The Electroadsorption Field Effect Transistor:
Numerical and Experimental Treatment of Chemisorption on Nanostructured Chemical Sensors

by

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Abstract

Chemisorption on semiconducting metal oxides is in general of great importance to the fields of clean energy, heterogeneous catalysis, nanoelectronics, and trace chemical detection. The purpose of this thesis is to illuminate this process by means of an investigation that utilizes the electric field effect to control surface chemistry and is both theoretical and experimental in nature. In addition, a fundamental semiconducting device is formally described by numerical derivation of its heterogeneous electrochemical properties at nanoscale.

This work concerns a chemical sensor that bears close similarity to a buried-gate thin film transistor (TFT) but differs conceptually in that it can control and measure charge density associated with chemisorption that occurs at an outer surface of the semiconducting channel. Similar device structures have been investigated experimentally within the chemical sensor community, without a thorough treatment of the complex interaction between surface forces and materials properties at the nanoscale. As a result, today there is not a widely accepted model for chemisorption based chemical sensors. This thesis employs a finite element analysis of chemisorption effects in nanostructured semiconductors, in an integrated analytical, numerical, and experimental approach, and applies it towards understanding the behavior of this device, which can be called an Electroadsorption Field Effect Transistor (EA-FET).

The EA-FET is a four terminal device (3 electrical, 1 chemical), possessing electronic and electrochemical properties that are derived numerically in this thesis work. In the case of the chemical terminal, charge is transferred by means of chemisorption and desorption processes. The device has been tested and compared to numerical simulations. As result of the analysis, key fundamental properties of the device are derived, regimes of operation are characterized, and a lumped element model is developed, in an effort to make the influence of chemisorption accessible in a practical electrical engineering context. In addition to studies of the EA-FET, related influences on chemical sensor performance are investigated, including the roles of illumination and thin film morphology.

Thesis Supervisor: Harry L. Tuller
Title: Professor of Ceramics and Electronic Materials
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1. Introduction

Chemisorption. It is a fundamental phenomenon: the reaction of a surface with a gas. Familiar examples of gas interaction with materials exist: the rusting of iron, the oxidation of silicon. These phenomena can be considered after-effects of chemisorption and are only visible after gas has diffused and reacted over a finite thickness of the material. Though invisible in our daily lives, its influence is ubiquitous, and chemisorption is at the beginning of any chemical reaction between a solid and a gas.

It is easy for chemisorption to be ignored in our casual experience, because as humans we care most about what we can see and touch. Silver is not tarnished until it turns black. A window has not fogged until water droplets nucleate in liquid phase. You may not know that you have inhaled a poisonous gas until the toxin enters your bloodstream and begins to impact your biological capacities. However, at the point of chemisorption on the cells of the lungs, a destructive chain of events has already begun. In numerous unfortunate examples, by the time the body’s reaction with a toxic gas is noticed, it is already too late to save the victim of inhalation poisoning from death or lifelong physical incapacitation.

A chemical sensor can save your life. There is a great need for chemical sensors that can quickly and reliably identify trace amounts of toxic chemicals that are present in the environment. Such systems need to be cheap and easy to use. They should be small, portable, and require low electrical power consumption for operation. The device should not get confused if it is placed in an environment that contains a complex mixture of gases. This is a very demanding set of operational requirements, but the ultimate goal of chemical awareness within our surrounding environment is of utmost importance, and it has motivated an enormous community of researchers to pursue the realization of practical devices.

When a gas chemisorbs upon a surface, there is often an exchange of electronic charge between the gas molecule and the bulk, in the process of forming the chemical bond, resulting in a buildup of electrical charge at the surface. This charge exerts an electrostatic potential on a volume of the material that lies just underneath the chemisorption surface, possessing a depth of influence on the order of nanometers to micrometers in the case of semiconductors. This effect has been utilized by the scientific community to create chemical sensors.

Chemical sensors based on semiconducting metal oxides (SMOs) are particularly attractive in many applications, due to ease of manufacturing, small size, portability, and high sensitivity compared to many alternative techniques. This sort of device gains a high chemical sensitivity with the surrounding environment when fabricated into a conductive structure that possesses a cross-sectional area that is on the order of nanometers. In this manner, electrostatic forces at the surface may influence electronic properties throughout a large volume fraction of the material. Because of this interaction, semiconducting metal oxide based chemical sensors are a hot area of research in the scientific field of nanotechnology.
Semiconducting metal oxides are further utilized as platforms for catalysis in many commercial and industrial applications. The catalytic converter found in automobile engine exhaust systems utilizes a semiconducting metal oxide as a catalytic support material. Considering the field of chemical engineering, large quantities of porous semiconducting metal oxides are routinely used as either the structural support or as a catalyst itself, in the bulk synthesis of organic compounds. The field of heterogeneous catalysis seeks to understand the phenomena of chemisorption in nanoscale and multi-component systems, with frequent application to chemical fabrication processes.

Besides industrial catalysts and chemical sensing, the study of chemisorption presented in this thesis has a much broader potential impact to inform the science and engineering of semiconductor based device design and fabrication process design. Oftentimes, when active semiconductor surfaces are exposed to the environment, they may exhibit a drift in electronic properties that may ultimately render the device unusable. To avoid these effects, engineers frequently go through great length to keep devices under well controlled environmental conditions. Semiconducting devices are often capped with a passivation layer after fabrication that seals the top surface from the outer environment because of the known effect of the device to interact with the environment in ways that are neither well understood nor controllable without use of the blocking layer. To date, fundamental models surrounding chemisorption have proven unwieldy, as is evident by the absence of a treatment of chemisorption in the nearly all modern literature on semiconductor device engineering.

In addition, chemisorption impacts many problems within the global energy crisis. In the pursuit of new and clean sources of energy, solar panels based on semiconductors such as silicon have grown into widespread use. Solar panels need to be stable and operate with high efficiency over long periods of time in order for them to be cost effective. However, the semiconductors themselves are commonly observed to gradually degrade over time when in contact with air, via processes that can only begin with chemisorption. Because of this, great care is taken to hermetically seal semiconductor based solar cells in the commercial fabrication of solar panels. The standard approach for elimination of chemisorption related drift and degradation in electronic and photonic devices is to simply, “cover it up.”

In contrast to solar cells or microelectronics, another clean technology operates explicitly by exposure of a material surface to a surrounding gas: the fuel cell, a device that converts a chemical fuel such as gaseous hydrogen directly into electrical power. Fuel cells operate by means of an electrolyte membrane that divides a chamber into two halves, one half containing hydrogen and the other containing oxygen. The membrane is ionically conductive, permitting hydrogen to travel across it and react with oxygen to form water. Electrical work may be extracted from the motion of ions acting under the chemical driving force of the hydrogen concentration gradient. In other implementations of fuel cells, the electrolyte conducts oxygen, and the electrode materials most commonly used in these cases are semiconducting metal oxides. In addition to fuel cells, similar principles of operation govern the behavior of batteries and ion
pumps. Such systems are largely affected by the rate at which chemisorption of gas occurs at the electrolyte surface, and many studies seek to maximize the rate of the chemisorption. However, broadly speaking there is not an agreement about the physical processes governing this critical step of system operation.

To date, the commercial success of semiconducting metal oxide based chemical sensors has relied heavily upon empirical studies that determine repeatable device response to gases of interest under a limited set of operating conditions. The current body of scientific research in this area includes largely phenomenological studies that may identify interesting materials of high sensitivity but stop short of proposing fundamental mechanisms to explain the trends that are observed. In certain isolated studies, progress has been made toward a more thorough understanding of sensor operation, but these works generally lack a unified perspective to account for relevant physical effects that influence performance under a diverse range of operating conditions. Furthermore, certain relevant, fundamental studies exist that have been overlooked by nearly the entire body of sensor literature, as for example, the work of F.F. Vol’kenshtein and of H. Gatos in the 1960s and 1970s.

Besides the limited understanding of chemisorption within the scientific community, some technological implementations have been encountered in prior studies of semiconducting metal oxide based chemical sensors. To obtain rapid and reversible sensor responses to the surrounding environment, high temperatures of operation are typically used to accelerate the kinetics of adsorption and desorption processes at the surface. This sample heating can additionally activate other processes within a materials structure such as grain boundary diffusion, bulk defect formation, and morphological evolution, which among other effects contribute to sample degradation. In addition, SMO sensors typically exhibit poor selectivity to specific gases of interest, due to promotion of multiple chemisorption reactions simultaneously at the film surface.\textsuperscript{5,6} Finally, the electronic properties of the film-substrate interface are often difficult to control, impacting sensitivity and repeatability of the devices.\textsuperscript{7} To address these limitations, this thesis applies several materials engineering approaches in parallel to increase sensitivity, selectivity, and speed of device operation while at the same time reducing temperatures of operation and improving device stability.

The following background section begins with a discussion of concepts that are necessary to understand the influences of charge transfer in chemisorption on semiconducting metal oxide materials, identifying relevant theories that in some cases have existed in scientific literature for more than 6 decades but to date have gone largely unappreciated. In addition to a treatment of fundamental mechanisms, state of the art research on chemical sensors is reviewed, including novel approaches that have been developed to seek improvements to device performance. Following the background, the goals of this thesis are described.

The present work includes both a significant numerical simulation component in addition to experimental investigations, and the relationship between the two is discussed. The experimental
portion begins by defining real sensor structures, fabrication techniques, materials characteri- 
ization techniques and relevant electrical characterization techniques. Particular emphasis is given 
towards characterization of highly sensitive thin film transistor based chemical sensors, which are demonstrated to possess a tunable sensitivity and response time via electroadsorption. Then, the modeling portion begins with evaluation of charge transfer in the process of chemisorption in finite element models of semiconducting metal oxide based sensor structures of practical dimensions. The influence of key materials, structural, and environmental variables are considered in detail. The devices treated by numerical simulation in this section are of the same structural dimensions and electronic properties of devices that were characterized experimentally, and correlation between models and experiments are considered in detail.

Numerical treatment of the thin film transistor based chemically active device elucidates several important properties of the heterogeneous electrochemical nanostructure, including an approximately linear relationship between voltage applied from gate to reference electrodes and the trapped charge density layer that accumulates at the semiconductor/gas surface, due to the electric field induced process of chemisorption, similar to the familiar $Q=CV$ relationship of a capacitor. However, the charged surface itself is tangential to the electric displacement from gate to reference electrodes, which differs from capacitors in the classical sense. In addition, both the applied voltage at the transistor gate and the charged surface layer of chemisorbed gas serve to influence conductance through the channel. Because the conductance of this transistor is influenced both by the electronic gate and chemisorption that occurs at the semiconductor/gas surface, this work refers to it as, the Electroadsorption Field Effect Transistor. A two-dimensional finite element numerical simulation of the electric potential field around the Electroadsorption FET is shown below in Figure 1 and discussed in later sections in detail. In the final chapters of this work, the combined numerical-experimental approach is discussed at length. Lumped element models of device conductance and surface charge density are derived from numerical simulation results, to make the trends in device performance practical and accessible in an electrical engineering context. Conclusions are provided, as are recommendations for future work.
Figure 1. Two dimensional plot of electric potential vs. position, in and around the Electroadsorption FET including several levels of voltage $V_G$ applied from gate electrode (bottom edge of each image) to reference electrodes (white regions, top left and right of thin film located at 0μm vertical position). Position scale bar is given at the bottom and left of figures in units of microns. $V_G$, from bottom to top: -5V, -2.5V, 0V, 2.5V, and 5V. The device possesses 2 microns channel length and 70 nanometers thickness. Electric potential is indicated in the color bar to the right, with isopotential lines shown in white (5 lines equally spaced in electric potential per image).
2. Background

2.1. Semiconductor Bulk

2.1.1. Energy Band Theory
The author notes the relevance of numerous prior works in the derivation of modern theories of semiconductor physics. Of great historic importance are the original works that describe the behavior of electrons within crystalline solids, including theory of linear combination of atomic orbitals (LCAO) and Bloch’s Theorem that describe the wave function of an electron in a periodic potential. Similar conclusions are arrived upon by means of the Tight Binding model, which describes the mechanisms by which weak interactions between neighboring atoms give rise to the formation of energy bands within a solid material. The energy band theory of crystalline solids is treated routinely in modern solid state physics curricula, and the reader is referred to the works of J.D. Livingston, of C. Kittel, and of N.W. Ashcroft and N.D. Mermin as a highly accessible and thorough basis. With energy band theory as a starting point, Sze provides a definitive reference text on semiconductor device physics, including thorough examination of numerous practical structures. R.F. Pierret provides a similar text from more of an introductory perspective, and R.T. Howe and C.G. Sodini further treat semiconductor devices in the context of electrical circuit engineering. In the proceeding sections, the author assumes a familiarity with the fundamental concepts covered in these works while taking care to identify equations of key relevance to the present work.

2.1.2. Bulk Space Charge Effects
Space charge formation commonly occurs in semiconducting or ionic systems at or adjacent to surfaces and interfaces. The origins of these charges are several and include, for example, the difference in work function at a heterojunction, e.g. metal/semiconductor interface, chemisorption of gaseous molecules at a semiconductor surface, or defect segregation to surfaces or interfaces driven either by intrinsic or extrinsic means. The end result of each of these phenomena is a redistribution of mobile species in response to a gradient in electrostatic and/or chemical potential across an interface. This in turn impacts the operation of various electroceramic devices that are subject to these phenomena. In the following, we first consider the origins of space charge potential. Then, we derive the resultant redistribution of charge carriers considering the case where ions are frozen in place and cannot redistribute. Having derived expressions describing charge redistributions in the vicinity of interfaces in bulk systems, we then move on to consider the consequences of shrinking dimensions to the nanoscale.

There are various driving forces that result in the formation of space charge across surfaces or interfaces. Perhaps the simplest example is the case of a Schottky diode that is formed from a metal-semiconductor heterojunction. For an ideal metal-semiconductor contact, the height of the potential barrier is given by
\[ \Phi_g = \Phi_m - \chi_s \]  
where \( \Phi_m \) is the work function of the metal and \( \chi_s \) is the electron affinity of the semiconductor\(^{17}\).

Space charge potentials also arise due to inhomogeneities that occur within a single material, as is the case of p-n junctions in single crystalline materials. The so-called built-in potential \( \phi_{bi} \) of a p-n junction is given by\(^{13}\)

\[ \phi_{bi} = \frac{kT}{q} \ln \left( \frac{N_D N_A}{n_i^2} \right) \]  
(2)

in which \( N_D \), \( N_A \) and \( n_i \) is the donor density on the n-side, the acceptor density on the p-side and the intrinsic carrier density, respectively.

A grain boundary is an interface between adjacent single crystalline grains, and in both ceramic and metallic polycrystalline materials, defects tend to segregate to such boundaries to lower their interfacial free energies, as first discussed by Gibbs\(^{18}\). In semiconducting oxides, these defects tend to form electron or hole traps within the band gap of the oxide, trapping free carriers from the adjoining grains. The barrier height of a back-to-back Schottky potential barrier formed at such electron blocking grain boundaries between grains with donor density of \( N_D \), is given by\(^{19}\):

\[ \phi_s(0) = -\frac{Q_s^2}{8\epsilon q N_D} \]  
(3)

in which \( \epsilon \) and \( Q_s \) are the dielectric constant and charge/area trapped at the grain boundary core respectively. Such grain boundary barriers are, for example, essential to the operation of ZnO varistors and positive temperature coefficient (PTC) thermistors. Both depend, in their operation, on the collapse of the space charge barrier, in the former case, at a characteristic breakdown voltage and in the latter case, in the vicinity of the ferroelectric Curie temperature.

In the case of gases adsorbing on the surface of a semiconductor (gas/semiconductor junction), the space charge potential arises from the charge transfer of electronic charge between the semiconducting oxide and the chemisorbed ions. Here, the magnitude of the potential is determined by charge per unit area of ions chemisorbed at the surface, \( Q_s \), as given by Equation 3 with a factor of 8 is replaced with 2 in the denominator. \( Q_s \) in turn is related to the partial pressure of gases, \( P \), in the surrounding environment by:

\[ Q_s = \frac{qN^* \beta P}{1 + \beta P} \]  
(4)

where \( N^* \) is the number of chemisorption sites per unit area and \( \beta \) is an adsorption coefficient that depends on the electronic properties of the semiconductor, as derived by Vol’kenshtein\(^{20}\).
This adsorption coefficient will be discussed in further detail later in this text, in the case study of chemical sensors.

Additional sources for potential barriers in ionic systems can be driven by intrinsic ionic processes. As first described by Frenkel, the formation of a net surface charge and a compensating space charge layer relates to the energy differences required to bring various ionic species to a surface\textsuperscript{21}. Indeed, while ionic solids are macroscopically charge-neutral, local variations in both structure and chemistry lead to internal electrostatic potentials and electric fields. Space charge layers are formed to compensate this excess charge and preserve electrochemical equilibrium. Subsequent work by Lehovec\textsuperscript{22} and Kliewer and Koehler\textsuperscript{23} led to the refinement and widespread adoption of space charge theory in ionic systems.

As an example, the space charge properties of TiO\textsubscript{2} were analyzed by Ikeda and Chiang\textsuperscript{24}. Assuming cation Frenkel disorder, i.e. cation vacancies and interstitials are the predominant defects, the free energy change due to the introduction of such defects into a perfect crystal is given by

\[
F = \int_0^\infty \left[ n_v(x)g_{v_n} + n_i(x)g_{i_n} + \frac{1}{2} \rho(x)\phi(x) \right] dx - TS_c
\]  

where \( n \) is the defect density, \( g \) the free energy per defect, \( \rho \) the charge density per unit volume, \( T \) the absolute temperature, and \( S_c \) the configurational entropy. The authors derived the potential difference between the grain boundary core and the bulk in TiO\textsubscript{2} to be:

\[
e\phi(0) = \frac{1}{8} (g_{v_n} - g_{i_n})
\]  

thus relating the polarity and magnitude of the space charge potential to the difference in defect formation energies of titanium vacancies and interstitials.

The impact of space charge regions on combined electronic and ionic transport was presented by Maier\textsuperscript{25}. The space charge potential, \( \Delta \phi = \phi(0) - \phi(\infty) \), where \( \phi(0) \) is the potential at the interface and \( \phi(\infty) \) is the reference value in the bulk, determines the charge carrier profiles in the space charge layer. The equilibrium condition for species \( j \) is given by the constancy of the electrochemical potential:

\[
\tilde{\mu}_j(x) = \mu_j(x) + z_j e\phi(x)
\]  

consisting of the chemical potential, \( \mu_j \), and electrostatic potential \( \phi(x) \) with \( z_j e \) the net charge. For dilute defect concentrations, the chemical potential term in Eq. 3 can be expanded to include the standard chemical potential, \( \mu_j^0 \), and concentration \( c_j \) (or activity for concentrated systems) of species \( j \).
\[ \mu_j = \mu_j^0 + kT \ln c_j \]  

(8)

By equating the electrochemical potential of species \( j \) at two different locations and solving, one finds that the ratio \( c_j \) at two locations, one at \( x \) and the other far from the interface (\( x=\infty \)), depends exponentially on the difference in potential between these two locations as described by:

\[
\left( \frac{c_j(x)}{c_{j\infty}} \right)^{\frac{1}{z_j}} = \exp \left( -\frac{e}{k_B T} \Delta \phi(x) \right)
\]

(9)

Equation 9 demonstrates that an electrical potential difference is compensated by non-uniform chemical profiles in order to preserve electrochemical equilibrium.

The importance of Eq. 9 is clear, as it demonstrates that carriers will either accumulate or deplete exponentially in the space charge layer in response to the space charge potential. In order to quantify the enhancement/depletion effects, one must first solve for the spatial variation of the electrical potential. Beginning with Gauss’ law,

\[ \nabla \cdot E = \frac{P}{\varepsilon} \]  

(10)

and the definition of the electric field:

\[ E = -\nabla \phi \]  

(11)

a partial differential equation is found as a specific example of Poisson’s equation:

\[ \nabla^2 \phi = -\frac{\rho}{\varepsilon_0 \varepsilon_r} = -\frac{z_j e c_j}{\varepsilon_0 \varepsilon_r} \]  

(12)

Poisson’s equation and equation 10 are combined to form the Poisson-Boltzmann differential equation that, for the case of electrostatic potential variation in one dimension and one predominant defect, results in:

\[ \frac{d^2 \phi}{dx^2} = -\frac{e z_j c_{j\infty}}{\varepsilon_0 \varepsilon_r} \exp \left( -\frac{z_j e}{kT} \Delta \phi(x) \right) \]  

(13)

Equation 13 represents an ordinary differential equation requiring two boundary conditions and a reference point for the potential, commonly set to zero in the bulk. If ionic defects are frozen in place and unable to move, the charge density in Poisson’s equation is determined only by redistribution of electronic charge carriers that are ionized from the dopants. This is known as the Mott-Schottky approximation\(^{26}\), which results in a simplification to Poisson’s equation: by setting \( c_j(x) = c_{j\infty} \):
\[
\frac{\partial^2 \phi}{\partial x^2} = -\frac{z_j e c_{jn}}{\varepsilon_0 \varepsilon_r}
\] (14)

With boundary conditions \( \phi'(\lambda^*) = 0 \) and \( \phi(\lambda^*) = \phi_\infty = 0 \), equation (14) can be integrated to yield (relative to the bulk reference potential, commonly set to zero):

\[
\Delta \phi(x) = -\frac{z_j e c_{jn}}{\varepsilon_0 \varepsilon_r} (x - \lambda^*)^2
\] (15)

where \( \lambda^* \) is the depletion (space charge) width:

\[
\lambda^* = \sqrt{\frac{2 \varepsilon_0 \varepsilon_r \Delta \phi(0)}{z_j e c_{jn}}}
\] (16)

Note, the Debye Length of the material is defined as:

\[
\lambda = \sqrt{\frac{\varepsilon_0 \varepsilon_r kT}{2z_j e^2 c_{jn}}}
\] (17)

Thus, \( \lambda \) and \( \lambda^* \) are directly related:

\[
\lambda^* = \lambda \sqrt{\frac{4z_j e}{kT} \Delta \phi(0)}
\] (18)

It is important to note that the ratio of depletion length to Debye length is largely determined by the magnitude of the space charge potential, as illustrated in Figure 1 for the case of a \( z_j = 1 \) and \( T = 300K \). At zero potential, the space charge vanishes, and for moderate space charge potentials of 10 mV and above, the space charge length will be larger than the Debye length.
Figure 2. Ratio of depletion length to Debye length vs. space charge potential at a depleted surface or interface. Note, $z_j = 1$ and $T = 300K$.

In order to find the spatial dependence of electronic charge carrier concentrations, the expression for the potential difference as a function of $x$, equation (15), can be substituted into the original equation for carrier enhancement/depletion, equation (9), yielding:

$$\frac{c_i(x)}{c_{ex}} = \exp \left[ - \frac{z_i}{z_j} \left( \frac{x - \lambda_*}{2\lambda} \right)^2 \right]$$  \hspace{1cm} (19)

where defect $i$ is enhanced or depleted, and defect $j$ is the majority defect that determines the space charge width.

Considering the simple example of an n-type semiconductor ($c_{\infty}$ being equal to the donor concentration, $N_D$), the electron concentration can be expressed as:

$$\frac{c_e(x)}{c_{\infty}} = \exp \left[ \left( \frac{x - \lambda_*}{2\lambda} \right)^2 \right]$$  \hspace{1cm} (20)

and the corresponding hole concentration is related to the electron concentration by:
\[
\frac{c_n(x)}{c_{p\infty}} = \left( \frac{c_p(x)}{c_{p\infty}} \right)^{-1}
\]  

(21)

Note that under static equilibrium, the electron and hole concentrations are additionally related by the familiar mass action law, \( c_n c_p = n_i^2 \), where \( n_i \) is the intrinsic charge carrier concentration of the material.

ZnO and TiO\(_2\) are examples of wide-bandgap (\( E_g \approx 3.2\)eV) semiconducting ceramics that are commonly used in temperature ranges at which ionic defects are not mobile. At room temperature, ZnO is widely used in varistors and thin film transistors, while TiO\(_2\) has become heavily investigated as an anode material for dye sensitized solar cells (see case study below). In addition, both materials can be used as chemical sensors that are operated from 200-400\(^\circ\)C, which is at sufficiently high temperatures to promote reversible surface reactions, but at still low enough temperatures to avoid motion of bulk defects during typical time scales of interest. Figure 2 illustrates the spatial dependence of electron and hole concentration in these two materials at various doping concentrations, under the Mott-Schottky approximation. It is interesting to note that since the relative permittivity of TiO\(_2\) is over 10 times larger than that of ZnO, depletion lengths will be significantly longer, according to equation (16). At constant space charge potential, materials with lower doping levels have longer depletion lengths and are easier to electronically invert, as illustrated by the cross-over in electron/hole concentration for \( N_D = 10^{17}\)cm\(^{-3}\).
Figure 3. Space charge profiles of electrons and holes according to the Mott-Schottky model, in two common semiconducting ceramics, (a) TiO$_2$ and (b) ZnO at 300°C. Both materials have band gap $E_g \sim 3.2$ eV, but relative permittivity $\varepsilon_r \sim 100$ in TiO$_2$ vs $\varepsilon_r \sim 8$ in ZnO. Varying doping levels ($10^{17}$, $10^{18}$, and $10^{19}$ cm$^{-3}$) are shown, for comparison at $\phi = 0.5$ volt space charge potential. (note, density of electronic states assumed equal to that of silicon.)
In certain materials and at sufficiently high temperatures, ionic defects become mobile enough to redistribute in response to an electric field. This situation was covered in an article co-authored by the author and can be found in Reference 16 but will not be treated further in this thesis.

2.1.3. Nanoscale Space Charge Effects

Nanoscale structures, as illustrated in Figure 4 imply the existence of high densities of surfaces and/or interfaces. For conductive materials, this in turn, results in the formation of adjacent space charge regions, discussed in detail above. One classifies nanostructures by their dimensionality; i.e. those that conduct in one, two, or three dimensions (1D, 2D or 3D systems, respectively). In contrast to transport in bulk materials, charge carriers in nanostructured materials are heavily influenced by interactions with surfaces and/or interfaces as they move along the conductive pathway. Canonical examples of 1D, 2D, and 3D systems are shown in Figure 4 as a nanowire, a thin film, and a nano-porous / nano-grained bulk material. In practice, nanostructured ceramic materials often contain a hierarchy of 1D, 2D, and 3D structures.

![Figure 4. Schematic depiction of 1D, 2D, and 3D nanostructures in which the diameter, thickness or particle size of the respective structures are typically on the order of 10s of nm or less in dimension. Modulation in the relative size and intensity of the depleted/accumulated regions (orange) with respect to the neutral (bulk) regions (green) can markedly influence the resistance or the overall structure. This effect is strongly multiplied as the dimensions of the space charge regions become comparable to the geometrical dimensions of the depicted structures.

As the characteristic dimension of a conducting nanostructure is decreased below the scale of the Debye length of the material, the semi-infinite approximation of a semiconductor bulk material is no longer applicable. Instead, it becomes necessary to consider the influence of charge screening by multiple surfaces on the conductive properties. In the case of a material with no mobile ionic defects, the space charge density compensating the fixed surface/interface charge will be

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*The following review of influence of nanostructure on carrier distribution and its impact on sensors is reproduced largely from a work co-authored by G.C. Whitfield, titled Electrical Conduction in Nanostructured Ceramics.*

36
approximately constant in magnitude throughout the depleted region. Consider the example of a nano-thin membrane with exposure at two free surfaces; as the membrane thickness approaches twice the Debye length, the membrane becomes nearly completely depleted. As the membrane thickness is further reduced the total amount of compensating space charge within the material becomes geometrically constrained to the dimensions of the membrane. This in turn reduces the intensity of electric fields that form perpendicular to the surface and limits the total change in electrostatic potential across this region. This results in an energy band profile, as calculated by Leonard and Talin for nanowires of different dimensions, that approaches flat band conditions as the diameter of the wire approaches the space charge width\(^2\)\(^8\) (see Figure 5).

**Figure 5.** The figure depicts energy band bending within a silicon nanowire that is covered in an outer shell of metal that forms a Schottky barrier. The calculation is for a nanowire of n-type doping density at \(10^{19}\) cm\(^{-3}\) and diameter equal to (a) 40 nm (b) 10 nm. Note that at smaller nanowire diameter, band bending nearly disappears and the Fermi Energy moves away from the conduction band towards mid gap. After Leonard and Talin\(^2\)\(^8\)

At even smaller dimensions, i.e., as the characteristic feature sizes decrease below 5 nm, quantum confinement begins to have a strong impact on the conductive properties of semiconducting materials. First, the reduction of device dimensions results in bulk energy bands splitting into discrete energy levels, accounting for an increase in the HOMO-LUMO separation or equivalently, an increase in the effective band gap. This quantization of states can be computed from a top-down approach by considering deviation from single-band conduction models\(^2\)\(^9\) or from a bottom-up approach by using a tight-binding model.\(^3\)\(^0\)

Typically, at small conducting channel dimensions (e.g. nanowire diameter) and high surface:volume ratios, the conductivity would be expected to drop due to the heightened influence of surface scattering on carrier mobility as is commonly observed at the channel/dielectric interface in field effect transistors.\(^2\)\(^7\) However, for sufficiently small dimensions, there appear to be several quantum effects that contribute toward reduced surface scattering upon continued downscaling of e.g. nanowire diameter. Zheng, et. al., calculated that a
restructuring of the energy bands decreases charge carrier effective mass in the direction along the nanowire axis and increases effective mass in directions transverse to the axis. This contributes to increased electron mobility along the nanowire axis and reduced mobility normal to the axis. Based on numerical solutions to coupled Poisson-Schrodinger equations at and below 5 nm nanowire diameter, the spatial density of electronic states are reported to shift toward the center of the nanowire, further serving to remove charge carriers from the region of the surface, as illustrated in Figure 6.

Figure 6. Electron density throughout the cross section of a 2nm diameter silicon nanowire, determined by coupled numerical solution of the Schrodinger and Poisson equations. After Gnani and Baccarani.

2.2. Semiconductor Surface

2.2.1. Chemisorption Theory

Chemisorption on semiconducting metal oxide materials relies on charge transfer between the SMO and the gas molecules that become bound at the surface. Chemical sensors that are based on thin film SMO materials make use of this fact and detect changes in the concentration of oxidizing or reducing gases present in the environment by measuring the change in film resistance as charge carriers are transferred to and from the film surface. The process is believed to proceed by means of the population and depopulation of mid-bandgap electronic states derived from the hybridized molecular orbitals of the gas molecules in contact with the material surface. An energy band diagram of the surface of a typical n-type semiconducting metal oxide during the process of chemisorption is displayed below, in Figure 7. As shown, the occupation of states in the gap increases or decreases depending on the nature and concentration of gases present in the environment, which in turn impacts the amount of band bending at the surface of the semiconductor. Depletion of electrons near the surface is reflected in an upward bending of the conduction band relative to the Fermi energy. Electron accumulation results instead in a downward band bending. Oxidizing gases tend to act as electron traps at the surface and thereby
increase the amount of upward band bending experienced by an n-type semiconductor, while reducing gases have the opposite effect, decreasing the amount of band bending at the semiconductor surface.

Figure 7. Schematic presentation of the effect of the ambient gas atmosphere on the energy band diagram of an n-type metal-oxide in air (a); reducing gases in air (b); and with additional oxidizing gases in air (c).

A detailed analytical theory of chemisorption, relating changes in semiconductor energy band structure to chemisorption of gas molecules on the semiconductor surface was proposed nearly 50 years ago by F.F. Vol’kenshtein.33 His theory proposed an explanation for the electronic driving forces of chemisorption including the roles that illumination and applied electric fields could have in altering the degree of binding of molecules to the surface, and today a growing number of studies have acknowledged the relevance of this model in particular in the area of chemical sensors. However, although a small number of studies cite Vol’kenshtein’s model, an even smaller fraction have attempted to evaluate its implications due possibly to the fact that the equations involved do not lend themselves to analytic evaluation. The following section reviews a portion of the introductory discussion presented by Vol’kenshtein in analysis of chemisorption processes.

The adsorption of gas at the surfaces of solid materials can be generally divided into two phenomena, physisorption and chemisorption, the distinction concerning the nature of the intermolecular forces that bind the adsorbed gas in place. As defined by F. F. Vol’kenshtein, chemisorption is “the combination reaction of a gas particle with a solid, which emerges in this process as a sort of single system.” In general, physisorption concerns the binding of a gas at a surface by means of a weak perturbation of the gas from its initial quantum mechanical state, whereas chemisorption results in the formation of new, hybridized quantum mechanical orbitals. Chemisorption also includes a charge transfer between the gas and the solid, either involving delocalized charge carriers from the bulk of the solid material or localized charge transfer from atoms at the solid surface.
Figure 8.1 illustrates the general form of an adsorption curve comprising energy $W$ of a gas molecule versus its distance $r$ from a surface with which it is binding. This takes its form from multiple forces of interaction that exist between a gas molecule in close proximity to a solid. In an adsorption process, there is an attractive interatomic potential that draws the gas molecule toward the surface. At the same time, there is repulsive potential resulting from a different physical interaction that repels the molecule from the surface. Both the attractive and repulsive forces generally increase in strength with closer proximity but relate in different functional form to the absolute distance between the molecule and the surface. The simultaneous action of attraction and repulsion results in the observed shape of the adsorption curve, which specifies an equilibrium adsorption length $r_0$ and the heat of adsorption $q$ (energy gained in the adsorption process).

In the case of physisorption (also called weak adsorption), the gas is held in place typically by van der Waal’s forces or forces resultant from electrostatic polarization. In this case, the electronic wave functions of the gas and the solid material do not overlap significantly, and no net electronic charge is transferred between the gas and the solid. The general form of the adsorption curve in this case is given by the Lennard-Jones potential, which takes the form\(^{34}\)

$$W(r) = -\frac{a}{r^6} + \frac{\beta}{r^{12}} \tag{22}$$

where $a$ is a constant related to attractive van der Waals forces and $\beta$ is a constant related to repulsive forces based on exchange coupling between the gas and solid molecules.
Figure 8. a) Schematic plot of an adsorption curve, i.e. energy $W$ vs. distance $r$ of an adsorbed gas molecule. $q$ is the heat of adsorption and $r_0$ is the equilibrium adsorption distance. b) schematic plot of an activated adsorption curve, where a weakly bonded state of bond length $r_0'$ and binding energy $A$ is separated from a strongly bonded state of bond length $r_0''$ and binding energy $B$ by an activation barrier of energy $C$. c) Two adsorption curves superposed, corresponding to weak (shallow curve) and strong (deep curve) binding.

Chemisorption, by comparison, involves one or more chemical reactions between the gas and the solid surface, which may be e.g. covalent or ionic in nature. Charge is exchanged with the lattice and a new quantum mechanical system is formed, i.e. a radicalized (having given or received an electron) and/or hybridized (having blended electronic orbitals with the binding species) gas molecule. Because the gas molecule is fundamentally altered, the energy vs. distance relationship of a chemisorbed molecule is entirely separate from that of a physisorbed molecule. Although the same exchange forces might repel the chemisorbed molecule from the solid, a stronger attractive force acts upon it, resulting in a bond length that is shorter and heat of adsorption that is larger than that of a physisorbed molecule. This is shown schematically in Figure 8.c.

A process of chemisorption may possibly involve a transition from the physisorbed state of a gas molecule (weakly interacting at a long distance) to the chemisorbed state (strongly interacting at
a short distance) and result in an activated chemisorption adsorption curve as shown in Figure 8.b. However, the derivation of this curve is not a matter of mere superposition of physisorption and chemisorption, as these correspond to entirely different quantum mechanical states. Furthermore, Vol’kenshtein notes that it is possible for non-activated chemisorption to occur and even for activated physisorption to occur. To begin to elucidate this complex picture, a discussion of the activation energy in adsorption is presented in the following section.

2.2.2. Activation Energy in Adsorption

Vol’kenshtein discusses several mechanisms that may result in a thermal activation of adsorption processes and importantly notes that both chemisorption and physisorption may be thermally activated. In general, thermal activation of adsorption corresponds to the presence of two distinct energy states, $A$ and $B$, of an adsorbed molecule before and after adsorption (respectively) that are separated by an activation barrier $C$. Heating of the material surface results in an increased vibration of the gas molecules in state $A$ and an increased probability of transition over the energy barrier $C$ and arrival in the adsorbed state $B$. Analysis of such a system by Boltzmann statistics results in an observed rate of chemisorption (number of adsorbed molecules per second) according to the following relationship:

$$
\frac{dN}{dt} \propto \exp\left(-\frac{E_C}{k_BT}\right)
$$

(23)

where $N$ is the number of adsorbed molecules, $t$ is time, $k_B$ is Boltzmann’s constant, $T$ is temperature, and $E_C$ is the activation energy of chemisorption corresponding to a transition above the effective barrier height $C$.

In a discussion of mechanisms that possibly contribute to the observed activation energy of chemisorption, Vol’kenshtein notes that under simplified conditions (in the case that desorption can be neglected, at the beginning of an adsorption process, and when the surface concentration of adsorbed species is small enough that adsorbed molecules do not interact with one another) the rate of chemisorption can be described as follows:

$$
\frac{dN}{dt} = N^* s \chi f_p
$$

(24)

where $N^*$ is the total number of available adsorption sites per unit area, $s$ is the effective surface area of an adsorbed gas molecule, $\chi$ is the probability that a gas molecule that is in the vicinity of an adsorption center at the surface will become chemisorbed, and $f_p$ is the frequency of collision of gas molecules with a material surface per unit area. The above expression may be simply related to the pressure of a gas in the environment through the kinetic theory of ideal gases, which results in the following expression for $f_p$:

$$
f_p = \frac{P}{\sqrt{2\pi M k_BT}}
$$

(25)
where $P$ is the gas pressure and $M$ is the mass of a gas molecule. The above expression for collision frequency of gas molecules includes weak dependence on temperature ($T^{1/2}$) and cannot account for the exponential dependence under consideration.

There are only two terms that may contribute to the activation energy: the probability of state transition $\chi$ and the concentration of surface sites $N^*$. Considering the former, this phenomenon may generally occur whenever there are multiple attractive forces and/or multiple repulsive forces at play. Vol’kenshtein noted that a classic example of this phenomenon was derived in much earlier work by Lennard-Jones, concerning the behavior of gas adsorption coupled with decomposition of the gas molecule into separate atoms, so called “dissociative adsorption.”

Figure 9 schematically illustrates a discussion of the dissociative adsorption of H$_2$ gas on a material surface.

Figure 9. Three graphs illustrating the phenomenon of dissociative adsorption as derived by Lennard-Jones and reproduced by Vol’kenshtein

(a) Plot of position of two hydrogen atoms as they each transition from quantum mechanical state 1 (weakly adsorbed) to state 2 (strongly adsorbed). The x axis depicts distance of a the atoms from the adsorbent surface and the y axis depicts distance of separation between the two hydrogen atoms.

(b) Plots of the interaction potential between the surface of a solid material and two different quantum mechanical systems: the H$_2$ gas molecule and a molecule that has been dissociated into two separate H atoms.

(c) A
two dimensional "Eyring" type diagram that illustrates a continuous transition from quantum
mechanical state $A$ to state $B$ through an activation energy $D$ that is less than the barrier height $C$
resulting from the intersection of the two plots shown in part (b).

As shown in Figure 9.a, the transition of a diatomic gas molecule (e.g. H$_2$) from a weakly
adsorbed state 1-1 to a strongly adsorbed state 2-2 is considered. As the H$_2$ molecule approaches
the surface, it first feels the influence of van der Waals forces that compel it toward a
physisorbed metastable state of equilibrium (state 1-1, corresponding to curve H$_2$ and binding
energy $A$ in Figure 9.b). Having arrived in this state, the H$_2$ molecule now feels a much stronger
influence of the substrate that tends to counteract the covalent bonding of the H$_2$ molecule and
pull it apart in order to bind to each of the H atoms individually. The origin of this driving force
can be considered a result of a quantum mechanical derivation of bonding energy of individual
atoms on the surface with the hydrogen atom, and its strength is specific to the particular
adsorbent material under consideration. As such, the system is generally driven toward an
adsorption curve shown schematically as "H+H" with stronger binding energy $B$ in Figure 9.b by
pushing the two hydrogen atoms apart. It must be noted that the transition from state $A$ to state $B$
represents a continuous change to the quantum mechanical potential landscape and the activation
energy of this process cannot be computed as the height $C$ above the original energy of the
hydrogen molecule. As shown in Figure 9.c, the hydrogen atoms will follow a path in two
dimensions (stretching the molecular bond and approaching the surface) that minimizes the
energy of the transition, noted as activation energy $D$.

Although the state transition depicted in Figure 9.c is merely a qualitative sketch, it is true in its
suggestion of a continuous transition of states intermediate to the start and end points. In earlier
days of physical chemistry, attempts were made to investigate specific cases of such transitions
through algebraically and computationally intensive analysis of simplified physical systems
consisting of a small number of molecules moving in constrained directions of motion. Such an
investigation is greatly helped by the power of modern computation, and today in the field of
chemical physics it is possible to calculate the adsorption curve (potential energy versus
position) in three dimensions for an arbitrary gas approaching the surface of a material and
interacting by means of known start and end electronic states. Although this is the active pursuit
of many research groups today, it is not the principal topic of this thesis. Rather, given the
increasing availability and accuracy of such information about materials surfaces, it is the goal of
this thesis work to develop a comprehensive physical model of chemisorption on semiconducting
metal oxide materials to be used in the design of high performance chemical sensors.

2.2.3. The Vol’kenshtein Chemisorption Coefficient
Vol’kenshtein presented a quantum mechanical treatment of the electronic structure of the
semiconductor surface in contact with gas molecules in order to derive an adsorption coefficient
on semiconductors that accounts for the electronic driving force, i.e. the Fermi Energy, in the
process of strong chemisorption on materials surfaces. This coefficient is referred within this
thesis as the Vol’kenshtein Chemisorption Coefficient, $\beta$:
\[
\beta = \beta_0 \left( \frac{g_A + \exp \left( \frac{E_F - E_{S_A}^{\text{S}}}{kT} \right)}{g_A + \frac{v^0}{v^-} \exp \left( - \frac{E_{S_C} - E_F}{kT} \right)} \right)
\]

where \( E_F \) is the Fermi energy, \( E_{S_C}^{\text{S}} \) is energy of the conduction band edge at the surface, \( E_{S_A}^{\text{S}} \) is the energy level of chemisorption-induced acceptor states at the surface, \( g_A \) is the degeneracy factor of chemisorption-induced states, \( v^0 \) is the oscillation frequency of neutral species, \( v^- \) is the oscillation frequency of charged chemisorbed species, and \( \beta_0 \) is an adsorption coefficient given by the well known Langmuir equation, modified to account for an activation energy \( (q_0) \) of weak chemisorption:

\[
\beta_0 = \frac{\kappa s_0 \exp(q_0/kT)}{v_0 \sqrt{2\pi M kT}}
\]

Where \( \kappa \) is the sticking probability, \( s_0 \) is the effective area of a chemisorbate, \( M \) is molecular mass of the gas, \( v_0 \) is the oscillation frequency of the neutral species and \( q_0 \) is the adsorption heat of the neutral (weakly bound) species. Intuitively, the above equations demonstrate that the adsorption coefficient \( \beta \) and surface coverage \( \Theta \) are higher when the Fermi energy \( E_F \) is at higher positions above the energy level of surface acceptor states \( E_{S_A}^{\text{S}} \). Similarly, as \( E_F \) increases and its separation from the conduction band edge at the surface \( E_{S_C}^{\text{S}} \) decreases, the adsorption coefficient \( \beta \) and surface coverage \( \Theta \) will increase. While \( E_{S_C}^{\text{S}} \) and \( E_{S_A}^{\text{S}} \) are properties of the semiconductor and its interaction with the chemisorbed gas, the position of \( E_F \) at the surface is will depend on the dimensions of the space charge region, which in turn can be heavily dependent on the geometry of the sensor film, especially at the nanoscale. Hence, the above equation states that there is a recursive relationship in the electronic processes governing chemisorption. As the amount of charge transferred to the surface of a semiconductor will influence the position of the Fermi Energy via band bending processes, and conversely the Fermi Energy influences \( \beta \). In Vol’kenshtein’s initial treatments he discussed this parameter in the context of a semi-infinite bulk material, and an iterative procedure is necessary even to calculate values of this coefficient as applied to bulk materials. However, that does not capture the complexity of a nanostructured semiconducting material. Other studies have emerged propose to evaluate nanoscale effects, but significant simplifications are made in consideration of practical device geometries and the recursive nature of the semiconductor-gas interaction is often overlooked.
2.2.4. Early Studies of Chemisorption

As solid state chemistry evolved throughout the 20th century, an increasing number of studies of chemisorption were performed on many different materials systems. Most initial studies were largely phenomenological, seeking to quantify experimental observations with models such as the Elovich Equation. For some time, the scientific community generally lacked experimental techniques that could properly test emerging theories on the role of charge transfer associated with chemisorption.

With the advent of semiconductor device microfabrication processes in the 1960s, the impact that chemisorption has on the electronic properties of materials became more broadly appreciated. Researchers developed new techniques to create very pure, bulk crystalline materials, and with advances in vacuum technology, were able to create materials with “clean” surfaces that enabled more reproducible experimental conditions for the study of chemisorption. Since that time, a large body of research activity has developed which studies the interaction of gases with the surfaces of semiconductor materials, driven in part, by the need to engineer reproducible manufacturing conditions for the microelectronics industry. One research group that stands out from that period was one headed by Professor Harry C. Gatos of the Department of Material Science and Engineering at MIT, who founded the Journal of Surface Science in 1964. Over the following two decades, Prof. Gatos’ research group developed new techniques that focused on characterizing the energy band structure, charge transfer, and thermodynamic properties related to chemisorption, demonstrating their utility on bulk crystalline materials such as GaAs, CdS, and ZnO.

A key technique refined by the Gatos group was surface photovoltage spectroscopy, which makes use of a Kelvin probe to measure changes in work function at a material surface, for example, as a result of illumination of the surface with monochromatic light exciting electrons between specific energy states. By scanning the illumination wavelength and measuring resultant changes in the work function, they demonstrated that it is possible to map out the density of occupied and unoccupied electronic surface trap states, accessible by photon absorption, in addition to associated recombination velocities. By performing these techniques in a vacuum chamber with controlled partial pressure of oxygen, they were able to conclusively establish the connection between certain electronic transitions and the presence or absence of oxygen chemisorbed at the material’s surface. Figure 10 shows an example of the influence that illumination with above-bandgap-energy (Figure 10.a) and below-bandgap-energy light (Figure 10.b) can have on the chemisorption of oxygen on the surface of ZnO, as measured by the Kelvin probe technique (note, changes in contact potential difference or surface photovoltage are proportional to changes in the work function of the material). In this case, illumination with light above bandgap energy was shown to induce desorption of chemisorbed oxygen from the surface of ZnO. In addition, probing via surface photovoltage spectroscopy revealed that the onset of such desorption occurred at photon energies significantly below the band gap energy, strongly
implicating the role of electronic transition among sub-bandgap surface energy states specifically associated with oxygen chemisorption.

Figure 10. (a) Changes in contact potential difference of the ZnO surface upon irradiation with above-bandgap-energy light in different oxygen partial pressures (b) Surface photovoltage spectrum in a vacuum of $10^{-7}$ Torr (preceded by exposure to oxygen pressure of 20 Torr). Curve (1): after irradiation with above-bandgap-energy light; Curve (2): prior to irradiation. 39

In Gatos’ studies, the piezoelectric effect was used to modulate the work function of ZnO and other piezoelectric materials and investigate the resultant changes in chemisorption of various gaseous species at their surfaces, a phenomenon they entitled the piezochemisorption effect. 40 Chemisorption of oxygen on bulk ZnO induces the buildup of negative charge on the surface along with a compensating depletion space charge distribution beneath the surface, thus establishing overall charge neutrality across the interface. Bending of the bulk crystal induces modulation of the space charge width at the material surface due to the piezoelectric effect, which in effect modulates the work function of the material, which was shown, in turn, to impact the oxygen chemisorption rate. The significance of this technique was that it facilitated achieving repeatable degrees of energy band bending (i.e. repeatable surface potential barriers) during variation of other environmental conditions that influenced chemisorption. Figure 3 illustrates the ability, in this manner, to measure contact potential difference (cpd; related to work function) transients in a ZnO crystal while keeping the height of the surface potential barrier at a constant level. This enabled the measurement of the thermal activation energy associated with chemisorption of oxygen at a fixed level of band bending at the surface. A
phenomenological description of the charge transfer rate of electrons from chemisorbed oxygen is captured in the following equation:

\[
R_{ct} = \frac{1}{\alpha V_{d} V_{s}} \frac{d(cpd)}{dt} = A_{e} \exp \left( \frac{q V_{d}}{kT} \right) N_{s} \exp \left( \frac{E_{a}^{*}}{kT} \right).
\]

(a) Schematic representation of the procedure for obtaining, \(d(cpd)/dt\) as a function of temperature for constant \(cpd\) from oxygen-induced work function (cpd) transients, and (b) extraction of the associated activation energy related to oxygen chemisorption under conditions of constant band bending.

The studies performed by the Gatos group directly demonstrated the important role that sub-bandgap energy states play during chemisorption, confirming some aspects of the theory proposed by Vol'kenshtein. In addition, the studies revealed additional phenomena that were not captured by early theories, including a non-electronic activation energy needed to excite physisorbed species into metastable surface states that participate in chemisorption. While these techniques were very useful for investigating chemisorption phenomena at the surfaces of large, flat single crystal piezoelectric materials, they were not readily adapted to the investigation of smaller device structures, such as those used in chemical sensor studies, nor on non-piezoelectric materials.
2.3. Nanostructured Semiconducting Metal Oxide based Gas Sensors

2.3.1. Conventional Theory of Operation
Many studies into the mechanisms of chemical sensor operation exist, and over multiple decades the conventional theory of semiconducting metal oxide (SMO) based chemical sensor operation has been developed within an ever growing body of literature.\textsuperscript{41,42} The typical approach employs a thin SMO thin film deposited on two metal electrodes and an insulating substrate, depicted schematically in . The substrate is typically heated to a temperature of several hundred (300 to 500) degrees Celsius in order to accelerate the rate of chemical reactions that can occur between the SMO and the surrounding environment. The metal electrodes are used to probe the resistance of the SMO film as it is exposed to various gases of interest. The fundamental phenomenon that is observed in all studies of this system is the effect of changes in gas composition to change total conductance (or resistance) measured between the electrodes, which is monitored as the main output signal of the sensor structure.

![Diagram of SMO based gas sensor film](image)

Figure 12. A schematic representation of the typical SMO based gas sensor film, with expanded views of A) the center of the film, B) the film/substrate interface and C) the film/substrate/electrode interface. As shown, the film may exist as a dense/compact layer that only interacts with gas at the outer surface or a porous layer that is open to gas interaction throughout the film thickness. Reproduced from Barsan and Weimar.\textsuperscript{43}
The mechanism by which gas is known to change the conductance of the SMO layer has to do with interaction between the surface and the bulk of the SMO material and is heavily dependent on SMO composition and film morphology. In general, the gas is expected to react with the surface of the material in a chemisorption (or desorption) process that changes the amount of charge that is trapped at the SMO surface. If the surface is oxidized, then an electron is transferred from bulk to the surface; conversely, in the case of reduction an electron is transferred back to the SMO. The net result is that the trapped charge at the surface affects either an enhancement or depletion of charge carriers in the bulk, typically electrons in an n-type semiconductor, via electrostatic interactions that result from the Poisson equation and the requirement of overall charge neutrality of the material. Studies have been performed wherein the work function of the material surface has been monitored by means of non-contact Kelvin probe techniques, confirming that the magnitude of the surface potential barrier is modulated by changes in the ambient environment, as described in the conventional theory of sensor operation.

Figure 13. A schematic representation of the mechanism by which the surface of a compact sensing layer interacts with gas in the environment, impacting layer conductance as measured by a current flow applied in the x direction. Electric potential vs thickness is sketched in the case of a) a thicker layer that is depleted by an oxidizing surface reaction in only a fraction of the total film thickness and b) a thinner layer that is depleted throughout the entire thickness of the film. Reproduced from Barsan and Weimar.32

Since the sensing phenomenon of interest concerns a surface-to-volume interaction, particular attention is given toward the engineering of micro- and nanostructured materials that possess high surface areas that may be influenced by the gas environment. Typical structures of interest include dense thin films (on the order of tens to hundreds of nanometers in thickness), porous thick films (several microns thick) with nanograin structure, suspended thin film membranes,
nanowires and nanobelt structures. The importance of nanoscale characteristic dimensions in all of these structures is examined in detail in proceeding sections.

In consideration of the operation of practical sensors that may be readily used in portable, handheld devices that are robust in the detection of small amounts of gases in a range of operating environments, a common set of performance metrics are adopted, which are of common interest to all studies of SMO based chemical sensor phenomena: sensitivity, selectivity, speed and stability.

2.3.2. Sensitivity
Sensor performance is characterized by sensitivity, selectivity, speed and stability, all of which must be engineered together to achieve an effective device.

Gas sensor sensitivity is formally defined as the fractional change in measurable sensor output (sensor resistance or conductance) per unit of change in concentration of gas in the surrounding environment:

\[ S_G = \frac{\Delta G}{G_0 X} \text{ or } S_R = \frac{\Delta R}{R_0 X} \]  

Where \( S_G \) is sensitivity defined in terms of conductance, \( S_R \) is sensitivity defined in terms of resistance, \( X \) is concentration of gas being detected by the sensor (partial pressure), \( \Delta G \) is the change sensor in conductance (Siemens) and \( \Delta R = 1/ \Delta G \) is the change in sensor resistance (ohms) when it is exposed to the concentration (\( X \)) of gas, and \( G_0 \) is sensor conductance and \( R_0 \) sensor resistance in air without the analyte gas present. The choice of whether to characterize sensitivity by means of resistance or conductance in many studies in the literature depends upon whether the semiconducting metal oxide based sensor is n-type or p-type or whether the gas is oxidizing or reducing. In case of an n-type material being used to detect a reducing gas, \( S_G \) is often used, and for a p-type material detecting an oxidizing gas, \( S_R \) is often used. Fundamentally, sensitivity is reported for the steady state response of the sensor to a gas, once the initial response transients have subsided or in some cases, when the sensor has reached 90% of its final steady state value.

The derivation of sensitivity within a given system is the topic of extensive discussion in the sensor literature. In general, the thickness of the oxide film is known to have a strong influence on sensitivity, which can be divided into two main regimes:

- **a) \( t > L_{\text{Debye}} \):** low sensitivity regime, since only a fraction of the film thickness, \( t \), is nominally influenced by changes occurring at the surface.

- **b) \( t < L_{\text{Debye}} \):** high sensitivity regime, and charge carrier concentration throughout the entire thickness of the sensor film, \( t \), is influenced by changes in the gas environment.

A rigorous derivation of sensitivity can be obtained in consideration of the nature of various steps involved in obtaining the conductance or resistance signal as the output of the chemical sensor. Changes in gas composition influence a space charge distribution within the sensor bulk.
and hence the carrier concentration throughout the film. Sensor conductance may be obtained directly if the sensor film geometry and carrier concentration distribution are known precisely. I.e., the carrier concentration multiplied by carrier mobility should be integrated over every differential cross sectional element that exists between the conductive electrodes of the sensor to obtain a differential. By then integrating the contribution of these elements over the conductive path length between sensor electrodes, the total sensor conductance is obtained as a function of carrier density throughout the film volume. The task then remains to calculate differential change in sensor conductance as a function of change in gas composition, via these parameters' interdependence on charge carrier distribution within the film. However, due to the general complexity of device geometries used in practical sensor structures, such a calculation is nontrivial, and to date the proper treatment of this parameter has posed a challenge within studies of nanostructured semiconducting metal oxide based sensors.

2.3.3. Selectivity

Selectivity of a chemical sensor refers to its capability to accurately detect and identify a particular analyte of interest and reject other environmental factors that may also influence the response of the sensor. Selectivity can be quantified by considering the sensitivity of a sensor to two different stimuli, for example its sensitivity $S_A$ to an analyte of interest, gas $A$, and its sensitivity $S_I$ to an interferant, gas $I$. The selectivity of this sensor, $\Gamma_{AB}$, to gas $A$ over gas $B$ can be defined as the ratio,

$$\Gamma_{AB} = \frac{S_A}{S_B} \quad (28)$$

In a changing environment where there are multiple influences on the output signal of a single sensor, it is desirable to have a sensor that possesses high selectivity to a gas of interest, i.e. maximizing the sensitivity to gas $A$ while minimizing sensitivity to gas $B$. In this manner, the ideal sensor would respond to the phenomenon of interest while blocking all other influences that are not pertinent to the desired measurement. In practice, no detection scheme is perfect, and sensor technologies are often judged by their capability to fundamentally single-out the preferred gas reactions of interest.

Semiconducting metal oxides are generally not considered to be highly selective to individual gases of interest, due to the presence of many chemical reactions that may be promoted when the device is heated to elevated temperatures. Although the reactions that occur are determined by the composition of the semiconducting metal oxide and the chemical properties of the gas, it is difficult to distinguish one reaction from another in a sensor that has only a single output parameter, the sensor conductance. Even if individual surface reactions are not easily isolated or blocked in semiconducting metal oxide based sensors, it is clear that certain reactions may be promoted in favor of others in consideration of the impact that the Fermi energy has on the ability of the material to become oxidized or reduced. A material may be tailored to become more reactive to oxidizing gases by increasing the electron density of the material and moving
the Fermi energy closer to the conduction band. Similarly, a semiconductor with a higher density of holes would be more readily react with reducing gases that will donate electrons to the material.

Multiple approaches have been investigated in attempts to overcome inherent limitations in selectivity of semiconducting metal oxide based sensors, and perhaps the most widely used in the area of miniaturized, portable sensors, is the integration of multiple materials that each possess differing selectivity to gases in the environment. If the sensitivity and selectivity of multiple sensors are well characterized in response to gases that might be present in the environment, it becomes possible to identify the occurrence of individual gases among the set of possible environmental influences by examination of the relative magnitude of each sensor signal. Generally speaking, pattern recognition algorithms are utilized in analysis of the relative response that each sensor gives to a particular analyte, in order to properly identify and quantify the amount of gas present in the environment. In such a system, the orthogonality of sensors within an array of materials is discussed as the quality of individual sensors to possess high selectivity to an individual gas of interest that is different from the gases that other sensors within the array exhibit selectivity toward. Sensor arrays that have a higher degree of orthogonality are able to more accurately classify individual gases of interest. Since this thesis concerns primarily enhancements in performance of individual chemical sensor structures, the concepts of pattern recognition and orthogonality in the engineering of sensor arrays will not be further treated.

Other approaches towards improving selectivity of individual semiconducting metal oxide based sensors include the modulation of temperature as a means to modulate device sensitivity and selectivity to various gases. Less commonly, the use of illumination and the electric field effect have been recently investigated as a means to influence these parameters, and are addressed in detail in later portions of this thesis.

2.3.4. Speed

It is important for a sensor to respond as rapidly as possible to a gas of interest, especially in the case that the device is being used in an application related to personal health or public safety. Speed is generally defined as a fraction of the time it takes for a device to transition from one steady signal baseline to another steady baseline when the gas environment is suddenly changed. Sensor response speed is generally divided into two subcategories: response time (when the environment is subjected to a transition from clean air to air containing the analyte) and recovery time (when the analyte is suddenly removed from the open environment and replaced with clean air). In a semiconducting metal oxide based sensor, signal response time is determined largely by rates of chemisorption of gases and recovery time is determined conversely by desorption processes, which can be governed by different reaction pathways. The baseline signal output of a sensor at a given time is considered to be a steady state between multiple reactions that are occurring at the surface in an environment of a given gas composition. When the environment is changed, the rates of multiple reactions are shifted, which is why in general the response and recovery times may differ. Another trend often observed is that if a gas reacts strongly with a
semiconducting metal oxide, the sensor may exhibit a rapid response time and a sluggish recovery time, conversely the case if a gas only weakly interacts with the material.

Several approaches have been used to quantify sensor speed. An engineering approximation that is often used is to examine a sensor’s transient response to a gas and note the time that it takes for the output to reach 90% of its new saturated value as the response or recovery time. Another common approach assumes that the process of sensor response relaxation to a new baseline signal takes the form of a decaying exponential signal. The response profile in this latter case is assigned a characteristic response time that is obtained by curve fitting the transient signal to an exponential dependence of the assumed form:

\[ G = G_0 + \Delta G \left( 1 - e^{-\frac{t}{\tau}} \right) \]  

(29)

where \( G \) is the sensor output conductance, \( G_0 \) is the initial sensor conductance before the transition has occurred, \( \Delta G \) is difference in conductance between the starting and final stable baseline sensor signals, \( t \) is time and \( \tau \) is the characteristic sensor response (or recovery) time.

In general, \( \tau \) is observed to occur as a thermally activated parameter that may be governed by one or more reaction mechanisms. To resolve the transient sensor response in a complex environment with multiple reactions present, some analyses have attempted to extract multiple response time constants from the surface, in which case a signal is assumed to be comprised of a linear combination of multiple terms of the above exponential form. Separate resolution of individual time constants from a single response may provide insight into the changing properties of individual underlying mechanisms. In addition, by varying the temperature of a sensor and repeatedly measuring its response or and recovery time in each case, the speeds of multiple reaction pathways may be influenced, and the activation energies of multiple processes may be determined. Besides temperature, the use of illumination and electric field applied in the vicinity of the semiconducting metal oxide surface have been investigated as means to influence the speed of sensor response, as discussed later in this work.

2.3.5. Stability

Sensor stability refers to the ability of a sensor to exhibit a consistent, reproducible response to gases a prolonged period of time. Considering a device’s response to a fixed set of stimuli, stability is quantified as a percentage of change in sensitivity, selectivity, or speed between measurements. It is of great practical importance to obtain a high stability of any chemical sensor that is to be used in a commercial setting over a prolonged period of time. Because SMO based chemical sensors rely upon the advance characterization of a known, predictable device response to specific gases of interest, any instability serves to invalidate the accuracy of decisions that are made based on the sensor response. In this manner, a sensor that is unstable over time might fail to identify certain gases in some cases or exhibit a “false positive” reading, indicating that a gas is present when there is none. Clearly, such phenomena not only render the sensor useless but might create a dangerous situation if the device was being used in a critical
applications such as the detection of toxic materials in a user’s environment or monitoring the progress of a volatile industrial process.

Instability in the long term operation of chemical sensors based on semiconducting metal oxides is recognized as a difficult problem to overcome due to changes in device properties that are accelerated as temperature is increased. The relevant changes in materials properties can include microstructural evolution of a material due to surface diffusion and grain coarsening, defect segregation and phase separation within the SMO bulk, slow reactions at the SMO/electrode/substrate interfaces, irreversible reactions with surrounding gases at the surface of an SMO, and the diffusion and reaction of gas from the material surface in the bulk. An idealized approach towards engineering highly stable SMO sensors would involve fabrication of structures comprising materials that are close to equilibrium in their phase stability at the temperature of operation. Since any practical device will not be perfectly at equilibrium, attempts have been made to kinetically limit the evolution of device properties by adding dopants to inhibit defect segregation and diffusion from the surface to the bulk. However, such changes also influence the sensitivity of the structure to gases, giving rise to trade-offs between sensitivity and stability in the process of device design. This problem is particularly evident in the cases of nano-grained, nano-porous or nano-fibrous materials that often possess heightened chemical sensitivity that is characteristic of their small dimensions (as reviewed in the proceeding section). These same structures also may exhibit more rapid changes in morphology due to higher driving forces for surface diffusion and grain boundary migration that exist along surfaces and interfaces of higher curvature.

It is clear that by reducing the temperature of operation of a semiconducting metal oxide based sensor, the stability of its operation may be improved by the simultaneous action of a number of underlying driving mechanisms. However, reductions in temperature also generally reduce the speed of sensor operation, due to the fact that the chemisorption reactions that govern device response time are thermally activated. There is a direct trade-off between speed and stability in selection of sensor operating temperature, and although a device may become much more stable at lower temperature, its response may become too slow for the device to be of practical use. Therefore, it is of great interest to find alternative means to accelerate the rate of the sensor response at lower temperatures of operation. Two such routes for influencing the rate of sensor response include the use of illumination to photoexcite specific surface reactions of interest and the use of electric fields to modify the degree of adsorption.

2.3.6. Enhanced Sensitivity at Nanoscale

The sensitivity of an SMO wire, film or porous layer to various gases depends on the fraction of the conductive channel modulated by the gas adsorption. It thus becomes obvious that sensitivity should depend on the ratio of the space charge to the conductive channel width. As discussed earlier, the penetration depth of the depletion region is closely related to the Debye length and ranges from tens to hundreds of nanometers for typical semiconducting metal oxides of interest. Thus, it is on the scale of nano-patterned features that enhancements to sensor
performance become significant. Many groups are exploiting novel processing techniques to achieve desired porous, hierarchical nanostructures that enable strong interaction of the sensor material with the surrounding environment. Several examples are briefly discussed below illustrating the anticipated trends with scale.

A common method for creating nano-grained porous structures is by sintering ceramic powder at reduced temperatures allowing individual grains to begin to form sinter necks with neighboring grains while maintaining overall porosity. The average grain size and porosity of the final product depend on the initial grain size of the starting powders and the sintering parameters such as temperature, pressure, and atmosphere. Xu et al. prepared SnO$_2$ based chemical sensors with average grain size ranging from 5 to 32 nm and reported significant improvements in sensitivity to both H$_2$ and CO for grain sizes below 10 nm.\textsuperscript{45} Later, Rothschild and Komem confirmed that Xu's results were in quantitative agreement with a sensor response model based on modulation of surface depletion layers.\textsuperscript{46} As predicted by the model, the trend in sensitivity is proportional to the surface to volume ratio, i.e. proportional to $1/D$ in the case of spherical grains, where $D$ is the characteristic grain diameter. Model predictions are shown plotted together with experimental data below, in Figure 14.

![Figure 14. Response of nanoporous SnO$_2$ elements to 800 ppm H$_2$ or CO in air at an operating temperature of 300°C as a function of the reciprocal diameter of the grains. Reproduced from Rothschild and Komem\textsuperscript{46}.](image-url)

The popularity of carbon nanotubes (CNT) has inspired, in turn, numerous means for preparing quasi-1D metal oxide nanostructures.\textsuperscript{47} This has included the preparation of nanofibers, wires, belts, tubes, and springs\textsuperscript{48,49} with the ability, quite often, to control the size, composition, and electronic properties of the metal oxide nanostructures during growth.\textsuperscript{50} Synthesis methods for metal oxide nanofibers have focused on electrospinning\textsuperscript{51,52} or vapor-liquid-solid and vapor-
solid growth with ability, in some cases, to incorporate longitudinal and coaxial heterostructures. Examples of recent efforts specifically directed towards metal oxide nanoscaled devices for gas sensing are summarized in the literature. Similar to the case of nano-grain chemical sensors, device sensitivity increases as nanowire diameter decreases, as illustrated in Figure 15 for oxygen detection by ZnO nanowires. Although such nanowires are highly sensitive, they are difficult to grow and contact reproducibly. Consequently, alternative methods for achieving wire or fiber like structures have been investigated. An alternative approach has been the preparation of nanofiber mats by electrospinning. These tend to be of larger diameter and more complex microstructurally, being polycrystalline and often porous (Figure 16). Nevertheless, they can also exhibit high sensitivity while remaining structurally robust and easy to contact.

Figure 15. ZnO nanowire sensitivity to chemisorption of 20% oxygen, as a function of nanowire radius. Sensitivity is defined as $\Delta G/G_0$, where $G_0$ is conductance of the nanowire in an environment of in $10^{-2}$ Torr vacuum and $\Delta G$ is change in nanowire conductance when it is exposed to 20% oxygen at atmospheric pressure. From: Fan and Lu.
Next moving to two dimensional structures, one would imagine that very thin films should be exceptionally sensitive given that the width of the space charge layer becomes comparable to the thickness of the film. Surprisingly, this is often not the case. The authors suspect that this is due to the space charge layer emanating from the substrate - film interface that largely pins the carrier density in the film. Consistent with this hypothesis, very thin films grown onto microsphere templates, which served to lift the films off of the substrate (Figure 17), indeed showed markedly enhanced sensitivity to hydrogen as compared to the identical film deposited onto a flat substrate.  

17. a. Hollow microsphere templated thin films of macroporous CaCu₃Ti₄O₁₂ made up of grains on the order of 30 nm. b. Relative conductance response to H₂ gas of CaCu₃Ti₄O₁₂ films grown on flat vs a microsphere templated surface. From Kim et al.  

Figure 16. a. As-spun TiO₂/PVAc 200~500 nm diameter fibers. b. Following calcination at 450 °C, 30 min, bundle structure of anatase TiO₂ composed of sheaths of 200~500 nm, cores filled with 10 nm fibrils. From Kim et al.  

Figure
2.4. Amorphous Oxide based Gas Sensors

2.4.1. Background on Amorphous Oxide Semiconductors
Amorphous semiconductors have come into widespread use in many applications due to unique properties that they exhibit in contrast to their crystalline counterparts. For decades, the conventional approach toward semiconductor engineering included fabrication of high purity materials that relied on long-range order to achieve the necessary properties. Disruption of the crystal lattice can result in decreased carrier mobility, creation of mid-gap trap states that reduce free carrier concentration, and breakdown of delocalized electron orbitals that comprise the semiconductor energy band structure. However, amorphous semiconductors retain short range order and overlapping orbitals that provide a conducting path among neighboring atoms. The introduction of amorphous silicon was enabled by a process of hydrogenation to passivate deep trap states, freeing charge carriers to conduct within overlapping orbitals. Although certain electronic properties are degraded, amorphous semiconductors possess key advantages that have spurred their widespread use:

- Uniformity and homogeneity of materials properties over wide area due to isotropic material structure and absence of grain boundaries
- High strain tolerance due to ability of short-range ordered material to restructure and absorb mechanical work without propagating cracks
- Low temperature processing sufficient to obtain the amorphous material phase
- Compatibility with polymeric substrates due to low processing temperatures
- Compatibility with sol-gel and solution based processing techniques such as spin coating, screen printing, and ink jet printing
- Reduced fabrication costs

Due to these advantages, amorphous semiconductors have found increasing use in commercial electronics, especially devices that require wide coverage areas at low cost. Photovoltaic solar cells based on amorphous materials are often more cost effective than crystalline solar panels, when installed in high volume. Field programmable displays based on LCDs utilize amorphous thin film transistors to turn pixels on and off. Due to their high strain tolerance and low processing temperature, amorphous semiconductors are also used in conjunction with flexible electronics and polymeric substrates.

2.4.2. High-Mobility Amorphous Oxides
In the mid 1990’s, amorphous oxide based semiconductors were realized to hold significant advantages over conventional amorphous silicon based devices, by means of significant increases in electronic mobility. In the case of a covalently bonded semiconductor such as silicon, the conduction and valence bands arise as a result of overlap between sp hybridized molecular orbitals. These orbitals are highly directional according to octahedral coordination of silicon’s diamond cubic structure, and once the material enters an amorphous state, disordering of the crystalline structure tends to reduce overlap between adjacent orbitals, resulting in
significant scattering of charge carriers. In contrast, oxide based semiconductors are formed from ionic bonding between metal cations and oxygen anions. The conduction and valence bands of a semiconducting metal oxide typically correspond to empty states of metal Ns orbitals \( (N > 2) \) and filled states of oxygen 2p orbitals, respectively. Since the s orbitals of the cations are spherical in shape, they are by comparison robust against disordering and able to retain a high degree of overlap even in the amorphous phase. This effect is further enhanced in the case of heavy metal cations that bond at longer lengths via additional higher s orbital shells. The comparison between an ionically bonded oxide based semiconductor in the crystalline vs. amorphous states is illustrated schematically, below (Figure 18).

![Figure 18. Comparison of an ionically bonded oxide based semiconductor in crystalline and amorphous states.](image)

In addition to increased mobility, amorphous metal oxide based semiconductors are further advantageous in many applications due to the large bandgap of the material, typically in the range of 3 eV. In the case of TFTs used in display technology, amorphous silicon based transistors may absorb light that is generated within the display, reducing output efficiency and also contributing to transistor aging over time. Since an amorphous oxide will not absorb visible light via a band-to-band electronic transition, it can be placed in close contact with devices that must maintain a high optical output efficiency. At the same time, the semiconductor bulk can remain stable under intense visible illumination due to low level photon absorption. For these reasons, amorphous oxide semiconductors have now become the material of choice in many applications and have begun to penetrate commercial markets for field programmable displays and flexible electronics.

### 2.4.3. Indium Gallium Zinc Oxide (IGZO)

In 2004, amorphous Indium-Gallium-Zinc-Oxide (a-IGZO) was discovered to possess particularly high carrier mobility within the class of amorphous oxide based semiconductors\(^{63}\), leveraging a large body of research which had previously been performed on polycrystalline ZnO based devices. At that time, ZnO had already become a strong candidate material for usage
in the flat panel display industry. TFTs based on ZnO were perceived as particularly advantageous in display applications, due to a relatively high electron mobility of the bulk material, combined with its wide bandgap that renders it transparent to visible light. However, polycrystalline ZnO suffers from the previously mentioned drawbacks resulting from grain-boundary related scattering, which results in mobility significantly lower than that of the single crystalline material.

a-IGZO improves upon polycrystalline ZnO with the addition of In$_2$O$_3$ and Ga$_2$O$_3$, which stabilizes the amorphous phase of the material at room temperature and over a wide range of compositions. As shown in the left chart of Figure 19, although ZnO is stable in crystalline form at room temperature, small additions of In$_2$O$_3$ and Ga$_2$O$_3$ result in an amorphous material. On the right hand side of Figure 19, mobility and carrier concentration of various compositions are shown. In general, a higher ratio of indium contains the largest mobility and carrier concentration, while higher concentrations of gallium show the lowest values of these parameters. An key benefit of including gallium in a-IGZO is that it functions as a carrier killer, tending to accelerate switching times when integrated into a TFT based device structure.

![Figure 19. Left: Ternary phase diagram of the ZnO-Ga$_2$O$_3$-In$_2$O$_3$ system (comprising IGZO) at room temperature. Right: corresponding mobility in cm$^2$/Vs.](image)

The following table provides a comparison of performance thin film transistor parameters based on amorphous and polycrystalline silicon versus similar devices formed from amorphous IGZO.

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61
2.4.4. Atmospheric Sensitivity of IGZO

During the course of many studies that followed its initial discovery, a-IGZO was later found to exhibit a gradual change in electronic properties over time when exposed to open air during device operation.\textsuperscript{66,67} Among the parameters observed to change, the TFT threshold voltage was shown to shift over time, which is particularly problematic for stable operation of transistors in logic circuitry, and was a primary problem in the early fundamental research of Ge based logic devices in the 1950s. In the case of a-IGZO, the shift in threshold voltage was shown to occur more rapidly during operation at higher levels of gate bias and at higher temperatures. To remedy these effects, the devices are often subjected to high temperature anneal parameters to accelerate device aging and stabilize the electronic properties of the material. In addition, the instabilities were conclusively linked to exposure of the semiconducting film to the open environment, and as a result a passivation layer is often used to shield the material from the open environment.\textsuperscript{65}

Besides changing the bulk material properties, further studies have linked the shift in threshold voltage to changes in density of occupied electronic states within the sub-mobility gap energy levels of the amorphous semiconductor, as opposed to a change solely in bulk properties. The technique used to determine this figure includes measurement of device capacitance over a range of frequency and DC bias applied from TFT gate to source, i.e. a $C-V$ measurement. In some of these studies, it was suggested that the subgap occupied electronic states are physically located at the interface between the semiconductor material and the gate electrode of the device.\textsuperscript{68} However, it is also possible that such electronic states arise from interaction of an exposed surface of the a-IGZO with the open environment. At least one study has suggested that a
depletion region related to oxygen adsorption may arise below the surface of the semiconductor, further highlighting the need to employ a passivation layer in the case of practical devices being used in TFT based display technology. 69

2.4.5. Advantages of Amorphous Oxide based Gas Sensors
It is important to note that a gas sensor derived from an amorphous semiconductor may also benefit from the key features of amorphous semiconductors in several ways. Improved uniformity of materials properties from device to device translates into higher reproducibility of sensor response, resulting in more reliable measurements. High strain tolerance further improves device reliability and ruggedness as a sensor is handled in portable applications or subjected to mechanical torture. The ability to deposit materials on flexible substrates and at low temperature broadens the landscape that sensors may cover and supports the vision of intelligent, pervasive devices that are deeply integrated with everyday human life. Flexibility in the selection of processing technique at low cost also results in a strong potential for commercialization. All of these reasons make amorphous semiconductors an attractive materials system to investigate for the development of low-cost, portable, and reliable gas sensors.

It is important that for the purpose of taking conductivity measurements, the electronic mobility of the material be as high as possible. This property lends the material to electrical measurement via DC probing techniques. To this end, a-IGZO is relatively unique by comparison to other amorphous semiconductors, it maintains a relatively high mobility while in the amorphous material phase.

Lastly, while the instability in TFT properties to exposure to gases, viewed as a negative phenomenon in the case of flat panel displays, is largely avoided via use of passivation layers, it identifies a potential of this material for use in gas sensing applications. Given its sensitivity to oxygen, it suggests similar sensitivity to other oxidizing gases. Nevertheless, this material has not been actively studied, to date for use as a gas sensor.

2.5. Thin Film Transistor (TFT) based Gas Sensors

2.5.1. Control of Fermi Energy at the Semiconductor/Substrate Interface
The Fermi Energy of a semiconducting material plays a critical role in the determination of the nature and amount of gases that chemisorb at the material surface. Precise control of material structure and composition are necessary in order to reproducibly position the Fermi Energy at the surface of the as-deposited semiconducting metal oxide film. These materials’ properties are largely defined in the fabrication process utilized to deposit the semiconducting material; often difficult to precisely control from run to run. For example, surface contamination existing on the substrate prior to film deposition may influence the position of the Fermi Energy via creation of buried charge at the semiconductor/substrate interface. In addition to sensitivity to fabrication parameters, the Fermi Energy is also influenced by the ambient operating conditions of the sensor, including temperature and atmosphere. Under conditions of illumination and electric
field, the system is perturbed from equilibrium and one can turn instead to consideration of how these externalities impact the quasi-Fermi energy.

The typical means of operating a semiconducting metal oxide based sensor includes heating of the device to elevated temperature (200 to 400°C), to accelerate the rate of chemisorption of gases at the device surface. The process of chemisorption includes the transfer of electronic charge from the semiconductor bulk to an electronic state of a chemically bound molecule (typically ionically bound) at the device surface. In SMO sensor operation, a key parameter is the relative number of electronic charge carriers in the material bulk available to participate in the chemisorption reaction at the surface of the device. In equilibrium (or quasi-equilibrium, when recombination rates are equal to generation rates and there is no carrier motion), the charge carrier concentration within the bulk is determined by the position (energy with respect to the conduction band edge) of the Fermi Energy with respect to the density of electronic states that exist within the material, e.g. as in the case of a non-degenerate semiconductor:

$$n = N_e \exp \left( \frac{E_C - E_F}{kT} \right)$$

(30)

Through its influence on charge carrier density, the position of the Fermi energy (or quasi-Fermi energy) governs the amount of chemisorption that may occur. Conversely, the chemisorbed charge at the SMO surface influences the Fermi Energy of the underlying SMO material by an induced space charge distribution that satisfies Poisson’s equation and the requirement of overall charge neutrality.

Among the available techniques for control of the (quasi) Fermi energy is the ability to utilize the electric field effect of a thin film transistor (TFT) presents a unique opportunity for rapid, programmatic enhancement to device performance in a compact electronic device structure. Thin film transistors are heavily studied for use in other applications besides sensing, and in these cases, preventative steps are frequently taken to ensure that the semiconducting bulk of the device does not interact with the surrounding environment. Figure 22 is taken from a review of typical TFT structures that have been investigated in the application of flat panel displays, and one structure that includes an exposed outer surface of the semiconductor is noted to exhibit significant instability in device properties as it interacts with the surrounding environment during device operation. In the case of a TFT based sensor, an exposed surface of the SMO conducting channel enables an interaction with the environment that is utilized to detect the presence of gases via chemisorption and changes in conductance of the channel. The sensor output is defined as the change in conductance of the semiconducting channel (from source to drain) in the TFT. Unlike thin film resistor based sensors whose sensitivity is fixed, an applied voltage bias from gate to source and/or drain of a TFT serves to modulate the charge carrier density in the channel and thereby enables the modulation of the sensitivity of the device.
Figure 21. (left) Energy band structure associated with thin film transistor type semiconducting metal oxide based chemical sensor, (Middle) transistor structure with gate bias applied, inducing electron accumulation and population of surface states. (Right) modified energy band structure associated with increased population of surface states associated with chemisorption, resultant from applied gate bias.

Top gate, top contact

Bottom gate, top contact

Inverted Staggered (etch stopper)

Inverted Staggered (channel etch)

Figure 22. Example of several thin film transistor (TFT) device structures that have been investigated with primary application in flat panel display systems. Counter-clockwise from the top-left, the “top gate, top contact”, “Inverted Staggered (etch stopper)” and “Inverted Staggered (channel etch)” with the latter two designs including blocking layers to isolate the semiconducting channel from the open gaseous environment. The final design shown at top-right (Bottom gate, top contact) exposes the semiconductor surface to air and can be used as a functioning gas sensor.65
2.5.2. TFT Concept of Operation

To understand the operation of a buried-gate thin film transistor (TFT) based gas sensor, it is instructive to begin by reviewing the operation of a well known model system: the long-channel field effect transistor (FET). A brief review of the long-channel FET is presented, within which the essential device-level parameters of interest are derived from the electronic properties of the metal-oxide-semiconductor heterostructure. In consideration of a simplified geometry, the differential equations resultant from the underlying physics governing the system may be further simplified into analytical expressions, providing insight into the relationship between materials properties, device dimensions, and operating conditions representative of a practical device structure. Furthermore, the application of analytically or numerically parameterized relationships between measurable properties of the FET provide the essential capability to perform carefully controlled experiments on the FET, the output of which are utilized to derive physical properties of the device. Key differences between the long-channel FET and buried-gate TFT, relevant to our investigation of TFT based gas sensors, are then considered.

The metal-oxide-semiconductor field effect transistor (MOSFET) is a fundamental building block in nearly all applications of analog and digital microelectronics. It is a three-terminal device consisting of a gate, source and drain; and the conductance from source to drain is determined by the amount of voltage applied from gate to source. In the case of analog circuitry, MOSFETs are frequently used as a high input-impedance amplifiers. In digital electronics, the device operates as a switch, within which the conducting channel from source to drain is turned on or off when the gate bias is switched from low to high or high to low voltage. A key feature of the MOSFET is the very high resistance from the gate to the source and drain, the insulating gate oxide layer providing this essential function. A schematic of the typical MOSFET transistor structure and I-V characteristics are shown in Figure 23.

Figure 23.(a) Schematic representation of a long-channel MOSFET structure. S, G, and D denote source, gate, and drain regions, respectively. As pictured, the semiconducting bulk is formed from p-type Si, with N+ wells implanted in the source and gate regions. Shaded regions indicate metal contacts, and an insulating gate oxide layer is present under the gate metal contact.
An idealized plot of drain current $I_D$ versus drain voltage $V_D$ as a function of gate bias $V_G$ is shown. Reproduced from Pierret.\textsuperscript{14}

A device is considered to be a “long channel” FET if the length of the conducting channel is much larger than the Debye length of the material. In this case, any depleted semiconductor region surrounding the source and drain contacts are not overlapping with one another, and the extent of the depleted zone in these areas is negligible relative to the overall distance separating the source from the drain. A charge-sheet approximation is made, in which the induced conductive region below the gate electrode consists of a layer of charge at the semiconductor/oxide interface, which extends in two dimensions. Electrical properties formally resultant from the charge sheet approximation and other assumptions appropriate to the long-channel MOSFET are presented in the following.

\begin{equation}
V_T = 2\phi_F + \frac{K_S x_o}{K_O} \sqrt{\frac{4qN_A}{K_S \varepsilon_0} \phi_F} \tag{31}
\end{equation}

and

\begin{equation}
\phi_F = \frac{1}{q} \left[ E_{(\text{bulk})} - E_F \right] \tag{32}
\end{equation}

where $K_S$ is the semiconductor relative permittivity, $K_O$ the oxide relative permittivity, $x_o$ the oxide thickness, $q$ the elementary charge, $N_A$ the concentration of acceptor doping in the p-type semiconductor substrate, and $\varepsilon_0$ the permittivity of free space. Capacitance across the oxide per unit area of the gate, $C_o$, is given by

\begin{equation}
C_o = \frac{K_O \varepsilon_0}{x_o} \tag{33}
\end{equation}

Consider two parameters that are of critical importance to the operation of the MOSFET as a switching device in logic and memory applications:

\begin{equation}
g_d = \frac{\partial I_D}{\partial V_D} \tag{34}
\end{equation}

and

\begin{equation}
g_m = \frac{\partial I_D}{\partial V_G} \tag{35}
\end{equation}

where $g_d$ is the channel conductance and $g_m$ the transconductance.

As the MOSFET switches between the OFF and ON states, it is desirable for $g_d$ to be as high as possible, in order to maximize the characteristic frequency $f_{out}$ associated with output switching and enable rapid device operation.

\begin{equation}
g_{d,mi} = \frac{Z \mu_C C_o}{L} (V_G - V_T - V_D) \tag{36}
\end{equation}

and
\[ f_{out} = \frac{g_{d,tri}}{C_{out}} , \]  

where \( C_{out} \) is a capacitive load connected at the output of the.

When the device is in the cut-off regime, \( g_m \) will also ideally be zero. Within the triode (transition) and saturation (ON) regimes, \( g_m \) is given as

\[ g_{m,tri} = \frac{Z\mu_s C_o V_D}{L} \]  

and

\[ g_{m,sat} = \frac{Z\mu_s C_o (V_G - V_T)}{L} . \]  

The cut-off frequency that limits the speed of charging and discharging the MOSFET gate (and thus the MOSFET switching speed) is derived from the transconductance and the oxide capacitance, given by

\[ f_G = \frac{g_m}{2\pi C_o} , \]  

where

\[ C_o = \frac{K_o \varepsilon_o Z L}{x_o} . \]  

2.5.3. **Electroadsorption**

Electroadsorption is a known effect in semiconducting metal oxide based gas sensors and concerns the influence of electric field on adsorption at the surface of a material. Numerous different types of sensors have been proposed that utilize this effect or related effects, including\(^70\):

1) Structures that utilize MEMS processing technology to fabricate an electrode in close proximity (nanometers to microns distance) to a SMO film used to modulate the level of chemisorption on the film.

2) Thin film transistor (TFT) structures that make use of a buried gate electrode to apply an electric field across the entire thickness of a very thin SMO film, thus impacting energy band bending and associated chemisorption processes at the free surface of the film.

The buried gate TFT based approach has some advantages over other techniques e.g. avoidance of the complexity of a microchannel electrode. To date, the buried gate thin film transistor based chemical sensor has been the topic of a growing number of studies.
Recently, separate studies were performed that explore the changes in sensitivity and selectivity of a SnO$_2$ based chemical sensor by application of gate bias, in thin film transistor and nanowire transistor based test structures. Both studies propose analytical models to support experimental data. However, in both cases the complex recursive relationship between surface charge and electric potential in the nanoscale device was neglected.

In other work, the electronic properties of a-IGZO based TFTs have been modeled in detail, utilizing an iterative scheme to apply finite difference models to the structure in multiple dimensions. Here, the authors accounted for the influence of sub-gap density of states of the amorphous material in creating charge screening effects within the conducting channel. However, this work treats the semiconductor simply as a “floating potential” surface, with no consideration for induced chemisorption.

Very recently, an article has been reported concerning the use of amorphous InGaZnO$_4$ thin film transistors as a room temperature chemical sensing platform. The authors achieved this by coating the surface with polymeric materials including CuPc, which absorbed gases from the air. In this case, the polymer acts as a second gate to the transistor structure, and the operation of their device is not explained via chemisorption processes, and the sensor is in fact not an electroadssorption based device.

Besides electric field effects, other approaches have been taken in recent literature to modulate chemical sensor electronic properties, including the use of illumination to enhance sensor operation. Researchers have used illumination in order to induce desorption, for example, enabling detection of NO$_2$ gas at room temperature with illuminated SnO$_2$ thin films sensors. Kelvin probe measurement techniques are also being used in the study of illumination effects on the operation of chemical sensor systems. These studies are largely qualitative but do reveal changes in energy band structure and electronic state population associated with the chemisorption of various gases.

Another related technique is the addition of noble metal based catalyst materials at the surface of the sensor.

In general, there is a great need for more careful studies that employ simultaneous control of multiple sample conditions that are known to influence chemisorption, including illumination, band bending, temperature, and gas environment. It is only then that it will be possible to employ fundamental models of chemisorption in the context of engineering chemical sensors and other practical device structures.

Although some reports regarding field effects on gas sensor behavior have been published in the literature to date, a great need still exists for detailed models that capture the complex interactions between the semiconductor and the gas at the surface of semiconducting metal oxides, in particular in the case of nanoscale device dimensions.
3. Thesis Goals

To address the need for a deeper understanding of the mechanisms of chemisorption on the surface of semiconducting metal oxides and realize the potential of such knowledge to enable the better engineering of practical devices, this thesis seeks to 1) develop computational models that couple semiconductor physical properties with surface chemistry in practical device structures and 2) utilize precise experimental control designed to isolate various environmental influences. It is the hope of the author that insight gained in this study may be applied in the engineering of chemical sensors with improved sensitivity, selectivity, and power consumption, beyond the conventional devices that are used today.

In the process of synthesizing a general understanding of sensor operation, a fundamental model of chemisorption is developed and applied to understand the performance of a diverse set of test structures in response to multiple types of environmental stimuli. The primary goal of the sensor model is to account for the relationship between the electronic properties of the semiconductor bulk and the occurrence of chemisorption at the semiconductor surface, in the presence of various environmental influences that impact the operation of a chemical sensor. In this process, a gas may either oxidize the surface by accepting an electron (creating localized negative charge) or reduce the surface by donating an electron (leaving behind localized positive charge), and the amount charge transferred is a function of the Fermi energy of the material. Conversely, trapped charge at the surface of the material, in turn, influences the magnitude of electric fields present near the surface and causes semiconductor band bending near the surface. Hence, there is a nontrivial, recursive relationship between mobile charge carrier concentration in the sensor bulk and trapped charge density at the surface of the chemical sensor. These effects are numerically simulated in detail on device structures of practical dimensions, using finite element model techniques. The modeling portion of this thesis work seeks to establish a formal description of the amount of chemisorption that occurs based on materials properties, gas properties, and environmental stimuli including temperature, illumination, and applied voltage. To this end, a systematic approach is adopted for analysis of systems of increasing complexity in the following manner:

1) Identification of the relevant physical and chemical interactions, closed form and differential equations, and analytical evaluation of simplified structures.
2) Formulation of a one dimensional finite element model for numerical analysis of the performance of practical device structures under realistic operating conditions.
3) Investigation of the effects of variation in the modeled parameters.

The electrochemical interaction between the surface and bulk of the model sensor structure is evaluated explicitly, including the effect of the trapped charge at the surface to induce changes in sensor conductance, and the effect of an applied transistor gate bias to induce changes in chemisorbed surface coverage. Numerical modeling of this nature is an essential component of
this thesis work, as some of the resultant conclusions would not be obvious and not directly obtainable without such tools.

Furthermore, in the proceeding experimental portion of this thesis, real devices are characterized and compared to numerical simulation results. The performance of semiconducting metal oxide based chemical sensors is investigated in a number of practical nanostructures, and devices are engineered for enhanced performance by means of several non-conventional approaches:

1) Use of thin film transistor based structures to programmatically influence sensor electrochemical properties and modulate sensitivity, selectivity, and speed; at the same time, reducing operating temperatures and increasing device stability.
2) Use of amorphous oxide materials to improve device uniformity and stability while at the same time enhancing sensitivity and speed
3) Use of illumination to photoexcite electronic charge carriers within the sensor material and programmatically modulate sensitivity, selectivity, and speed of operation at reduced temperature.

A strong emphasis is placed on novel experimental techniques for the investigation of the above effects in fabricated chemical sensor structures. Several new environmentally controlled test chambers have been designed, constructed, and utilized to enable characterization of device properties relevant to the performance of chemical sensors. In addition, custom software was developed and used to vary environmental conditions systematically and parameterize sensor response to a range of stimuli. Extensive characterization of device properties was enabled by means of automated experimental control systems that were developed during this thesis work, including:

1) A highly parallelized sensor test stand for characterization of up to 8 sensor structures simultaneously under identical environmental conditions including control of temperature up to 400°C, gas composition in parts-per-million and electronic resistance measurement.
2) A highly miniaturized test stand (1 cm³ chamber) for rapid changes in gas composition, temperature control above 500°C, programmatic modulation of electric fields within a transistor based sensor and automatic extraction of transistor electronic properties.
3) Environmentally contained, illumination controlled sensor test chamber for programmed exposure to broadband and scanned monochromatic light of energy ranging from IR to UV, with integrated microheater platform and software control.

Together with novel device structures, systematic experimental control, and an analysis approach that integrates insight from numerical simulations, this thesis seeks to demonstrate a major step forward in the general approach to chemical sensor research and further illuminate fundamental mechanisms related to chemisorption phenomena on nanostructured semiconductors.
4. Experimental Setup

4.1. Model Systems

To investigate the influence of chemisorption under conditions of controlled levels of band bending, the author makes use of lithographically defined model thin film resistor (TFR) and transistor (TFT) structures with reproducible dimensions and electronic properties. While transistor based structures provide an added level of control over device properties through use of the field effect, resistors have the added benefit of being simpler to fabricate and measure. All devices in the present study consist of a semiconducting metal oxide (SMO) thin film that is exposed to the open gas environment. In some cases, the SMO film has been fabricated with a porous nanostructure that enhances its interaction with surrounding gases, and in other cases the film is dense and lies flat on the underlying substrate. Beneath the SMO film are two electrodes that are used to measure film electrical resistance, labeled “source” and “drain” in the case of TFT structures. The electrodes and SMO film are deposited onto a thicker substrate material that is provided for mechanical support and electrical isolation of the sensor from external forces, made of alumina in the case of some samples and a thin layer of SiO₂ on Si in other samples. In the case of TFTs, the underlying Si is conductive and serves as a buried gate, an electrical contact to induce variations in the conducting channel by application of electric field across the SiO₂ insulating layer. By utilizing a sufficiently thin semiconducting film (on the order of 70 nm), the electric field induced via the gate electrode is can induce changes in band bending at the exposed surface of the semiconducting channel, enabling an impact on chemisorption processes to be realized.

Two semiconducting metal oxide systems have been selected for study: zinc oxide (ZnO), and InGaZnO₄ (IGZO). ZnO was selected given that 1) it is known to be sensitive to many gases and have been studied extensively as chemical sensors and 2) their electronic and optical properties are well characterized. InGaZnO₄ (IGZO) is an amorphous semiconductor system that has recently been the subject of many investigations given its transparency in the visible and it relatively high electron mobility, features of interest for the display industry. Our research group recently discovered that IGZO reacts with several gases at temperatures significantly lower than that of ZnO, a feature of general interest. Besides the variation in selection of materials composition (ZnO, IGZO) and device design (thin film resistor vs. transistor) certain of the thin film resistor devices were further modified via deposition on a sacrificial template that enabled formation of suspended, highly porous sensor films that are more open to surrounding gases. In the proceeding sections, the preparation of each of the different types of samples studied in this thesis work is described in detail.

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b Y.S. Jin, H.L. Tuller, Toxic Gas Sensors using Thin Film Transistor Platform at Low Temperature, 2009 M.S. Thesis, Department of Materials Science and Engineering, MIT.
4.2. Sample Preparation

4.2.1. Amorphous InGaZnO$_4$ Thin Film Resistors

Amorphous InGaZnO$_4$ sensors were prepared for the purpose of studying chemical sensitivity at elevated temperature.\(^c\)

All sensors in this study utilized Au interdigitated electrodes that were deposited and patterned on an Al$_2$O$_3$ substrate, the electrode pattern consisting of individual fingers that were 200\(\mu\)m wide and spaced apart by 200\(\mu\)m. In the case of microsphere-templated InGaZnO$_4$, PMMA microspheres of diameter 0.8\(\mu\)m were first suspended in a mixed solution of deionized water and ethanol (3 wt \% PMMA) and treated with ultrasonic vibration with 20 minutes to obtain a uniform dispersal. The mixture was then deposited onto the electrode pattern via micropipette. Following the deposition, the samples were dried in a dessicator at room temperature.

Following preparation of sample substrates (with and without microspheres) both types of samples were loaded into a sputtering chamber. Thin films were deposited on Al$_2$O$_3$ substrates containing Au interdigitated electrodes via RF magnetron sputtering from an InGaZnO$_4$ polycrystalline target. The sputtering was performed at room temperature, which in the case of InGaZnO$_4$ results in films that are amorphous in nature. Samples were deposited as thin films and also using a PMMA microsphere colloidal template in the same manner that SnO$_2$ samples were deposited. In addition, separate samples were fabricated at two different film thicknesses: 100 and 200 nm. Following deposition, samples were annealed at 450°C to remove the PMMA template. As shown in the results section, the InGaZnO$_4$ remained amorphous through the annealing process. The variation types of samples are depicted schematically in Figure 24.

![Figure 24. Schematic representation of thickness and morphology variation of the amorphous InGaZnO$_4$ based thin film resistors.]({"type":"image"})

\(^c\) Amorphous InGaZnO$_4$ based thin film resistors were fabricated by collaborators at KAIST.
InGaZnO₄ based chemical sensors: a) 100nm thin film b) 200nm thin film c) 100nm microsphere templated film and d) 200nm microsphere templated film.

4.2.2. Amorphous InGaZnO₄ Thin Film Transistors

The InGaZnO₄ materials system was further utilized as the semiconducting channel material in model thin film transistor (TFT) device structures. Devices were patterned with a general layout of device features as depicted schematically in Figure 25. The fabrication process began with a heavily p-doped silicon wafer that is used as the bottom gate electrode of the TFT. 100nm of thermal silicon oxide was grown uniformly across the wafer surface, to provide the insulating gate oxide material. Then, a 70nm thick layer of InGaZnO₄ was deposited via sputtering and patterned to provide the conducting channel material utilized in all devices within the present study. The thickness was selected at 70nm in order to provide a sufficiently thin layer to enable the gate bias to influence conductivity throughout the entire thickness of the film. The final step of sample preparation included deposition and patterning of Pt metal with a Ti adhesion layer as source and drain electrodes. As a variable parameter in the fabrication process, conducting TFT channels were created possessing width in the range of 10 to 300 μm and length in the range of 2 to 20 μm, as indicated in Figure 26.a.

Figure 25. Schematic depiction of model InGaZnO₄ TFT device structure, a) cross sectional view and b) top-down planar view.

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Amorphous InGaZnO₄ thin film transistor structures were provided by Dr. Il-Doo Kim at the Korea Institute of Science and Technology and originally studied within our research group during earlier Master’s thesis work of Yoon-Sil Jin, in the Crystal Physics and Electroceramics Laboratory at MIT.

Figure 26. a) Schematic depiction of placement of fabricated TFT structures on silicon wafer, possessing TFT channel width varied in the range of 10 to 300 μm and channel length varied in the range of 2 to 20 μm.

4.2.3. Photoactivated ZnO Thin Film Resistors

The ZnO thin film resistor based sensors used in this study were fabricated and extensively characterized for their electronic properties and chemical sensor properties in prior research conducted within the author's research group. A select number of these samples were revisited and utilized in the present study, primarily for investigation of ZnO photochemical properties and the influence of illumination on chemical sensor performance. For completeness, the details of sample design and preparation are reproduced in this section.

The first step in processing consisted of deposition and patterning of Pt/Ta metal onto an insulating Si/SiO2 substrate, via a lift-off process that included a 280 nm sacrificial Al layer to increase smoothness of the resultant Pt/Ta pattern edges, illustrated schematically in Figure 27. 200 nm of Pt was deposited via evaporation atop 25 nm of Ta, which served to enhance adhesion to a 1 μm thick SiO2 layer, which was formed on top of a Si substrate of 350 μm nominal thickness. This layer was formed into multiple functional structures via this patterning process, including 1) buried interdigitated electrode fingers for measurement of ZnO film resistance, 2) an integrated on-chip heating element and 3) a separate, electrically isolated on-chip temperature sensing element. The metalized ZnO sensor chip is illustrated schematically in Figure 28, including planar dimensions of the interdigitated electrode fingers and overlaying ZnO sensor thin films.
Figure 27. Schematic illustration of Pt/Ta liftoff process using photoresist/Al sacrificial layers:
1) bare SiO₂/Si wafer 2) Al deposition 3) Photoresist deposition 4) Photoresist exposure patterning via developer 5) Al patterning via wet etch 6) Pt/Ta layer deposition 7) Pt/Ta liftoff via photoresist strip 8) Al sacrificial layer removal.

The ZnO sensor film was similarly patterned, using only photoresist as the sacrificial layer. ZnO was deposited via reactive sputtering of a Zn metal target within a sealed chamber that contained a controlled mixture of oxygen and argon gas. The films were further doped with Al via co-sputtering. The substrate was unheated during the sputtering to preserve the stability of the sacrificial photoresist layer, and afterward the photoresist was stripped away to leave the ZnO film patterned within the electrode regions. Finally, the ZnO die was annealed for 12 hours at 700°C in synthetic air to obtain the desired ZnO crystalline phase.

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Figure 28. a) Top-down view of ZnO sensor die including 4 thin-film ZnO sensor elements of planar dimensions as given, buried Pt/Ta electrodes for ZnO film electrical measurement, integrated Pt/Ta heater and temperature sensor elements b) planar dimensions of buried Pt/Ta interdigitated electrode structure c) schematic illustration of the completed ZnO sensor structure.

4.3. Materials Characterization Techniques

A number of techniques were employed to determine structure, composition, and phase of the sensor materials prior to sensor response studies. These include scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in determination device structural dimensions and film morphology, x-ray diffraction (XRD) for bulk materials composition and phase analysis, and selected area electron diffraction (SAED) in examination of crystallinity.

4.4. Sensor Measurement Systems

4.4.1. Multiplexed Thin Film Resistor Measurement System

The SnO$_2$ and InGaZnO$_4$ thin film resistor samples were measured in a tube furnace based measurement chamber that enabled simultaneous measurement multiple sensors under uniform sample temperature and gas composition. The sensors were measured within a Lindberg Blue box furnace in a gas-sealed temperature controlled environment. DC conductance was measured using an Agilent 34970A data acquisition and switch unit through an Agilent 34901a 20 channel multiplexer module. The system was designed to test up to 8 sensors in parallel via use of multiple mounting structures and electrical interconnection to a multiplexed electronics interface.
Each sensor was mounted to an alumina rod (McDanel Ceramics, Inc.) and inserted into a quartz tube (Technical Glass Products Ltd.). A 1 inch long flat surface was cut along the length of the tip of the alumina rod, to enable mounting of sensor substrates. 1mm diameter holes were bored along the length of the alumina rod and Pt wire was inserted throughout the rod’s length (26”) for electrical interconnection to the sensors. In addition, a Pt-Rh thermocouple was formed at the alumina rod tip to provide temperature readout of the sensors. Sensors were mounted to the rod using silver paste (SPI Corporation), and Pt wires were additionally connected to sensor contact pads using silver paste. In total, 8 alumina rods were inserted into the quartz tube (4 on each side) were inserted into the complete tube furnace measurement setup.

Swagelok Ultratorr fittings were used for gas sealing at each end of the quartz tube, and Swagelok metal compression fittings provided a sealed gas flow path from mass flow controllers to the quartz tube and out to the building exhaust ventilation. For gas flow, two mass flow controllers (MKS Instruments) were connected in parallel to the inlet of the flow path to the chamber. Each mass flow controller was connected to a gas cylinder (Airgas Corporation) that contained a pre-mixed gas, dry air in one case and 1000 ppm H₂ in air, for use in studying the InGaZnO₄ sensor responses. The constant composition of the gas cylinder was then diluted via mass flow to a maximum ratio of 80:1 (minimal gas composition of 12.5 ppm H₂ in air).

A customized electrical interconnection enclosure was designed and assembled to interface electrical measurement systems with sensors within the heated quartz tube while maintaining gas seals. The base of each alumina tube was epoxy sealed, and Pt wires were soldered to parallel pins of a DB25 bulkhead connector. The 25 pin connector cable provided connection of 4 sensors and 2 thermocouples on each side of the furnace to the Agilent measurement hardware. To facilitate the measurement, custom LabVIEW software applications were designed and implemented within this thesis work in order to programmatically control mass flow rates and to log sensor electrical measurements and temperature. Photographs of the completed measurement setup are provided in Figure 29.
Figure 29. Photographic detail of the macro-scale enclosure and electrical measurement interconnections, used for characterization of SnO$_2$ and InGaZnO$_4$ thin film resistor sensors.

4.4.2. Miniaturized Thin Film Transistor Measurement System

As an important distinction of the present experimental approach, all InGaZnO$_4$ thin film transistor measurements were carried out in an environmentally sealed test chamber of volume on the order of 1 cm$^3$ (supplied by Boston MicroSystems, Inc). The small chamber volume enabled rapid purging of gases and switching from one composition to the next, to accurately measure time constants associated with sensor response and recovery processes. Prior to experiments performed in a controlled gas environment, electrical properties were measured on-wafer using microprobes, to confirm device electronic functionality. Then, TFTs were diced from the wafer and bonded to a custom designed alumina stick heater (Boston MicroSystems, Inc.). The alumina stick heater contained platinum electrodes deposited via screen printing along the stick length in two separate material layers, separated by a screen printed alumina layer in a sandwiched structure. One platinum layer provided the stick heating element and temperature sensor, and one platinum layer provided electrical contact to the TFT. On the TFT electrical contact layer the TFT die was bonded to a large-area Pt contact pad (3 x 3 mm square) using silver paste, providing the TFT backside gate contact, and then the source and drain were contacted by wirebonding Au wires from the Pt source and drain contact pads of the TFT to screen printed Pt electrode leads (200μm wide with 200μm spacing) on the alumina stick. The gross dimensions of the alumina heater stick were 6mm width and 70mm length, facilitating insertion of the TFT into the miniaturized, environmentally sealed test chamber. The stick heater and measurement chamber are shown in Figure 30.

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Custom LabVIEW software applications were developed in order to control experimental parameters and measure the TFT response. Control of gas flow rate and composition was achieved in similar manner to the approach used for other sensors studied in this thesis work (MKS mass flow controllers). An HP 4142B modular DC source meter was used to apply voltage and monitor current, from gate to source \((V_{GS}, I_{GS})\) and from drain to source \((V_{DS}, I_{DS})\). TFT channel conductance \((G)\) and rate of change in channel conductance \((dG/dt)\) were recorded during application of programatically controlled gate bias.

**4.4.3. Sensor Photoconductance Measurement System**

Figure 31 illustrates the experimental test stand used to measure the ZnO thin film resistor based chemical sensor response in an environment of controlled gas composition, temperature and illumination conditions. A chamber of low gas volume (less than 10 cm\(^3\)) was used to rapidly
change gas concentrations. Heater and temperature sensor elements are integrated on the sensor die, which is bonded with ceramic paste to a TO can type package and wirebonded for electrical interconnection. Gas composition is provided via a metal compression sealed flow path from MKS mass flow controllers, through the chamber and out to exhaust. At the front of the chamber is a glass lid to permit photoexcitation of the sensors from an externally controlled source. Monochromatic illumination was applied using an Newport Oriel Instruments model 74100 monochromator powered by a 100W quartz tungsten halogen lamp. Diffraction gratings within the monochromator provided generation of illumination of 25 nm bandwidth in the range of 2000 to 200 nm wavelength, and optical filters were utilized to remove higher order harmonic components of light when longer wavelengths were generated (285 nm, 550, and 1000 nm cut-on filters from Newport Oriel Instruments). An electronically controlled shutter was used switch the on-off state of the light. Conductance measurement was performed using a constant voltage source and logarithmically scaled current sensors, in a custom electronic measurement system. LabVIEW software was developed to enable programmed scanning of pulsed monochromatic light while recording sensor conductance (G) and rate of change in conductance (dG/dt).

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*ZnO conductance measurement electronics and LabVIEW readout developed and provided by David Bono, MIT Department of Materials Science and Engineering.*
Figure 31. (a) Cross sectional schematic view of ZnO sensor thin film between two electrodes (b) optical micrograph of a thin film resistor based chemical sensor with 19 interdigitated electrode fingers (c) several thin film chemical sensors fabricated on a single chip and packaged with an integrated heater and temperature sensor (d) packaged array of heatable chemical sensors in sealed chamber with controlled illumination and gas concentration and (e) schematic of the sensor measurement system.
5. Experimental Results

5.1. Materials Characterization
In general the materials properties of InGaZnO₄ are increasingly well known due to the growing number of studies that are performed on the material in the investigation of electronics and display applications. As an additional point of reference, the following section includes materials characterization results of the thin film resistor amorphous InGaZnO₄ based samples that were used in the proceeding study. Besides this, numerous studies including AFM, XRD, and SEM of the ZnO based thin film samples used in the photoactivated experiments can be found in prior work of our research group.

Following the sputter deposition of the InGaZnO₄ thin film sample, its X-ray diffraction (XRD) spectrum was measured. The sample was then annealed at 450°C and its XRD spectrum was remeasured. In addition, samples were prepared and annealed at 650°C and 850°C, for collection of XRD spectra. The results are shown in Figure 32, illustrating by the absence of diffraction peaks that the films are amorphous when deposited and at anneal temperatures up to 650°C. Since the sensor tests were performed below 400°C, this is a good indication that the film would remain amorphous throughout its electrical characterization.

The micrographs in Figure 33 show evidence of a continuous, interconnected film morphology attained in the microsphere templating technique. The SEM image illustrates the short range hexagonal order of microspheres, and the TEM image shows that neighboring microspheres are connected via bridged neck structures. The diffuse ring visible in the selected area electron diffraction pattern (SAED) and the lack of lattice fringing in the high resolution transmission electron micrograph (HR-TEM) further indicate the amorphous nature of the final InGaZnO₄ films, in agreement with XRD results.

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Materials characterization was performed by colleagues in collaborations with the Korea Institute for Science and Technology (KIST) and Korea Advanced Institute for Science and Technology (KAIST).
Figure 32. XRD Spectra of InGaZnO$_4$ thin films as deposited at room temperature and annealed at 450°C, 650°C, and 850°C.
5.2. **Amorphous Oxide based Gas Sensors**

The sensor response of multiple IGZO films was characterized in the presence of increasing concentrations of H\textsubscript{2} gas in a background of dry air. The following figures show the gas response of 3 different sensor films to increasing concentrations (1.25 to 50 ppm) of H\textsubscript{2} gas. The tests were performed at temperatures in the range of 200 to 400 degrees Celsius, and the resultant curves are shown below.
Figure 34. Response of 100nm thick InGaZnO$_4$ thin film resistor based sensor to increasing concentrations of H$_2$ gas (1.25, 2.5, 5, 12.5, 25, and 50 ppm) at 200 to 400 °C.

Figure 35. Response of 200nm thick InGaZnO$_4$ thin film resistor based sensor to increasing concentrations of H$_2$ gas (1.25, 2.5, 5, 12.5, 25, and 50 ppm) at 200 to 400 °C.
Figure 36. Response of 200 nm thick InGaZnO₄ hollow hemispherical resistor based sensor to increasing concentrations of H₂ gas (1.25, 2.5, 5, 12.5, 25, and 50 ppm) at 200 to 400°C.

In the first figure above, the device exhibits the typical response of an n-type device to reducing gases, increasing in conductance (decreasing in resistance). Of particular note is the apparent inversion of the direction of response that is clear as gas concentration is increased and temperature is decreased in the 200 nm thick thin film and 200 nm thick hollow hemisphere template devices. For an n-type material responding to a reducing gas such as hydrogen, a decrease in resistance is expected, as observed e.g. in the IGZO 100 nm thin film sample. An inversion in the direction of response, i.e. an increase in sensor resistance in the presence of H₂ gas is consistent with a change in the nature of sensor material from n-type to p-type. Such a change may be due to the influence of temperature or environment on the electronic properties of the material.
Figure 37. Sensitivity of a-InGaZnO₄ based chemical sensors to increasing exposure of NO₂ gas in the range of 1.25 to 50 ppm at several temperatures of operation: 350, 300, 250 and 200°C. Types of sensors shown: 100 nm thin film, 200 nm thin film, and 200 nm hollow hemisphere devices.

The amorphous InGaZnO₄ thin film and hollow hemisphere resistive sensors were characterized in increasing concentrations of NO₂ gas in a background of dry air, at temperatures decreasing from 350°C to 200°C, over a period of 80 hours. All devices showed a significant response, generally increasing in resistance when exposed to the oxidizing gas, as is expected for an n-type material. Notably, the hollow hemisphere template sensors exhibit a much higher response than the other devices, exhibiting a sensitivity of over 2000% change in resistance at 250°C. Although the responses are large and the rate of change in resistance during introduction of NO₂ is fast, the response does not saturate within the time of exposure to gas (20 minutes), indicating that the ultimate sensitivity could be even larger than shown here. After the response of the hollow hemisphere template sensor, the next largest response to NO₂ gas was exhibited by the 100 nm thin film device, and the lowest response was exhibited by the 200 nm thin film.
5.3. Thin Film Transistor based Gas Sensors

Utilizing the miniaturized stick heater based test stand, IGZO thin film transistors were subjected to a series of experiments, with a goal of determining the device’s electronic properties, chemical sensitivity, and the influence of gate bias on chemical sensitivity in particular at room temperature. Prior to this sequence of experiments, a number of thin film transistors were characterized at room temperature and evaluated for their relative suitability. The primary criteria included 1) high device resistance from gate to source/drain and 2) the ability to clearly resolve device transfer characteristics including threshold voltage within the limits of the measurement instrumentation. In this manner, a single device was selected for detailed characterization of transistor operating properties as a function of temperature, gas composition, and gate bias strain.

A suite of software applications was designed and developed, specifically to enable a detailed characterization of thin film transistor properties, while controlling a range of environmental properties. The software was developed using National Instruments LabVIEW running on a windows based desktop PC. The software enabled programmatic variation of the following:

- Variation of gas concentration by control of relative flow rates of mass flow controllers.
- Control of device temperature by supplying current to the heating element of the alumina stick heater while using the resistance of the element as measurement of temperature.
- Control of voltages applied to the thin film transistor, including drain voltage ($V_{DS}$) and gate voltage ($V_{GS}$).

In these studies, particular emphasis was focused on the investigation of the influence of gate bias ($V_{GS}$) on the device electrical properties and gas sensitivity. A total of three measurement approaches of increasing complexity were developed in order to monitor TFT electrical response to variation in $V_{GS}$. This includes:

- **TFT I-V Transfer Curve Measurement:** In this measurement approach, device drain current ($I_{DS}$) is measured while drain voltage ($V_{DS}$) and gate voltage ($V_{GS}$) are swept within specified ranges. Threshold voltage ($V_{TH}$) is determined by comparison of the square root of $I_{DS}$ to swept values of $V_{GS}$ at constant $V_{DS}$, as illustrated in the results section.

- **TFT Gate Bias DC Response Measurement:** The TFT channel conductance and threshold voltage are measured while a sequence of gate biases (tens of minutes per pulse) is applied. In certain tests, the gate bias was held constant for the entire duration and the gas concentration only was varied.

- **TFT Gate Bias Transient Response Measurement:** A periodic gate voltage is applied (period of several seconds) while monitoring the TFT channel conductance and slope in channel conductance over time.
5.3.1. **TFT Current-Voltage Transfer Characteristics**

Figure 38 provides the current-voltage (I-V) transfer characteristics of the TFT, measured at room temperature, in an environment containing N$_2$. Gate bias was held at constant values within the range of -10 to 10 volts while drain voltage was swept from -1 to 1 volt and drain current was measured. As shown in Figure 39, the threshold voltage is extracted from the transfer curve using a common engineering approximation, by plotting the square root of drain current (y axis) vs. gate bias (x axis). A line is fit to the measurement data at the higher values of gate bias and then extrapolated to the x axis intercept to determine the threshold voltage. At the time of this measurement, the device shown in Figure 39 exhibited a threshold voltage of -10.3 volts at room temperature, measured in N$_2$ gas. However, in general the measured threshold voltage is observed to be a function of the measurement history, including conditions of gate bias, gas environment, and temperature over time.

In addition to the above representations of the TFT electrical response, it is useful to consider variation in TFT film conductance in response to changes in applied gate bias. In the separate numerical simulation of TFT based sensor electronic and electrochemical properties in this thesis work, this representation of the TFT electronic response (conductance vs. gate bias) was selected as a preferred means for investigation of changes device properties in response to electronic and chemical stimuli. Several sample plots are shown in Figure 40, including conductance measured at several values of drain voltage in the range of \{0.25, 0.5, 0.75, 1\} volt. At zero volts gate bias, the measured values of conductance at varying drain bias are consistent with one another to better than 10%, with the deviation becoming smaller at more positive values of gate bias. A larger spread in measured sensor conductance at negative gate voltage in the range of -5 to -10 volts is due in part to limitations on the accuracy in the measurement of small values of current in the test stand that was used. The independence sensor conductance on drain bias in this range of operating voltage is an important feature of this device, as the proceeding experimental studies and also the numerical models investigate changes in sensor conductance and largely neglect the influence of variation in drain voltage.

The values of conductance shown in Figure 40 were measured in dry air at 150°C, before and after series of experiments that were performed over the course of 48 hours, during which time the device was subjected to numerous exposures of oxidizing gas and varying levels of gate bias. Qualitatively, the figure shows that the film is not permanently oxidized by prolonged testing in oxidizing gas, evident by the higher level of conductance observed after the testing sequence. However, in general the conductance is dependent on the history of gas exposure and gate bias.
Figure 38. Representative TFT transfer curves: drain current vs. drain voltage (-1 to 1 volts) as a function of gate bias (-10 to 10 volts) in linear scale (upper plot) and log scale (lower plot).
Figure 39. Plot of square root of drain current ($I_{DS}$, amps) vs. gate voltage ($V_{GS}$). Threshold voltage is extracted by fitting a linear function (dashed blue line) to the measurement data (black squares) and extrapolating to the x axis. The pictured device exhibits $V_{TH}$ of $-10.3\, V$. 

4E-3 - sqrt($I_{DS}$) at $V_{DS} = 1$ volt

-15 -10 -5 0 5 10 15 VGS

-15 -10 -5 0 5 10 15 VGS

-15 -10 -5 0 5 10 15 VGS

-15 -10 -5 0 5 10 15 VGS
Figure 40. InGaZnO$_4$ TFT conductance vs. gate bias measured in air, at $150^\circ$C, measured before and after 48 hours of testing in various concentrations of oxidizing gas, with varying conditions of applied gate bias. Thin film conductance is measured at multiple levels of applied drain voltage $V_{DS}$: 0.25, 0.5, 0.75, and 1 volt.

5.3.2. TFT Sensor Response to N$_2$ and O$_2$ gas
Prior to detailed studies of TFT responses to varying levels of gate bias, its response as a sensor to prolonged operation in O$_2$ and N$_2$ atmospheres was probed. The device was held at a constant temperature of $100^\circ$C, and gate bias was held constant at one of three levels: -10 V, 0 V or 10 V. Then, the sensor was exposed to 12 hour cycles of exposure to 100% N$_2$ gas followed by 100% O$_2$ gas. The results are shown in Figure 41, illustrating a slow drift in sensor response during the entire period of exposure to each gas (each 12 hour period). In addition, there is a longer drift in conductance that occurs over the entire course of the measurement period, more than 70 hours in each of the three measurements. This longer drift is dependent on the level of gate bias, with negative gate bias causing the signal to gradually drift upwards (higher conductance over time) and a positive gate bias causing the signal to drift downwards (lower conductance over time). The sample with 0 V gate bias exhibited the least amount of drift, trending downwards slightly over time.
5.3.3. **TFT DC Gate Bias Response Measurement in N₂ and O₂ gas**

In this series of measurements, a programmed sequence of gate biases ($V_{GS}$) in the range of -10 to 10 volts was applied to the transistors in a series of experiments that each lasted approximately 24 hours. A constant drain voltage ($V_{DS}$) of 1 volt was applied to measure TFT channel conductance over time, and periodically, the programmed gate bias ($V_{GS}$) was interrupted in order to sweep gate bias rapidly (less than 1 second) in the range of -10 to 10 volts and measure threshold voltage. The threshold voltage was determined as illustrated in the previous section, by extrapolation of the square root of $I_{DS}$ at high values of current to the x axis. Figure 43 shows the sequence of gate biases and also the threshold voltage over time of a single device that was measured at several temperatures (25, 100, and 150°C) and in two different gas environments (100% N₂ and 100% O₂). In all test cases, the devices exhibit a reproducible change in threshold voltage in response to the applied gate bias. In general, application of a negative DC gate bias tends to shift the threshold voltage to a more positive value, and conversely application of a positive DC gate bias shifts the threshold voltage to a more negative value. The magnitude of change in threshold voltage increases for higher values of applied gate bias. Furthermore, as a constant gate bias is held at a constant value for up to 30 minutes in duration, the threshold voltage continues to drift in the same direction of the initial transient.
Figure 42. TFT Gate bias $V_{GS}$ over 24 hours between measurements of threshold voltage $V_{TH}$. Note, at each measurement of $V_{TH}$, $V_{GS}$ was rapidly swept from -10V to 10V (not shown).

Figure 43. TFT threshold voltage over time at 3 different temperatures (25, 100, and 150°C) and in gas environments of 100% $N_2$ and 100% $O_2$ as labeled above.
There are notable differences in the response of TFT threshold voltage to applied gate bias, under the different conditions of temperature and gas environment. As shown, the TFT response at room temperature exhibits a stable baseline level in both \( \text{N}_2 \) and \( \text{O}_2 \), with the threshold voltage returning to a value on the order of 1.9 volts when DC gate bias returned to 0 volts. The TFT threshold voltage tends to decrease as temperature is increased, dropping from a range of \( \{0, 5\} \) volts at 25°C to a range of \( \{-5, -15\} \) volts at 100°C and \( \{-10, -50\} \) volts at 150°C. In addition, a drift in the value of baseline threshold voltage is observed to increase as temperature is increased. Although no significant drift over the course of the experiment is perceivable at room temperature, in \( \text{N}_2 \) atmosphere at 100°C the threshold voltage drifts from approximately -7V to -10V, and at 150°C the change is much larger, dropping from approximately -17.5V to -35V. Interestingly, the direction of drift in threshold voltage is a function of the gas environment, as shown in Figure 43 in \( \text{O}_2 \) atmosphere at 150°C where \( V_{TH} \) drifts upward from a level of -30V to -17.5V.

Since the observable effects of long-term drift are largely absent at room temperature, it is possible in this case to perform a more detailed comparison of TFT DC electrical response in an \( \text{N}_2 \) vs an \( \text{O}_2 \) environment. Figure 45 displays an expanded view of threshold voltage measured within the first 7 hours of the above experiment. While in general both curves follow a similar trend, the gate bias response in nitrogen appears to exhibit a slightly higher threshold voltage on the order of tens of mV, in particular when positive gate bias is applied and released.

In the process of measuring each data point of threshold voltage, the TFT gate bias \( V_{GS} \) is swept rapidly (less than 1 second) in the range of -10V to 10V while holding drain bias \( V_{DS} \) at a constant value of 1V. Because of this, it is also possible to calculate channel conductance at each value of swept gate voltage, and Figure 46 displays the result of this calculation performed at a gate voltage of 10V. In this case, there is a more pronounced difference between the curves measured in nitrogen and oxygen, and it is clear that the channel conductance of the TFT in nitrogen is significantly higher than the channel conductance in oxygen in all cases except for negative applied gate bias.
Figure 44. TFT Gate bias $V_{GS}$ over 6 hours between measurements of threshold voltage $V_{TH}$. Note, at each measurement of $V_{TH}$, $V_{GS}$ was rapidly swept from -10V to 10V (not shown).

Figure 45. Expanded view of TFT threshold voltage vs. time at room temperature in $O_2$ (blue) and $N_2$ (red) gas environments.
Figure 46. Channel conductance measured during brief application of $V_{GS} = 10$V gate bias, with $V_{DS} = 1$V drain bias at room temperature in $O_2$ (blue) and $N_2$ (red) gas environments. During the period of time between measured data points of channel conductance, the gate bias was held at nominal constant values according to the programmed sequence displayed in Figure 45.

A more detailed examination of the trends in TFT channel conductance is possible in consideration of values that were measured during application of constant gate bias, between the measurements of threshold voltage that were performed. As displayed in Figure 45 and Figure 46, individual measurements of threshold voltage were repeatedly performed over time at a measurement interval of approximately 2 minutes between datapoints. Each measurement of threshold voltage involved a rapid sweep in gate bias voltage $V_{GS}$ from -10V to 10V, which took less than 1 second to complete. During the ~2 minute interval between threshold voltage measurements, when the gate bias was not being rapidly swept from -10 to 10V, the gate bias was held at a constant value as indicated in the upper graph of while continuing to measure channel conductance at a sample rate on the order of 10 Hz. The resultant trend in channel conductance over time between threshold voltage measurements is shown in Figure 47. From this perspective, the channel conductance is observed to be a strong function of gate bias, decreasing as expected to a low value when -10V is applied to the gate and increasing by at least 4 orders of magnitude to the range of $10^{-6}$ Siemens when +10V is applied to the gate. Measured values of conductance during application of -10V gate bias are very noisy and essentially below the minimum detection limit of measurement instrument, on the order of $10^{-10}$ Siemens. However, the signal to noise ratio of the measured conductance is significantly improved at higher levels of gate bias.
Figure 47. Channel conductance measured at 10 Hz sample rate between measurements of threshold voltage at room temperature in O₂ (blue) and N₂ (red) gas environments. Nominal TFT gate bias VGS between threshold voltage measurements in this time frame is as shown in Figure 45.

The repeated measurement of threshold voltage is apparent in Figure 47 as an intermittent interruption in the continuous observed trend in channel conductance. When a nominal value of VGS = 0V gate bias is applied, each occurrence of a threshold voltage measurement causes an upward decay in channel conductance, in effect a recovery of the channel conductance back to the baseline level of measured channel conductance. To examine this phenomenon in greater detail, Figure 48 displays an expanded view of channel conductance in the time frame of 0.5 hours to 1.65 hours experiment time. Here, channel conductance in N₂ gas is again observed to be significantly higher than conductance in O₂, with the greatest difference between the two curves observed following transition from relatively negative to relatively positive gate bias. In addition, when gate bias is changed from a relatively negative voltage to a relatively positive voltage, the channel conductance following this transition tends to trend downward (negative slope). In the case of the transition shown close to 1.5 hours experiment time, there is a pronounced overshoot in conductance in N₂ gas which then decays in value to approach the level of conductance shown for the TFT in O₂. This sort of trend is further illustrated in Figure 49 whereupon repeated measurement of threshold voltage following application of a negative gate bias prior to 2.8 hours experiment time, the measured conductance in N₂ continues to recover to a baseline value that eventually approaches the essentially the same value as the conductance in O₂ gas.
Figure 48. Expanded view of channel conductance in the time frame of 0.5 to 1.65 hours experiment time, at room temperature in $O_2$ (blue) and $N_2$ (red) gas environments.

Figure 49. Expanded view of channel conductance in the time frame of 0.5 to 1.65 hours experiment time, at room temperature in $O_2$ (blue) and $N_2$ (red) gas environments.
To summarize, the channel conductance and threshold voltage were measured while systematically varying gate bias in the range of -10 to 10 volts, characterizing device response at three different operating temperatures (25, 100, and 150°C) and in two different gas environments (100% N₂ and 100% O₂). Significant drift in device electrical characteristics over time was shown to occur at higher temperatures of operation, and this drift is shown to be a function of gas composition, trending towards lower threshold voltage in nitrogen and higher threshold voltage in oxygen. At room temperature, the baseline level of threshold voltage was stable in nitrogen and oxygen, facilitating a more detailed comparison of device response characteristics over a prolonged period of experiment time. Expanded views of experiment data over time reveal that the calculated values of threshold voltage and measured values of channel conductance of the TFT in nitrogen are significantly higher than measured values in oxygen. Furthermore, the data illustrates a complex transient response of channel conductance to changes in applied gate bias. In general, difference between channel conductance in nitrogen and oxygen is observed to be largest when transitioning from -10V gate bias to 0V gate bias, and the higher level of conductance in N₂ gas gradually decays over time towards the value of conductance that is measured in O₂. When gate bias is changed to a more positive value, the measured channel conductance is observed to suddenly increase in value but then more slowly decay towards a negative value. Conversely, a change in gate bias towards a more negative value corresponds to a negative jump in channel conductance followed by a more gradual positive drift in measured channel conductance.

5.3.4. TFT Transient Response Measurement in N₂ and O₂ gas

It is clear from the above measurements of the previous section that the observed channel conductance and threshold voltage vary over time when excited with a constant gate bias, and measured values depend on the frequency and duration of the gate bias that is applied. In addition, there was a larger observable difference between TFT conductance in N₂ and O₂ gas during the period of time that followed transition from relatively negative to relatively positive gate bias. The preceding section more explicitly investigates the transient response of the TFT to changes in gate bias, with particular attention toward the influence of the gas environment in changing the TFT transient electrical response.

The preceding figures illustrate the transient measurement approach. Figure 50 shows a periodic waveform that is applied to the TFT in the present experiment, varying from between two levels of gate bias, V_LOW (0V) and V_HIGH (10V), with a period of less than 7 seconds. Figure 51 illustrates representative values of TFT conductance measured during the applied sequence of gate bias. As shown in earlier data, application of a positive gate bias V_HIGH generally corresponds to a positive jump in channel conductance followed by a downward trend in conductance (negative slope) over time, conversely the case during application of a negative gate bias V_LOW. The transient measurement involves extraction of two key parameters related to each transition in gate bias, 1) nominal value of conductance at the end of each cycle of applied gate bias and 2) slope in conductance during the period of time that constant gate bias is held. These
values are extracted separately for the low and high values of applied gate bias. Accordingly, the blue squares in Figure 51 illustrate extracted values of channel conductance during application of higher gate bias, and the red squares illustrate extraction of channel conductance during the application of the more negative gate bias. These extracted parameters are then grouped each into separate plots over time, to more clearly resolve the changes in TFT electronic properties under various conditions over time.

Figure 50. Representative periodic voltage signal applied as the TFT gate bias $V_{GS}$. In this case, the signal is varied between a level of $V_{LOW} = 0V$ and $V_{HIGH} = 10V$ at a period of less than 7 seconds.
Figure 51. TFT transient conductance response to gate bias shown in Figure 50. Extracted values of channel conductance during application of $V_{\text{HIGH}}$ are shown in blue squares, and extracted channel conductance values during application of $V_{\text{LOW}}$ are shown in red squares.

To investigate the influence of gas composition on the transient electrical properties of the TFT, gas concentration was varied between 0% and 20% oxygen on a period of 5 minutes, much longer than the period of the transient gate bias applied to the TFT, as shown in Figure 52.

Figure 52. Periodic variation in oxygen concentration of the ambient environment during TFT transient conductance response measurement.
Figure 53 shows representative values of TFT conductance measured during application of the $V_{\text{HIGH}}$. In this particular experiment, gate bias was varied periodically within the range of $V_{\text{LOW}}=0V$ and $V_{\text{HIGH}}=10V$. The changing concentration of oxygen in the environment is plotted on a secondary axis, and a corresponding shift in channel conductance is observed in response to changes in gas concentration. Channel conductance shifts to a more negative value when oxygen is introduced to the environment and reversibly recovers towards the baseline value when oxygen is removed. Similarly, slope in channel conductance during application of $V_{\text{HIGH}}$ in this case is plotted in the following chart. In the presence of oxygen, the slope of change in channel conductance is observed to become steeper, noticeably shifting to a more negative value. When oxygen is removed from the environment, the slope in conductance over time becomes more shallow.

![Conductance vs. Time](image)

Figure 53. Representative changes in $G_{\text{HIGH}}$, conductance measured during application of $V_{\text{HIGH}}$, in response to variation in oxygen content of the environment. In this case, $V_{\text{LOW}} = 0V$ and $V_{\text{HIGH}} = 10V$. 
Figure 54. Variation in slope $dG_{HIGH}/dt$, during variation in oxygen content of the environment. $V_{LOW} = 0V$ and $V_{HIGH} = 10V$.

The above experiment was repeated on the same device at room temperature under varying conditions of applied gate bias. $V_{HIGH}$ was kept constant at a level of 10V, and $V_{LOW}$ was varied at the following levels of gate bias: $V_{LOW} = -15, -10, 0, and 5$ volts, and the results are shown in Figure 55. Since the nominal values of channel conductance change as a function of both $V_{LOW}$ and $V_{HIGH}$, the measured channel conductance was normalized to its initial value, and percent change in conductance for each of these experiments is shown in the following plot. The largest reversible response in conductance to changes in $O_2$ concentration is observed in the case of $V_{LOW} = -15V$, and the magnitude of the response decreases as $V_{LOW}$ is increased to -10V and 0V. Interestingly, in the case of $V_{LOW} = 5V$, a downward trend in conductance is observed during exposure to oxygen, however negligible signal recovery is observed when the environment is returned to nitrogen. In addition, the sensor exhibits diminishing changes in conductance upon successive exposures to oxygen. These final two points indicate that under the condition of $V_{LOW} = 5V$, the sensor is able to respond to exposure to oxygen but not able to effectively recover when exposed to nitrogen. This would prevent the operation of a practical device, as the sensor would saturate upon any initial exposure to oxygen ultimately lose its ability to respond to the gas. However, this situation is remedied by selection of more negative value of $V_{LOW}$, as illustrated in the case of -15V which provides a reversible sensor response to variation in oxygen concentration.
Figure 55. Normalized plot of percent change in channel conductance $G_{\text{HIGH}}$ in response to changes in oxygen content of the environment during multiple experiments. In each experiment, $V_{\text{HIGH}}$ was kept at a constant value of 10V, and $V_{\text{LOW}}$ was varied in the range of \{-15, -10, 0, and 5\} volts.

5.3.5. TFT DC Response Measurement in NO$_2$ gas

After measurements were completed in that characterized TFT response to oxygen, a multiple studies were performed to measure TFT response to varying concentration of a stronger oxidant: NO$_2$ gas. First in this series of measurements is Figure 56, which shows the device’s conductance response to increasing gas concentration in the range of 1.25 to 100 ppm (parts per million) NO$_2$. The test was performed with the sensor at a constant operating temperature of 150°C, under volumetric gas flow of 200 standard cubic centimeters per minute [sccm] that was held constant for nearly the entire duration of the experiment (the total flow rate was dropped to 100 sccm in the final ~5% of the experiment, when 100 ppm NO$_2$ gas was flowed). Alternating pulses of NO$_2$ gas and dry air were exposed to the sensor, of 30 minutes and 60 minutes in duration, respectively. The sensor exhibits a relatively rapid initial response to the gas, reaching a level of 90% of the saturated value of conductance e.g. in the first exposure to NO$_2$ gas. The sensor recovery is by comparison much slower, and over the course of one hour of flowing dry air, the sensor conductance never quite reaches the same baseline level that was observed initially in dry air. The occurrence of a rapid response coupled with slow recovery is commonly observed in chemisorption based sensor response to strongly oxidizing gas.
Figure 56. InGaZnO$_4$ TFT DC Conductance Response (solid line, left axis) to increasing concentrations of NO$_2$ gas (dashed line, right axis), in the range of 1.25, 2.5, 5, 12.5, 25, 50, and 100 ppm.

5.3.6. TFT Transient Response Measurement in NO$_2$ gas

Using the newly developed TFT transient response measurement approach, the InGaZnO$_4$ TFT was tested for its sensitivity to 1.25 ppm NO$_2$ gas at an operating temperature of 150°C. Three different experiments were performed to test the impact of pulsed gate bias on the NO$_2$ sensitivity:

- Sensor measurement during pulses of gate bias from 0 to 10 volts
- Sensor measurement during pulses of gate bias from 0 to -10 volts
- Sensor measurement with gate bias held constant at 0 volts

In order to obtain a uniform test condition for comparison of sensor response within the experiments, only one sensor reading was taken per cycle of gate voltage applied, at the end of application of 0V gate bias. During the pulsed experiments, gate bias was pulsed for approximately 2.5 seconds and then returned to 0 volts for 2.5 seconds, and at the end of this latter period (after having held gate bias for 2.5 seconds) a sensor reading was recorded for that
cycle. This measurement procedure was repeatedly cyclically throughout the course of each pulsed \( V_{GS} \) experiment. Figure 57 illustrates the measurement procedure, indicating the point within each cycle where a sensor reading was taken. In the case of the experiment with constant gate bias of 0 volts, a single reading was taken once every 5 seconds (not shown in Figure 57).

![Graph showing sensor conductance and gate bias over time for pulsed \( V_{GS} \).](image)

Figure 57. \( \text{InGaZnO}_4 \) TFT based sensor measurement during pulsed gate bias \( V_{GS} \). Sensor conductance over time is shown in a solid black line and gate bias is shown as a dashed black line.
Sensor readings are taken once per cycle, and the point of measurement is shown as a solid square, a) in blue for \( V_{GS} \) pulsed 0 to 10 V and b) in red for \( V_{GS} \) pulsed from 0 to -10 V.

Following this measurement procedure, the TFT based gas sensor was measured during cyclic exposure to 1.25 ppm NO\(_2\) gas, with 30 minutes of exposure and 60 minutes recovery per cycle. The resultant sensor response is shown in Figure 58. As shown, although there are clearly visible sensor responses, the signal continues to change slowly after an initial more rapid transient, and there is no clear saturation of the response. Nevertheless, it is possible to compare the relative magnitude and rate of response under these conditions. The experiment with the TFT held at 0 V shows a significant response, dropping in resistance by a factor of 6 during NO\(_2\) exposure from 300 to 50 nano Siemens and recovering to 78\% the initial value (240 nanoSiemens) during 60 minutes of recovery in air. During pulsing of the gate bias to 10 volts, the sensor exhibits a much larger response, decreasing in conductance by nearly a factor of 30 from 410 nanoSiemens to 13 nanoSiemens. However, the recovery is much slower and the device only reaches 25\% its initial value in 60 minutes. The third bias condition of \( V_{GS} \) pulsed from 0 to 10 V provides an interesting comparison to the other two conditions. In this case, although the response magnitude is much smaller (conductance decreasing only by a factor of 2) the signal is completely reversible within the timeframe of 60 minutes recovery from the 30 minutes of exposure to NO\(_2\).

![TFT Conductance Measured at VGS=OV, during pulsed VGS Operation](image)

Figure 58. Sensor response to 1.25PPM NO\(_2\) gas during three different conditions of transient gate bias: \( V_{GS} \) pulsed from 0 to 10 V, \( V_{GS} \) held constant at 0 V, and \( V_{GS} \) pulsed from 0 to -10 V.
In all cases, sensor conductance readings were taken during $V_{GS} = 0$ V, whether constant or during cyclic exposure.

The above results have demonstrated the significant influence that gate bias can have over both sensor sensitivity and response time. As shown, a positively pulsed gate bias induced a stronger response to NO$_2$ gas but a slower recovery, as compared to the TFT when it was not subjected to a pulsed gate bias. Conversely, pulsing gate bias at -10V resulted in a weaker response to NO$_2$ gas but enabled the signal to recover more rapidly. However, this is not the complete picture. An additional important effect to consider is the selection of the gate bias at which sensor readings are taken. The sensor readings shown above were measured at 0 V gate bias, but in general two sensor readings are taken per cycle when the device is exposed to cyclic gate bias: one reading at $V_{LOW}$ and one reading at $V_{HIGH}$. As illustrated in Figure 59, the values of conductance measured at these points in the cycle will be referred to as $G_{LOW}$ and $G_{HIGH}$, respectively. In the following figures, measured values of $G_{LOW}$ and $G_{HIGH}$ for each individual pulsed gate bias experiment are plotted in a single chart, along the TFT conductance as measured with 0 volts constant gate bias (marked as “Reference”). Figure 60 shows the case of $\{V_{LOW} = -10, V_{HIGH} = 0\}$ and Figure 61 provides $\{V_{LOW} = 0, V_{HIGH} = 10\}$. In addition, a third case is shown, $\{V_{LOW} = -10, V_{HIGH} = 10\}$ in Figure 62.

![Graph](image-url)

Figure 59. Schematic illustration of the transient gate bias measurement approach. Transistor gate bias is pulsed from $V_{LOW}$ and $V_{HIGH}$ and channel conductance is measured over time. Two sensor readings are taken per cycle, indicated above as $G_{LOW}$ and $G_{HIGH}$.
Figure 60. InGaZnO$_4$ TFT transient responses $G_{\text{LOW}}$ and $G_{\text{HIGH}}$, measured during cyclic exposure to NO$_2$ gas. $V_{\text{LOW}} = -10\text{V}$ and $V_{\text{HIGH}} = 0\text{V}$. DC response with $V_{\text{GS}} = 0\text{V}$ is shown for reference.

Figure 61. InGaZnO$_4$ TFT transient responses $G_{\text{LOW}}$ and $G_{\text{HIGH}}$, measured during cyclic exposure to NO$_2$ gas. $V_{\text{LOW}} = 0\text{V}$ and $V_{\text{HIGH}} = 10\text{V}$. DC response with $V_{\text{GS}} = 0\text{V}$ is shown for reference.
In general, lower values of gate bias serve to turn the TFT off by depletion of the conducting channel and reduce the measured conductance. Because of this, although the TFT at a higher (more positive) gate bias will be able to chemisorb an oxidizing gas more readily due to an abundance of electrons to be accepted by the oxidizing gas at the surface, the TFT when held at a lower (more negative) gate bias will be more sensitive to incremental changes in surface charge (due to chemisorption / desorption). As will be demonstrated, the benefits of both of these effects (increased chemisorption at positive gate bias and increased sensitivity in the channel conductance measurement at negative gate bias) may be obtained by appropriate selection of modulated gate bias voltages.

In addition to the above conductance data that has been shown, the present measurement approach enables a more detailed analysis sensor performance by examination of the slope in sensor response over time. As will be shown in later discussion sections, this measured slope can be utilized along with knowledge of the equilibrium behavior of the system in order to obtain a measurement of the rate of charge transfer occurring at the semiconducting metal oxide surface. The LabVIEW based control application was further developed to measure the slope in conductance, designated $\frac{\partial G_{LOW}}{\partial t}$ and $\frac{\partial G_{HIGH}}{\partial t}$ within each cycle of gate bias pulsing, as illustrated in Figure 63.

Figure 62. InGaZnO$_4$ TFT transient responses $G_{LOW}$ and $G_{HIGH}$, measured during cyclic exposure to NO$_2$ gas. $V_{LOW} = -10V$ and $V_{HIGH} = 10V$. DC response with $V_{GS} = 0V$ is shown for reference.
Figure 63. Schematic illustration of the method used to extract slope of $G_{\text{LOW}}$ and $G_{\text{HIGH}}$ from each cycle in the transient gate bias measurement approach.

The extracted values of slope from each of the three experiments of pulsed gate bias are shown in Figure 64 through Figure 66.
InGaZnO$_4$ TFT slope $dG_{\text{HIGH}}/dt$ in NO$_2$ | $V_{\text{LOW}} = -10\ V$, $V_{\text{HIGH}} = 0\ V$

Figure 64. Slopes $\partial G_{\text{LOW}}/\partial t$ and $\partial G_{\text{HIGH}}/\partial t$ extracted during the TFT transient measurement process, during cyclic exposure to 1.25ppm NO$_2$ gas | $V_{\text{LOW}} = -10\ V$, $V_{\text{HIGH}} = 0\ V$. 

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Figure 65. Slopes $\partial G_{\text{LOW}}/\partial t$ and $\partial G_{\text{HIGH}}/\partial t$ extracted during the TFT transient measurement process, during cyclic exposure to 1.25ppm NO$_2$ gas | $V_{\text{LOW}} = 0$ V, $V_{\text{HIGH}} = 10$ V.
Figure 66. Slopes $\partial G_{\text{LOW}}/\partial t$ and $\partial G_{\text{HIGH}}/\partial t$ extracted during the TFT transient measurement process, during cyclic exposure to 1.25ppm NO$_2$ gas | $V_{\text{LOW}} = -10\text{ V}$, $V_{\text{HIGH}} = 10\text{ V}$. 

InGaZnO$_4$ TFT slope $dG_{\text{HIGH}}/dt$ in NO$_2$ | $V_{\text{LOW}} = -10\text{ V}$, $V_{\text{HIGH}} = 10\text{ V}$

InGaZnO$_4$ TFT slope $dG_{\text{LOW}}/dt$ in NO$_2$ | $V_{\text{LOW}} = -10\text{ V}$, $V_{\text{HIGH}} = 10\text{ V}$
5.4. Illumination Enhanced Gas Sensors

5.4.1. Impact of Broadband Illumination on Chemisorption on ZnO

Studies to date have focused on experimentally demonstrating the various physical effects that are hypothesized to control chemisorption processes in the selected model systems. In Figure 67 below, broadband illumination (including above bandgap UV light) on ZnO thin films is observed to induce desorption of oxygen from the surface of the material. In this experiment, a thin film of ZnO was first subjected to an anneal for 1 hour at 300°C, in order to induce adsorption of oxygen at the surface. Then, the sample was cooled to room temperature and measurement of the film conductance was initiated. When light is first turned on at approximately 0.75 hours experiment time, a large, irreversible change in conductance is observed, believed to be associated with desorption of a large amount of oxygen from the material surface. Subsequent cycles of light being switched on and off induce smaller changes in conductance that do not return to the original level observed after the anneal in oxygen, indicating that the process of re-adsorption occurs very slowly at room temperature. These results are in agreement with studies observed in literature.

Figure 68 illustrates the impact that the same level of broadband illumination can have on the chemisorption of NO₂ gas on ZnO at room temperature. Normally, NO₂ reacts very strongly with ZnO, and at room temperature it binds in an irreversible manner, as shown to the left of the figure where the sample is held in the dark. However, under broadband illumination, the sample is seen to respond reversibly to the presence of NO₂ gas, indicating that energy states associated with chemisorption are able to populate and depopulate due to the presence of illumination generated charge carriers.

Together, these measurements demonstrate that broadband illumination can be used in order to influence the process of chemisorption on ZnO, and that the influence of the light will depend on the composition and concentration of gases present. In addition, by showing that illumination can be used to desorb material from the sample surface, this indicates a path toward achieving a repeatable and reproducible clean initial state of the ZnO surface, thereby facilitating subsequent studies in the presence of various gases of interest. Further investigations within the thesis work will seek to model this behavior quantitatively, establishing correlations between absorption properties, electronic properties, and reaction rate equations influencing chemisorption.
Figure 67. Impact of broadband (above bandgap) illumination on chemisorption of oxygen on ZnO at room temperature. A large, irreversible increase in conductance is associated with irreversible desorption of oxygen.

Figure 68. Response of ZnO thin film resistor to pulses of .1% NO₂ gas concentration (left) in the dark and (right) under the presence of broadband (above bandgap) illumination.
5.4.2. Impact of Monochromatic Illumination on Chemisorption on ZnO

Given the known influence that broadband illumination has to promote desorption of gases including O₂ and NO₂ from the surface of ZnO, it is of interest to determine the energy of illumination necessary to induce this desorption event and correlate this to the known energy band structure of the material. The following figures show ZnO film conductance at room temperature in the presence of monochromatic illumination, following an anneal of the film at 260°C in the presence of 50 ppm NOₓ/N₂ gas for 2 hours to induce NOₓ chemisorption. The wavelength was scanned from long (sub-bandgap) down to short wavelength (above bandgap) and then back to long wavelength. Following exposure of the ZnO film to each wavelength, the illumination was briefly halted by means of a shutter, in order to measure film conductance in the dark, in addition to measurement in the light.

Figure 69 shows plots of ZnO film conductance under illumination and in the dark, as a function of the wavelength. As is shown in the graph, the conductance was initially low. As wavelength was scanned to sufficiently low levels (sufficiently high energy), the conductance began to increase. Since this conductance increase is observed both in the dark and under illumination, it can be conclusively associated with irreversible desorption of NOₓ from the surface of the ZnO film. It is also of interest to note that this desorption event begins at energy levels significantly below the band gap energy.

Figure 70 illustrates more precisely how monochromatic illumination of the sample is varied over time during this experiment and also shows an interesting phenomenon associated with the act of turning the light on and off. A close examination of the transient response in conductance of the sample reveals that there are multiple time constants associated with turning the light on and off. Qualitatively, a “fast” and a “slow” response time can be separately identified. Based on the response times observed, it may be the case that the fast process is more directly associated with carrier generation / recombination and the slow process associated with population / depopulation of surface states. A primary goal of this study will be to more precisely identify, model, and control these phenomena through additional experimentation and numerical/analytical tools.

Fast vs Slow Response Regimes in During Monochromatic Pulses

- Figure 69 shows sensor response over time during illumination pulses
- Expanded view shows distinct fast and slow sensor responses during periodic illumination and transition back to dark
- Rate of sensor response over time in each 2.5 minute light/dark half cycle is extracted from each of the response regimes:
  - Fast response during first 15 seconds of exposure
- Slow response during final 1 minute 30 seconds of exposure
- Results of slope analysis (S/min) are plotted vs. wavelength in Figure 70.

Figure 69. (a) Photoconductance spectrum of thin film ZnO at room temperature in N₂ environment following anneal in the presence of NOₓ gas and (b) measurement of the same sample in the dark during the reverse scan to high wavelength.
Figure 70. (a) Conductance vs time as monochromatic illumination is being scanned in wavelength and pulsed on/off (b) magnified view of the same and (c) larger magnification, illustrating clearly the presence of two distinct response regimes (referred to as fast and slow).
Figure 71. Slope of change in conductance resultant from each pulse of monochromatic illumination, resolved into two components, a “fast” response slope that is extracted within the first 15 seconds (top) and a “slow” response slope that is extracted in the last 1 minute 30 seconds of pulses of monochromatic light that are each 2.5 minutes in duration.
Figure 72. Extracted data from each cycle illumination: sensor response rates in (a) rapid and (b) slow response regimes, and change in conductance in (c) rapid and (d) slow response regimes.
Influence of Illumination on Desorption

- Exposure of the ZnO film to broadband illumination results in irreversible increase in conductance, associated with desorption of gases such as O$_2$ and NO$_2$ (Figure 67).
- During monochromatic illumination, onset of change in conductance occurs at wavelengths significantly longer than the bandgap of ZnO (388nm)

Fast vs Slow Response Regimes

- During pulsing of light, two regimes are observed in the sensor response:
  - A faster response occurring when light is first turned on or off
  - A slower response that occurs during the entire pulse period
- In Figure 5, a select features of these responses are extracted and shown:
  - Rate of change in sensor signal is calculated via linear approximation
  - The relative amount of change in conductance occurring in each regime is calculated
- From sensor response kinetics in Figure 71, we observe the onset of a slow sensor response regime at about 875nm light, followed by onset of a larger signal in the rapid regime at about 500nm light.

Phenomenological Observations

- The rate of the fast response is higher in light than it is in the dark. (Figure 71)
- Based on Figure 72, it appears that the rapid response regime produces a change in conductance that approximately recovers reversibly at each cycle of light and dark exposure.
- Figure 72 shows that the change in conductance seen in the slow response regime is not reversible in light vs dark.

It appears that the gradual increase in conductance that is observed during scanning of monochromatic light (as in Figure 3) appears to occur primarily during the slow response regime

Key Results

- While chemisorption of O$_2$ and NO$_2$ on ZnO is normally irreversible at room temperature, light is observed to accelerate the desorption process.
• Onset of changes in conductance related to desorption occurs at wavelengths significantly longer than the bandgap.

• Fast and a slow sensor conductance response regimes are observed during pulsing of light at wavelengths longer than the bandgap.
6. Numerical Modeling

6.1. Overview
This section describes the results of numerical simulation of an InGaZnO$_4$ thin film transistor structure. A finite element approach is used for calculation of the electric field distribution throughout the conducting channel, implemented in COMSOL. The quantity of gas that chemisorbs is voltage-dependant, due to the relationship with Fermi Energy (as described earlier in theory sections of this thesis by the Vol’kenshtein chemisorption coefficient), and the surface charge density, induced by chemisorption, is solved self-consistently with the Poisson-Boltzmann equation under the influence of the gate electrode (in 1D) and under interactions between gate, source, drain and the surrounding air (in 2D). Charge carrier concentration is calculated throughout the thin film transistor nanoscale thickness and integrated to calculate changes in sensor conductance.

The modeled transistor possesses structural dimensions identical to the devices tested in this thesis, including a conducting IGZO channel of 70 nm thickness and an underlying SiO$_2$ gate dielectric material of 100 nm thickness. Initial values for the electronic properties of IGZO and SiO$_2$ are taken from the literature and varied during the course of the numerical investigation. Key geometric and materials properties of the modeled device are listed at the start of each of the proceeding sections. Parameters held constant in all studies include an assumed relative permittivity of IGZO (11.8), electron affinity of IGZO (4.3 eV) and relative permittivity of SiO$_2$ (4.2).

In order to utilize the Vol’kenshtein equation for chemisorption, it is necessary to identify the energy levels (relative to the vacuum level) of surface states that are associated with chemisorption of the gas of interest (e.g. oxygen or NO$_2$). This parameter, in general, is a function of the semiconductor and also of the gas itself. In the case of an oxidizing gas adsorbed on a semiconducting metal oxide, the energy level typically lies within the band gap of the semiconductor, with more oxidizing gases yielding energy levels that are deeper below the conduction band edge. Since this data is not available for IGZO, the energy level of the gas associated surface state is initially assumed in this study to be placed at 1.2 eV below the conduction band edge. Later, in this chapter, the energy level of surface states is varied to investigate its impact on device performance.

Besides the energy level of surface states associated with the gas, there are numerous other materials properties that significantly impact the calculation of the Vol’kenshtein adsorption coefficient. The relevant parameters (and assumed values) include the total number of adsorption sites per unit of surface area ($10^{15}$ cm$^{-3}$), oscillation frequency of adsorbates ($10^{13}$ Hz), mass of the adsorbate (32 amu in the case of O$_2$) and binding energy of the neutral (uncharged) adsorbate (0.1 eV). For simplicity in the present analysis, these parameters are assumed constant at the listed values taken from literature in a work that treated SnO$_2$. 

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Within the large body of scientific literature available on chemical sensors today, there is a great lack of studies that apply rigorous numerical analysis towards understanding of device properties at nanoscale. A search of the Compendex\textsuperscript{1} online database of scientific literature reveals that search criteria containing the words, “chemical sensor”, “oxide” and “finite element” yield only 81 results among the thousands of articles published on chemical sensors. The majority of the articles that include finite element modeling concern modeling of temperature distributions induced by heating elements, and none of them apply finite element models to the semiconductor itself. Due to the nanoscale dimensions of the chemical sensor and complex interaction with the surface, it is critical to have a calculation of electric field distribution within the device that is able to accurately resolve the electric field distribution throughout the film thickness. Such a problem calls for a numerical approach.

At least one earlier work reported application of a finite difference models toward calculation of changes in surface coverage of oxygen on ZnO.\textsuperscript{79} Another recent thesis work suggests the use of finite element modeling in calculating sensor response to gases.\textsuperscript{80} However, in both cases the discussion is brief and does not explicitly investigate changes in the chemisorption coefficient itself, which result from recursive interaction between the semiconductor surface and nanoscale material bulk. The author believes that the present thesis work represents the first application of finite element techniques towards a detailed investigation of the heterogeneous electrochemical nature of chemisorption on nanostructured semiconductor based chemical sensors.

A recent article treated numerical modeling of InGaZnO\textsubscript{4} based thin film transistors.\textsuperscript{73} In this study, instead of a finite element approach, the authors developed a finite difference based numerical code to evaluate charge carrier density throughout a film of nanoscale dimensions. Important in their work, the authors included the effect of sub-gap density of states intrinsic to the amorphous material structure, which has the effect of charge screening and impacts conductive properties in particular when the doping density of the device is low (5 x 10\textsuperscript{16} cm\textsuperscript{-3} in their case). Similarly, a thesis work was recently published that applied finite element analysis towards the understanding of amorphous properties of InGaZnO\textsubscript{4}.\textsuperscript{81} However, in all cases the models did not consider gas-related electrochemical charging and discharging that occurs at the surface of the material. For simplicity in the present analysis, sub-gap states related to the amorphous material are not modeled. In future work, the present model may be readily adapted to consider other properties of the amorphous material.

The proceeding sections begin by considering that the operation of a thin film transistor possesses a weak coupling between the gate electrode and the chemisorption process, which occurs in the case of a thick or heavily doped device (in this case, 10\textsuperscript{18} cm\textsuperscript{-3}). After that, the doping density is decreased to 3.1 x 10\textsuperscript{17} cm\textsuperscript{-3} to demonstrate a strongly coupled device, and the section then more generally examines how variation in donor density influences the electroadsorption process, through consideration of variation in the Vol’kenshtein chemisorption

\textsuperscript{1} Compendex Engineering Village online searchable database of scientific literature: www.engineeringvillage2.org

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coefficient and surface charge density as they relate to channel conductance over a range of gate bias. Then, with the electron donor density determined at a constant value, the energy level of gas surface states is swept within a range of 1 to 2.5 eV below the conduction band edge, to investigate the impact on the same parameters. The variation in electrochemical properties is considered as partial pressure is swept over 12 orders of magnitude from $10^{-12}$ atm up to 1 atm in the cases of a relatively weakly bound ($E_a = 1$ eV) and strongly bound ($E_a = 2.5$ eV) adsorbate. Finally, the impact of gate bias, in changing the amount of chemisorbed gas over a range of partial pressure ($10^{-12}$ atm to 1 atm), is considered separately for the cases of weak ($E_a = 1$ eV) and strong ($E_a = 2.5$ eV) chemisorption.

Three key parameters are examined with respect to the results derived for each case of the model: the Vol’kenshtein chemisorption coefficient, the surface charge density of chemisorbed gas, and the transistor channel conductance. The Vol’kenshtein chemisorption coefficient is an intrinsic property of the system and quantifies the strength of the interaction between the semiconducting metal oxide and the surrounding gas. The surface charge density is accumulated at the semiconductor/gas interface due to charge transfer in the chemisorption process and is proportionate to the fractional surface coverage of charged adsorbate. The channel conductance calculation is also of great importance in this study because it is the measureable output of the chemical sensor.

Because it was found that two dimensional models match closely to 1D models in the present system, unless otherwise stated, the proceeding sections will present 1D modeling results of interaction along the center of the film at a point equidistant between source and drain electrodes, through film thickness and to the buried gate electrode. At the end of this chapter, a 2D model is presented to illustrate the equivalency with this model and consider edge effects arising due to the influence of the source, drain and fringing fields through the air. In addition, capacitance vs. voltage characteristics of the nanoscale metal-oxide-semiconductor structure are derived, including the notable influence of the chemisorbed gas.

6.2. Finite Element Model Procedure and Implementation

All one dimensional calculations in the proceeding section were performed using a finite element basis. In the region of the semiconducting InGaZnO$_4$ channel, the semiconductor was modeled at a resolution of 1 element per nm i.e. 70 elements. In the region of the gate oxide underneath the conducting channel a much coarser grid was used, resulting in less than 100 total elements in the model. This small number of elements enabled rapid iterative solution to and permutation of the nonlinear equations describing surface and bulk parameters, to explore the above desired phenomena. A subset of the calculations were performed with the grid resolution increased 10x for a total of over 700 elements in the model. In this case, no impact was observed on model results within 4 significant digits of calculation of the dependent variables.

As described previously, the equations implemented in the finite element model include Gauss’ Law, the Poisson Equation, charge neutrality condition in the bulk of the semiconductor, and
Vol’kenshtein’s chemisorption coefficient for interaction with the surrounding environment. Electronic states of the conduction and valence bands were calculated as populated by the Fermi Function, evaluated with a Maxwell-Boltzmann approximation appropriate for non-degenerate materials. Convenient to this study, an equal voltage from source to drain was applied and as such the metal oxide structure was considered under static equilibrium. Channel conductance was determined by integrating carrier densities over the conducting channel thickness and multiplying by respective mobility, electronic charge, and channel dimensions. Charge neutrality was applied throughout the conducting channel including both space charge of ionized donors and mobile species (electrons, holes) again in light of static equilibrium.

Boundary conditions of this model included zero flux of charge carriers at the top semiconductor / gas surface and at the semiconductor / gate oxide interface. Gate bias was applied at the end of the gate oxide to influence the semiconductor layer. At the semiconductor/gas interface, a fixed surface charge density condition was applied, which is as determined in calculation of surface coverage using the Vol’kenshtein chemisorption coefficient. The buildup of charge at the outer surface in effect imposes an electric field on the rest of the bulk, and the entire system was solved in using a non-linear iterative finite element approach.

For further information on implementation of the finite element model, the reader is directed to the appendix of this thesis work, where the numerical simulation procedure is described in detail. In addition, the COMSOL Multiphysics Reference Guide provides a very thorough and detailed description of the finite element modeling approach and the capabilities of the software used to perform the present calculations.

6.3. Weak Coupling of the Transistor Gate in Chemisorption

The initially considered structure in the model concerns a thin film transistor that is dubbed, “weakly coupled” to the chemisorption process that occurs at the surface, as an initial point of reference. This represents a device of sufficiently high doping density or sufficiently large conducting channel thickness.

Table 1. Model parameters: Weak Coupling of Transistor Gate in Chemisorption

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGZO Channel length</td>
<td>2 μm</td>
</tr>
<tr>
<td>IGZO Channel width</td>
<td>40 μm</td>
</tr>
<tr>
<td>IGZO Donor density</td>
<td>$10^{15}$ cm$^{-3}$</td>
</tr>
<tr>
<td>IGZO Electron mobility</td>
<td>23.5 cm$^2$/Vs</td>
</tr>
<tr>
<td>Energy level of surface states induced by gas (position below $E_C$)</td>
<td>1.2 eV</td>
</tr>
<tr>
<td>Partial pressure of gas</td>
<td>1 atm</td>
</tr>
<tr>
<td>Device temperature</td>
<td>300 K</td>
</tr>
</tbody>
</table>
In this case, a voltage bias applied by the gate (left hand side of Figure 73) has little influence on the amount of band bending occurring at the surface (right hand side). An expanded view of the IGZO layer in the following figure (Figure 58) reveals that the potential only barely begins to influence the surface in the range of gate bias applied, because accumulated / depleted region of the SMO (left hand side) occurs over a length scale that does not reach the region depleted underneath the free surface that is exposed to the gas (right hand side). With the system in quasi-equilibrium under application of gate bias, the carrier concentrations are directly related to the electrical potential via Poisson-Boltzmann equation. The following figures further present electron and hole concentration through the IGZO film thickness in log scale. The inset of the electron concentration figure shows a linear scale plot, highlighting the distribution of delocalized electrons towards the center of the film thickness.

The final 3 figures in this section show key parameters derived from the finite element model of the TFT based chemical sensor. Channel conductance vs. gate bias, determined to be a linear relationship, as the accumulated or depleted zone of the IGZO film near the gate oxide is modulated and the surface potential barrier, resulting from chemisorbed states, remains largely unaffected. A closer examination of the Vol’kenshtein chemisorption coefficient directly reveals that there is indeed a small influence of gate bias on chemisorption states, in particular at the most negative (strongly depleted) gate biases. A corresponding small variation in surface charge density is also observed. Essentially, in all cases of gate bias the TFT remains turned on (in the saturation regime) and there is little influence of the gate on the surface because the electric fields that extend from both do not intersect.
Figure 73. Electrical potential throughout the thickness of the thin film transistor structure, from the bottom gate electrode (Si, left-hand side), through the gate oxide (SiO₂) and through the InGaZnO₄ film, to the top surface (right hand side), with gate bias as a parameter (legend). Numerically modeled in an InGaZnO₄ TFT that exhibits a relatively weak interaction with the surface (high donor density).
Figure 74. Electrical potential through the thickness of the InGaZnO$_4$ film, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). Numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively weak interaction with the surface (high donor density).
Figure 75. Electron concentration through the thickness of the InGaZnO₄ film, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). Main graph: log scale. Inset: linear scale. Numerically modeled in an InGaZnO₄ TFT that exhibits a relatively weak interaction with the surface (high donor density).
Figure 76. Hole concentration through the thickness of the InGaZnO$_4$ film, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). Numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively weak interaction with the surface (high donor density).
Figure 77. Channel Conductance vs. Gate Bias, numerically modeled in an InGaZnO$_4$ TFT that exhibits a weak interaction with the surface (high donor density).
Figure 78. Vol’kenshtein Chemisorption Coefficient (1/Pa) vs. Gate Bias, numerically modeled in an InGaZnO₄ TFT that exhibits a weak interaction with the surface (high donor density).
6.4. Strong Coupling of Transistor Gate in Chemisorption

This section contains 1D modeling results of an IGZO thin film transistor structure that is identical to the case of the previous section in every way except that here the doping density of the device is changed from $10^{18}$ cm$^{-3}$ to $3 \times 10^{17}$ cm$^{-3}$. Corresponding figures are provided relating to all of the parameters plotted in the previous section. It is evident that with a decreased doping density, the electrical potential, over the entire thickness of the IGZO film, is influenced by gate bias within the range of $-10$ V to 5 V. As a result, the charge carrier concentration throughout the bulk is heavily influenced by gate bias, and we see a strong relationship between gate bias and surface charge density corresponding to populated (chemisorbed) gas molecules. Interestingly, outside the accumulated regime of positive gate bias, both the surface charge density and the Vol’kenshtein chemisorption coefficient exhibit a linear dependence on applied gate voltage, as charge buildup at the gate electrode is directly balanced across the gate oxide and depleted IGZO film by charged, chemisorbed species at the IGZO surface. Channel conductance is also heavily modulated, varying nonlinearly by more than 10 orders of magnitude over the investigated range.

Figure 79. Surface Charge Density (Coulombs/meter) vs. Gate Bias, numerically modeled in an InGaZnO$_4$ TFT that exhibits a weak interaction with the surface (high donor density).
Figure 80. Electrical potential throughout the thickness of the thin film transistor structure, from the bottom gate electrode (Si, left-hand side), through the gate oxide (SiO$_2$) and through the InGaZnO$_4$ film, to the top surface (right hand side), with gate bias as a parameter (legend). Numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively strong interaction with the surface (low donor density).
Figure 81. Electrical potential through the thickness of the InGaZnO$_4$ film, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). Numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively strong interaction with the surface (low donor density).
Figure 82. Electron concentration through the thickness of the InGaZnO$_4$ film, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). Main graph: log scale. Numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively strong interaction with the surface (low donor density).
Figure 83. Hole concentration through the thickness of the InGaZnO₄ film, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). Numerically modeled in an InGaZnO₄ TFT that exhibits a relatively strong interaction with the surface (low donor density).
Figure 84. Channel Conductance vs. Gate Bias, numerically modeled in an InGaZnO$_4$ TFT that exhibits a strong interaction with the surface (low donor density).
Figure 85. Vol’kenshtein Chemisorption Coefficient ($1/\text{Pa}$) vs. Gate Bias, numerically modeled in an InGaZnO$_4$ TFT that exhibits a strong interaction with the surface (low donor density).
Figure 86. Surface Charge Density (Coulombs/meter) vs. Gate Bias, numerically modeled in an InGaZnO$_4$ TFT that exhibits a strong interaction with the surface (low donor density).
6.5. Influence of Electron Donor Density on Electroadsorption

Table 2. Constant parameters: Influence of Electron Donor Density on Electroadsorption

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel length</td>
<td>4 µm</td>
</tr>
<tr>
<td>Channel width</td>
<td>20 µm</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>2.6 cm²/Vs</td>
</tr>
<tr>
<td>Partial pressure of gas</td>
<td>1 atm</td>
</tr>
<tr>
<td>Energy level of surface states induced by gas</td>
<td>1.2 eV</td>
</tr>
<tr>
<td>(position below Ec)</td>
<td></td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 K</td>
</tr>
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</table>

Table 3. Varied Parameters: Influence of Electron Donor Density on Electroadsorption

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron donor density</td>
<td>4.4 to 5.6*10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>Gate Voltage</td>
<td>-10 to 5 Volts</td>
</tr>
</tbody>
</table>

In this section, the density of electronic donors is varied in a relatively small range, from (4.4 10¹⁷ cm⁻³ to 5.6 10¹⁷ cm⁻³), and the impact on channel conductance, Vol’kenshtein chemisorption coefficient and chemisorption induced surface charge density is investigated. As is shown in Figure 87, when the TFT is in the accumulation regime (positive VGS), only a very small change in conductance is observed, in response to the small change in electron donor density. When the channel is fully depleted in the subthreshold regime of the TFT, however, as is the case below VGS= -5V, the channel conductance varies by 3 orders of magnitude in response to relatively minute variation in doping density on the order of 20%.

Looking to the Vol’kenshtein chemisorption coefficient, at higher doping density, the chemisorption coefficient is also higher (Figure 88), resulting in a larger amount of surface coverage (Figure 90) and higher magnitude of surface charge density (Figure 89). Note that this increase in surface charge then acts to further deplete the TFT conducting channel in addition to the negative applied gate voltage. This explains why such a large variation in channel conductance is observed in response to such a small variation in doping density and also illustrates the complex interactions that arise between surface and bulk due to the electrostatic influence of chemisorption in nanostructured materials.
Figure 87. Channel conductance as a function of gate bias in a TFT of varied doping density. From bottom to top: $4.47 \times 10^{17}$ cm$^{-3}$, $4.73 \times 10^{17}$ cm$^{-3}$, $5.01 \times 10^{17}$ cm$^{-3}$, $5.31 \times 10^{17}$ cm$^{-3}$, and $5.62 \times 10^{17}$ cm$^{-3}$. 
Figure 88. Vol'kenshtein Chemisorption Coefficient vs. gate bias in a TFT of varied doping density. From bottom to top: $4.47 \times 10^{17}$ cm$^{-3}$, $4.73 \times 10^{17}$ cm$^{-3}$, $5.01 \times 10^{17}$ cm$^{-3}$, $5.31 \times 10^{17}$ cm$^{-3}$, and $5.62 \times 10^{17}$ cm$^{-3}$.
Figure 89. Surface Charge Density (Coulombs / cm²) vs. gate bias, in a TFT of varied doping density. From top to bottom: $4.47 \times 10^{17}$ cm$^{-3}$, $4.73 \times 10^{17}$ cm$^{-3}$, $5.01 \times 10^{17}$ cm$^{-3}$, $5.31 \times 10^{17}$ cm$^{-3}$, and $5.62 \times 10^{17}$ cm$^{-3}$. 
Figure 90. Surface coverage of chemisorbed (charged) species vs. gate bias, in a TFT of varied doping density. From bottom to top: $4.47 \times 10^{17} \text{ cm}^{-3}$, $4.73 \times 10^{17} \text{ cm}^{-3}$, $5.01 \times 10^{17} \text{ cm}^{-3}$, $5.31 \times 10^{17} \text{ cm}^{-3}$, and $5.62 \times 10^{17} \text{ cm}^{-3}$. 


6.6. Influence of Gas Energy Level on Electroadsorption

Table 4. Constant parameters: Influence of Gas Energy Level on Electroadsorption

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel length</td>
<td>4 μm</td>
</tr>
<tr>
<td>Channel width</td>
<td>20 μm</td>
</tr>
<tr>
<td>Electron donor density</td>
<td>$4 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>2.6 cm$^2$/Vs</td>
</tr>
<tr>
<td>Partial pressure of gas</td>
<td>0.2 atm</td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 K</td>
</tr>
</tbody>
</table>

Table 5. Varied Parameters: Influence of Gas Energy Level on Electroadsorption

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy level of surface states induced by gas</td>
<td>1 to 2.5 eV</td>
</tr>
<tr>
<td>(position below $E_c$)</td>
<td></td>
</tr>
<tr>
<td>Transistor gate voltage</td>
<td>-10 to 10 V</td>
</tr>
</tbody>
</table>

In this section, the energy level of surface states induced by the chemisorbed gas is varied from 1 to 2.5 eV below the conduction band edge, and the impact on conductance, Vol’kenshtein chemisorption coefficient and surface charge density is investigated. Figure 91 shows that as the energy level (separation from the conduction band) is increased, the conductance of the TFT decreases at $V_{GS} > 0$V. At higher energy levels (deeper surface states), the film thickness is fully depleted by the action of chemisorption at the surface at $V_{GS} = 0$V and moderate positive voltage. At negative gate bias, this trend continues except that at very negative values of gate bias and high binding energy (2 eV and 2.5 eV), an inversion in thin film conductance is observed, such that further decreases in gate bias result in an observed increase in conductance, with holes as the dominant charge carrier. As shown in Figure 91, the case of 2.5 eV energy position is particularly interesting, because variation in applied gate voltage in the range of -1.25V to -7.5V results in nearly no change in conductance (slightly increasing conductance at increasingly negative gate bias). This reflects the fact that at each increment of gate bias within this range, the decrease in integral electron concentration over film thickness is compensated by an increase in integral hole concentration of nearly the same magnitude, resulting in very little change in conductance.

Figure 92 shows that higher values of energy level (deeper levels of chemisorption trap states) result in higher values of the Vol’kenshtein chemisorption coefficient. This is consistent with the fact that deeper trap states are known to correspond to gases that bind more strongly to a given material (e.g. the energy level of NO$_2$ trap states on InGaZnO$_4$ would be expected to be significantly deeper than that of oxygen states, as it is a much stronger oxidant). In addition, in
the case of deeper trap states, the saturated value of the Vol'kenshtein chemisorption coefficient increases (Figure 92), as does the surface charge density (Figure 93). This is understood by noting that the saturation occurs in general when the TFT structure transitions from the depleted to the accumulated regime. Comparison of Figure 82, Figure 85 and Figure 86 illustrates that when the TFT is in accumulation, the gate loses its influence over chemisorption at the surface and hence the both the Vol’kenshtein chemisorption coefficient and the surface charge density reach saturated values. At higher values of chemisorption binding energy (deeper surface trap states), a stronger electric field is formed beneath the surface at equilibrium, and more gate voltage is required to bias the TFT into accumulation. In this manner also, the saturated values of the Vol’kenshtein chemisorption coefficient and the surface charge density are also heterogeneous properties of the system. A thicker semiconductor film would be expected to have lower saturated values of both of these parameters, because the ionized donors provide charge screening and lessen the impact that the gate has on changing the electrical potential at the surface, and vice versa.

Figure 91. Channel Conductance vs. Gate Bias, in a TFT that interacts with gases of varied energy position of surface states associated with chemisorption, from top to bottom: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 92. Vol’kenshtein Chemisorption Coefficient vs. Gate Bias, in a TFT that interacts with gases of varied energy position of surface states associated with chemisorption, from bottom to top: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 93. Surface Charge Density (Coulombs / cm$^2$) vs. Gate Bias, in a TFT that interacts with gases of varied energy position of surface states associated with chemisorption, from top to bottom: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 94. Surface coverage of chemisorbed (charged) species vs. gate bias, in a TFT that interacts with gases of varied energy position of surface states associated with chemisorption, from bottom to top: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
6.7. Influence of Gas Energy Level on Gas Sensitivity

Table 6. Constant parameters: Influence of Gas Binding Energy on Gas Sensitivity

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGZO channel length</td>
<td>4 [µm]</td>
</tr>
<tr>
<td>IGZO channel width</td>
<td>20 [µm]</td>
</tr>
<tr>
<td>IGZO donor density</td>
<td>4*10^{17} [cm^{-3}]</td>
</tr>
<tr>
<td>IGZO electron mobility</td>
<td>2.6 [cm^2/Vs]</td>
</tr>
<tr>
<td>Transistor gate voltage</td>
<td>0 [V]</td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 [K]</td>
</tr>
</tbody>
</table>

Table 7. Varied Parameters: Influence of Gas Binding Energy on Gas Sensitivity

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pressure of gas</td>
<td>10^{-12} to 1 [atm]</td>
</tr>
<tr>
<td>Energy level of surface states induced by gas</td>
<td>1 to 2.5 [eV]</td>
</tr>
<tr>
<td>(position below Ec)</td>
<td></td>
</tr>
</tbody>
</table>

In this section the gas sensitivity of the model structure is investigated, by varying partial pressure of the chemisorbed gas in the range of 10^{-12} to 1 atm and considering gases with energy position of gas induced surface states varied in the range of 1, 1.5, 2, and 2.5 eV below the conduction band edge. Figure 95 shows that channel conductance decreases as the concentration of oxidizing gas in the environment is increased. In addition, the sensor conductance is lower when the surface states exist at deeper energy levels below the conduction band edge, corresponding to the formation of a larger surface potential barrier for a given amount of surface coverage of chemisorbed species. At very low partial pressure, there is a common saturation level of maximum sensor conductance that is reached as the gas pressure is decreased. Figure 99 reveals that this correlates to the surface coverage reaching zero, and Figure 97 shows that once this occurs, the Vol’kenshtein chemisorption coefficient saturates at a constant value for decreasing partial pressure of the gas.

Figure 97 further illustrates the fact that as partial pressure of the gas increases, the Vol’kenshtein chemisorption coefficient decreases, which is a result of the nonlinear relationship between electronic properties of the sensor film and the chemisorption process occurring at the surface. Essentially, as more gas is chemisorbed, the electric potential barrier at the semiconductor/gas surface gets larger in magnitude, depleting the semiconductor thin film. This shifts the Fermi energy within the material towards the valence band in the vicinity of the top surface, decreasing the number of electrons that are available to participate in the chemisorption process. The net effect is that as partial pressure of the gas increases, the surface coverage of
chemisorbed molecules continues to increase (Figure 99) even though the chemisorption coefficient decreases. When the surface coverage is higher, the device tends to resist chemisorption of additional gas molecules, as is evident by the decreasing slope in surface coverage vs. partial pressure.

The tendency for the sensor to resist chemisorption of additional gas at high partial pressure is stronger in the case of gases that create sub-bandgap energy levels that are deeper below the conduction band edge. This is because deeper trap states deplete the semiconductor more heavily, decreasing the concentration of electrons that are needed for chemisorption to occur. In this manner, the gas possessing chemisorption-induced energy levels 2.5 eV below the conduction band saturates in surface coverage at about $10^{-2}$ atm (Figure 99), while other gases associated with shallower energy levels are still able to increase surface coverage at higher partial pressures. This is consistent with the fact that the 2.5 eV gas has decreased the conductance of the film far below the conductance observed in other gases at $10^{-2}$ atm (Figure 95). Interestingly, although the surface coverage of the 2.5 eV gas has nearly saturated at $10^{-2}$ atm, its conductance continues to drop rapidly as partial pressure is increased. In fact, this range of partial pressure exhibits both the smallest change in surface coverage and also the largest change in sensor conductance, when compared to other ranges.

To analyze the sensitivity of sensor response to the gas, it is instructive to extract the power law dependence of sensor resistance on gas pressure. Since an oxidizing gas is being detected, changes in resistance (inverse of conductance) are considered. For this analysis, the sensor resistance is assumed to be an exponential function of partial pressure of the gas:

$$ R = A p^\alpha $$  \hspace{1cm} (42)

where $R$ is sensor resistance, $p$ is the gas pressure, $A$ is a constant, and $\alpha$ is an exponent that characterizes the dependence of $R$ on $p$. In this case, the exponent $\alpha$ can be extracted from Figure 95 by the following calculation:

$$ \alpha = \frac{\log (R_x) - \log (R_0)}{\log (P_x) - \log (P_0)} $$  \hspace{1cm} (43)

where $R_x$ is sensor resistance at a given pressure, $P_x$, with increments in $x$ indicating adjacent datapoints in Figure 95. The resultant calculation of the resistance exponent $\alpha$ vs. gas pressure is shown in Figure 96, with higher values of $\alpha$ indicating a stronger sensitivity of sensor resistance to gas pressure. This figure highlights the fact that the highest sensitivity (in the case of the gas with energy states 2.5 eV below the conduction band edge) is obtained at a range of partial pressure that effects the least amount of change in surface coverage, as shown by Figure 99 above $10^{-2}$ atm. In this range, the exponent $\alpha$ approaches a value of 1, indicating that the resistance (and conductance) of the film is almost directly proportionate to the partial pressure of gas. At lower partial pressures of gas and for shallower energy states of the gas, there is a plateau in $\alpha$ of approximately 0.05, as is shown for a 1eV gas in the range of $10^{-3}$ to 1 atm, a 1.5
eV gas from $10^{-9}$ to $10^{-1}$ atm, and a 2 eV gas from $10^{-11}$ to $10^{-7}$ atm. It is interesting to note that this plateau occurs at the same level of $\alpha$, over different ranges of partial pressure for different gases. Finally, a third regime is clearly visible, where as previously noted, at sufficiently low gas pressure and energy level the gas sensitivity decreases rapidly (below $10^{-3}$ atm for a 1 eV gas and below $10^{-9}$ atm for a 1.5 eV gas), tending towards zero as seen in a 1 eV gas below $10^{-6}$ atm, when the surface becomes completely depleted of chemisorbed gas.

To summarize, in the present range of different gas energy levels (1, 1.5, 2, and 2.5 eV below the conduction band edge) and different partial pressures ($10^{-12}$ to 1 atm) that are simulated, there are three clear regimes of sensitivity that are observed, as quantified by the sensitivity exponent, $\alpha$:

\[ \alpha = 1 \] maximum sensitivity at high gas pressure and deep energy levels  
\[ \alpha = \alpha_0 \] plateau in sensitivity at intermediate energy levels and moderate gas pressure  
\[ \alpha = 0 \] no sensitivity at sufficiently low gas energy level and gas pressure

In this section, $\alpha_0$ was equal to 0.05 and did not change as a function of the position of the energy level associated with binding of the gas. The following sections will investigate other possible influences on sensitivity as quantified by $\alpha$, including the roles of gate bias and film thickness.
Figure 95. Channel Conductance vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with the binding energy of the gas varied in the following range (from top to bottom): 1 eV, 1.5 eV, 2 eV, and 2.5 eV.
Figure 96. Exponent $\alpha$ in the power law dependence of resistance on gas pressure ($R=Ap^\alpha$) vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with the binding energy of the gas varied in the following range (from bottom to top): 1 eV, 1.5 eV, 2 eV, and 2.5 eV.
Figure 97. Vol'kenshtein Chemisorption Coefficient vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with the binding energy of the gas varied in the following range (from bottom to top): 1 eV, 1.5 eV, 2 eV, and 2.5 eV.
Figure 98. Surface Charge Density vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with the binding energy of the gas varied in the following range (top to bottom): 1 eV, 1.5 eV, 2 eV, and 2.5 eV.
Figure 99. Surface coverage of chemisorbed (charged) species vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with the binding energy of the gas varied in the following range (bottom to top): 1 eV, 1.5 eV, 2 eV, and 2.5 eV.
6.8. Influence of Transistor Gate Voltage on Sensitivity to Weak Binding Gas

Table 8. Constant parameters: Influence of Transistor Gate Voltage on Sensitivity to Weak Binding Gas

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGZO channel length</td>
<td>4 [µm]</td>
</tr>
<tr>
<td>IGZO channel width</td>
<td>20 [µm]</td>
</tr>
<tr>
<td>IGZO donor density</td>
<td>4*10^{17} [cm^{-3}]</td>
</tr>
<tr>
<td>IGZO electron mobility</td>
<td>2.6 [cm²/Vs]</td>
</tr>
<tr>
<td>Energy level of surface states induced by gas</td>
<td>1 [eV]</td>
</tr>
<tr>
<td>(position below E_c)</td>
<td></td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 [K]</td>
</tr>
</tbody>
</table>

Table 9. Varied Parameters: Influence of Transistor Gate Voltage on Sensitivity to Weak Binding Gas

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pressure of gas</td>
<td>10^{-12} to 1 [atm]</td>
</tr>
<tr>
<td>Transistor gate voltage</td>
<td>-10, 0, and 10 [V]</td>
</tr>
</tbody>
</table>

In this section, the influence of gate voltage on the sensitivity of sensor response to a relatively weak binding gas is investigated. The energy level of surface states located associated with the weak binding gas is assumed to be located 1 eV below the conduction band edge, as is the case of oxygen on SnO₂. Negative gate voltage decreases channel conductance, and positive increases it, as expected (Figure 100). Important to note is the impact on the Vol’kenshtein chemisorption coefficient. A negative gate bias causes the chemisorption coefficient to decrease (Figure 102), which will reduce the amount of chemisorbed gas, hence causing the surface coverage of charged species to decrease (Figure 104) and the surface charge density to move towards a more positive value (Figure 103). On the other hand, a positive gate bias does not influence the Vol’kenshtein coefficient or the surface charge density, because the device is biased into accumulation. As is seen in other simulation data (Figure 74, Figure 81), when the electroad sorption FET is biased sufficiently far into accumulation such that the depletion region from the top surface does not meet the depletion region from the bottom surface, the gate electrode loses its influence over the process of chemisorption.

As the partial pressure of the gas is decreased initially from the range of one atmosphere, all values of conductance in Figure 100 are observed to increase until the surface coverage of charged species reaches zero (Figure 104) and effectively all of the chemisorbed gas is removed from the surface. The slope that is observed in conductance vs. partial pressure of the gas is
determined by the relative fraction of total conductance that the chemisorbed gas at the surface tends to influence by means of depletion of electrons. To investigate sensitivity explicitly, Figure 101 plots the exponent $\alpha$ of $R = Ap^\alpha$ as was examined in the previous section, where $R$ is sensor resistance, $p$ is pressure and $A$ is a constant. Application of 10 volts of positive gate bias causes the sensitivity exponent $\alpha$ to decrease by about a factor of 2.5 from 0.05 to 0.02 at 1 atm of gas pressure. As was previously seen, the positive gate bias will cause a fraction of the semiconductor film near the semiconductor / oxide interface to be driven into accumulation, and the conductance this region of the film will not be sensitive to depletion occurring at the semiconductor / gas surface. Conversely, when -10 volts bias is applied to the gate, the sensitivity exponent $\alpha$ increases by 19x, increasing to a value of $\alpha = 0.95$ at 1 atm of gas pressure.

Figure 100. Channel conductance vs. partial pressure of weakly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from bottom to top): -10V, 0V, 10V.
Figure 101. Exponent $\alpha$ in the power law dependence of resistance on gas pressure ($R = A p^\alpha$) vs. partial pressure of weakly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from top to bottom): -10V, 0V, 10V.
Figure 102. Vol'kenshtein chemisorption coefficient vs. partial pressure of weakly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from bottom to top): -10V, 0V, 10V. Note, the 0V and 10V lines overlay so that only the 10V curve is visible.
Figure 103. Surface charge density (Coulombs/cm²), vs. partial pressure of weakly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from top to bottom): -10V, 0V, 10V. Note, the 0V and 10V lines overlay so that only the 10V curve is visible.
Figure 104. Surface coverage of chemisorbed (charged) species vs. partial pressure of weakly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from top to bottom): $-10V$, $0V$, $10V$. Note, the $0V$ and $10V$ lines overlay so that only the $10V$ curve is visible.
6.9. Influence of Transistor Gate Voltage on Sensitivity to Strong Binding Gas

Table 10. Constant parameters: Influence of Transistor Gate Voltage on Sensitivity to Strong Binding Gas

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGZO channel length</td>
<td>4 [μm]</td>
</tr>
<tr>
<td>IGZO channel width</td>
<td>20 [μm]</td>
</tr>
<tr>
<td>IGZO donor density</td>
<td>$4 \times 10^{17}$ [cm$^{-3}$]</td>
</tr>
<tr>
<td>IGZO electron mobility</td>
<td>2.6 [cm$^2$/Vs]</td>
</tr>
<tr>
<td>Energy level of surface states induced by gas</td>
<td>2.5 [eV]</td>
</tr>
<tr>
<td>(position below $E_C$)</td>
<td></td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 [K]</td>
</tr>
</tbody>
</table>

Table 11. Varied Parameters: Influence of Transistor Gate Voltage on Sensitivity to Strong Binding Gas

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pressure of gas</td>
<td>$10^{-12}$ to 1 [atm]</td>
</tr>
<tr>
<td>Transistor gate voltage</td>
<td>-10, 0, and 10 [V]</td>
</tr>
</tbody>
</table>

Similar to the previous section, changes in device properties in response to changes in the partial pressure of gas in the environment are calculated, and the influence of gate bias is additionally investigated, with the only difference in this case being that the position of the energy level of the chemisorbed gas within the bandgap of the semiconducting metal oxide is moved to a deeper level below the conduction band (i.e. 2.5 eV below the conduction band edge in this case vs. 1 eV examined in the previous section). Hence the film conductance of the electroadsorption FET shown in at 0V is lower than the respective plot in Figure 100.

Notably, when a negative gate bias is applied, the conductance exhibits a more complex trend with respect to partial pressure of the gas as compared to other cases: when the partial pressure is increased from $10^{-12}$ to $10^{-7}$, the conductance decreases with a constant slope and above that pressure it increases at a constant slope. This is understood by examination of Figure 106 and Figure 107, which show that at a partial pressure of $10^{-7}$ atm the electron and hole concentrations are approximately equal. Hence, lower partial pressure below $10^{-7}$ atm causes electron concentration and film conductance to increase. Conversely, at higher pressures above $10^{-7}$ atm, the film becomes inverted from n-type to p-type, and film conductance continues to increase with holes as the dominant electronic charge carrier. Figure 108 illustrates that in the n-type regime, the sensitivity exponent $\alpha=0.94$, and in the p-type regime $\alpha=-0.8$, both of these cases corresponding to gate bias of -10 V. When 10V positive bias is applied, the sensitivity drops
from $\alpha=0.82$ to $\alpha=0.02$ at 1 atm, which is approximately the same level of sensitivity that was observed previously for a weak binding gas under 10V positive gate bias.

Figure 109 shows that although application of positive gate bias has little effect on the Vol’kenshtein chemisorption coefficient (it increases slightly), negative gate bias of -10V decreases the chemisorption coefficient roughly by a factor of 2 as compared to its value at 0V gate bias. Similarly, Figure 110 illustrates that with 10V positive gate bias causes the surface charge density to increase in magnitude by a little over 10% at 1 atm, whereas -10V gate bias decreases it in magnitude by about a factor of 3. The same can be said of the surface coverage of charged species (which is proportionate to the surface charge density), as shown in Figure 111.

In general, the emergence of the inversion phenomenon within the conductance vs. pressure trend is due to a stronger depletion of the film thickness by the chemisorbed species at the top surface. Because as the energy states associated with chemisorption are deeper below the conduction band edge, the same surface concentration of chemisorbed gas induces a stronger band bending into the depth of the InGaZnO$_4$ film. With the film already heavily depleted by chemisorption at the semiconductor / gas surface, less gate bias is required to ultimately bias film into inversion and cause holes to become the dominant electronic charge carrier.
Figure 105. Channel conductance vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from bottom to top): -10V, 0V, 10V.
Figure 106. Electron concentration vs. thickness through the semiconducting metal oxide film, from the bottom SMO/gate interface (left) to the top SMO/gas interface (right) at increasing partial pressure of strongly chemisorbed in the range of $10^{-12}$ to 1 atm (top to bottom, each line representing a change in pressure of one decade), with transistor gate bias varied in the range (color coded) -10V, 0V, 10V.
Figure 107. Hole concentration vs. thickness through the semiconducting metal oxide film, from the bottom SMO/gate interface (left) to the top SMO/gas interface (right) at increasing partial pressure of strongly chemisorbed in the range of $10^{-12}$ to 1 atm (bottom to top, each line representing a change in pressure of one decade), with transistor gate bias varied in the range (color coded) -10V, 0V, 10V.
Figure 108. Exponent $\alpha$ in the power law dependence of resistance on gas pressure ($R=A \rho^\alpha$) vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from bottom to top): -10V, 0V, 10V.
Figure 109. Vol’kenshtein chemisorption coefficient vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from bottom to top): $-10V$, $0V$, $10V$. 
Figure 110. Surface charge density (Coulombs/cm²), vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from top to bottom): -10V, 0V, 10V.
Figure 111. Surface coverage of chemisorbed (charged) species vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with transistor gate bias varied in the range (from bottom to top): $-10V$, $0V$, $10V$. 
6.10. Influence of Film Thickness on Sensitivity to Strong Binding Gas

Table 12. Constant parameters: Influence of Film Thickness on Sensitivity to Strong Binding Gas

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGZO channel length</td>
<td>4 [μm]</td>
</tr>
<tr>
<td>IGZO channel width</td>
<td>20 [μm]</td>
</tr>
<tr>
<td>IGZO donor density</td>
<td>$4 \times 10^{17}$ [cm$^{-3}$]</td>
</tr>
<tr>
<td>IGZO electron mobility</td>
<td>2.6 [cm$^2$/Vs]</td>
</tr>
<tr>
<td>Energy level of surface states induced by gas</td>
<td>2 [eV]</td>
</tr>
<tr>
<td>(position below $E_c$)</td>
<td></td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 [K]</td>
</tr>
<tr>
<td>Transistor gate voltage</td>
<td>0 [V]</td>
</tr>
</tbody>
</table>

Table 13. Varied Parameters: Influence of Film Thickness on Sensitivity to Strong Binding Gas

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pressure of gas</td>
<td>$10^{-12}$ to 1 [atm]</td>
</tr>
<tr>
<td>Film thickness</td>
<td>20, 30, 40, 50, 60, 70, 100, and 200 [nm]</td>
</tr>
</tbody>
</table>

In this section, the gas under consideration is defined to have energy states that are located 2 eV below the edge of the conduction band. Partial pressure of the gas is varied within the range of $10^{-12}$ atm to 1 atm to characterize gas sensitivity (change in conductance vs. change in gas pressure) and the thickness of the film is varied in the range of 20 nm to 200 nm as shown in Table 13, to determine the influence of film thickness on gas sensitivity. Note that as a point of reference in the present study, the case of 70 nm film thickness modeled in this section is similar to the model result for a gas of the same energy level (2 eV below the conduction band edge) as shown in section 6.7 Influence of Gas Energy Level on Gas Sensitivity.

The resulting calculation of film conductance vs. gas partial pressure over the range of specified sensor thicknesses is shown in Figure 112. From the figure, it is clear that the 70 nm thick film exhibits a weak sensitivity to the gas, changing by approximately one order of magnitude in resistance over 12 orders of magnitude of variation in partial pressure of the gas. Thicker films (100 and 200 nm) exhibit an even weaker relationship between gas pressure and sensor conductance, because the gas is only able to deplete a fraction of the total thickness of the film. Significant increases in gas sensitivity are observed as film thickness is decreased below 70 nm, which is sufficiently thin to enable the depleted region of the film at the exposed semiconductor surface to penetrate the entire film thickness. For sufficiently thin films and high gas pressure,
the film sensitivity tends to increase from a low value associated with partial depletion of the film to a higher value of sensitivity associated with complete depletion of the film.

Figure 113 provides a calculation of the sensitivity exponent \( \alpha (R=A\rho^\alpha) \), which demonstrates clearly that the observed plateaus in sensitivity are a function of film thickness. By observation of \( \alpha \) calculated at 1 atm pressure, it is clear that films possessing thickness of 20, 30, 40, 50 and 60 nm each reach separate plateaus in the sensitivity exponent \( \alpha \) of 0.94, 0.92, 0.89, 0.86 and 0.84 respectively. On the other side of this figure, it is clear that the 200, 100, 70 and 60 nm films each approach a lower plateau in the sensitivity exponent \( \alpha \) at approximately 0.01, .03, 0.05, and 0.07 respectively. It is interesting to contrast these observations to the earlier section (6.7. Influence of Gas Energy Level on Gas Sensitivity), because in this previous case the values of \( \alpha \) observed at the lower plateau were not influenced by changes in energy position of the gas. Here, the sensitivity exponent \( \alpha \) is shown to be a strong function of film thickness an upper and lower plateau of sensitivity. At the upper plateau, the entire film thickness is more strongly controlled by depletion of the film that occurs at the semiconductor / gas interface when the film is thinner. Conversely, at the lower plateau in sensitivity, a thicker film contributes a relatively larger fraction of total film conductance that is not influenced by the depletion that occurs at the semiconductor / gas interface.

The Vol’kenshtein chemisorption coefficient is shown in Figure 114, illustrating slightly lower values for thinner films due to stronger depletion of charge carriers throughout the entire film thickness. Similarly, Figure 116 shows that due to the lower Vol’kenshtein chemisorption coefficient, the surface coverage at a given partial pressure of gas is also decreased significantly. Importantly, even though the surface coverage is lower in the case of thinner films, the continues to increase as noted above, due to a strong influence of surface depletion on the total conductance of the film.
Figure 112. Channel conductance vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with film thickness varied in the range of (from bottom to top) 20 (dashed), 30, 40, 50, 60, 70, 100, and 200 [nm].
Figure 113. Exponent $\alpha$ in the power law dependence of resistance on gas pressure ($R = A p^\alpha$) vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with film thickness varied in the range of (from top to bottom) 20 (dashed), 30, 40, 50, 60, 70, 100, and 200 [nm].
Figure 114. Vol’kenshtein chemisorption coefficient vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with film thickness varied in the range of (from bottom to top) 20 (dashed), 30, 40, 50, 60, 70, 100, and 200 [nm].
Figure 115. Surface charge density (Coulombs/cm$^2$), vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with film thickness varied in the range of (from top to bottom) 20 (dashed), 30, 40, 50, 60, 70, 100, and 200 [nm].
Surface Coverage of Charged Species vs. Partial Pressure of Gas (atm)

Figure 116. Surface coverage of charged chemisorbed species (fraction of total sites), vs. partial pressure of strongly chemisorbed gas in the range of $10^{-12}$ to 1 atm, with film thickness varied in the range of (from bottom to top) 20 (dashed), 30, 40, 50, 60, 70, 100, and 200 [nm].
6.11. The Electroadsorption FET Capacitance vs. Voltage

Table 14. Constant parameters: the Electroadsorption FET Capacitance vs. Voltage

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel length</td>
<td>4 μm</td>
</tr>
<tr>
<td>Channel width</td>
<td>20 μm</td>
</tr>
<tr>
<td>Electron donor density</td>
<td>$4 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>2.6 cm$^2$/Vs</td>
</tr>
<tr>
<td>Partial pressure of gas</td>
<td>0.2 atm</td>
</tr>
<tr>
<td>Device temperature</td>
<td>450 K</td>
</tr>
</tbody>
</table>

Table 15. Varied Parameters: the Electroadsorption FET Capacitance vs. Voltage

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy level of surface states induced by gas (position below $E_c$)</td>
<td>1 and 2 eV</td>
</tr>
<tr>
<td>Transistor gate voltage</td>
<td>-20 to 10 V</td>
</tr>
</tbody>
</table>

In this section, the capacitance vs. voltage relationship is calculated. The modeled parameters for this section are essentially reproduced from the earlier section, 6.6. *Influence of Gas Energy Level on Electroadsorption*, which examined sensor properties as a function of gate bias from -10V to 10V at various levels of energy placement of chemisorption-induced surface states (1 eV, 1.5 eV, 2 eV and 2.5 eV below the conduction band edge). In this case the device is swept lower to -20V, which is sufficiently negative to drive the Electroadsorption FET into electronic inversion at the semiconductor / gate oxide interface for all energy levels considered. The corresponding calculations of sensor film conductance (Figure 117), Vol’kenshtein chemisorption coefficient (Figure 118), surface charge density (Figure 119) and surface coverage (Figure 120) are provided for reference. Capacitance vs. voltage relationship is calculated for two cases, including energy position of surface states located 1 eV and 2 eV below the conduction band edge, and the result is shown in Figure 121.

Capacitance is calculated from the voltage applied at the gate electrode as compared to the associated electronic charge that builds up at the gate electrode, according to the relationship $Q = CV$, where $Q$ is the charge at the gate electrode, $V$ is voltage applied from the gate to the reference (source and drain) electrodes and $C$ is capacitance from gate to reference electrodes. Since the charge $Q$ is calculated in the system at a state of equilibrium, the associated capacitance would be observed only when the system is given enough time to fully equilibrate with each new setpoint of voltage measurement. In other words, the present capacitance calculation corresponds to the system measured at very low frequency, perturbed sufficiently
slower than the longest time constant necessary for the system to relax into a state of equilibrium as described by the present model for chemisorption. The calculation in Figure 121 evaluates the electronic charge at the gate electrode at a resolution of 0.5 volts per increment in gate voltage in the range of -20 to 10 volts, so that the derivative of $Q$ vs. $V$ may be clearly calculated within this range using a three point center difference approximation.

Considering first the calculation of capacitance vs. voltage for a gas that induces surface states that are located 2 eV below the conduction band edge, there are three clear regimes of capacitance observable. At gate biases above 5V and below -15V, the capacitance reaches a value of $2.95 \times 10^{-14}$ Farads, as the semiconductor is driven into electronic accumulation and inversion, respectively, at the semiconductor / gate oxide interface. In between these two extremes, the capacitance decreases to a plateau of approximately $2.37 \times 10^{14}$ Farads, when the entire thickness of the film is depleted (Figure 117) and variation in gate bias is able to cause a linear change electronic charge density at the semiconductor / gas surface (Figure 119). These two values of capacitance are in good agreement with dielectric capacitance as is estimated from device dimensions. Considering the first case, the capacitance across the oxide is calculated from the well known relationship:

$$C = \frac{\varepsilon_0 \varepsilon_r WL}{t_{ox}}$$

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the oxide, $W$ is device width, $L$ is device length, and $t_{ox}$ is thickness of the gate oxide layer. The above calculation yields a value of $C=2.98 \times 10^{14}$ F, which is very close to the numerical value in accumulation and inversion, as expected. In addition, the dielectric capacitance across the depleted semiconductor layer can be calculated and combined in series with the gate capacitance to calculate total dielectric capacitance from the gate electrode to the semiconductor / gas surface:

$$C_{tot} = \frac{C_{ox}C_{semi}}{C_{ox} + C_{semi}}$$

Where $C_{semi}$ is capacitance across the semiconductor layer, $C_{ox}$ is capacitance across the gate oxide, and $C_{tot}$ is the total capacitance across both layers. In this manner, $C_{tot}$ is calculated as $2.38 \times 10^{-14}$ F, which is only 0.4% higher than the numerically computed value in the center plateau region of capacitance. Considering the above comparison, it is fair to conclude that the center plateau region of capacitance vs. voltage corresponds to a capacitive charging and discharging of chemisorption-induced surface states, across the gate oxide and depleted semiconductor dielectric layers.

Next, the calculated $C$ vs. $V$ curve is considered in the case of a gas that has surface energy states that are 1 eV below the conduction band edge, i.e. a weaker bonding gas than was considered above. The result of this calculation is shown overlaid with the calculation of a stronger binding gas energy states located 2 eV below the conduction band edge (Figure 121), with several
notable differences. Firstly, the two calculations are observed to be similar in that the calculated values of capacitance under heavy accumulation and inversion are the same, as is the value of capacitance in the center plateau region. However, beginning with positive values of gate bias and proceeding in the direction of negative voltage, it is clear that a more negative value of gate bias is necessary to reach the center plateau of capacitance in the weaker binding (1 eV) gas. In addition, the capacitance of the structure transitions more gradually from the higher value ($2.95 \times 10^{-14}$ F) to the lower plateau ($2.37 \times 10^{-14}$ F), indicated by a lower slope in C vs. V in the case of the weaker binding gas (1 eV) over the range of $V_{GS}=2V$ to $V_{GS}=-5V$, compared to a steeper slope for the transition of the stronger binding gas between $V_{GS}=2V$ and $V_{GS}=-1V$. As is expected, the weaker binding gas depletes a smaller fraction of the total film thickness, and application of increasingly negative gate bias gradually depletes the remainder of the film. During this transition, the capacitance gradually decreases as the depleted zone extends outward from the gate oxide / semiconductor interface until it intersects the depletion zone extending from the semiconductor / gas surface, completely depleting the film of charge carriers and capacitively coupling the gate electrode to the semiconductor / gas surface.

The most drastic difference between the C-V curve of the weak binding gas and the stronger binding gas is observed at -14 V, where the capacitance of the weak binding gas (1 eV below the conduction band edge) drops sharply to a calculated lower spike of $1.17 \times 10^{-14}$ Farads before increasing to the upper plateau value of capacitance as gate voltage is decreased. The meaning of this phenomenon is understood by examination of Figure 120, which shows that at this voltage, the surface coverage of charged species has decreased to a value of nearly zero. As was seen in previous sections, this complete depletion of surface coverage occurs more readily in weaker binding gases, which create a smaller surface potential barrier that is easier for a negative applied gate bias to overcome the process of inducing desorption. Hence, the stronger binding gas has not become completely depleted of surface coverage at this same level of gate bias (-14 V) as is also clearly visible in Figure 120. The reason for a sudden drop in capacitance of the weaker binding gas may be then understood simply due to the absence of any electronic states at the surface to charge or discharge (Figure 119). Because a very negative gate bias was necessary to induce this depleted condition at the semiconductor / gas surface, an increasingly negative gate bias rapidly drives the semiconductor / gate oxide interface into electronic inversion, significantly decreasing sensitivity of the surface to any further changes in gate bias.
Figure 117. Thin film conductance vs. gate bias of an Electroadsorption FET that interacts with gases of varied energy position of surface states associated with chemisorption, from top to bottom on the right hand side: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 118. Vol’kenshtein chemisorption coefficient (1/Pa) vs. gate bias of an Electroadsorption FET that interacts with gases of varied energy position of surface states associated with chemisorption, from bottom to top: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 119. Surface charge density (Coulombs per cm$^2$) vs. gate bias of an Electroadsorption FET that interacts with gases of varied energy position of surface states associated with chemisorption, from top to bottom: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 120. Surface coverage of chemisorbed (charged) species vs. gate bias of an Electroadsorption FET that interacts with gases of varied energy position of surface states associated with chemisorption, from bottom to top: 1 eV, 1.5 eV, 2 eV, and 2.5 eV below the conduction band edge.
Figure 121. Capacitance vs. voltage of the Electroadsoption FET as calculated in the presence of two different gases: a gas that creates surface trap states that are 1 eV (blue) below the conduction band edge and one with surface trap states that are 2 eV (red) below the conduction band edge.
6.12. The Electroadsorption FET in 2D

With the 1D model having been used for investigations of the various operating regimes of chemisorption device, a 2D model was constructed to further consider the influences of electric field fringing near the source and drain, around the electrodes and in the vicinity in the chemisorbed charged layer. All physical device dimensions were considered to be the same as in the 1D model, with the addition of source and drain electrodes of the same thickness (70nm) as the conducting channel. In addition, all model parameters such as doping density, environment temperature, energy level of surface states were specified to be identical to the case shown previously in section 6.4 titled, “Strong Coupling of Transistor Gate in Chemisorption”, hence facilitating a direct comparison of results in this case to the 1D model.

The model contained approximately 80,000 elements. The grid size was varied and concentrated in the vicinity of the semiconducting channel and at corners of structures where fringing fields occur.

A plot of electric potential vs. position in 2D is shown in Figure 122, with the device evaluated at several values of gate bias, \( V_{GS} = -5, -2.5, 0, 2.5, \) and \( 5 \) volts. The chart illustrates electric potential inside the device and also fringing fields above EA-FET. The chemisorbed gas on the surface exerts its own influence on the electric potential in the region of the device, as is clearly observable from the soft-blue shaded region in the center of the pictures.

It was considered to be of particular importance to utilize this 2D model to validate the assumption that the 1D model provides an accurate description of device properties. Comparison of Figure 123 to Figure 81 demonstrates that the 1D model indeed does provide an accurate calculation of electric potential through thickness at the center of the conducting channel of 2\( \mu \)m length. In consideration of fringing fields that arise close to the source and drain electrodes, Figure 124 shows the electric potential vs through film thickness at a distance of 100 nm from the source electrode, which is nearly identical to the calculation taken at the center of the film. Significant deviation from the above two calculations is observable in Figure 125, which is taken at a distance of 10 nm of the film. However, this location represents only a small fraction of the conducting length. Hence, the 1D calculations are validated by analysis of the electric potential in 2D.
Figure 122. Two dimensional plot of electric potential, vs. cross sectional position of the thin film transistor as gate bias is varied in the range of -5, -2.5, 0, 2.5 and 5 V (from bottom to top). Transistor dimensions are 2 microns channel length and 70 nanometers thickness. Electric potential is indicated in the color bar, with isopotential lines shown in white (5 lines equally spaced in electric potential per image). The center of the device experiences chemisorption, which creates a sheet of chemisorbed charge at the TFT surface. The equilibrium concentration of this charge sheet is a function of applied gate bias, temperature, gas concentration and gas binding energy, all of which are captured in the two dimensional finite element numerical model.
Figure 123. 1D cross section of electrical potential through the thickness of the InGaZnO$_4$ film, taken at the center of the conducting channel of length 2µm modeled in 2D, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). This is numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively strong interaction with the surface (low donor density).
Figure 124. 1D cross section (of 2D model) of electrical potential through the thickness of the InGaZnO$_4$ film, taken 100 nm distance from the source electrode, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). This is numerically modeled in an InGaZnO$_4$ TFT that exhibits a relatively strong interaction with the surface (low donor density).
Figure 125. 1D cross section (of 2D model) of electrical potential through the thickness of the InGaZnO₄ film, taken 10 nm distance from the source electrode, from the gate oxide interface (left hand side) to the top surface (right hand side), with gate bias as a parameter (legend). This is numerically modeled in an InGaZnO₄ TFT that exhibits a relatively strong interaction with the surface (low donor density).
6.13. The Chemisorption Capacitor (Chemiresistive Sensor) in 2D

It is further of great interest to apply this model towards the operation of thin film resistor based chemical sensors, as are very widely studied in the field of chemical sensor technology. This is achieved by considering a structure identical to the above and simply causing the gate electrode to float. Note that in order to make such a calculation, it is essential that the structure be treated in at least two dimensions, to establish a reference level of electric potential as is exerted by the source and drain electrodes. This sort of device is commonly described within sensor literature as a chemiresistive device, because of the influence that the chemisorbed species at the surface has in changing the resistance that is measured by the source and drain electrodes. Given the additional electronic influence that the chemisorbed gas has in charging and discharging the surface and thereby influencing the electrical potential of the surrounding environment, this device can be appropriately titled a chemisorption capacitor.

An oxidizing gas possessing an energy level of the surface states at 2 eV below the conduction band was considered, identical to conditions of section 6.7 Influence of Gas Energy Level on Gas Sensitivity, with concentration of the oxidizing gas varied from $10^{-12}$ to 1 atm. The result of the calculation is shown in Figure 126, illustrating changes in electric potential in the range of -4.5 to -6 volts in the region surrounding the chemically active surface in response to chemisorption of the oxidizing gas. Notably, at higher concentrations of the gas especially, there is a significant change in electrical potential drop in the air surrounding the sensor surface addition to the film.

![Figure 126. Two dimensional plot of electric potential, vs. cross sectional position of the chemiresistive sensor (chemisorption capacitor) structure at several concentrations of oxidizing gas in the surrounding environment: 1 ppm, 100 ppm, and 10,000 ppm. Resistor dimensions are 2 microns channel length and 70 nanometers thickness. Electric potential is indicated in the color bar to the right of the image.](image-url)
7. Discussion

7.1. Numerical Results

7.1.1. Electroadsoption FET Regimes of Operation
As discussed earlier, the conventional nanoelectronic device that bears closest semblance to the EA-FET is the thin film transistor. Both devices are also based on the MOS capacitor. However, with the addition of the interaction with the gas, there is a new state variable that must be accounted for: the surface charge associated with chemisorption, $Q_s$.

The following approach considers regimes of operation when the applied drain current is sufficiently low not to result in any observable pinch-off effect (due to voltage drop along the channel length). The proceeding discussion will describe regimes of operation of the EA-FET on this basis, proposing the following regimes (for an n-type semiconductor):

- $V_G > V_{DEP}$: Electronic Accumulation
- $V_{DEP} > V_G > V_{PT}$: Electronic Depletion
- $V_{PT} > V_G > V_{CHD}$: Electrochemical Punchthrough
- $V_{CHD} > V_G > V_{INV}$: Electrochemical Depletion
- $V_{INV} > V_G$: Electronic Inversion

Note, all of the above threshold voltages are directly resultant from parameters of the numerical model evaluated on a particular materials system at nanoscale. In addition these following evaluations apply to the model structure considered at in a state of equilibrium with the environment. Kinetic processes will be discussed later, as will possible non-idealities in the above.

With $V_G$ below $V_{DEP}$, the device enters the electronic depletion regime, wherein the depletion regions extend from both the semiconductor/gate oxide interface and semiconductor/top surface and together modulate the width of a conducting channel in the semiconductor bulk.

When the two depletion regions intersect (for $V_G > V_{PT}$), the device enters electrochemical punchthrough. In this regime, the surface is heavily modulated by changes in the electric potential at the buried gate. In addition, by the same relation, the electric potential of the gate electrode may be influenced by chemisorption induced charge at the semiconductor/gas interface. Both surfaces modulate the charge carrier concentration of the bulk, and the dominant charge carrier within the semiconducting thin film in this regime can be converted from n- to p-type at sufficiently strong levels of negative (depletive) gate bias.

When the device enters the electrochemical depletion regime, the surface coverage of charged chemisorbates tends to zero, and then the buried gate electrode completely controls the
conductance of the film. Note, this regime is titled, “electrochemical” depletion and not “chemical” depletion because it refers to the electronic influence of gate bias to deplete the surface concentration of charged chemisorbed species. Besides this means of depleting the surface coverage, there is another regime that can be titled, chemical depletion, which is entered when the partial pressure of the gas that is chemisorbed at the surface drops to a sufficiently low level, as is seen in Figure 95 and Figure 98 in a gas of energy position 1 eV below the conduction band for partial pressures below $10^{-6}$ atm (1ppm). This regime is omitted from the present list because it is not electronically induced by means of the gate electrode.

Note that $V_{PT}$ and $V_{CHD}$ are numerically derived parameters relating to the interaction between the surface, the bulk, concentration of surrounding gas, the gas binding energy, and temperature of operation, among other parameters. However, these points may be approximated by a graphical analysis of numerical model results. In addition, the order of progression through the proposed regimes of operation may not occur exactly as listed above. If the surface heavily depletes the bulk due to high binding energy or high concentration of gas, the device may proceed directly from electronic accumulation to electrochemical punchthrough and skip the electronic depletion regime. Similarly, it is possible for the device to progress directly to electronic inversion prior to the surface reaching the chemical depletion regime, if the electronic inversion threshold voltage $V_{INV}$ is larger than the chemical depletion threshold voltage $V_{CH}$. Once the semiconductor / gate oxide interface is inverted, the gate loses its capability to deplete the surface, and the system will also lose its chemical sensitivity, as conduction through the film channel will be dominated by the inversion layer. In this manner, the operation of the EA-FET may reduce to a minimum of the following regimes:

\[
V_G > V_{PT} \quad \text{Electronic Accumulation}
\]
\[
V_{PT} > V_G > V_{INV} \quad \text{Electrochemical Punchthrough}
\]
\[
V_{INV} > V_G \quad \text{Electronic Inversion}
\]

7.1.2. Analytical Model Derivation and Parameterization

This section seeks to derive a set of equations that approximate the response of the Electroadsorption FET within each regime of operation. Where appropriate, analytical models are employed that link electronic measurements of the EA-FET to its underlying geometric, electronic, and electrochemical properties. In addition, numerical simulation results are analyzed and parameterized to obtain expressions for device operation that are otherwise nontrivial to obtain by simple analytical techniques.

The model predicts that in the electrochemical punchthrough regime, (when the thin film transistor conducting channel is completely depleted) there is an approximately linear relationship between gate bias and the equilibrium level of surface charge density induced by chemisorption, as depicted in . In other words, in the depleted regime:
\[ Q_s = X_{CH} V_{GS} \]  

(44)

where \( Q_s \) is the surface charge density induced by chemisorption, \( V_{GS} \) is the gate bias and \( X_{CH} \) is a numerically derived, linearized relationship between the above two parameters. Note that \( X_{CH} \) is similar to a capacitance in that it defines a linear relationship between an applied voltage and a buildup of charge on the semiconductor top surface. However, this \( X_{CH} \) itself is not a capacitance in the electrostatic sense. In a normal capacitor, an applied voltage across two electrodes results in a buildup of charge across those same electrodes. However, in this case, the applied voltage causes trapped charge to accumulate along a surface that is not in the direct path of the applied electric field. The chemisorption based device also bears similarity to the classical MOSFET transistor, in that a voltage applied at the gate electrode induces charge along a surface that is parallel to the gate. However, as noted above, the charged layer is not induced by the electric field effect alone. Rather, it is resultant from the process of chemisorption occurring on the heterogeneous semiconductor/gas interface. In addition, conventional models of thin film transistors do not include a voltage-controlled layer of trapped charge at the top surface of the conducting channel. Even within in the global chemical sensor community, which deals specifically with studies of devices that use this principle of operation to detect chemicals, there is no broad consensus on quantitative models for how these devices work.

Hence, \( X_{CH} \) represents a fundamental phenomenon related to chemisorption on semiconductor surfaces that that to date is not included in classical descriptions of semiconductor device operation. It involves the electrochemical coupling of electronic properties of the device bulk to chemical properties of the surface. In addition, it states that an applied voltage across two terminals will cause trapped charge to buildup at a third exposed surface in the process of chemisorption. In addition, it further indicates that the buildup of charge on the surface will result in a measurable change in potential across the gate and reference electrodes. \( X_{CH} \) is titled, the \textit{electrochemical transcapacitance}.

The physical meaning of \( X_{CH} \) may be understood immediately in consideration of other capacitances within the system. Earlier in section 6.11. \textit{The Electroadsorption FET Capacitance vs. Voltage}, the electronic capacitance observed at the gate electrode was considered, and the capacitance calculated in the \textit{electrochemical punchthrough} regime was shown to be equal to the dielectric capacitances of the gate oxide and semiconducting layers in series, approximately \( 2.4 \times 10^{-14} \) F. Examination of the slope in charge density of Figure 119 results in a calculation of \( X_{CH} = 3 \times 10^{-8} \) F/cm\(^2\), which when normalized to the area of the conducting film also results in a calculation of \( 2.4 \times 10^{-14} \) F. Hence, the \textit{electrochemical transcapacitance}, although different in nature from a strictly dielectric capacitance (in that charging and discharging corresponds to chemisorption and desorption processes), is shown to be equal in magnitude to the dielectric capacitance across the gate oxide and semiconductor layers.
As an additional result of the TFT modeled in the *electrochemical punchthrough* there is an approximately exponential dependence of TFT channel conductance on gate bias, as observed in Figure 84 and Figure 87 and described by the following equation:

\[ G_{CH} = G_0 \exp(\alpha_{CH} V_{GS}) \]  

(45)

\( G_0 \) is a reference level of conductance numerically determined by materials parameters (doping density and mobility) and geometry of the conducting channel. \( G_{CH} \) is titled the *chemisorption conductance* and parameterizes the channel conductance in the *electrochemical punchthrough* regime of operation.

\( \alpha_{CH} \) is titled the, *chemisorption coupling coefficient*, and is a parameter that may be extracted simply by linearizing the numerical model result, since in general the channel conductance when the device is fully depleted will depend both on space charge layers at the gate oxide / semiconducting metal oxide and the semiconducting metal oxide / gas interfaces. Rearranging equation 41 illustrates a convenient means for extracting \( G_{CH} \) directly from the model results, by extraction of the following slope

\[ \alpha_{CH} = \frac{\partial \ln(G)}{\partial V_{GS}} = \frac{1}{G_{CH}} \frac{\partial G_{CH}}{\partial V_{GS}} \]  

(46)

the derivative in the above expression being defined as,

\[ \Gamma_{CH} = \frac{\partial G_{CH}}{\partial V_{GS}} = \alpha_{CH} G_{CH} \]  

(47)

where \( \Gamma_{CH} \) is the *electrochemical transconductance*.

Hence, by substituting equation 40 into 41 and eliminating \( V_{GS} \) we can obtain a direct relationship between the equilibrium values of channel conductance and chemisorption induced surface charge density, which is parametrically extracted from finite element model results of the physical, electronic, and electrochemical properties of the TFT:

\[ G_{CH} = G_0 \exp \left( \frac{\alpha_{CH}}{\chi_{CH}} Q_s \right) \]  

(48)

The above equation provides a particularly useful relationship between changes in a measurable parameter (the channel conductance) and changes in a fundamental property of the system at equilibrium (surface coverage of charged species) when the conducting channel is in the *electrochemical punchthrough* regime.

It is important to note that the approximately exponential relationship between sensor conductance and applied gate bias in *electrochemical punchthrough* appears valid in cases where there is a single charge carrier type (i.e. electrons) and the gate is able to effect a continuous / linear change in surface concentration of chemisorbed species. If a sufficiently negative gate bias is applied, the channel may be depleted strongly enough to change the dominant charge
carrier from electrons to holes, in which the original approximation of conductance in the 
*electrochemical punchthrough* regime no longer holds. In this case, the polarity of the 
*chemisorption coupling coefficient* $\alpha_{CH}$ is observed to invert its polarity, with negative voltages 
resulting in a nearly exponential increase in conductance as observed in Figure 117.

In addition, in certain cases of a relatively weak binding gas and large negative gate bias, it is 
possible for the device to enter the *electrochemical depletion* regime, i.e. the situation where the 
entire thickness the semiconductor film has become depleted of charge carriers and the 
semiconductor / gas interface has also become depleted of surface charge density due to 
desorption of chemisorbed gas molecules. Since no electronic states associated with 
chemisorption are available at the semiconductor surface to compensate for voltage applied at 
the FET gate, the device can be considered to proceed more rapidly through the electrochemical 
punchthrough regime for increasingly negative gate bias. This is also observed in Figure 117 in 
the case of a gas that creates surface states that are 1 eV below the conduction band edge. When 
a sufficiently negative gate bias is applied to fully the deplete the semiconductor of surface 
coverage of charged species (Figure 120), increasingly negative voltage results in an exponential 
increase in conductance that is significantly steeper than is seen in other regimes of operation. 
Judging again by the slope seen in this transition in Figure 117, the device conductance in the 
chemical depletion regime may be described by a similar exponential equation as was used in the 
*electrochemical punchthrough* regime, with a modified value of the *chemisorption coupling 
coefficient* $\alpha_{CH}$, to capture the higher sensitivity to gate bias in this case.

When the electroadsorption FET is biased sufficiently far into the *electronic accumulation* 
regime, the picture is very different from the above scenarios. In this case, changes in gate bias 
can only influence the electrical potential and charge carrier concentration in a region very close 
to the semiconductor/gate oxide interface, as was discussed. In this regime, the channel 
conductance only exhibits a weak linear dependence on gate bias as the number of charge 
carriers under accumulation are modulated. In addition, without the influence of the gate bias in 
an equilibrium gaseous environment the chemisorbed surface charge density will not change. 
This scenario is analogous to the conducting channel of a long-channel MOSFET during 
operation within the triode regime, as reviewed earlier in this thesis. Therefore, from the 
equation for MOSFET transconductance in the triode regime (Equation 34), we can derive the 
following expression for sensor conductance under accumulation, $G_{acc}$:

$$G_{acc} = G_{0,acc} + \left( \frac{W \mu_{chm} C_o}{L} \right) V_G$$

(49)

Where $\mu_{chm}$ is effective mobility of electrons in the accumulation region, $C_o$ is capacitance per 
unit area across the gate oxide, $L$ is the channel length and $W$ is the channel width. $G_{0,acc}$ is then 
the remaining contribution toward sensor total conductance besides the accumulated charge at 
the semiconductor / gate oxide interface. $G_{0,acc}$ includes the remainder of the semiconductor film
thickness that has not been depleted by the surface and by application of the delta depletion approximation to the space charge regions beneath the surface is calculated as follows:

$$G_{acc,0} = \frac{q\mu_nN_DW}{L}(Z_F - Z_S)$$  \hspace{2cm} (50)$$

where the additional parameter $Z_F$ is film thickness and $Z_S$ is the extent of the depletion zone beneath the surface, given by:

$$Z_S = \frac{Q_S}{\varepsilon_0\varepsilon_sN_D}$$  \hspace{2cm} (51)$$

Where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_s$ is the relative permittivity of the semiconductor, $N_D$ is the donor doping density in the semiconductor and $Q_S$ is surface charge density.

Similar to the electronic accumulation regime, the conductance under electronic inversion can be described as:

$$G_{inv} = G_{0,inv} + \left(\frac{W\mu_{chp}C_0}{L}\right) V_G$$  \hspace{2cm} (52)$$

with the difference here being that $\mu_{chp}$ is effective mobility of holes in the inverted region and $G_{0,inv}$ is a reference level of conductance that is much lower than $G_{0,acc}$ because of an additional depleted layer that extends into the semiconductor film from the semiconductor / oxide interface. $G_{0,inv}$ can be considered close to zero in the case of a completely depleted thin film.

In the case of a thin film that is partially depleted from the semiconductor / oxide interface and partially depleted from the semiconductor / gas surface, the device is defined to be operating within the electronic depletion regime. Again applying the delta depletion approximation, conductance in this case is given by:

$$G_{dep} = \frac{q\mu_nN_DW}{L}(Z_F - Z_S - Z_G)$$  \hspace{2cm} (53)$$

Where $Z_G$ is the extent of the depleted region at the semiconductor / gate oxide interface. Drawing an analogy to the MOS capacitor, $Z_G$ can be expressed as a function of gate voltage$^{14}$:

$$Z_G = \frac{\varepsilon_s}{\varepsilon_{ox}Z_{ox}}\left[\sqrt{1 - \frac{V_G}{V_\delta}} - 1\right]$$  \hspace{2cm} (54)$$

Where $\varepsilon_{ox}$ is the relative permittivity of the gate oxide material, $Z_{ox}$ is thickness of the gate oxide, and $V_\delta$ is given by the following expression:

$$V_\delta = \frac{q\varepsilon_sZ_{ox}^2N_D}{2\varepsilon_{ox}^2\varepsilon_0}$$  \hspace{2cm} (55)$$

The above equations lend themselves to the conceptualization of a general lumped element model for device operation.
7.1.3. Lumped Element Model

The state variables of interest in this four terminal device are conductance from source to drain \( G \), and surface charge density, \( Q_s \), at a given value of applied gate voltage \( V_G \). Based on the above discussions, expressions for DC values of \( G \) and \( Q_s \) are provided in Table 16 and Table 17 respectively.

Table 16. Lumped Element Model for Electroadsorption FET Conductance, \( G_x \), where \( x \) denotes the regime of operation.

<table>
<thead>
<tr>
<th>Regime of Operation</th>
<th>Gate Voltage Range</th>
<th>Lumped Element Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic Accumulation</td>
<td>( V_G &gt; V_{AT} )</td>
<td>( G_{acc} = G_{0,acc} + \left( \frac{W \mu_{chn} C_D}{L} \right) V_G )</td>
</tr>
<tr>
<td>Electronic Depletion</td>
<td>( V_{AT} &gt; V_G &gt; V_{PT} )</td>
<td>( G_{dep} = \frac{q \mu_{n} N_D W}{L} (Z_F - Z_S - Z_G) )</td>
</tr>
<tr>
<td>Electrochemical Punchthrough</td>
<td>( V_{PT} &gt; V_G &gt; V_{CHD} )</td>
<td>( G_{CH} = G_{0,CH} \exp (\alpha_{CH} V_{GS}) )</td>
</tr>
<tr>
<td>Chemical Depletion</td>
<td>( V_{CHD} &gt; V_G &gt; V_{IT} )</td>
<td>( G_{CHD} = G_{0,CHD} \exp (\alpha_{CHD} V_{GS}) )</td>
</tr>
<tr>
<td>Electronic Inversion</td>
<td>( V_{IT} &gt; V_G )</td>
<td>( G_{inv} = G_{0,inv} + \left( \frac{W \mu_{chn} C_D}{L} \right) V_G )</td>
</tr>
</tbody>
</table>

Table 17. Lumped Element Model for Electroadsorption FET Surface Charge Density \( Q_{S,x} \), where \( x \) denotes the regime of operation.

<table>
<thead>
<tr>
<th>Regime of Operation</th>
<th>Gate Voltage Range</th>
<th>Lumped Element Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic Accumulation</td>
<td>( V_G &gt; V_{AT} )</td>
<td>( Q_{S,acc} = Q_{S,HIGH} )</td>
</tr>
<tr>
<td>Electronic Depletion</td>
<td>( V_{AT} &gt; V_G &gt; V_{PT} )</td>
<td>( Q_{S,dep} = Q_{S,HIGH} )</td>
</tr>
<tr>
<td>Electrochemical Punchthrough</td>
<td>( V_{PT} &gt; V_G &gt; V_{CHD} )</td>
<td>( Q_{S,CH} = \alpha_{CH} V_{GS} )</td>
</tr>
<tr>
<td>Chemical Depletion</td>
<td>( V_{CHD} &gt; V_G &gt; V_{IT} )</td>
<td>( Q_{S,CHD} = 0 )</td>
</tr>
<tr>
<td>Electronic Inversion</td>
<td>( V_{IT} &gt; V_G )</td>
<td>( Q_{S,inv} = Q_{S,LOW} )</td>
</tr>
</tbody>
</table>

The equations in Table 16 provide quantitative expressions for film conductance in all possible regimes of operation. Although many of the related parameters are numerically derived, certain terms in the equations for sensor conductance in the electronic accumulation, depletion and inversion regimes may be obtained from analytical expressions, as provided in the previous section. As noted previously, the conductive nature of the semiconductor film may change from p-type to n-type while the device is in the electrochemical punchthrough regime, and the
electrochemical coupling coefficient $\alpha_{CH}$ will change in magnitude and also invert in polarity when this occurs. In certain cases of sufficiently weak binding gas (shallow surface energy states), the device may enter a chemical depletion regime, and due to a depletion of surface states, the electrochemical coupling coefficient in this regime, $\alpha_{CH_D}$, is generally larger in magnitude than $\alpha_{CH}$ seen in the electrochemical punchthrough regime.

Table 17 includes the corresponding relationships for surface charge density of the Electroadsorption FET. The maximum and minimum values of surface charge density, $Q_{S, HIGH}$ and $Q_{S, LOW}$ are observed when the device is biased sufficiently far into the electronic accumulation and electronic inversion regimes, wherein additional gate bias is largely compensated by charge at the semiconductor/gate oxide interface and does influence the charge density at the semiconductor/gas interface. In the case of a sufficiently weak binding gas and negative gate bias, $Q_{S, LOW}$ will be equal to zero as the surface becomes completely depleted. Within the electrochemical punchthrough regime, the surface charge density is modulated linearly with respect to gate voltage according to the electrochemical transcapacitance $X_{CH}$, which was found to be equal to the electronic capacitances of the gate oxide and depleted semiconductor layers taken in series.

### 7.1.4. Kinetic Processes

In general, the InGaZnO$_4$ sensor does not sit at equilibrium but is constantly drifting from one state to another. The numerical model results may further be utilized to interpret kinetic processes involved in device operation in various regimes of operation. The analytical and numerically derived expressions of the previous section are assumed as a description of the device at equilibrium, and the proceeding analysis examines time dependence.

First, the regime of electrochemical punchthrough is considered. By taking equation 48 in differential form, a relationship is obtained between small changes in surface charge density, $\partial Q_S$ and small changes in film conductance, $\partial G_{GS}$:

$$\partial Q_S = \frac{x_{CH}}{\alpha_{CH}} \partial \ln \left( \frac{G_{CH}}{G_0} \right) = \frac{x_{CH}}{\alpha_{CH}} \frac{\partial G_{CH}}{G_{CH}}$$

Then, taking the derivative with respect to time produces:

$$\frac{\partial Q_S}{\partial t} = \frac{x_{CH}}{\alpha_{CH}} \frac{1}{G_{CH}} \frac{\partial G_{CH}}{\partial t}$$

Let us take a moment to reflect on the implications of the above equation: it states that if $X_{CH}$ and $\alpha_{CH}$ are known, then the rate of charge transfer at the semiconductor surface when the device is in electrochemical punchthrough may be determined from a time resolved analysis of conductance. $X_{CH}$ and $\alpha_{CH}$ are calculated in the numerical model results. $X_{CH}$ may be additionally estimated from the dielectric capacitance across the gate oxide and depleted semiconductor layers, and $\alpha_{CH}$ can further be obtained by measurement of conductance vs. gate
bias when the device is close to equilibrium with its environment. In this manner, the rate of change in conductance with respect to time can be considered to be a direct measurement of the rate of charge transfer occurring at the surface.

Next, the kinetic response of the system is considered when the semiconductor channel is only partially depleted, which is includes the electronic accumulation and electronic depletion regimes of operation. In these cases, the conductance of the semiconductor film will be comprised of 1) the accumulated/depleted layer near the semiconductor/gate oxide interface, 2) any non-depleted layer that exists in the film, and 3) the depleted layer near the semiconductor/gas top surface. Assuming that the device is subjected to a constant gate bias and that electronic processes within the bulk occur much more rapidly than chemisorption processes, the rate of change in conductance over time can be calculated using only the contribution of the depleted layer at the semiconductor/gas interface. Whether the system is considered in electronic accumulation or electronic depletion, the result will be the same as computed from equation 49 or 53:

$$\frac{\partial Q_s}{\partial t} = -\frac{L}{W} \frac{\epsilon_0 \epsilon_s}{q \mu_n} \frac{\partial G_s}{\partial t}$$  \hspace{1cm} (58)

The above relationship states that when operating in the electronic accumulation and electronic depletion regimes, the rate of change in conductance is proportionate to the rate of charge transfer at the semiconductor/gas interface.

To determine the effect of gate bias on the response/recovery time of the TFT based chemical sensor, the behavior of the system is considered as it is suddenly driven away from equilibrium. The TFT gate voltage and the partial pressure of gas in the environment can together be considered to exert an electrochemical driving force over the chemisorption process. When gate voltage or partial pressure is changed suddenly to a new value, a new surface charge density associated with chemisorbed species is defined as the equilibrium state. Given the assumption that the system will respond linearly to perturbations in gate bias, a step function of applied bias will cause the chemisorbed charge density at the surface to vary with a time dependence that is initially linear with respect to time (at short time interval with respect to the relaxation time of the system) as the surface charge approaches the new equilibrium state. This would be the case, for example, if the system followed a time dependence that was described by an exponential decay. Hence, the response time of the system may be estimated by linearization of the rate of change in conductance at short time.

In the transient TFT measurement approach, a square wave AC voltage waveform was applied to the transistor gate, resulting in orders of magnitude change in charge carrier concentration and sensor conductance in each cycle. This has the effect within each cycle of voltage to drive the system toward two very different states of electrochemical equilibrium. Specifically, for sufficiently positive gate bias $V_{HIGH}$ and sufficiently negative gate bias $V_{LOW}$, within each cycle
of gate bias, the semiconductor can be considered to be driven towards alternating states of increased \( V_{\text{HIGH}} \) and decreased \( V_{\text{LOW}} \) surface coverage. Such a periodic driving force may be expected to promote a reversible sensor response to gases that are present, since the surface will tend to chemisorb an oxidizing gas more readily when present in the environment and desorb more rapidly when the gas is absent.

Within each half cycle of constant gate voltage in the transient measurement approach, the rate of change in conductance was determined by least squares estimation of a linear slope in each cycle, \( dG_{\text{LOW}}/dt \) and \( dG_{\text{HIGH}}/dt \). In addition, nominal values of conductance \( G_{\text{LOW}} \) and \( G_{\text{HIGH}} \) were, separately for \( V_{\text{LOW}} \) and \( V_{\text{HIGH}} \). It was observed that under prolonged application of a given AC voltage waveform, the system generally approaches a steady state, wherein the nominal conductance within each half-cycle of gate voltage become nearly constant over time, even though the slope in conductance within each half-cycle is nonzero. Under this set of conditions, it may be appropriately assumed that the system undergoes a reversible processes within each cycle. In addition, if multiple processes are responsible for the observed changes in conductance, in steady state each individual process may be considered to operate reversibly.

When the concentration of gas in the ambient environment is changed, the chemical driving force that acts upon the system of chemisorbed surface charge is also suddenly changed. The resultant flux in chemisorbed species within this system (i.e. chemisorption or desorption) may be considered the direct result of the change in gas concentration. Similarly, the deviation in conductance and rate of change in conductance from the previously observed values at steady state may be ascribed solely to the influence of changes in surface coverage of the chemisorbed gas. By introduction of controlled concentrations of gas in the sensor’s environment, changes in the sensor conductance and conductance slope may be measured, which are solely resultant from changes in charge transfer that occurs at the surface. In this scenario, the charge transfer rate can be estimated directly, utilizing the above derived equations that provide the relation to sensor conductance and conductance slope over time. By allowing the system to deviate from steady state under the controlled influence of a change to the gas environment, numerous alternate influences on sensor conductance are essentially eliminated, isolating a measurement of the rate of charge transfer associated with chemisorption at the semiconductor / gas interface.

7.1.5. **Non-Idealities**

Many non-idealities could arise that would cause the threshold voltage to shift, the channel conductance to change or even the surface charge to vary from the numerically predicted values. In general, it is known that at times there may be an accumulated layer of fixed (trapped charge) at the gate oxide / semiconductor interface that tends to influence the threshold voltage. However, in past studies and without the present model, it is possible that the surface charge layer under discussion may have been mistaken for a buried layer.

The present model considers the interaction of the surface with a single gas of interest, however in general there the surrounding air is a multi-component system there will be multiple reactions
present that are possible. Besides additional chemisorption reactions, there will be in many cases a diffusion from the surface into the bulk and a bulk reaction that occurs over time, which will cause the described device to vary largely from the model within this work, as it considers only surface phenomena. A precise numerical treatment of this scenario would further be very useful in seeking to obtain well engineered chemical sensors in the future.

Surface morphology will have a role also in causing the model to vary away from the trends that are described thus far. In general, a roughened surface with a higher surface to volume ratio exposed to the environment may actually cause some desirable effects with respect to device sensitivity, as are suggested in some of the experimental results of this work and numerous others.

Conveniently, the finite element approach lends itself to an investigation of much more complex device structures than can be practically treated through simple analytical techniques. Each of the above suggested non-idealities provide a direction for future work in development of the present models, as opposed to indicating any fundamental limitation in the present approach.

7.2. Experimental Results

7.2.1. **TFT based Sensor Conductance vs. Gate Bias in Air**

The goal of the proceeding sections is to apply the analytical and numerical models that have been developed towards an understanding of experimentally measured properties of the **EA-FET** and other chemical sensor test structures. As a first step in this process, **EA-FET** conductance vs. gate bias is examined as experimentally measured in air, and a correlation to numerical simulations of device properties in the presence of weak binding gas is considered. For an assessment of similarity in device properties, Figure 40 and Figure 87 are overlaid directly with one another, and the resulting chart is shown in Figure 127. Note that at this point, no attempt has been made to adjust fitting parameters to match the experimental data. However, already certain similarities between simulation and experiment are already clearly evident. The calculated and measured slope in conductance vs. voltage are very to one another in the shown range of data, the correlation being closest at higher positive values of gate bias and persisting as low as zero volts gate bias. In addition, the absolute value of sensor conductance in this range of gate voltage is within an order of magnitude of agreement between simulation and measurement, clearly outside of the margin of error in measurement of TFT conductance but clearly illustrating the appropriateness of the initial values of materials properties and device geometry that were selected.
Figure 127. Channel conductance as a function of gate bias a) in numerically simulated TFT of varied doping density (from bottom to top, $4.47 \times 10^{17}$ cm$^{-3}$, $4.73 \times 10^{17}$ cm$^{-3}$, $5.01 \times 10^{17}$ cm$^{-3}$, $5.31 \times 10^{17}$ cm$^{-3}$, and $5.62 \times 10^{17}$ cm$^{-3}$) and b) in a fabricated device of equivalent dimensions measured in air at 150°C at two different times in a 48 hour sequence of continuous tests. Drain voltages $V_{DS}$ applied to the TFT during measurement are listed in the legend to the right. Further information about simulation and measurement parameters are provided in earlier sections.

At sufficiently positive gate bias, the measured TFT can be assumed to operate within the electronic accumulation regime of operation. Based on the lumped element model summarized earlier, the mobility can be estimated in this regime from the slope of conductance vs. gate bias $\frac{\partial G}{\partial V_{GS}}$, given known values of transistor width $W$ (20 μm), length $L$ (4 μm), and gate oxide capacitance per unit area, $C_o$ (37 nF/cm$^2$):

$$\mu_n = \frac{L}{WC_o} \frac{\partial G}{\partial V_{GS}}$$  \hspace{1cm} (59)$$

The resulting value of mobility is $\mu_n=3.9$ cm$^2$/Vs, which is within a factor of two of the initial estimate of mobility used in the above calculation (2.6 cm$^2$/Vs) and within a factor of three of literature references on InGaZnO$_4$ that possesses the same composition ratio of the material used in the present study, In:Ga:Zn of 1:1:1 (9 cm$^2$/Vs as shown in Figure 19).

It is observed that variation in the doping density of the material within the numerical model largely impacts the calculated device conductance at negative gate bias in the electronic depletion and electrochemical punchthrough regimes, with little observable impact on the
**electronic accumulation** regime (positive gate bias). Hence, the modeled value of doping density may be varied to obtain better agreement with experimental data in regions of large negative gate bias but will have little impact on the conductance at positive gate bias (in electronic accumulation). With the mobility and device dimensions at their assumed values, the possibility of including a scalar coefficient in an attempt to adjust the simulated magnitude of conductance and bring it into the range observed by experiment. Such an adjustment may for instance represent deviation of the effective device dimensions from those that have been lithographically defined. The result of this adjusted calculation, with new values of doping density, mobility as calculated above, and a scalar coefficient of 5 applied to the calculated conductance (to reduce calculation to the range of measurement), is shown in Figure 128.

![Figure 128](image)

**Figure 128.** Channel conductance as a function of gate bias in numerically simulated TFT of varied doping density (dotted lines from bottom to top, 3.76 $10^{17}$ cm$^{-3}$, 3.98 $10^{17}$ cm$^{-3}$, 4.22 $10^{17}$ cm$^{-3}$, 5.96 $10^{17}$ cm$^{-3}$, 6.31 $10^{17}$ cm$^{-3}$, and 6.68 $10^{17}$ cm$^{-3}$) with a nominal scale factor of 5 applied to reduce simulated conductance to the range of measured conductance, overlaid with measurements of a fabricated device of equivalent dimensions measured in air at 150°C at two different times in a 48 hour sequence of continuous tests. Drain voltages $V_{DS}$ applied to the TFT during measurement are listed in the legend to the right. Further information about simulation and measurement parameters are provided in earlier sections.

Another possible explanation for the observed difference magnitude of simulated and measured conductance in the electronic accumulation and electronic depletion regimes may be the
amorphous nature of the InGaZnO$_4$ film. Prior works have demonstrated that the film conductance is dependent strongly dependent on the density of acceptor like states that exist in an exponential tail near the conduction band edge and extend to a lesser extent throughout the amorphous semiconductor mobility gap.$^{73}$ These acceptor states can serve to significantly modify the slope in film conductance vs. gate bias through electronic depletion and electronic accumulation regimes, which would be a reasonable cause for the observed difference in this case. The influence of these amorphous states is typically stronger in materials that are more lightly doped (on the order of $5 \times 10^{16}$ cm$^{-3}$), as are often used of modern InGaZnO$_4$ based electronics. Such a refinement to the model is left for future work, the feasibility of such studies having already been demonstrated in the prior literature.$^{81}$

7.2.2. TFT based Sensor Response to NO$_2$ Gas

In the experimental section, the EA-FET conductance response to NO$_2$ gas was characterized in the range of 1.25 to 100 ppm concentration in a background of dry air at 150°C, and results were provided in Figure 56. In Figure 129, the measurement result is further summarized in a plot of the nominal sensor conductance vs. partial pressure. The measurement data has been overlaid with calculations of the partial pressure dependence of sensor conductance, with the energy position of the chemisorbed gas with respect to the conduction band edge varied in the range of 1 eV to 2.5 eV, as was calculated in the numerical modeling section. The measured resistance of the sensor is increased again by a factor of 5, as was observed to be necessary in the previous section to obtain comparable values of nominal measured and modeled sensor conductance, with the other materials and geometric parameters assumed to be constant values.
Figure 129. Channel Conductance vs. partial pressure of gas in the range of $10^{-12}$ to 1 atm, with the energy position of chemisorbed the gas varied in the following range (solid lines from top to bottom): 1 eV, 1.5 eV, 2 eV, and 2.5 eV. Numerical data is overlaid with measured values of InGaZnO$_4$ TFT based chemical sensor response to NO$_2$ gas in the specified range, with the magnitude of measured conductance increased by a factor of 5.

Comparing the measured data to the numerical model indicates correlation to the numerically modeled gas that was positioned 2.5 eV below the conduction band edge. This is consistent with the fact that NO$_2$ is known to be a strong oxidant and expected to create energy states that lie deep within the band gap (or in this case, mobility gap). As was seen earlier, however, the correlation is not precise. Here also the amorphous nature of the film may have a role in the necessity of the scalar factor that is applied. In addition, the nature of the experiment is to expose the sensor to a gas for a fixed amount of time and then measure its conductance. If the exposure time is not sufficient for the gas to equilibrate with the material surface, deviation with the equilibrium model will be observed. Finally, the model is designed to consider chemical equilibration with the gas only at the semiconductor surface, and if there is any subsequent redistribution of atoms within the sensor bulk, this also can influence the accuracy of the correlation in the present model, especially during the course of longer gas exposure.
7.2.3. Experimental Results in Context of Numerical Simulation

It is seen in general that when a voltage bias is applied to the gate of the TFT based chemical sensor, typically there will be a sudden jump in sensor channel conductance followed by a much slower relaxation of conductance. As seen for example in Figure 63, when a negative gate bias is applied, the conductance decreases to a very low level initially and then gradually increases over time to a new steady state value. Conversely, when a positive gate bias is applied to the device, conductance increases suddenly but then decays to a lower value. This can be understood in terms of the thermodynamic driving forces at play in combination with kinetic limiting factors. As shown in Figure 110, when a negative gate bias is applied to the structure in the presence of a gas at a given concentration, the equilibrium surface coverage of that chemisorbed species decreases (pictured in the figure as decrease in the magnitude of surface charge density of chemisorbed species, which is proportionate to surface coverage). Conversely, when a positive gate bias is applied, the system is driven towards higher surface coverage. Looking to Figure 105, this does not correlate to the same trend in channel conductance, because the device is a TFT and while negative gate bias tends to induce desorption of gas (which effects an increase in channel conductance due to the electroadsorption transconductance) the TFT is also driven farther into depletion by the negative gate bias and hence the net measured conductance will be lower. In this manner, the sudden jump in conductance when the a gate voltage is applied can be explained in this model as primarily the electric field effect of the transistor gate to rapidly change the charge carrier concentration of the device while the surface charge density of chemisorbed species remains approximately constant. Then, the gradual change in conductance over time may be attributed to gradual change in the surface charge density in response to the electrochemical driving force exerted by the transistor gate.

It is important to consider the possibility that the observed gradual trends in sensor conductance in response to applied gate bias are not resultant from the action of chemisorption at the surface but rather from other gradual charging and discharging effects that may be intrinsic to the device structure itself. The authors of [62] note that gradual drift and instability in InGaZnO₄ based thin film transistors are often observed, and they note several mechanisms for this phenomenon that have been suggested, including the charging and discharging of mid-bandgap interfacial trap states at the semiconductor / gate oxide interface or the separate possibility of redistribution of defect states within the film. In general, there may be a number of parallel kinetic processes governing the operation of the InGaZnO₄ thin film transistor. To address the possibility of multiple additional influences on the TFT response to gate bias, this thesis adopts an experimental approach that isolates the contribution of chemisorption at the surface by introducing controlled amounts of gas into the environment and then characterizing changes in kinetics of the sensor response.

Figure 46 gave an indication of the role that oxygen has in influencing the sensor response in comparison to other mechanisms that may be intrinsic to the device, by rapidly interrogating the sensor conductance at one value of gate voltage, $V_{GS,meas}$, while otherwise holding the gate
voltage constant at a second, nominal level over time, \( V_{GS,nom} \). Because the level \( V_{GS,nom} \) was held for two minutes between measurements at the gate voltage \( V_{GS,meas} \) (each of which took less than a second to perform) we may state that for more than 99% of the time the TFT based sensor was being exposed to the driving force of the gate voltage specified by \( V_{GS,nom} \), and hence in this analysis it will be assumed that this value of gate voltage approximately specifies the equilibrium state toward which the system was being driven. The experiment was performed in both \( O_2 \) and \( N_2 \) gas separately at room temperature, and interestingly, reversible responses of the device conductance to gate bias are observed in both cases, indicating that the phenomenon responsible for the transient response is not solely due to the influence of oxygen. There is an observable effect of the gas, in that although a positive gate bias drives the conductance downwards to a value that is the same in both \( N_2 \) and \( O_2 \), the measured conductance in \( N_2 \) at 0V gate bias and positive gate bias was noticeably higher. This indicates that there is a measurable effect resulting distinctly from interaction of the device with the surrounding environment.

The goal of the studies of the TFT based chemical sensor was to determine the component of sensor response that is resultant from chemisorption. Hence, it was also important to identify other influences of gas composition on the device behavior outside of chemisorption, and it is conceivable that the environment may influence the sensor conductance through a process that primarily influences the device bulk, such as a change in the oxygen stoichiometry of the sensor film itself. For most semiconducting metal oxide materials, this is not expected to occur very rapidly at room temperature, and Figure 41 does show that there is a very slow response of the device to varying concentration of oxygen when heated to 100°C. This reaction continues to proceed without showing any sign of saturation over the course of 12 hours for each cycle and was repeatable over the course of three experiments that were each over 70 hours in duration. Hence, the effect observed at 100°C over long periods of time might be attributed to bulk reaction of the TFT based sensor with the surrounding environment. However, the difference between signals in \( N_2 \) and \( O_2 \) responds much more rapidly. Hence, we may conclude that the difference in sensor conductance response in \( N_2 \) vs. \( O_2 \) in the short time period (30 minutes) of pulsing the gate bias at room temperature is indeed related to chemisorption. The response is observable, but seems very slow. At this point, the question arises as to whether it is possible to utilize the influence of gate bias to effect an accelerated response of the sensor to the surrounding gaseous environment. This was a primary goal of the transient TFT measurement approach that was developed in this work.

In the transient TFT measurement approach provided an effective means to overcome potential sensor drift mechanisms and accelerate sensor response to gas. Application of an AC gate bias caused the system to be continuously and rapidly driven away from equilibrium, with the electrical signal of the gate electrode exerting a large driving force on the exposed surface of the film. Although it may take a long time for the system to come to equilibrium, its initial chemisorption and desorption response will vary rapidly. In addition, the use of AC gate voltage avoids the occurrence of long-term drift in sensor properties associated with DC gate voltage, by
rapidly exciting reversible reactions within the sensor. The oxygen testing at room temperature in the transient measurement approach (Figure 55) demonstrates a much more rapid response time (on the order of seconds) to oxygen than was observed in the other experiments (on the order of hours at 100°C and barely observable if at all at room temperature). This test also shows that a rapid, reversible response to oxygen was induced by gate bias at room temperature, and it makes sense that when the gate bias was pulsed only to positive values, the sensor responded downward only and did not recover. However, the magnitude of the response was very small. The approach was demonstrated more thoroughly at elevated temperature (~150°C), where the influence of various gate bias parameters were investigated. Both sensor response magnitude and response time were improved compared to the device without gate bias. As a final important point, kinetic information can be extracted from the transient TFT measurements, and it is of great interest to examine the slope information contained in Figure 64, Figure 65, and Figure 66 with a goal of direct measurement of the rate of charge transfer involved in chemisorption. In addition, it may be possible to determine parameters for the lumped element model by examination of the magnitude and rate of signal responses in the transient exposure experiment.

It is also of interest to consider photoconductance properties of the sensor as they relate to the band structure that determines the process of chemisorption at the material surface. A photodesorption experiment was performed in a related materials system, ZnO desorbing NO₂ gas, and results were presented that indicate irreversible changes in conductance occur at sub-bandgap wavelengths of 500 and 860 nm (Figure 69), i.e. approximately 1.4 and 2.5 eV energy. There are many sub-bandgap transitions that could possibly occur within the material structure in response to the absorption of light, including electronic excitation among intrinsic states of the material, from the valence band to vacancy related states in the material or transition among intrinsic (surface reconstruction related) materials surface states. In this case, it is interesting to compare the observed energy of transition to the modeled results of the EA-FET, which was also observed to chemisorb NO₂ gas at an energy level of 2.5 eV. In the monochromatic photodesorption experiment, the 2.5 eV desorption transition was further correlated to a change in conductance that was markedly slower than other observable processes in the system, based on quantitative extraction of the rate of change in conductance. This is consistent with the expectation that desorption of a strongly oxidizing gas such as NO₂ gas will occur particularly slowly.

For comparison to the thin film transistor measurements that were performed, several studies were performed on thin film resistor based chemical sensors. The InGaZnO₄ devices were measured for their sensitivity in both oxidizing (NO₂) and reducing (H₂) gas. In general, the trends that are expected in the model are observed, in that thinner devices are more sensitive in particular in the case of oxidizing gases. In addition, the templated structure was shown to be significantly more sensitive than either of the thin film structures that were tested. This is consistent with the fact that it has a larger amount of surface area that is exposed to the environment, which exerts a greater electronic influence on the semiconductor bulk. These
experiments provide a useful reference point regarding the utility of InGaZnO$_4$ in general as a chemical sensor to multiple gases and also indicate a starting point for more detailed investigations. Besides the electronic characterizations that were performed, a materials and structural analysis of the InGaZnO$_4$ thin films was also presented, supporting the conclusion that the material remains amorphous over the entire range of operating conditions that the device experiences. This validates the assumption of constant bulk materials properties during chemisorption processes on the Electroadsorption FET.
8. Conclusion

8.1. Summary
This thesis work presents a unified experimental and numerical investigation of chemisorption in a nanostructured semiconductor device titled, the Electroadsortion Field Effect Transistor. This work is strongly motivated by a need to improve the understanding and technological advancement of chemical sensor technology. In addition, the chemical sensor served as a well controlled model system for investigation of chemisorption processes, both by means of experimental characterization and numerical simulation. Although the underlying electronic relationship between a bulk semiconductor and the surrounding gas was analyzed in early semiconductor literature, the quantitative role of nanostructure in determination of heterogeneous system properties was to date not widely understood. The numerical approach employed in this thesis is a vital step towards understanding the interaction between chemisorption processes at a semiconductor surface and the electronic properties of a nanostructured semiconductor bulk material.

The implications of the insight gained in this thesis extend far beyond the context of this particular application. In general the very broad advancement of modern nanoelectronic semiconductor technology relies on the controlled engineering of electronic properties of devices at the nanoscale. This work identifies a fundamental physical phenomenon that is shown to have a great influence on the electronic properties of a material that is today heavily investigated in the area of thin film displays. Modern and state of the art investigations of this material omit any quantitative model of the interaction between the material surface and the surrounding gases. The lack of understanding of the interaction between gases and nanoelectronic devices is not surprising, given the fact that modern studies of chemical sensors also do not present a widely agreed upon model for the role of nanostructure in chemisorption on semiconductors. Looking beyond these applications, the present study has the potential to inform any investigation of the influence of nanostructure on the chemisorption of gas at a semiconductor surface, including heterogeneous catalysis and emerging areas of clean energy.

Initial emphasis was placed on development of the necessary fundamental understanding of this device, including the appropriate background on chemisorption, chemical sensors, and the role of nanostructure. This was then applied in a detailed investigation of the relationship between chemisorption processes at the semiconductor surface and electronic properties of the nanostructured bulk, in order to derive fundamental descriptions of the heterogeneous system. With the ultimate goal being attainment of a practical understanding of the interaction between the environment and nanostructured electronic devices, numerous variations in materials, structure and environmental stimulation were simulated, to thoroughly characterize device response. Measurable device properties were examined including sensor conductance and gate capacitance vs. gate bias of the FET structure, providing an opportunity for correlations to
measurement in the present and future work. In addition the Vol’kenshtein chemisorption coefficient was identified as a critical surface property of the heterogeneous system, and it was related quantitatively to changes in applied fields, environmental influences, and other measurable electronic device properties. Importantly, the tendency of the device to resist increasing amounts of surface coverage as the nanostructure becomes depleted of electronic charge was illustrated quantitatively, by the tendency of the chemisorption coefficient to decrease with increasing partial pressure of gas. Large enhancements that are observed in chemical sensor sensitivity at the nanoscale were derived and shown to occur in spite of the fact that these nanoscale structures only exhibit small changes in surface coverage due to strong depletion of the bulk by the semiconductor/gas surface. In an effort to make the analysis accessible, the numerical results were analyzed and parameterized in development of a lumped element model.

In addition to studies based on numerical simulation, the Electroadsorption FET was fabricated and its electronic and chemical properties were characterized in a controlled range of environmental conditions. Its response was measured in oxygen gas and also in the presence of NO$_2$ gas at moderate temperatures. In addition, the role of gate bias was investigated. In the process of device characterization, a novel measurement approach was developed that illustrated the ability of applied gate bias to increase device sensitivity and also influence the kinetic reversibility of sensor response. All of the experimental results were discussed in detail as they relate to the numerical model, with clear correlations identified to numerical results, including identification of chemisorption related energy levels in the expected range (2.5 eV below the conduction band) for a strongly oxidizing gas. Where necessary, opportunities for improvement to the model have been identified, the most immediate among them being the explicit inclusion of amorphous states in the description of electronic properties. Because the described physical chemisorption phenomenon is general to semiconductors that are not only of an amorphous nature, the detailed initial investigation was appropriately focused on a more traditional crystalline semiconductor band structure. However, this presents a straightforward direction to pursue, as this amorphous system is already investigated by many other groups without the context of chemisorption.

The following sections outline key conclusions that were obtained within the related experimental and numerical investigations of this work. The final section of this chapter discusses future work recommended, building upon the results of this thesis.

8.2. Electroadsorption FET – Key Conclusions from Experimental Work
- Reversible detection of NO$_2$ gas is demonstrated in InGaZnO$_4$ at 160°C.
- Electroadsorption FET conductance and threshold voltage are heavily influenced by the concentration of NO$_2$ gas in the surrounding environment.
- Transistor gate bias is shown to influence both the sensitivity and the speed of InGaZnO₄ based chemical sensor operation.

- Proper selection of gate bias is shown to significantly accelerate the sensor response and recovery.

- A novel control technique has been developed for high sensitivity, reversible operation of thin film transistor based chemical sensors at reduced temperature, through use of a varying (AC) bias applied to the transistor gate.

- In the process of applying the new TFT control technique, a novel analysis approach was developed to directly determine changes in the rate of charge transfer occurring at the surface of the thin film transistor.

- Approaches are suggested for determining the rate of charge transfer in chemisorption directly from measured data.

- Application of DC transistor gate bias is shown to influence sensor sensitivity by changes in the Fermi energy, as seen in other studies of TFT based gas sensors.

- Application of AC transistor gate bias is shown to controllably and separately influence both sensor response and recovery rates, with response times directly linked to the rate of charge transfer processes in chemisorption and desorption at the device surface, enabling rapid, highly sensitive and reversible detection of NO₂ gas at reduced operating temperatures.

8.3. Electroadsorption FET – Key Conclusions from Numerical Analysis

- The Electroadsorption Field Effect Transistor (EA-FET) was proposed as a model system for study of chemisorption on nanostructured semiconductors.

- The EA-FET was measured experimentally and simulated using a finite element approach that incorporated the Vol’kenshtein model for chemisorption at the device surface.

- Although the Vol’kenshtein model has been long recognized as highly relevant to charge transfer processes that occur on semiconducting metal oxides, only a handful of prior studies within the chemical sensor literature have attempted to analytically or numerically evaluate its implications in chemical sensing.

- The implications for an improved understanding of chemisorption on nanostructured semiconductors are of general and far reaching impact.

- Fundamental properties of the heterogeneous nanostructured system were derived:

  - The chemisorption coefficient decreases at higher partial pressures of oxidizing gas and thinner layers of depleted semiconductor material.
  - Nanostructured sensors exhibit large enhancements in sensitivity despite possessing a lower chemisorption coefficient and lower surface coverage than their larger counterpart.
Three regimes of chemical sensitivity were identified in nanostructured semiconductor chemisorption, corresponding to low, medium and high plateaus in the power law relationship between partial pressure of gas and sensor conductance. The plateau values of sensitivity were shown to be a function of film thickness.

The surface states were shown to charge and discharge under the influence of gate bias, corresponding to chemisorption and desorption of gas, with a linear charge-voltage relationship titled the Electrochemical Transcapacitance. This parameter was shown to be quantitatively equivalent to the dielectric capacitance of the gate oxide and semiconductor in series, although it is fundamentally electrochemical in origin.

Capacitance vs. Voltage of the EA-FET was derived and shown to be dependent on the surface coverage.

The device was modeled in two dimensions inside and outside of the semiconductor bulk, demonstrating equivalence to 1D models.

Relationships between sensor conductance, doping density, surface coverage, surface charge density, energy level of the binding gas, and partial pressure of the binding gas were derived.

- 5 regimes of operation were identified in EA-FET operation: electronic accumulation, electronic depletion, electrochemical punchthrough, chemical depletion, and electronic inversion.

- The numerical model was parameterized in derivation of a lumped element model of device DC conductance and surface charge density, to make the conclusions of this thesis practical and accessible in an electrical engineering context.

8.4. Future Work

It is of great importance to rapidly pursue additional studies that build upon the foundation of this thesis, which has presented a new framework for deeper understanding of the relationship between chemisorption processes and electronic properties of semiconductors at the nanoscale. Along these lines, it is essential to test every assumption made during the course of this work and further refine both numerical and experimental techniques, to enable a more precise understanding of the behavior of practical material structures. Based on insight gained, it is anticipated that rapid technological advancements may be made in the engineering of new materials and devices that accurately predict, measure, and control the process of chemisorption.

The following sections recommend key additional studies to perform, divided into five main areas:

- Determination of Surface Energy Levels of Additional Gases
- Optimization of Gas Sensitivity vs. Materials Properties and Device Geometry
- Electric Field Programmed Chemisorption and Desorption
Surface Spectroscopy and Gas Composition Analysis
- Refinement of the Numerical Simulation Approach

In the first four sections, key experiments are proposed, both as a validation of the numerical model, and also as an application of the model towards engineering of systems and devices of improved performance. The final section focuses on future modeling work and simulation of systems of increasing complexity. This includes three dimensional device structures, anisotropy of materials properties, and the coupling of additional differential equations related to other known physical phenomena.

8.4.1. Determination of Surface Energy Levels of Additional Gases

As discussed earlier in the thesis, a key parameter of the numerical model is the energy position of surface states related to chemisorption of gases, $E_{SS}$, which is considered to be an electrochemical property of a specific gas that reacts at the surface of a specific semiconducting material. In the case of oxidizing and reducing gases that chemisorb at the surface of semiconducting metal oxide materials, $E_{SS}$ generally specifies energy levels associated with chemisorption that are closer to the valence band and conduction band, respectively. In general, $E_{SS}$ is not known for a wide range of materials and gases, and hence it is of interest to experimentally measure this parameter in systems of scientific and technological interest. This can be accomplished through application of the simulation and experimentation approaches presented in the present thesis work:

1. Construct a model of the EA-FET as described within this thesis work.
2. Select the semiconductor, gas, and device geometry such that all system properties except for $E_{SS}$ are known.
3. Select a temperature of operation within which a rapid, reversible response of the sensor to the gas is expected. Operating temperatures within the range of 200 to 400°C are suitable for many polycrystalline semiconducting metal oxide based sensors.
4. Vary $E_{SS}$ and calculate device conductance as a function of partial pressure of the gas as shown in Figure 95 of this thesis work.
5. Construct the device and measure device conductance as a function of partial pressure within the specified range according to the experimental approaches outlined in this thesis.
6. Compare experiment to numerical simulation in order to determine the value of $E_{SS}$, by selection of the best fit between experiment and simulation (as shown in Figure 129).

Materials that would be of immediate interest in this follow up study include semiconducting metal oxides that are known to respond to oxidizing and reducing gases of practical importance in chemical sensing applications. This includes materials such as SnO$_2$, TiO$_2$, ZnO, WO$_3$, and In$_2$O$_3$ operating in response to oxidizing gases such as O$_2$ and NO$_2$ or reducing gases such as CO and H$_2$. Gas concentrations should be controlled over as wide a range as possible within the
limits of conductance measurement sensitivity and saturation of the semiconductor surface concentration. Example recommended ranges of gas concentration for follow up studies include:

- $10^{-12}$ to 1 atm of O$_2$ in a background of N$_2$ gas.
- $10^{-9}$ to $10^{-3}$ atm of NO$_2$ in a background of N$_2$ or air.
- $10^{-9}$ to $10^{-3}$ atm of H$_2$ gas in a background of N$_2$ or air.
- $10^{-9}$ to $10^{-3}$ atm CO gas in a background of N$_2$ or air.

Note that great care should be taken in handling NO$_2$ and CO, as they are known to be toxic to humans upon inhalation. In addition, H$_2$ and CO are explosive upon mixture with oxygen at certain concentrations and become even more explosive (at lower concentrations of gases) when mixed with a strong oxidant such as NO$_2$. However, certain sensor reaction models for H$_2$ and CO consider these reducing gases to react with chemisorbed oxygen directly and form vapor phase water and CO$_2$. Hence, it is of interest to compare the response of sensors to a varying concentration of reducing gases in a background of air and a background of inert gas such as nitrogen. A strongly oxidizing gas such as NO$_2$ is generally expected to react with the semiconductor with a response significantly greater than the device’s response to oxygen, and hence a background of air or inert gas is appropriate. In addition, because NO$_2$ is a strong oxidant, a chemical sensor of typical dimensions as defined in this thesis may become heavily depleted and difficult to measure due to high resistance at sufficiently high NO$_2$ concentration.

8.4.2. Optimization of Gas Sensitivity vs. Materials Properties and Device Geometry

The numerical model of this thesis may be used as a tool to optimize chemical sensor performance as a function of the materials system and device geometry that are selected. This is possible because the numerical model calculates the amount of chemisorption that occurs on a semiconductor surface as a function of the Fermi Energy at the material surface. The model additionally captures the dependence of the Fermi Energy at the surface on materials properties and device geometry. Hence, a chemical sensor based on device structures such as the Electroadsorption FET or Chemisorption Capacitor (i.e. thin film transistor or thin film resistor based chemical sensor) will possess a chemical sensitivity that is heavily influenced by the choice of semiconductor bandgap, semiconductor doping density, semiconductor work function, the work function of the underlying substrate (whether it is a conductive buried gate electrode or an insulating substrate), and the thickness of the semiconducting film. Examples of these dependences are shown in Figure 87 through Figure 90 in the case of doping density dependence and Figure 112 through Figure 116 in the case of semiconductor film thickness dependence. The substrate work function, semiconductor work function and semiconductor band gap influence all of the numerical results that were investigated, and these may also be parametrically varied in future work, to simulate the performance of different materials systems.

To optimize chemical sensitivity with respect to a materials property or device dimension, the following procedure is proposed:
1. Select a gas to measure with the chemical sensor, where the position of the surface states, \( E_{SS} \) is known (i.e. measured via techniques outlined in the previous section and earlier in the thesis).
2. Select a temperature of operation of the chemical sensor, as this also influences the Fermi Energy of the material bulk.
3. Select a materials property or device dimension, such as semiconductor bandgap, semiconductor doping density, semiconductor work function, substrate work function, or semiconductor film thickness.
4. Calculate chemical sensitivity as a function of the parameter being varied, by calculating device conductance a) in the presence of the gas of interest (\( G_a \)) and b) in the presence of air (\( G_b \)), i.e. with the gas removed. As discussed earlier in this thesis, conductance sensitivity can be calculated as \( S=(G_a-G_b)/G_b \).
5. Examine the finite element calculations and identify the range of values of the parameter being varied that results in maximal device sensitivity.
6. Select several values of each parameter to be optimized about the expected maximum in sensitivity. At a bare minimum, three values around the maximum should be selected, but a data set of 5 elements or larger is preferred. In addition, it is important to select a variation of materials parameters or device geometry that is practically attainable within experimental control.
7. Construct devices wherein which the selected parameters are varied.
8. Measure the sensitivity of each fabricated device to a range of concentrations of the gas of interest. Recommended concentrations for various gases of interest are provided in the preceding section on Determination of Surface Energy Levels of Additional Gases.

According to the above procedure, an improved sensitivity of the chemical sensor structure to a given gas of interest may be predicted by the numerical model and then measured, to compare device performance to the model predictions. As discussed, there are a number of parameters of interest that may be optimized by this procedure. The following paragraphs suggest experimental approaches to explore in the variation of each parameter.

The doping density may be varied within the semiconductor by adding trace concentrations of chemicals to standard fabrication techniques such as co-depositing multiple semiconducting metal oxide materials (e.g. co-sputtering of Al with ZnO), preparation of material sputtering or pulsed laser ceramic deposition targets that include trace concentrations of the dopant, or ion implantation techniques as are used in doping of silicon with boron or phosphorous. It is expected that there is a large available body of literature on the appropriate selection of chemical elements and deposition techniques that are necessary to obtain doping densities in a wide range of materials systems of practical interest to the present problem. A second means for variation of dopant density is to control the oxygen partial pressure during deposition of a semiconducting metal oxide, so as to influence oxygen vacancy concentration in the resultant film. Oxygen
vacancies ionize as electron donors in many semiconducting metal oxides of practical interest to chemical sensing, such as ZnO and SnO₂.

The band gap of the material may be largely influenced by selection of the composition of the semiconductor. Certain materials systems may be selected wherein gradual changes in band gap may be influenced by means of gradual changes in materials composition, as is the case in binary or terenary materials systems such as strontium ferrite or strontium titanium ferrite. If this parameter is explored experimentally, the materials system should be selected carefully so that the bandgap may be varied gradually while keeping the crystalline phase of the material constant, as crystal structure and orientation is expected to influence the reactions that occur at the surface of the semiconductor (i.e. this may influence measured values of $E_{SS}$).

Work function of the semiconductor is varied implicitly in the process of selecting a material system to utilize as the sensor material, e.g. ZnO vs. SnO₂ vs. TiO₂. This change in work function may be accounted for simply in the numerical model. In addition, the change in materials system may influence a host of other materials parameters, which also must be considered in the process of obtaining an accurate device model.

The work function of the substrate may also be varied by selection of the substrate material. It is important to note that the EA-FET possesses a buried gate dielectric (in this case, SiO₂) that insulates the semiconductor film from the conductive substrate (which serves as the buried gate electrode). When the underlying conductive substrate material is changed, the change in work function will result in a change in the built-in voltage from the substrate to the semiconductor, which will in turn have an impact on the device chemical sensitivity. This may be achieved by selecting different materials as the conductive substrate, for example Si vs. Pt vs. Au, etc. However, changes in substrate material will have a strong impact on compatibility with the gate oxide layer and may complicate subsequent fabrication of the device on top of the substrate. Another way to vary the work function of the substrate would be to vary its doping density, from heavily doped p-type Si (as was the case in the present thesis) to heavily doped n-type Si. Because of the availability of silicon wafers over a range of well controlled doping density, this latter case may provide the best means for systematic variation of substrate work function.

Lastly, the thickness of the semiconductor should be varied to investigate the impact on device sensitivity. As was seen earlier in this thesis work, device sensitivity is heavily influenced by the thickness of the semiconductor. As device thickness is decreased, the power law dependence of semiconductor conductance on partial pressure of the gas increases until it reaches a maximum plateau. In addition, as the thickness decreases, the sensor becomes overall more resistive, which may complicate the matter of obtaining device measurements if the device falls out of the range of sensitivity of electronic instrumentation. In practice, it is expected that there will be a critical thickness of the semiconductor film, at which the sensor is most sensitive in response to a given gas of interest while still providing a strong, measurable signal above other noise sources that are present in the system. As was shown in the numerical simulation section, these transitions in
device sensitivity largely occurred at device thickness significantly thinner than 100 nm. For an EA-FET of electronic properties similar to the device modeled in this thesis, a range of thickness of 20 to 60 nm would be of high interest for further investigation.

8.4.3. Electric Field Programmed Chemisorption and Desorption

It is evident from numerical simulation and experiments concerning the EA-FET that application of a bias voltage to the buried gate electrode can have a drastic impact on chemisorption that occurs at the surface of the semiconductor. The modeling work shows that the influence of gate bias changes as a function of the energy position $E_{SS}$ of the gas that is chemisorbed on the surface (as discussed in section 6.8. Influence of Transistor Gate Voltage on Sensitivity to Weak Binding Gas and section 6.9. Influence of Transistor Gate Voltage on Sensitivity to Strong Binding Gas). In one case, the surface concentration of a strongly binding oxidant ($E_{SS} = 2.5$ eV) was shown to change by nearly 5x in response to a variation in gate bias of +/- 10 V. In another case, the surface concentration of a weakly binding oxidant ($E_{SS} = 1$ eV) was shown to change by orders of magnitude within the same range of applied gate voltage (+/- 10 V), and a bias of -10 V was sufficiently strong to remove nearly all of the chemisorbed species from the device surface. The fact that a single level of gate voltage can be used to cause a relatively small change in concentration of one chemisorbed gas while nearly completely desorbing a second gas illustrates the potential of this technique to significantly improve the selectivity of the EA-FET to a single gas of interest in a complex environment that contains multiple gases of varying oxidizing or reducing reactivity. Hence, the following procedure is proposed to illustrate the utility of electric field to control the process of chemisorption and increase sensor sensitivity and selectivity to specific target gases of interest:

1. Fabrication of an EA-FET, wherein all relevant materials properties and device dimensions necessary to inform a numerical model of the device are known.
2. Selection of a single gas to be detected, and one or more interfering gases that will serve to confound the measurement of the first gas.
3. Determination of the position of the surface energy levels, $E_{SS}$, of each gas gases under consideration individually, according to the procedure outlined earlier in this chapter. Note that this procedure will also determine the sensitivity of the EA-FET to each gas.
4. Comparison of numerical model results for each of the gases considered in contact with the EA-FET, and selection of bias voltage at an appropriate level to suppress cross sensitivity to one or more interfering gases while retaining sensitivity to the primary gas of interest.
5. Measurement of EA-FET sensitivity to each gas under consideration individually, during application of the selected bias voltage.
6. Comparison of EA-FET sensor response to all gases, before and after application of gate bias, to quantify the electric field induced change in selectivity.

The above procedure enables the principle of electric field induced enhancement to device selectivity to be tested directly. Such an enhancement can serve to significantly improve the
viability of semiconducting metal oxides as chemical sensors in open and uncontrolled operating environments, since it is normally difficult to identify a gas being detected based on an observed change in conductance of the sensor film, alone. To effectively study this phenomenon, the typical sensor films of interest are again recommended for future work (as discussed earlier in this chapter), in addition to the primary material studied within this thesis, InGaZnO$_4$. In addition, gases may be selected as suggested earlier (O$_2$, NO$_2$, H$_2$, and CO) with concentrations experimentally controlled at similar levels. In general, a stronger effect of gate bias upon selectivity is expected for gases that possess very different values of $E_{ss}$. Appropriate levels of gate bias in the above experiments will be determined by examination of numerical simulation results including the selected materials and gases. However, a significant impact of gate bias on changes in device sensitivity were previously observed within the range of +/- 10 V, and similar results might be expected for the presently suggested future work, which will depend also strongly upon electronic properties and physical dimensions of the EA-FET.

The above selectivity experiments may be repeated multiple times, wherein a different gas in the set of gases under consideration is each time identified as the primary gas of interest. In this manner, a different voltage may be necessary to enhance the sensitivity of each while suppressing sensitivity to the other gases as much as possible, according to the numerical model. Besides this technique for selection of the applied gate bias, it would be instructive to perform additional experiments that vary the applied voltage around each selected setpoint voltage, to determine whether further improvements beyond the predictions of the model are attainable. Because of variations in geometry and materials properties that may occur in device fabrication processes, it is expected that there may be deviation in device performance from the predictions of the model. Hence, some variation away from theoretically ideal measurement conditions might result in the measurement of further improvements to performance.

The above approach for selectivity measurement assumes that each gas in the environment will independently influence the sensor response, which may not always be the case. For example, H$_2$ and CO are commonly known to react with O$_2$ that is chemisorbed on certain sensor surfaces of interest. Because multiple gases in the environment may react with one another in addition to reacting directly with the semiconductor surface, it is important to perform additional experiments that test the EA-FET sensitivity to a gas of interest during simultaneous introduction of controlled concentrations of one or more interfering gases. Sensor response to each gas of interest should be collected and compared to earlier cases of the sensor responding to the same gas in a background of relatively inert balance gas (e.g. either air or nitrogen). If the observed sensor response appears similar to a linear combination of responses each gas present, then the model is considered a reasonable approximation for this particular system. However, if the measurement differs significantly from this expected trend, then additional complexity is necessary in the model to account for cross-sensitivity effects. In consideration of the direct interaction between various gases, it is of great importance to thoroughly research the
flammability and reactivity of all gases and avoid mixture of gases that may explode or otherwise violently react.

Experiments that were performed within this thesis on the fabricated EA-FET additionally illustrated that appropriate control of gate bias over time can result in preferentially accelerated chemisorption or desorption reactions on the device surface in steady state. The gate voltage itself creates an increased electrochemical driving force for chemisorption or desorption to occur, which enables a larger change in surface coverage over time in response to changes in response to a changing concentration of gas in the environment. While this effect was shown in the experimental work to result in a significant increase in reversible chemisorption and hence an increase in device sensitivity to NO\textsubscript{2} gas, there was also a significant drift in device response due to charge relaxation that was internal to the sensor film. This charge relaxation process was mitigated in part by application of an AC transient gate bias to the fabricated EA-FET, effectively elevating the driving force for adsorption and desorption processes at the semiconductor surface while allowing internal charge relaxation processes to occur over shorter time scales under the same AC voltage. Whether the internal charge relaxation process originated due to the amorphous nature of InGaZnO\textsubscript{4} or due to some other property of the semiconducting film, it reasonable that the observed charge relaxation might be eliminated by selection of a different semiconductor materials system. Hence, it is of interest to pursue additional experiments that investigate the influence of gate voltage on the performance of EA-FET structures that are fabricated out of alternative semiconductor materials systems that are expected to possess an internal structure that is stable under application of electric field.

8.4.4. Surface Spectroscopy and Gas Composition Analysis

In addition to experiments that are geared towards measurement of improved sensor selectivity in the conductance response to gas concentrations, it is also of interest to perform experiments that would directly confirm changes in the surface coverage that are predicted by the model. One approach towards achieving this is to measure the surface coverage of atoms using spectroscopic techniques such as low energy electron diffraction (LEED), fourier transfer infrared spectroscopy (FTIR), or ultraviolet photoelectron spectroscopy (UPS). Each of these techniques may offer different information of use in confirming predictions of the relationship between the electronic properties of the bulk material and changes in surface coverage of a given gas:

- LEED is a technique that is commonly used in semiconductor fabrication and characterization to measure the surface coverage of a monolayer of crystalline material. This technique might similarly inform the characterization of a layer of chemisorbed gas.
- FTIR measurements are expected to aid in identification of chemical species at the surface of the EA-FET, through the influence of molecular resonance on the attenuation of transmitted and reflected IR illumination.
- UPS provides information about the energy band structure of a semiconductor and may provide input regarding the interaction of the bulk semiconductor with energy states associated with the chemisorbed gas.

Besides the above spectroscopic tests, it is also of high interest to directly measure the composition of the gas that is being chemisorbed and desorbed at the surface of the chemical sensor. Mass spectrometry may be utilized to identify the composition of gases in the surrounding environment. To take full advantage of this approach, it is necessary to completely isolate a volume of air around the EA-FET in a sealed chamber that is sufficiently small. In this experiment, chemisorption and desorption must have a sufficiently strong impact on the surrounding volume of air to influence the concentration of gas within the measurable limit of the mass spectrometer. The goal of this experiment would be to measure changes in the surrounding gas concentration while characterizing an EA-FET according to normal procedures as outlined earlier. Knowledge of the composition of surrounding gases may be used to further develop models of chemisorption reactions that occur at the surface.

8.4.5. Refinement of the Numerical Simulation Approach

As was seen in numerous earlier discussions, the new numerical simulation approach developed within this thesis has proven to be very useful in understanding the mechanisms of chemisorption and informing the selection of meaningful experiments to perform. None the less, this work still only represents the starting point of the greatly improved insight into materials properties that may be gained if the model is further refined and made to more accurately reflect physical effects occurring in actual device structures of interest. Since the present thesis has considered models of the EA-FET in 1D and 2D, the most straightforward generalization of this work would include more complex device geometries that may be described in 3D.

Along these lines, it is also important to account for the possible occurrence of anisotropic materials properties as may occur in a crystalline material. Parameters such as relative permittivity and electronic mobility can be a function of crystal orientation, affecting the properties of the semiconductor bulk. Also, the position of surface energy levels, $E_{SS}$, is expected to be influenced by the crystallographic orientation of the exposed semiconductor surface. A modified version of the model can account for these effects. It would be useful to contrast the performance of such polycrystalline structures to EA-FET devices that are made of single crystalline layers, which may also be fabricated utilizing modern epitaxial growth techniques.

Polycrystalline devices may be modeled explicitly by creating subregions of the modeled semiconductor that possess different crystallographic orientation and are separated by grain boundaries that each may possess an accumulated or depleted space charge layer. Such materials structures are of practical interest to model, due to the fact that many other common sensor materials (SnO$_2$, ZnO) occur in polycrystalline phase when deposited via sputtering at room temperature. Other nonuniformities are of interest to the refinement of the numerical models,
including the consideration of discontinuous materials layers, the roughened semiconductor surfaces, and porous layers of material. The finite element techniques used in this thesis are sufficiently flexible and robust to capture relatively arbitrary variations in device geometry and materials properties of different regions of the EA-FET device structure.

As noted earlier, the model of this particular materials system (InGaZnO₄) would be greatly helped by an explicit treatment of sub-bandgap electronic states that arise due to the amorphous nature of the semiconductor. This includes accounting for a mobility gap within the semiconductor, rather than a band gap, and calculation of fixed charge and mobile charge carriers that are distributed in energy across the range of the semiconductor energy band gap. Recent works have emerged that consider the task of numerically modeling amorphous semiconductor based transistors,⁷³,⁸¹ and these approaches may be readily incorporated into the present work.

Besides the above techniques for analysis of the equilibrium behavior of the EA-FET, it is important to refine the numerical model to consider the time dependence changes in surface coverage and attempt to develop predictions of chemical sensor response time, directly from calculated results. To begin to address this, specific chemical reactions of importance may be first characterized experimentally via spectroscopic techniques or mass spectrometry. Then, equilibrium reaction rate constants may be entered into the numerical model, to predict the rate of every possible chemical reaction that occurs at the surface of the EA-FET. Then, the parameters such as ambient temperature and gas concentration may be varied, causing the various chemical reactions to evolve, driving the EA-FET to approach a steady state response to the environment. This reaction rate is of primary interest to the optimization of chemical sensor response time.

In addition to fundamental models of kinetic reaction rates associated with EA-FET chemical sensitivity, other kinetic influences on device nonlinearities should be considered in the model. As noted previously, some drift in device properties was observed experimentally during prolonged exposure to constant gate bias. Other works have identified possibility of electromigration effects through the semiconductor film in influencing drift in sensor response over time. These effects also may be readily incorporated into the numerical model by considering the diffusion of gases that are chemisorbed of the surface of the film, throughout the bulk.

By refinement of the numerical model, the ability to gain a more accurate description of the EA-FET as implemented in practical device structures and natural operating environments is significantly improved. As the numerical simulation becomes increasingly accurate, it also becomes more powerful as a tool that may be applied in better understanding chemisorption and applying that knowledge towards the engineering of markedly improved chemical sensors.
8.5. Broader Impact

Looking beyond the context of chemical sensors, it is of great interest to apply the numerical models developed in this thesis work toward the investigation of any system in which a nanostructured semiconductor interacts with a gaseous environment, be it for the specific purpose of detecting properties of the environment or otherwise. Process models that are utilized in semiconductor device fabrication may benefit from improved knowledge of the relationship between device dimensions, electric field, gas concentration, and electrochemical properties of the material. Electronic device designers may incorporate the numerical and lumped element models developed in this thesis work when predicting the performance of devices that expose a semiconductor surface to a gaseous environment. Researchers investigating nanostructure related enhancements in catalytic properties of semiconductors may use either the lumped element approach or a numerical treatment of semiconductor properties as they relate to chemisorption to better understand heterogeneous behavior of the system.

This thesis has presented a new approach for quantifying the influence of chemisorption on the electronic properties of materials that are formed into structures and devices of practical interest. Conversely, this thesis has also shown that changes in the electronic properties of nanostructured materials, whether originating from changes in structural geometry or application of electronic gate bias voltage, have a significant effect on the amount of chemisorption that occurs at the surface of a material. With this newfound insight in hand, it will be possible for other researchers to view their own semiconductor based systems in a new light, with knowledge of the fact that the choice of materials and nanostructure has a great impact not only on electronic properties of the bulk but also on electrochemical properties of the surface. Now that the Electroadsorption FET has been studied in detail, the door is opened for the invention of new devices that take advantage of the newly understood heterogeneous and nanoelectrochemical nature of chemisorption.
Appendix - Numerical Simulation Procedure

Finite element numerical simulation results presented within this thesis were performed using COMSOL Multiphysics version 4.2. This appendix summarizes the procedure utilized to construct the models, in both 1D and 2D finite element meshes. Variables, geometry, equations and solver parameters are all entered into the simulation software by means of a graphical user interface (GUI), as shown in the following figure.

The appendix provides a detailed description of each variable and equation that was entered into the GUI for computation of electronic carrier concentration and electric potential in the electroadsortption FET. 1D and 2D geometry were defined by means of finite element meshes, with mesh generation parameters such as minimum element size, growth rate, and refinement provided. The equations utilized in the solution are defined explicitly the 1D and 2D Model Definitions section of the appendix, including boundary conditions that couple electrostatics of the bulk material to chemisorption reactions occurring at the surface by means of the Vol’kenshtein chemisorption isotherm. An outline of the contents of the appendix is provided, followed by a detailed description of all relevant model parameters. The information contained within this appendix may be used to reproduce the numerical studies of this thesis, by re-entry of variables, geometry, equations and solver parameters into COMSOL.
Appendix Outline

1. **Global Definitions**
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   1.2. Variables

2. **2D Model**
   2.1. Definitions
   2.2. 2D Geometry
   2.3. 2D Electrostatics
   2.4. 2D Mesh

3. **1D Model**
   3.1. Definitions
   3.2. 1D Geometry
   3.3. 1D Electrostatics
   3.4. 1D Mesh

4. **2D Study**
   4.1. Parametric Sweep
   4.2. Mesh and Physics Selection
   4.3. Solver Configurations

5. **1D Study**
   5.1. Parametric Sweep
   5.2. Mesh and Physics Selection
   5.3. Solver Configurations
1. Global Definitions

Global definitions within COMSOL are divided into two categories: parameters and variables. For the purpose of the present model, parameters may be generally considered to be scalar numeric values that are held constant during the entire process of evaluation of a finite element model. The value of every parameter is defined prior to the start of the nonlinear finite element solver. This includes constant materials properties (e.g. bandgap, electron affinity), device geometry (e.g. transistor channel length, width) and environmental conditions (e.g. ambient temperature, partial pressure of gas). In contrast, variables define values that are derived from other calculated properties of the model. For example, this channel conductance, which is calculated by integration of electron and hole density over the entire thickness of the SMO film. Globally defined parameters and variables are provided in the following two tables.

1.1. PARAMETERS

PARAMETERS

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>q</td>
<td>1.602e-19[C]</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>T_0</td>
<td>300[K]</td>
<td>Temperature</td>
</tr>
<tr>
<td>k</td>
<td>1.38e-23[J/K]</td>
<td>Boltzman Constant</td>
</tr>
<tr>
<td>mun_smo</td>
<td>23.5[cm^2/(V*s)]</td>
<td>Electron mobility of IGZO (from Kim et al, DeAOTS Simulator, IEEE Trans Elec Dev 57 (2010) 2988)</td>
</tr>
<tr>
<td>mup_smo</td>
<td>mu_n/2</td>
<td>Hole mobility (assumed half of mu_n)</td>
</tr>
<tr>
<td>X_smo</td>
<td>4.3 [V]</td>
<td>SMO electron affinity</td>
</tr>
<tr>
<td>X_go</td>
<td>0.3[V]</td>
<td>Gate oxide electron affinity</td>
</tr>
<tr>
<td>X_g</td>
<td>5[V]</td>
<td>Gate work function (heavily doped Si: Eg_Si + X_Si)</td>
</tr>
<tr>
<td>epsr_smo</td>
<td>11.8</td>
<td>Relative permittivity of IGZO (approx correct according to Kim et al, Bulk-limited current cond in IGZO TFs, ECS 11 (2008) 1151)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Value</td>
<td>Description</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>epsr_go</td>
<td>4.2</td>
<td>Relative permittivity of gate oxide</td>
</tr>
<tr>
<td>Eg_smo</td>
<td>3.1[V]</td>
<td>Band gap of IGZO (or ZnO)</td>
</tr>
<tr>
<td>tao_n</td>
<td>0.1[us]</td>
<td>Electron lifetime</td>
</tr>
<tr>
<td>tao_p</td>
<td>0.1[us]</td>
<td>Hole lifetime</td>
</tr>
<tr>
<td>V_t</td>
<td>k*T_0/q</td>
<td>Thermal voltage</td>
</tr>
<tr>
<td>N_exp</td>
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<td>Exponent of factor to determine doping density, i.e. N_D=10^(N_exp)*N_D0</td>
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<tr>
<td>N_D0</td>
<td>1e17[1/cm^3(3)]</td>
<td>Starting doping density in parametric sweep</td>
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<tr>
<td>ND_SMO</td>
<td>10^(N_exp)*N_D0</td>
<td>Donor concentration in SMO</td>
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<tr>
<td>V_g</td>
<td>-10[V]</td>
<td>Gate voltage</td>
</tr>
<tr>
<td>V_d</td>
<td>0[V]</td>
<td>Drain voltage</td>
</tr>
<tr>
<td>t smo</td>
<td>70[nm]</td>
<td>Thickness of SMO</td>
</tr>
<tr>
<td>t go</td>
<td>100[nm]</td>
<td>Thickness of Gate Oxide</td>
</tr>
<tr>
<td>t sub</td>
<td>2[um]</td>
<td>Thickness of Si substrate</td>
</tr>
<tr>
<td>L_CH</td>
<td>2[um]</td>
<td>Conducting channel length</td>
</tr>
<tr>
<td>L_OVLP</td>
<td>1[um]</td>
<td>Length of S/D overlap with SMO</td>
</tr>
<tr>
<td>L_PAD</td>
<td>1[um]</td>
<td>Length of S/D contact pads</td>
</tr>
<tr>
<td>L_EDGE</td>
<td>1[um]</td>
<td>Length of edge of substrate</td>
</tr>
<tr>
<td>N_avogadro</td>
<td>6.02214129E23[mol^(-1)]</td>
<td>Avogadro's number</td>
</tr>
<tr>
<td>mu_n</td>
<td>mun_smo</td>
<td>Electron mobility in SMO</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>mu_p</td>
<td>Hole mobility in SMO</td>
<td></td>
</tr>
<tr>
<td>D_n</td>
<td>Electron diffusivity</td>
<td></td>
</tr>
<tr>
<td>D_p</td>
<td>Hole diffusivity</td>
<td></td>
</tr>
<tr>
<td>n_init</td>
<td>Electron concentration at thermal equilibrium (fully ionized donors)</td>
<td></td>
</tr>
<tr>
<td>p_init</td>
<td>Hole concentration at thermal equilibrium</td>
<td></td>
</tr>
<tr>
<td>phi_init</td>
<td>Initial guess for $\phi_0$ in SMO</td>
<td></td>
</tr>
<tr>
<td>W_CH</td>
<td>Conducting channel width</td>
<td></td>
</tr>
<tr>
<td>N_c</td>
<td>Effective DOS in conduction band of IGZO (from Kim et al., DeAOTS Simulator, IEEE Trans Elec Dev 57 (2010) 2988)</td>
<td></td>
</tr>
<tr>
<td>N_v</td>
<td>Effective DOS in valence band, assumed half of $N_c$</td>
<td></td>
</tr>
<tr>
<td>n_i</td>
<td>Intrinsic charge carrier concentration in SMO</td>
<td></td>
</tr>
<tr>
<td>ML</td>
<td>Assumed total number of surface sites (A. Rothschild, Y. Komem / Sensors and Actuators B 93 (2003) 362–369)</td>
<td></td>
</tr>
<tr>
<td>Q_s0</td>
<td>Surface charge density (assumed)</td>
<td></td>
</tr>
<tr>
<td>s0</td>
<td>condensation coefficient</td>
<td></td>
</tr>
<tr>
<td>NStar</td>
<td>number of adsorption sites per unit</td>
<td></td>
</tr>
</tbody>
</table>
1.2. VARIABLES

1.2.1. Variables 1

SELECTION

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Entire model</th>
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<tbody>
<tr>
<td>Name</td>
<td>Expression</td>
</tr>
<tr>
<td>n0_avg1D</td>
<td>mod2.intop2(n0_smo1D)/t_smo</td>
</tr>
<tr>
<td>p0_avg1D</td>
<td>mod2.intop2(p0_smo1D)/t_smo</td>
</tr>
</tbody>
</table>
### SMO Variables

SMO Variables are defined within “Domain 5”, which is the volume of the SMO film itself. SMO variables include relative permittivity (constant over film cross sectional area) and electron and hole concentration as a function of position.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{ch1D}$</td>
<td>$q_{t,smo}W_{CH/L,CH}(*mu_{n,n0,avg1D}+mu_{p,p0,avg1D})$ SMO channel conductance</td>
</tr>
<tr>
<td>$beta_{1D}$</td>
<td>mod2.aveop1(beta) Volkenstein Adsorption Coefficient</td>
</tr>
<tr>
<td>$theta_{1D}$</td>
<td>mod2.aveop1(theta) Surface Coverage (non-dissociative chemisorption)</td>
</tr>
<tr>
<td>$thetaMinus_{1D}$</td>
<td>mod2.aveop1(thetaMinus) Surface coverage of charged chemisorbates</td>
</tr>
<tr>
<td>$Q_sVolkenstein1D$</td>
<td>mod2.aveop1(Q_sVolkenstein) Surface charge density</td>
</tr>
<tr>
<td>$beta_{2Davg}$</td>
<td>mod1.aveop2D(beta) Volkenstein Adsorption Coefficient</td>
</tr>
<tr>
<td>$theta_{2Davg}$</td>
<td>mod1.aveop2D(theta) Surface coverage (non-dissociative adsorption)</td>
</tr>
<tr>
<td>$thetaMinus_{2Davg}$</td>
<td>mod1.aveop2D(thetaMinus) Surface coverage of charged chemisorbates</td>
</tr>
<tr>
<td>$Q_sVolkenstein2Davg$</td>
<td>mod1.aveop2D(Q_sVolkenstein) Surface charge density</td>
</tr>
</tbody>
</table>

### 2D Model

This section (2) contains information specific to the setup of a 2D finite element model of the Electroadsorption FET in COMSOL. This model is referenced elsewhere in the appendix solver section as “mod1”. All information necessary for setup of the 2D model is presented in the current section, including variable definitions specific to subdomains of the 2D model, model geometry, mesh generation, equation definitions, and boundary conditions.

#### 2.1. DEFINITIONS

2D model specific definitions are contained in the proceeding subsections.

#### 2.1.1. Variables

### SMO Variables

SMO Variables are defined within “Domain 5”, which is the volume of the SMO film itself. SMO variables include relative permittivity (constant over film cross sectional area) and electron and hole concentration as a function of position.
Gate Oxide Variables

Gate oxide variables are defined within “Domain 2”, the volume of the gate oxide. This includes relative permittivity of the gate oxide and an initial approximation of electric potential. This initial approximation is given to the finite element solver as an initial value, from which the solver iterates to search for values that accurately solve the defined physical equations of the system.

Volkenstein Chemisorption Variables

Volkenstein Chemisorption Variables are defined along “Boundary 18”, which is the top surface of the SMO film that is exposed to the open gas. The surface charge density is defined as a function of the electric potential along the boundary, which serves to shift the Fermi Energy from its initial value. The surface charge density and electric potential are via this
boundary condition in a recursive relationship, defined according to Vol’kenshtein chemisorption statistics.

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>beta</td>
<td>beta0*(1+1/g_A<em>exp((E_F-E_SS+(phi0-phi_init))/V_t))/(1+vminus/v0/g_A</em>exp(-(E_bc-E_F-(phi0-phi_init))/V_t))</td>
<td>Volkenstein Adsorption Coefficient</td>
</tr>
<tr>
<td>theta</td>
<td>(beta<em>p_gas)/(1+beta</em>p_gas)</td>
<td>Surface Coverage (non-dissociative chemisorption)</td>
</tr>
<tr>
<td>fMinus_A</td>
<td>1/(1+g_A*exp(-(E_F-E_SS+(phi0-phi_init))/V_t))</td>
<td>Fermi Distribution at the Surface, Evaluated over Trap Sites</td>
</tr>
<tr>
<td>thetaMinus</td>
<td>theta*fMinus_A</td>
<td>Surface coverage of charged chemisorbates</td>
</tr>
<tr>
<td>Q_sVolkenstein</td>
<td>-q<em>thetaMinus</em>NStar</td>
<td>Surface charge density</td>
</tr>
</tbody>
</table>

**Air Variables**

The permittivity of the air (1) is defined above the film, in order to consider fringing between electrodes.

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>eps_r</td>
<td>1</td>
<td>permittivity of air</td>
</tr>
</tbody>
</table>

2.1.2. Model Couplings
Various model couplings are defined, including average, maximum and minimum operators that may be used to analyze the nominal values of variables along the exposed boundary of the SMO/gas surface.

**Average 2D**

<table>
<thead>
<tr>
<th>Coupling type</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operator name</td>
<td>aveop2D</td>
</tr>
</tbody>
</table>

**SOURCE SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 18</td>
</tr>
</tbody>
</table>

**Maximum 2D**

<table>
<thead>
<tr>
<th>Coupling type</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operator name</td>
<td>maxop2D</td>
</tr>
</tbody>
</table>

**SOURCE SELECTION**

<table>
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<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 18</td>
</tr>
</tbody>
</table>

**Minimum 2D**

<table>
<thead>
<tr>
<th>Coupling type</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operator name</td>
<td>minop2D</td>
</tr>
</tbody>
</table>

**SOURCE SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 18</td>
</tr>
</tbody>
</table>

2.1.3. Coordinate Systems

**Boundary System 1**
Coordinate system type | Boundary system
---|---
Identifier | sys1

**SETTINGS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordinate names</td>
<td>{t1, n, to}</td>
</tr>
<tr>
<td>Reverse normal direction</td>
<td>On</td>
</tr>
<tr>
<td>Create first tangent direction from</td>
<td>Global Cartesian</td>
</tr>
</tbody>
</table>

**2.2. 2D GEOMETRY**

Geometry is programmatically defined within this section according to global model parameters that were provided in earlier sections of this appendix. Relevant geometric equations are listed. The following graph provides an image of the entire 2D geometric structure.
2D Geometry

UNITS

<table>
<thead>
<tr>
<th>Length unit</th>
<th>µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular unit</td>
<td>deg</td>
</tr>
</tbody>
</table>

GEOMETRY STATISTICS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space dimension</td>
<td>2</td>
</tr>
<tr>
<td>Number of domains</td>
<td>6</td>
</tr>
<tr>
<td>Number of boundaries</td>
<td>31</td>
</tr>
</tbody>
</table>

2.2.1. SMO (r1)
### 2.2.2. Gate Oxide (r2)

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>{-(L_{CH}/2+L_{PAD}+L_{OVL})+L_{EDGE}, -t_{go}}</td>
</tr>
<tr>
<td>x</td>
<td>-(L_{CH}/2+L_{PAD}+L_{OVL})+L_{EDGE}</td>
</tr>
<tr>
<td>y</td>
<td>-t_{go}</td>
</tr>
<tr>
<td>Layers on bottom</td>
<td>Off</td>
</tr>
<tr>
<td>Width</td>
<td>(L_{CH}/2+L_{PAD}+L_{OVL})+L_{EDGE})*2</td>
</tr>
<tr>
<td>Height</td>
<td>t_{go}</td>
</tr>
<tr>
<td>Size</td>
<td>{(L_{CH}/2+L_{PAD}+L_{OVL})+L_{EDGE})*2, t_{go}}</td>
</tr>
</tbody>
</table>

### 2.2.3. Substrate (r3)

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.4. Rectangle 4 (r4)

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>{-(L_{CH}/2+L_{PAD}+L_{OVLP}+L_{EDGE}), -t_{sub}-t_{go}}</td>
</tr>
<tr>
<td>x</td>
<td>-(L_{CH}/2+L_{PAD}+L_{OVLP}+L_{EDGE})</td>
</tr>
<tr>
<td>y</td>
<td>-t_{sub}-t_{go}</td>
</tr>
<tr>
<td>Layers on bottom</td>
<td>Off</td>
</tr>
<tr>
<td>Width</td>
<td>((L_{CH}/2+L_{PAD}+L_{OVLP}+L_{EDGE}))*2</td>
</tr>
<tr>
<td>Height</td>
<td>t_{sub}</td>
</tr>
<tr>
<td>Size</td>
<td>{((L_{CH}/2+L_{PAD}+L_{OVLP}+L_{EDGE}))*2, t_{sub}}</td>
</tr>
</tbody>
</table>

2.2.5. Rectangle 5 (r5)

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>{-(L_{CH}/2+L_{OVLP})-t_{smo}, 0}</td>
</tr>
<tr>
<td>x</td>
<td>-(L_{CH}/2+L_{OVLP}-t_{smo})</td>
</tr>
<tr>
<td>Width</td>
<td>L_{OVLP}+t_{smo}</td>
</tr>
<tr>
<td>Height</td>
<td>t_{smo}</td>
</tr>
<tr>
<td>Size</td>
<td>{L_{OVLP}+t_{smo}, t_{smo}}</td>
</tr>
</tbody>
</table>
2.2.6. Union 1 (uni1)

**SETTINGS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Create selections</td>
<td>On</td>
</tr>
<tr>
<td>Keep interior boundaries</td>
<td>Off</td>
</tr>
<tr>
<td>Edge</td>
<td>All</td>
</tr>
</tbody>
</table>

2.2.7. Rectangle 6 (r6)

**SETTINGS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>{-\frac{L_CH}{2}+L_OVLP, 0}</td>
</tr>
<tr>
<td>x</td>
<td>{-\frac{L_CH}{2}+L_OVLP}</td>
</tr>
<tr>
<td>Width</td>
<td>L_OVLP</td>
</tr>
<tr>
<td>Height</td>
<td>t_smo</td>
</tr>
<tr>
<td>Size</td>
<td>{L_OVLP, t_smo}</td>
</tr>
</tbody>
</table>

2.2.8. Difference 1 (dif1)

**SETTINGS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Create selections</td>
<td>On</td>
</tr>
</tbody>
</table>

2.2.9. Mirror 1 (mir1)
2.2.10. Rectangle 7 (r7)

**SETTINGS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keep input objects</td>
<td>On</td>
</tr>
<tr>
<td>Point in plane</td>
<td>{0, 0}</td>
</tr>
<tr>
<td>Plane normal</td>
<td>{1, 0}</td>
</tr>
</tbody>
</table>

2.2.11. Difference 2 (dif2)

**SETTINGS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keep input objects</td>
<td>On</td>
</tr>
</tbody>
</table>

2.3. 2D ELECTROSTATICS

This section defines the electrostatic problem that is solved throughout the 2D finite element mesh. As indicated in the proceeding subsections, the relevant equations include Poisson’s equation solved in all highlighted regions (SMO bulk, gate oxide and the surrounding air), space charge density defined within the SMO bulk, and surface charge density defined according to Vol’kenshtein chemisorption statistics at the SMO/gas surface. In addition, the source and drain are held at a nominal zero volts bias and a gate voltage is applied from the bottom surface of the gate oxide to the source and drain. Based on all of this, the nonlinear
finite element solver determines electric potential throughout all relevant regions of the model geometry, as indicated by the highlighted region of the model below.

2D Electrostatics

SELECTION

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 2-3, 5</td>
</tr>
</tbody>
</table>

EQUATIONS

\[ \nabla \cdot D = \rho \]

\[ E = -\nabla \phi_0 \]

SETTINGS

| Description | Value |
2.3.1. Charge Conservation: SMO, Gate Oxide

Charge Conservation: SMO, Gate Oxide

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 2-3, 5</td>
</tr>
</tbody>
</table>

**Equations**

\[ \nabla \cdot (\varepsilon_0 \varepsilon_r E) = \rho_v \]

\[ E = -\nabla \phi_0 \]

**Settings**

SETTINGS
Variables

The proceeding variables are implicitly defined within COMSOL in selection of the present electrostatic problem. General 3D vector values are defined for relevant system properties including electric field, electric displacement, polarization, permittivity, and current density. Certain of the following variables are referenced explicitly in the definition of various boundary volumetric materials parameters or area specific boundary conditions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.Ex</td>
<td>-phi0x</td>
<td>V/m</td>
<td>Electric field, x component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Ey</td>
<td>-phi0y</td>
<td>V/m</td>
<td>Electric field, y component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Ez</td>
<td>0</td>
<td>V/m</td>
<td>Electric field, z component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.normE</td>
<td>sqrt(realdot(init.Ex,init.Ex)+realdot(init.Ey,init.Ey)+realdot(init.Ez,init.Ez))</td>
<td>V/m</td>
<td>Electric field norm</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Dx</td>
<td>epsilon0_const*init.ccn1.input.Ex+init.Px</td>
<td>C/m^2</td>
<td>Electric displacement field, x component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Dy</td>
<td>epsilon0_const*init.ccn1.input.Ey+init.Py</td>
<td>C/m^2</td>
<td>Electric displacement field, y component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Dz</td>
<td>epsilon0_const*init.ccn1.input.Ez+init.Pz</td>
<td>C/m^2</td>
<td>Electric displacement field, z component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.normD</td>
<td>sqrt(realdot(init.Dx,init.Dx)+realdot(init.Dy,init.Dy)+realdot(init.Dz,init.Dz))</td>
<td>C/m^2</td>
<td>Electric displacement field</td>
<td>Domains 2-3, 5</td>
</tr>
</tbody>
</table>

Relative permittivity

User defined

\[
\{\{\text{eps}_r, 0, 0\}, \{0, \text{eps}_r, 0\}, \{0, 0, \text{eps}_r\}\}
\]
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.normJ</td>
<td>\text{sqrt}(\text{real} \cdot \text{dot}(\text{init.Jx,init.Jx})+\text{real} \cdot \text{dot}(\text{init.Jy,init.Jy})+\text{real} \cdot \text{dot}(\text{init.Jz,init.Jz}))</td>
<td>A/m²</td>
<td>Current density norm</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.tEx</td>
<td>-\phi \text{OTx}</td>
<td>V/m</td>
<td>Tangential electric field, x component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.tEy</td>
<td>-\phi \text{OTy}</td>
<td>V/m</td>
<td>Tangential electric field, y component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.tEz</td>
<td>0</td>
<td>V/m</td>
<td>Tangential electric field, z component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.Px</td>
<td>\epsilon_0 \text{_const} \cdot ((-1+\epsilon_0 \cdot \text{init._epsilon}<em>\text{rx} \cdot \text{init._epsilon}</em>\text{cx} \cdot \text{init._epsilon}<em>\text{cy} \cdot \text{init._epsilon}</em>\text{cz} \cdot \text{init._input.E} \cdot \text{r} A^2)</td>
<td>C/m²</td>
<td>Polarization, component x</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Py</td>
<td>\epsilon_0 \text{_const} \cdot ((\text{init._epsilon}<em>\text{ry} \cdot \text{init._epsilon}</em>\text{cx} \cdot \text{init._epsilon}<em>\text{cy} \cdot \text{init._epsilon}</em>\text{cz} \cdot \text{init._input.E} \cdot \text{r} A^2)</td>
<td>C/m²</td>
<td>Polarization, component y</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Pz</td>
<td>\epsilon_0 \text{_const} \cdot ((\text{init._epsilon}<em>\text{rz} \cdot \text{init._epsilon}</em>\text{cx} \cdot \text{init._epsilon}<em>\text{cy} \cdot \text{init._epsilon}</em>\text{cz} \cdot \text{init._input.E} \cdot \text{r} A^2)</td>
<td>C/m²</td>
<td>Polarization, component z</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init._input.E1</td>
<td>\text{model._input.E1}</td>
<td>V/m</td>
<td>Electric field, x component</td>
<td>Global</td>
</tr>
<tr>
<td>init._input.E2</td>
<td>\text{model._input.E2}</td>
<td>V/m</td>
<td>Electric field, y component</td>
<td>Global</td>
</tr>
<tr>
<td>init._input.E3</td>
<td>\text{model._input.E3}</td>
<td>V/m</td>
<td>Electric field, z component</td>
<td>Global</td>
</tr>
<tr>
<td>init.epsilonrxx</td>
<td>eps_r</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>xx</td>
</tr>
<tr>
<td>----------------</td>
<td>-------</td>
<td>---</td>
<td>----------------------------------</td>
<td>----</td>
</tr>
<tr>
<td>init.epsilonryx</td>
<td>0</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>yx</td>
</tr>
<tr>
<td>init.epsilonrzx</td>
<td>0</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>zx</td>
</tr>
<tr>
<td>init.epsilonrxy</td>
<td>0</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>xy</td>
</tr>
<tr>
<td>init.epsilonryy</td>
<td>eps_r</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>yy</td>
</tr>
<tr>
<td>init.epsilonrzy</td>
<td>0</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>zy</td>
</tr>
<tr>
<td>init.epsilonrxyz</td>
<td>0</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>xz</td>
</tr>
<tr>
<td>init.epsilonryz</td>
<td>0</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>yz</td>
</tr>
<tr>
<td>init.epsilonrzz</td>
<td>eps_r</td>
<td>1</td>
<td>Relative permittivity, component</td>
<td>zz</td>
</tr>
<tr>
<td>init.normP</td>
<td>sqrt(realdot(init.Px,init.Px)+realdot(init.Py,init.Py)+realdot(init.Pz,init.Pz))</td>
<td>C/m^2</td>
<td>Polarization norm</td>
<td></td>
</tr>
<tr>
<td>init.eps.rAv</td>
<td>0.5*(init.epsilonrxx+init.epsilonryy)</td>
<td>1</td>
<td>Relative permittivity, average</td>
<td></td>
</tr>
<tr>
<td>init.Jx</td>
<td>0</td>
<td>A/m²</td>
<td>Current density, x component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>---------</td>
<td>---</td>
<td>-------</td>
<td>-------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>init.Jy</td>
<td>0</td>
<td>A/m²</td>
<td>Current density, y component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.Jz</td>
<td>0</td>
<td>A/m²</td>
<td>Current density, z component</td>
<td>Domains 2-3, 5</td>
</tr>
<tr>
<td>init.unTex</td>
<td>0.5<em>dnx</em>(up(init.Dx)*up(init.Ex)+up(init.Dy)*up(init.Ey)+up(init.Dz)<em>up(init.Ez))+up(init.Dx)</em>(up(init.Ex)*dnx+up(init.Ey)*dny)</td>
<td>Pa</td>
<td>Maxwell upward electric surface stress tensor, x component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.unTey</td>
<td>0.5<em>dny</em>(up(init.Dx)*up(init.Ex)+up(init.Dy)*up(init.Ey)+up(init.Dz)<em>up(init.Ez))+up(init.Dy)</em>(up(init.Ex)*dnx+up(init.Ey)*dny)</td>
<td>Pa</td>
<td>Maxwell upward electric surface stress tensor, y component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.unTez</td>
<td>up(init.Dz)*(up(init.Ex)*dnx+up(init.Ey)*dny)</td>
<td>Pa</td>
<td>Maxwell upward electric surface stress tensor, z component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.dnTex</td>
<td>0.5<em>unx</em>(down(init.Dx)*down(init.Ex)+down(init.Dy)*down(init.Ey)+down(init.Dz)<em>down(init.Ez))+down(init.Dx)</em>(down(init.Ex)*unx+down(init.Ey)*uny)</td>
<td>Pa</td>
<td>Maxwell downward electric surface stress tensor, x component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.dnTey</td>
<td>0.5<em>uny</em>(down(init.Dx)*down(init.Ex)+down(init.Dy)*down(init.Ey)+down(init.Dz)<em>down(init.Ez))+down(init.Dy)</em>(down(init.Ex)*unx+down(init.Ey)*uny)</td>
<td>Pa</td>
<td>Maxwell downward electric surface stress tensor, y component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.dnTez</td>
<td>down(init.Dz)*(down(init.Ex)*unx+down(init.Ey)*uny)</td>
<td>Pa</td>
<td>Maxwell downward electric surface stress tensor, z component</td>
<td>Boundaries 3-28, 30-31</td>
</tr>
<tr>
<td>init.un</td>
<td>init.un</td>
<td>Pa</td>
<td>component</td>
<td>Boundaries</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>----</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>Tx</td>
<td>init.unTex</td>
<td>Maxwell upward surface stress tensor, x component</td>
<td>6, 8-13, 15, 17-19, 21, 23-28</td>
<td></td>
</tr>
<tr>
<td>Ty</td>
<td>init.unTey</td>
<td>Maxwell upward surface stress tensor, y component</td>
<td>6, 8-13, 15, 17-19, 21, 23-28</td>
<td></td>
</tr>
<tr>
<td>Tz</td>
<td>init.unTez</td>
<td>Maxwell upward surface stress tensor, z component</td>
<td>6, 8-13, 15, 17-19, 21, 23-28</td>
<td></td>
</tr>
<tr>
<td>Tx</td>
<td>0</td>
<td>Maxwell upward surface stress tensor, x component</td>
<td>3-5, 7, 14, 16, 20, 22, 30-31</td>
<td></td>
</tr>
<tr>
<td>Ty</td>
<td>0</td>
<td>Maxwell upward surface stress tensor, y component</td>
<td>3-5, 7, 14, 16, 20, 22, 30-31</td>
<td></td>
</tr>
<tr>
<td>Tz</td>
<td>0</td>
<td>Maxwell upward surface stress tensor, z component</td>
<td>3-5, 7, 14, 16, 20, 22, 30-31</td>
<td></td>
</tr>
<tr>
<td>Tx</td>
<td>init.dnTex</td>
<td>Maxwell downward surface stress tensor, x component</td>
<td>3-7, 14-16, 18, 20, 22, 28, 30-31</td>
<td></td>
</tr>
<tr>
<td>Ty</td>
<td>init.dnTey</td>
<td>Maxwell downward surface stress tensor, y component</td>
<td>3-7, 14-16, 18, 20, 22, 28, 30-31</td>
<td></td>
</tr>
<tr>
<td>Tz</td>
<td>init.dnTez</td>
<td>Maxwell downward surface stress tensor, z component</td>
<td>3-7, 14-16, 18, 20, 22, 28, 30-31</td>
<td></td>
</tr>
</tbody>
</table>
2.3.2. Zero Charge 1

A zero charge boundary condition is assumed at the outer extents of the air surrounding the modeled film, in addition to the outer edges of the gate oxide.
Zero Charge 1

SELECTION

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundaries 3, 5, 7, 30-31</td>
</tr>
</tbody>
</table>

Equations

\(-n \cdot D = 0\)

Variables

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.nD</td>
<td>0</td>
<td>C/m(^2)</td>
<td>Surface charge density</td>
<td>Boundaries 3, 5, 7, 30-31</td>
</tr>
</tbody>
</table>

2.3.3. Initial Values: SMO
Initial value of electric potential within the SMO and above the SMO is defined as shown. The nonlinear solver iterates following this initial value, to determine numerically accurate values of electric potential.

Initial Values: SMO

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 3, 5</td>
</tr>
</tbody>
</table>

**Settings**

**SETTINGS**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric potential</td>
<td>phi_init</td>
</tr>
</tbody>
</table>

2.3.4. Initial Values: Gate Oxide
Initial value of electric potential within the gate oxide is defined as shown. The nonlinear solver iterates following this initial value, to determine numerically accurate values of electric potential.

**Initial Values: Gate Oxide**

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 2</td>
</tr>
</tbody>
</table>

**Settings**

**SETTINGS**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric potential</td>
<td>phi_init_go</td>
</tr>
</tbody>
</table>

2.3.5. *Space Charge Density: SMO*
Space charge density within the SMO film is defined, based on ionized electron donor concentration in addition to mobile electron and hole concentrations in static equilibrium across the metal-oxide-semiconductor structure.

**Space Charge Density: SMO**

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 5</td>
</tr>
</tbody>
</table>

**Equations**

\[ \nabla \cdot D = \rho_v \]

**Settings**

**SETTINGS**

| Description | Value |
Space charge density \( q^*(p_0\text{smo-n smo}+ND_{\text{SMO}}) \)

**Variables**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.rhoq</td>
<td>( q^*(p_0\text{smo-n smo}+ND_{\text{SMO}}) )</td>
<td>C/m^3</td>
<td>Space charge density</td>
<td>Domain 5</td>
</tr>
</tbody>
</table>

2.3.6. *Space Charge Density: Gate Oxide (Zero)*

Zero space charge density exists within the gate oxide.

*Space Charge Density: Gate Oxide (Zero)*

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 2</td>
</tr>
</tbody>
</table>

**Equations**
\[ \nabla \cdot D = \rho_v \]

### Variables

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.rhoq</td>
<td>0</td>
<td>C/m^3</td>
<td>Space charge density</td>
<td>Domain 2</td>
</tr>
</tbody>
</table>

#### 2.3.7. Electric Potential: Gate

Gate voltage is defined at buried electrode, at the SMO/substrate interface.

**Electric Potential: Gate**

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 4</td>
</tr>
</tbody>
</table>

**Equations**
\[ \phi_0 = V_0 \]

**Settings**

**SETTINGS**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric potential</td>
<td>( V_{g-X_g} )</td>
</tr>
</tbody>
</table>

**Variables**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.nD</td>
<td>( \text{unx} \cdot \text{down(init.Dx)} - \text{uny} \cdot \text{up(init.Dx)} ) \ + ( \text{uny} \cdot \text{down(init.Dy)} - \text{up(init.Dy)} )</td>
<td>C/m^2</td>
<td>Surface charge density</td>
<td>Boundary 4</td>
</tr>
<tr>
<td>init.V0</td>
<td>( V_{g-X_g} )</td>
<td>V</td>
<td>Electric potential</td>
<td>Boundary 4</td>
</tr>
</tbody>
</table>

**2.3.8. Electric Potential: Source, Drain**

Electric potential of the source and drain are assumed to be zero in the present problem, satisfying the condition of static equilibrium.
Electric Potential: Source, Drain

**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundaries 8-14, 16-17, 19-27</td>
</tr>
</tbody>
</table>

**Equations**

\[ \phi_0 = V_0 \]

**Settings**

**SETTINGS**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric potential</td>
<td>( \phi_{\text{init}} )</td>
</tr>
</tbody>
</table>

**Variables**
<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.nD</td>
<td>$u_{nx}(\text{down}(\text{init.Dx})-\text{up}(\text{init.Dx}))+u_{ny}(\text{down}(\text{init.Dy})-\text{up}(\text{init.Dy}))$</td>
<td>C/m$^2$</td>
<td>Surface charge density</td>
<td>Boundaries 8-14, 16-17, 19-27</td>
</tr>
<tr>
<td>init.V0</td>
<td>$\phi_{\text{init}}$</td>
<td>V</td>
<td>Electric potential</td>
<td>Boundaries 8-14, 16-17, 19-27</td>
</tr>
</tbody>
</table>

### 2.3.9. Surface Charge Density 1

At the upper SMO/gas surface a surface charge density is defined according to Vol’kenshtein chemisorption statistics. The value of this surface charge density depends on electric potential along the surface, as listed earlier in this appendix, in geometry-specific model definitions of the SMO/gas surface.
Geometric entity level | Boundary
---|---
Selection | Boundary 18

**Equations**

\[ \mathbf{n} \cdot (\mathbf{D}_1 \mathbf{D}_2) = \rho_s \]

**Settings**

**SETTINGS**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface charge density</td>
<td>( Q_{sVolkenstein} )</td>
</tr>
</tbody>
</table>

**Variables**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>init.nD</td>
<td>( Q_{sVolkenstein} )</td>
<td>C/m^2</td>
<td>Surface charge density</td>
<td>Boundary 18</td>
</tr>
</tbody>
</table>

2.4. 2D MESH

The following graphs illustrate the resultant 2D finite element mesh, shown at three lengths scales of increasing magnification from top to bottom. Each magnified section of the 2D finite element mesh is indicated by a blue boxed region. In addition, the upper-most graph indicates the region of the 2D mesh that in later calculations is primarily considered when converting the 2D finite element model into a 1D model. Mesh generation parameters are provided within this section, including element size, resolution of curvature, and refinement. These parameters are applied to the geometry defined programmatically in previous sections, resulting in the mesh as shown below.
1D model considers cross section at film center

2D Mesh

2.4.1. Size (size)

SETTINGS

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum element size</td>
<td>0.08</td>
</tr>
<tr>
<td>Minimum element size</td>
<td>1.6E-4</td>
</tr>
<tr>
<td>Resolution of curvature</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Predefined size | Extremely fine

2.4.2. Refine 3 (ref3)

SETTINGS

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of refinements</td>
<td>1</td>
</tr>
</tbody>
</table>

2.4.3. Refine 4 (ref4)

SETTINGS

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of refinements</td>
<td>2</td>
</tr>
</tbody>
</table>

3. 1D Model

The proceeding section of the appendix defines the 1D finite element model that was setup in direct analogy to the 2D finite element model shown in the previous sections of the appendix. For further clarification on the meaning of any model definition within this 1D model section, the reader may refer to the preceding section of the appendix for clarification in context of the 2D model.

3.1. DEFINITIONS

3.1.1. Variables

Domain specific variables are defined in this section.

SMO Variables

SELECTION

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>eps_r1D</td>
<td>epsr_smo</td>
<td>Relative permittivity of the SMO</td>
</tr>
<tr>
<td>Name</td>
<td>Expression</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>eps_r1D</td>
<td>epsr_go</td>
<td>Relative permittivity of gate oxide</td>
</tr>
<tr>
<td>phi_init_go1D</td>
<td>( V_g-X_g+(x_t+g_0)*(phi_init-V_g+X_g)/t_0 )</td>
<td>Initial approximation of electric potential in gate oxide</td>
</tr>
</tbody>
</table>

**Gate Oxide Variables**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>n0_smo1D</td>
<td>( n_i \cdot \exp((\phi_1 + X_{smo} + 0.5E_{smo})/V_t) )</td>
<td>Electron concentration in SMO at thermal equilibrium</td>
</tr>
<tr>
<td>p0_smo1D</td>
<td>( n_i \cdot \exp(-(\phi_1 + X_{smo} + 0.5E_{smo})/V_t) )</td>
<td>Hole concentration in SMO at thermal equilibrium</td>
</tr>
</tbody>
</table>

**Volkenstein Chemisorption Variables**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>beta</td>
<td>( \beta_0 \cdot (1 + 1/g_A \cdot \exp((E_F-E_{SS}+(\phi_1 + \phi_{init})/V_t)))/(1 + v_{minus}/v_0/g_A \cdot \exp(-E_{bc-E_F-(\phi_1 + \phi_{init})/V_t})) )</td>
<td>Volkenstein Adsorption Coefficient</td>
</tr>
<tr>
<td>theta</td>
<td>( (\beta_p \cdot p_{gas})/(1 + \beta_p \cdot p_{gas}) )</td>
<td>Surface Coverage (non-dissociative chemisorption)</td>
</tr>
<tr>
<td>fMinus_A</td>
<td>( 1/(1 + g_A \cdot \exp(-(E_F-E_{SS}+(\phi_1 + \phi_{init})/V_t)) )</td>
<td>Fermi Distribution at the Surface, Evaluated over Trap Sites</td>
</tr>
</tbody>
</table>
thetaMinus \* theta*fMinus_A \\
Q_sVolkenstein \* -q\*thetaMinus*NStar

3.1.2. Model Couplings

Model couplings are used to integrate carrier density throughout the thickness of the SMO film and calculate nominal channel conductance.

**Integration 2**

<table>
<thead>
<tr>
<th>Coupling type</th>
<th>Integration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operator name</td>
<td>intop2</td>
</tr>
</tbody>
</table>

**SOURCE SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 2</td>
</tr>
</tbody>
</table>

**Average 1**

<table>
<thead>
<tr>
<th>Coupling type</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operator name</td>
<td>aveop1</td>
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</table>

**SOURCE SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 3</td>
</tr>
</tbody>
</table>

3.2. 1D GEOMETRY

A 1D geometry is defined as shown in the following figure. The SMO is defined, shown as a 70 nm long region on the right hand side of the model. The gate oxide is defined as a 100 nm long region on the left side of the model. Note, the thickness of each region may be varied programmatically via modification of the variables, t_smo and t_go.
1D Geometry

UNITS

<table>
<thead>
<tr>
<th>Length unit</th>
<th>μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular unit</td>
<td>deg</td>
</tr>
</tbody>
</table>

GEOMETRY STATISTICS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space dimension</td>
<td>1</td>
</tr>
<tr>
<td>Number of domains</td>
<td>2</td>
</tr>
<tr>
<td>Number of boundaries</td>
<td>3</td>
</tr>
</tbody>
</table>

3.2.1. SMO (ii)
3.2.2. Gate Oxide (i2)

3.3. 1D ELECTROSTATICS

Electric potential is calculated throughout the thickness of the SMO and gate oxide.
1D Electrostatics

SELECTION

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 1-2</td>
</tr>
</tbody>
</table>

EQUATIONS

\[ \nabla \cdot D = \rho_v \]

\[ E = -\nabla \phi_i D \]

SETTINGS

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Show equation assuming std1/stat</td>
<td></td>
</tr>
</tbody>
</table>

3.3.1. Charge Conservation 1
**SELECTION**

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 1-2</td>
</tr>
</tbody>
</table>

**Equations**
\[
\nabla \cdot (\varepsilon_0 \varepsilon_r E) = \rho_v \\
E = -\nabla \phi_1 \mathbf{D}
\]

**Settings**

**SETTINGS**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative permittivity</td>
<td>User defined</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>{{\text{eps}_r^{1D}, 0, 0}, {0, \text{eps}_r^{1D}, 0}, {0, 0, \text{eps}_r^{1D}}}</td>
</tr>
</tbody>
</table>

**Variables**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>es2.Ex</td>
<td>-\phi_{1D}x</td>
<td>V/m</td>
<td>Electric field, x</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.Ey</td>
<td>0</td>
<td>V/m</td>
<td>Electric field, y</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.Ez</td>
<td>0</td>
<td>V/m</td>
<td>Electric field, z</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.nor</td>
<td>sqrt(real dot(es2.Ex,es2.Ex)+real dot(es2.Ey,es2.Ey)+real dot(es2.Ez,es2.Ez))</td>
<td>V/m</td>
<td>Electric field norm</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.Dx</td>
<td>\epsilon_0\text{const}\cdot\text{ccn1.input.Ex}+\text{es2.Px}</td>
<td>C/m^2</td>
<td>Electric displacement field, x component</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.Dy</td>
<td>\epsilon_0\text{const}\cdot\text{ccn1.input.Ey}+\text{es2.Py}</td>
<td>C/m^2</td>
<td>Electric displacement field, y component</td>
<td>Domains 1-2</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
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<th>Unit</th>
<th>Component</th>
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<tr>
<td><strong>es2.Dz</strong></td>
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<td>C/m$^2$</td>
<td>y component</td>
<td>Domains 1-2</td>
</tr>
<tr>
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<td>$\sqrt{\text{realdot}(\text{es2.Dx},\text{es2.Dx}) + \text{realdot}(\text{es2.Dy},\text{es2.Dy}) + \text{realdot}(\text{es2.Dz},\text{es2.Dz})}$</td>
<td>C/m$^2$</td>
<td>Electric displacement field, z component</td>
<td>Domains 1-2</td>
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<tr>
<td><strong>es2.tEx</strong></td>
<td>$-\phi_1 \text{DTx}$</td>
<td>V/m</td>
<td>Tangential electric field, x component</td>
<td>Boundaries 1-3</td>
</tr>
<tr>
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<td>V/m</td>
<td>Tangential electric field, y component</td>
<td>Boundaries 1-3</td>
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<tr>
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<td>V/m</td>
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<td>C/m$^2$</td>
<td>Polarization, x component</td>
<td>Domains 1-2</td>
</tr>
<tr>
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<td>Polarization, y component</td>
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<td>Polarization, z component</td>
<td>Domains 1-2</td>
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<tr>
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<td>V/m</td>
<td>Electric field, z component</td>
<td>Global</td>
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<tr>
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<td>Pressure Unit</td>
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<td>es2.unTex</td>
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<tr>
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<td>es2.unTey</td>
<td>Pa</td>
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</tr>
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<td>$es2.unT_z$</td>
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<td>Pa</td>
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<td>es2.dnTz</td>
<td>es2.dnTez</td>
<td>Pa</td>
<td>Maxwell downward surface stress tensor, z component</td>
<td>Boundaries 2-3</td>
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<tr>
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<td>-----------</td>
<td>----</td>
<td>---------------------------------------------------</td>
<td>---------------</td>
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<td>Maxwell downward surface stress tensor, y component</td>
<td>Boundary 1</td>
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<tr>
<td>es2.dnTz</td>
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<td>Pa</td>
<td>Maxwell downward surface stress tensor, z component</td>
<td>Boundary 1</td>
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<td>es2.We</td>
<td>0.5*(es2.Dx<em>model.input.E1+es2.Dy</em>model.input.E2+es2.Dz*model.input.E3)</td>
<td>J/m^3</td>
<td>Electric energy density</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.W</td>
<td>es2.We</td>
<td>J/m^3</td>
<td>Energy density</td>
<td>Domains 1-2</td>
</tr>
<tr>
<td>es2.intWe</td>
<td>es2.intccn119(es2.We)</td>
<td>J</td>
<td>Total electric energy</td>
<td>Global</td>
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</table>

### 3.3.2. Zero Charge 1

The Zero Charge boundary condition is not applied to any regions of the present 1D model.
Zero Charge 1

SELECTION

<table>
<thead>
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<th>Boundary</th>
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</tbody>
</table>

Equations

\[-n \cdot D = 0\]

3.3.3. *Initial Values in SMO*
Initial Values in SMO

SELECTION

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<th>Domain</th>
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Settings

SETTINGS

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3.3.4. Initial Values in Gate Oxide
Initial Values in Gate Oxide

SELECTION

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<th>Domain</th>
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Settings

SETTNGS

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3.3.5. Space Charge Density in SMO
Space Charge Density in SMO

SELECTION

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<thead>
<tr>
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<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domain 2</td>
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</tbody>
</table>

Equations

\[ \nabla \cdot D = \rho_v \]

Settings

SETTINGS

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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<tbody>
<tr>
<td>Space charge density</td>
<td>( q*(p0_smo1D-n0_smo1D+ND_SMO) )</td>
</tr>
</tbody>
</table>
3.3.6. Electric Potential of Gate

Gate voltage is defined at the leftmost extent of the model, i.e. at the point of the buried gate electrode.

**Equations**

\[ \phi_{1D} = V_0 \]
3.3.7. Surface Charge Density on SMO

Surface charge density at the rightmost extent of the model (the SMO/gas surface) is defined according to Vol’kenshtein chemisorption statistics.
Surface Charge Density on SMO

SELECTION

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Boundary 3</td>
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</tbody>
</table>

Equations

\[ n \cdot (D_1 - D_2) = \rho_s \]

Settings

SETTINGS

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<th>Description</th>
<th>Value</th>
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</thead>
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<td>Q_sVolkenstein1D</td>
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Variables

286
3.3.8. Space Charge Density: Gate Oxide (Zero)

<table>
<thead>
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<th>Unit</th>
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<th>Selection</th>
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<td>Q_sVolkenstein1D</td>
<td>C/m^2</td>
<td>Surface charge density</td>
<td>Boundary 3</td>
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**Equations**

\[ \nabla \cdot (D) = \rho_v \]

**Variables**
### 3.4. 1D MESH

#### SETTINGS

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<td>Resolution of curvature</td>
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</table>
3.4.2. Size l (size1)

**SETTINGS**

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<td>Resolution of narrow regions</td>
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4. **2D Study**

The following 2D study parameters are provided to define selection of the 2D problem within a single COMSOL model file that has defined both 2D and 1D problems. Configuration of the nonlinear finite element solver is defined as shown. In addition, a parametric sweep of gate voltage is defined.

**4.1. PARAMETRIC SWEEP**
Parameter name: \( V_g \)
Parameters: range(-10,2.5,5)

**4.2. MESH AND PHYSICS SELECTION**
MESH SELECTION

<table>
<thead>
<tr>
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<th>Mesh</th>
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PHYSICS SELECTION

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4.3. SOLVER CONFIGURATIONS

4.3.1. Solver 1

Compile Equations: Stationary (st1)

SETTINGS

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<tr>
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<th>Value</th>
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<td>Use study step</td>
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Dependent Variables 1 (v1)

SETTINGS

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Mod1.phi0 (mod1_phi0)

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Mod2.phi_1D (mod2_phi_1D)
The following 1D study parameters are provided to define selection of the 2D problem within a single COMSOL model file that has defined both 2D and 1D problems. Configuration of the nonlinear finite element solver and parametric sweep of gate voltage are defined as shown.
5.1. PARAMETRIC SWEEP
Parameter name: \( V_g \)
Parameters: range(-10,2.5,5)

5.2. MESH AND PHYSICS SELECTION

MESH SELECTION

<table>
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PHYSICS SELECTION

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5.3. SOLVER CONFIGURATIONS

5.3.1. Solver

Compile Equations: Stationary (st1)

SETTINGS

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Dependent Variables 1 (v1)

SETTINGS

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\textit{Mod2.phi\_1D (mod2\_phi\_1D)}

\textbf{SETTINGS}

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\textit{Mod1.phi0 (mod1\_phi0)}

\textbf{SETTINGS}

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\textbf{Stationary Solver 1 (s1)}

\textbf{SETTINGS}

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\textit{Fully Coupled 1 (fc1)}

\textbf{SETTINGS}

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