Electrical Studies of Silicon and Low K Dielectric Material

by

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Abstract

Junction capacitance measurement is a well-established powerful characterization technique that allows one to explore electrical and physical properties of defects in bulk and interface of electronic materials. Capacitance-Voltage (CV) measures the overall net carrier concentration and a built-in voltage for a diode junction. Deep level transient spectroscopy (DLTS) as one of the most sensitive electrical measurement techniques can detect electrically active impurity concentration on the level of $10^{-1}$ to $10^{-5}$ of substrate doping concentration. The characteristic energy level and capture cross-section of the traps in the semiconductor energy gap can be extracted from DLTS temperature scans. Coupled with CV free carrier concentration profile, isothermal profiling by DLTS can determine the distribution of electrically active defects in the semiconductor. CV can also measure dielectric constant, K, on a metal-oxide-silicon structure. In this thesis, the junction capacitance technique is a primary tool used to study Er, Fe, and Mo in silicon. Si:Er is a candidate system for a light emitter in Si-based microphotonic. Fe is one of the most troublesome elements that degrade integrated circuit performance and solar cell
efficiency. Mo is a fairly unknown contaminant typical of integrated circuit processing. Fluorosilicate glass is being used as a dielectric material for inter-metal levels in the current generation microprocessor. By measuring the reaction kinetics of the Er-related donor state, a defect structure for Si:Er light emitter center was deduced. The role of heterogeneous precipitation in Fe internal gettering was observed and modeled by measurement of residual [FeB] associates following [Fe] saturation, quench, and annealing processing. The diffusivity of Mo was determined and models for both the substitutional and the kick out diffusion mechanism were constructed. Finally, a predictive model for the F-content dependent dielectric constant variation of SiO₂ was established.

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Chapter 1

Introduction

Electronic revolution has started since a bipolar transistor was invented to replace the traditional bulky vacuum tube about fifty years ago. With the advent of Integrated Circuit, semiconductor industry has embarked on its journey of device miniaturization for speed, performance, and economy. The number of components has doubled every two years since 1975 [1]. Now, the number of components per chip is over 10 million and projected to be more than 1 billion components in the early 21st century [2,3]. Accordingly, the device dimensions including gate oxide thickness and minimum feature size have shrunk exponentially, and are expected to be 40Å and less than 0.2μm, respectively.

Miniaturization sets various challenges for the different levels of a chip operation. On the system level, ultra-small size means higher IC capacitance and wiring resistance, which is translated into high power consumption and lower speed. Both short term and long term approaches are being made to address these challenges. To increase clock speed, short-term approaches involve decreasing both resistance and capacitance by
replacing Al line with Cu line and substituting low K dielectric materials for SiO$_2$. But these make only marginal progress.

Silicon-based optical interconnect has been rigorously developed as a long-term approach. Optical transmission can deliver high density of information at light speed without resistance and capacitance, seemingly to overcome all the challenges set by high density electrical interconnect. However, optical counterparts for a signal source, wire, and a receiver for transmission must be developed. The proposed optical components are Si:Er light emitters, modulators, poly silicon waveguides, bends, splitters, and SiGe detectors.

On the device level, miniature devices impose more stringent limits for defect and contamination levels as well as require a precise device structure. In order to control the device performance precisely, it's imperative to understand the mechanisms underlying each processing step such as cleaning, film growth, pattern etching, junction placement, and contamination prevention and removal. To address these challenges, more sensitive, reliable characterization tools and simulation are necessary.

1.1 Junction Capacitance Measurements

In the field of electrically active defect characterization, Deep Level Transient Spectroscopy (DLTS) is still one of the most powerful tools because of its sensitivity and spectroscopic nature with a well-documented defect library. Since its invention by Lang and Kimerling in the early 1970s, DLTS has greatly contributed to elucidating electrical properties of point and line-defects in semiconductors and help to understand physical properties of defects in semiconductors.

1.2 Thesis Organization

Junction capacitance measurement is employed as a primary tool to explore the following electrically active defects in silicon and low dielectric constant of fluorinated SiO$_x$ that are of both scientific and technological interest: Er, Fe, Mo and fluorosilicate glass (FSG). This thesis addresses each topic in the subsequent chapters after chapter 1.
describes the junction capacitance measurement techniques, both steady state and transient, in detail. In Chapter 2, electrical properties of Er were investigated and a possible defect structure for optically active Er in a Si:Er emitter was deduced. In Chapter 3, well-established Fe properties in silicon allowed us to study the heterogeneous precipitates in Fe gettering mechanism and its limit in p-type CZ silicon. Chapter 4 tackled Mo in silicon whose thermodynamic and kinetic properties remain fairly unknown. This thesis modeled Mo diffusion by interstitial-substitutional exchange mechanism combined with substitutional Mo diffusion and examined it with DOPDEES simulation, which showed a good consistency. In Chapter 5, measurements by capacitance-voltage on a metal-insulator semiconductor (MIS) structure shed light on the FSG/Si interface qualities and dielectric constant, K, of FSG. The relationship between F and K or n was expressed by applying a pseudo alloy model of SiO₂ and Si₂O₃F₂ to Clausius-Mossotti equation and the theoretical prediction and experimental data were compared. Appendix A derives the non-linear differential equations that describe Mo diffusion by interstitial-substitutional exchange mechanism. Appendix B presents DOPDEES codes that incorporate those equations into a partial differential solver to simulate Mo diffusion behavior.
Chapter 2

Junction Capacitance measurements

2.1 Electrical Defects in semiconductor

Silicon material at the core of the electronics revolution in this century becomes interesting only after they are doped with group III or V elements. As these dopants are incorporated into silicon, they form an energy level in the energy gap of silicon but quite close to either conduction band (group V element) or valence band edge (group III element) since they have an electronic structure that is similar to that of silicon. However, other elements such as transition metals form a deep level because they have an electronic structure quite different from that of silicon. Typically dopants are tens of meV apart from the band edges while deep levels are hundreds of meV away from the band edges. These deep levels are called traps or recombination centers depending on whether they interact with only one or both types of free carriers. Traps are defined to be deep levels that interact preferentially with either holes or electrons and recombination centers deep levels that interact with both electrons and holes as schematically shown in Figure 2-1.
2.2 Junction Capacitance

2.2.1 Junction Fabrication

2.2.1.1 Schottky Junction

Junction capacitance techniques allow one to measure concentration for dopants and trap/recombination centers. First of all, semiconductor of interest must form either a metal-semiconductor Schottky or n⁺-p or p⁺-n junction. Schottky junction is preferred over an asymmetric pn junction for simpler processing steps. The success of Schottky junction formation depends on its interface qualities and built-in voltage. To achieve high quality interface, semiconductor surface needs to be thoroughly cleaned and smooth. The surface preparation consists of organic cleaning, oxide etching, metal removal, and final oxide etching. Organic cleaning involves trichloroethane, acetone, and methanol cleanings in an ultrasonic bath for at least 5 minutes per solution in order. After a silicon sample is rinsed in de-ionized water, dilute hydrofluoric acid [100:1=H₂O:HF(49%)] removes a native oxide layer on silicon. The termination of oxide etching can be indicated by the hydrophobic nature (beading of water) of silicon surface. After another de-ionized water rinse, metal contaminants are removed in piranha (H₂O₂:H₂SO₄=1:3) for 10 minutes. It's important to note that one always has to add H₂SO₄ to H₂O₂ to avoid a violent acid reaction. Stirring will help metal removal. Silicon sample will go through
another de-ionized water rinse before its oxide is etched by this final dilute HF dip. The
built-in voltage is theoretically defined to be the difference between metal work function
and electron affinity of semiconductor as shown in Figure 2-2. Many times the Fermi
level is pinned by the interfacial defect states and the built-in voltage does not exactly
follow what the theory would predict. Still one uses metal that the theory predicts gives a
large enough built-in voltage. Al or Ti is thermally or deposited by e-beam through a thin
Molybdenum shadow mask on p-type silicon under a high vacuum around mid 10⁻⁷ mbar
while Au₃Pd alloy or Au is evaporated on n-type silicon. As a result, a circular metal
contact forms, defining the cross sectional area of Schottky junction. Al tends to form
oxide and to dope Si p-type around the contact, bringing about surface effects, which
results in a DLTS peak in a sign opposite to a majority peak. Ti is preferred over Al for
p-type silicon due to its sturdiness and inertness. The adhesion problem of Au makes
Au₃Pd a better metal alloy for n-type silicon. To deposit Au₃Pd, one puts Au and Pd in
three to one ratio into a resistive crucible and melts them at the eutectic temperature
lower than the melting temperature of either metal. After Au₃Pd wets the crucible, one
evaporates it at a higher temperature. Once Schottky junction, for example, on n-type
silicon, is formed, electrons diffuse to the metal side leaving a positively charged space
charge region and are soon stopped by the opposing electric field that is created by initial
electron diffusion. This space charge region is the region depleted of holes and electrons.
The presence of space charge region within the depletion width from the junction can be
modeled as a parallel plate capacitor shown in Figure 2-2. One can calculate built-in
voltage and carrier concentration profile in semiconductor from CV measurements.

2.2.1.2 Metal Oxide Semiconductor (MOS) Structure

To fabricate a MOS structure, one more intermediate step of oxide deposition is
required prior to Al contact deposition. Depending on the sample thermal budget, one
can decide oxide growth temperature and time duration, referring to the oxide growth
parameters [4]. After silicon surface cleaning, furnace annealing under either O₂ or H₂O
grows thermal oxide on silicon. Dry oxide is slow to grow but has a better quality.
Figure 2-2 Models and band diagrams for Schottky diode and MOS structure: \( W \): depletion width, \( t_{ox} \): oxide thickness, \( \Phi_M \): metal work function, \( \chi_S \): electron affinity for Si.
As-grown oxide/Si interface tends to have high interstitial trap density $D_{it}$ on the order of $10^{11}$ to $10^{12}$ cm$^{-3}$. To reduce the interfacial states, one anneals MOS sample in the furnace at 450°C under N$_2$ ambient for 5 to 10 minutes [5]. Residual vapor oxidizes Al, generating hydrogen to passivate the interface. SiO$_2$/Si samples can undergo an anneal under hydrogen ambient, for example, forming gas (N$_2$/H$_2$=99:1) at a temperature less than 500°C. As a result, $D_{it}$ reduces to less than $10^{10}$ cm$^{-2}$. MOS structure can be modeled as two parallel capacitors connected in a series as in Figure 2-2. Voltage dependent capacitance can be divided into three regimes: accumulation, depletion and inversion. The built-in voltage or flat band voltage can be defined as $\phi_{M} - \chi_{Si}$. The presence of interfacial traps, fixed charge, and mobile ions in oxide can change the flat band voltage. The accumulation regime which is characterized by constant capacitance of oxide allows one to measure the dielectric constant of oxide, whereas depletion regime provides silicon bulk and SiO$_2$/Si interface properties. The quantitative analytic treatments of CV measurements are handled in the subsequent sections.

### 2.2.2 Capacitance-Voltage Analysis

The capacitance can be expressed in the following manner.

$$C = C(N_A, N_D, K, N_T, V, A, t, f)$$  \hspace{1cm} \text{Eq. 2-1}

where $N_A$, $N_D$, $K$, $N_T$, $V$, $A$, $f$, $t$ are acceptor and donor concentration, dielectric constant, trap concentration, voltage, cross sectional area, measurement frequency (typically 1MHz) and depletion width/oxide thickness depending on the structure. When $N_T$ is on the order of dopant concentration, it can change CV profile significantly. It needs further analysis. The effect of deep traps on the measurement of free carriers is extensively treated in reference [6]. Effects of deep traps become important when interpreting implanted Er and Mo profiles in Chapter 2 and 4. A rule of thumb is that measuring an enhanced free carrier profile at a high temperature and a compensated free carrier profile at a low temperature to avoid the anomaly due to the presence of traps.
2.2.2.1 Schottky Junction

Assuming an abrupt junction and uniform doping in p-type silicon, capacitance is reduced to a simpler form.

$$C = \frac{A \varepsilon_0 K_{Si}}{w}$$  \hspace{1cm} Eq.2-2

$$w = \left( \frac{2 \varepsilon_0 K_{Si} (V_{bi} - V)}{q N_A} \right)^{\frac{1}{2}}$$  \hspace{1cm} Eq.2-3

where \(w\), \(q\), \(\varepsilon_0\) and \(V_{bi}\) are depletion width, electron charges, permittivity and built-in voltage, respectively. According to the above equations, the slope of plot \(1/C^2\) vs. \(V\) is proportional to \(1/N_A\) as in Figure 2-3. The straight line implies the doping concentration is indeed uniform. Unless the doping concentration is expected to increase with the depth of sample, a sublinear bending of the plot toward high reverse voltage indicates the presence of stray capacitance. It needs to be corrected by recalculating the deviation in terms of capacitance. The derivative of \(1/C^2\) with respect to \(V\) leads to the general expression for \(N(x)\).

$$x = \frac{A \varepsilon_0 K_{Si}}{C}$$  \hspace{1cm} Eq.2-4

$$N(x) = -\frac{\left( C/A \right)^3 \Delta V}{q \varepsilon_0 K_{Si} \Delta C}$$  \hspace{1cm} Eq.2-5

where \(\Delta V\) and \(\Delta C\) are an incremental voltage change and the corresponding capacitance change. The equation for \(N(x)\) can be also derived without assuming uniform doping concentration. Higher resolution of \(N(x)\) results from smaller \(\Delta V\) usually on the order of 0.01V. However, the resolution of \(N(x)\) is inherently limited by Debye length, which originates from the carrier spill over the depletion region. That is, in reality, the junction is not abrupt and some carriers penetrate through the depletion region by roughly Debye length [7].
\[ L_D = \left[ \frac{\varepsilon_0 K_{Si} k_B T}{q^2 N(x')} \right]^{\frac{1}{2}} \]

Eq. 2-6

where \( k_B \), \( T \), and \( x' \) are Boltzmann constant, temperature in Kelvin and the distance toward the junction from the edge of the depletion region.

\[ C \quad 1/C^2 \]

\[ V \]

\[ \text{Accumulation} \quad \text{Depletion} \quad \text{Inversion} \]

\[ V \]

\[ C \quad 1/C^2 \]

\[ V \]

\[ \text{slope} = 1/N \]

Figure 2-3 Schematic plot of \( C \) vs \( V \), \( 1/C^2 \) vs \( V \) for Schottky junction and MOS structure.

2.2.2.2 MOS structure

As shown in Figure 3-3, expression for overall capacitance takes a different form at each regime

\[ a) \text{Accumulation:} \quad C = C_{ox} = \frac{A \varepsilon_0 K_{ox}}{t_{ox}} \quad \text{Eq. 2-7} \]

\[ b) \text{Depletion:} \quad C = \frac{C_{ox}}{\left[ \frac{w_g K_{ox}}{t_{ox} K_{Si}} \right] + 1} \quad \text{Eq. 2-8} \]
c) Inversion: \[ C = \frac{C_{ox}}{\left[ \frac{w_d}{t_{ox}} K_{ox} K_{Si} + 1 \right]} \] for high \( \omega \)  
Eq.2-9

\[ C = C_{ox} \] for low \( \omega \)

where \( C_{tot}, C_{ox}, t_{ox}, K_{ox}, w_{Si}, w_d \) and \( \omega \) are total, and oxide capacitance, oxide thickness and dielectric constant, depletion width to Si, maximum depletion width to Si, and measurement frequency, respectively. The same formalism can apply to MOS structure to calculate dopant or free carrier concentration in silicon. But one needs to replace \( C \) in Eq.2-4 and 2-5 with \( (1/C_{tot} - 1/C_{ox})^{-1} \). The capacitance in an accumulation regime is employed to calculate dielectric constant of oxide after oxide thickness is measured by an ellipsometer. Dektek can also measure thickness of oxide by selectively removing oxide and measuring the step height of oxide on silicon.

### 2.2.3 Transient Capacitance

#### 2.2.3.1 Theory

Transient capacitance can measure energy level \( E_T \), capture cross section, \( \sigma \), and concentration of traps, \( N_T \). Coupled with carrier concentration profile from CV, deep level transient capacitance (DLTS) technique can generate a trap profile. Before going into details of DLTS technique, it's important to understand physics behind the interaction between free carriers and a trap. Even though all the following discussion and equations are dedicated to electrons in n-type silicon for simplicity, they remain true for holes with the corresponding physical constants and variables for holes. Traps can either capture or emit free carriers. If free carriers are available with \( E_F \), Fermi energy, above \( E_T \), traps tend to capture free carriers. Capture rates for an electron trap are expressed in the following manner.

\[ c_n = \sigma_n v_e n \]  
Eq.2-10

where \( \sigma_e, v_n, \) and \( n \) are a capture cross section of electron trap, thermal velocity and concentration of electrons in conduction band. With thermal or optical energy enough to
overcome the energy difference between the conduction band edge and trap energy level, a trap can emit free carriers in a rate given by Eq.2-11.

\[ e_n = \frac{N_c \sigma_v e_n}{g} \exp \left[ -\frac{(E_c - E_T)}{k_B T} \right] \]  

Eq.2-11

where \( N_c \) and \( g \) are effective density of states and a degeneracy factor for conduction band. For simplicity, \( g \) is assumed to be 1. The rate of trap occupation can depend on the net capture and emission rates of both electrons and holes.

\[ \frac{\partial N}{\partial t} = (c_n + e_p + e_p^o)(N_T - N) - (e_n + c_p + e_n^o)N \]  

Eq.2-12

where \( e \) and \( c \) means emission and capture rates, \( n \) and \( p \) indicates electrons and holes, and superscript "o" means optically activated and \( N_T \) and \( N \) are total trap concentration and occupied trap concentration, respectively. If the process involves an electron trap under the dark, the above equation can be vastly simplified.

\[ \frac{\partial N}{\partial t} = (c_n)(N_T - N) - (e_n)N \]  

Eq.2-13

\[ N(t) = \frac{c_n}{(e_n + c_n)} N_T + \left( N(0) - \frac{c_n N_T}{(e_n + c_n)} \right) \exp \left[ -t(e_n + c_n) \right] \]  

Eq.2-14

If \( E_T < E_F \) in a neutral region and trap is initially empty(i), \( e_n \approx 0 \) and traps are filled up.

\[ N(t) = N_T \left[ 1 - \exp(-t c_n) \right] \]  

Eq.2-15

If \( E_T > E_F \) in a depletion region and trap is initially full(ii), \( c_n \approx 0 \) and traps emit free carriers.

\[ N(t) = N(0) \exp(-t e_n) \]  

Eq.2-16

Controlling reverse bias and pulse to Schottky junction readily realize the above conditions. Traps can only emit free carriers as reverse bias lowers \( E_F \) below \( E_T \). On the other hand, traps can only capture free carriers as reduced reverse bias by a pulse voltage.
raises \( E_F \) above \( E_T \). These phenomena are schematically illustrated in Figure 2-4. Free carrier trapping and de-trapping involves charge transfer, which can be measured through transient capacitance.

![Diagram](image)

\[ V = V_r \]

\[ V = V_r + V_p \]

\[ V = V_r \]

**Figure 2-4 Emission and capture by traps in a n-type Si Schottky diode. Traps within a depletion width emit free carriers as \( V = V_r \), and capture them as \( V = V_r + V_p \).**

### 2.2.3.2 Conventional DLTS - signal processing in time domain

To measure transient capacitance, a variety of ways are available but all of them, basically, measure the change in capacitance in time domain or frequency domain. Conventional DLTS uses a lock-in amplifier or double boxcar averagers to take the difference of capacitance values at fixed time \( t_1 \) and \( t_2 \), a set of which defines a rate window. One rate window sets one time constant or rate and DLTS signal takes the following form.

\[
S(T) = \int_0^{T_r} C_{\tau}(T,t) f(t) dt \quad Eq.2-17
\]

\[
C_{\tau} = \sum_{trap,i}^{\text{all}} \Delta C_{s,i} \exp\left(-t / \tau_{e,i}\right) \quad Eq.2-18
\]

where \( S \), \( T_w \), \( C \), \( \Delta C_s \) and \( f \) are DLTS signal, period width (inverse of pulse frequency), capacitance, maximum transient capacitance and a signal processing function, respectively. The signal processing function can be any of those shown in Figure 2-5. This processing scheme averages the transient signal with respect to the reference signal to give a large signal to noise ratio. High sensitivity of DLTS results from this signal
process. If double boxcar averagers are used, time constant set by a rate window \( t_1 \) and \( t_2 \) is following.

\[
\tau = (t_2 - t_1) \ln \left( \frac{t_2}{t_1} \right)
\]

\textit{Eq.2-19}

DLTS shows a peak at a temperature where an emission rate of a trap is equal to the rate set by a rate window. The peak temperature changes with a rate window. More than four sets of (\( \tau \), \( T_{\text{peak}} \)) determine trap emission rate described by Eq. 2-11. On the Arrhenius plot of \( \ln(1/\tau T^2) \) vs \( 1/T \), slope and intercept are \( E_c - E_T \) and \( \sigma_n \) as shown. Although a capture cross section has been assumed to be temperature-independent, if it changes with

\[\text{Figure 2-5 Lock-in amplifier, double box-car averagers, and correlator function are shown in order.}\]

temperature, the slope of Arrhenius plot also includes the activation energy of capture and \( E_T \) needs its correction to avoid its overestimation. Another more accurate way of measuring capture cross section is to take Isothermal DLTS with varying filling pulse widths. Dividing Eq. 2-15 by incremental measurement voltage from capacitance meter, capture kinetics can be expressed in terms of capacitance.

\[
\Delta C = \Delta C_s \left[ 1 - \exp(-c_n t) \right]
\]

\textit{Eq.2-20}

where \( \Delta C \) and \( \Delta C_s \) is general and saturated DLTS signal.
Figure 2-6 Arrhenius plot of \( \ln(e/T^2) \) vs \( 1/T \) and \( \ln((\Delta C_s - \Delta C)/\Delta C_s) \) vs \( t \).

From the slope of the unsaturated part of plot \( \ln((\Delta C_s - \Delta C)/\Delta C_s) \) vs \( t \), \( \sigma \) can be obtained. \( \Delta C_s \) is proportional to traps density and can be roughly estimated by the simple equation.

\[
\frac{\Delta C_s}{C_R} \approx \frac{N_T}{2(N_D - N_A)} \quad \text{Eq.2-21}
\]

where \( C_R \) is a capacitance at reverse bias. Once trap energy and \( \sigma \) are measured, one can profile the spatial distribution of trap as deep as a junction structure permits, i.e. depletion width at break down voltage. There are three ways of doing profiling.

1) constant \( V_r \) and variable \( V_p \)

2) variable \( V_r \) and constant \( V_p \)

3) variable \( V_r \) and \( V_p \) with constant pulse height

For example, for method one, exact trap concentration can be calculated using the following equation [7].

\[
\delta \left( \frac{\Delta C}{C_R} \right) = \frac{\varepsilon_0 K}{qW_R^2N^+} \frac{N_T(x)}{N^+(x)} \delta V_p \quad \text{Eq.2-22}
\]

where \( W_R, N^+, N_T(x) \), and \( \delta V_p \) are depletion width and free carrier concentration under reverse bias, trap concentration at pulse voltage, and incremental pulse voltage.
2.2.3.3 Fourier Transform DLTS- signal processing in frequency domain

The difference between conventional DLTS and Fourier Transform DLTS (FDLTS) is how to process transient capacitance. All other analyses of how to get trap properties are in principle the same. Fourier Transform DLTS (FDLTS) Fourier-transforms capacitance transient to express transient capacitance in terms of Fourier series of 8 sine’s and cosine’s with either a fixed period width or variable period widths [8].

\[ C = \Delta C_s \exp(-t/\tau_e) = \Delta C_s \sum_n \left[ (a_n \sin(2\pi n / T_w)) + (b_n \cos(2\pi n / T_w)) \right] \]  
Eq.2- 23

where \( \tau_e \) and \( T_w \) are emission time constant and period width, respectively. Eight sets of independent coefficients are the following.

\[
\begin{align*}
    a_1(T_w/n) & \quad b_1(T_w/n) & \quad \text{where } n=1,2,8,16,32 \\
    a_2(T_w) & \quad b_2(T_w) \\
    a_1(T_w/2+T_o, T_o=T_w/2) & \quad b_1(T_w/2+T_o, T_o=T_w/2) \\
    a_1(T_w/2+T_o, T_o=T_w/16) & \quad b_1(T_w/2+T_o, T_o=T_w/16)
\end{align*}
\]

In one temperature scan, FDLTS records 16 independent coefficients in addition to two from six double boxcar averagers equivalent outputs to give a complete analysis. With up to 3 period widths that can be recorded simultaneously, total of 48 data points on the Arrhenius plot can be generated. Fixed period width technique is analogous to a conventional DLTS but with 18 times more data points on Arrhenius plot per a temperature scan. In a variable period width, the period width is constantly varied according to the temperature dependent exponential transient up to 30s to give an Arrhenius plot over several orders of magnitude. Biorad Digital DLTS assumes an exponential capacitance transient with a certain time constant. There are three independent methods to calculate the assumed time constant [9].

\[
\tau(a_n, a_k) = \left( \frac{2\pi}{T_w} \right) \sqrt[4]{\frac{a_n - a_k}{k^2 a_k - n^2 a_n}}
\]  
Eq.2- 24
\[ \tau(b_n, b_k) = \left( \frac{2\pi}{T_w} \right) \sqrt{\frac{b_n - b_k}{k^2 b_k - n^2 b_n}} \quad n < k \quad \text{Eq. 2-25} \]

\[ \tau(a_n, a_k) = \left( \frac{2\pi b_n}{T_w na} \right) \quad \text{Eq. 2-26} \]

If the transient is indeed exponential, all the three methods result in the same time constant. If those time constants that are calculated from different sets of coefficients are consistent, the transient capacitance is indeed exponential. To evaluate how exponential capacitance transient is, FDLTS employs its "class" system. Class 75 is excellent, class 50-65 is good, and 40-45 indicates overlapping peaks. Reliability of data for a trap presence can be judged from class values.

FDLTS has two main inherent advantages over conventional DLTS. First of all, it can save measurement time at least by a factor of two. Each term of Fourier series can be treated as a signal processing function for conventional DLTS and each Fourier coefficient of FDLTS is practically DLTS signal using slightly different rate window. "b_1," the first coefficient of cosine term is equivalent to conventional DLTS signal that uses double boxcar averagers. One temperature scan generates 18 coefficients and two temperature scans provide enough data to get a reliable Arrhenius plot. Another advantage is that it has a far better energy resolution. In case that multiple traps are present, FDLTS separates out contributions from different traps with similar emission rates by evaluating 9 coefficients that represent individual contribution to total transient capacitance from each harmonic of the emission rate set by a period width. For example, a shallower trap thus with a faster emission, is dominant in higher order coefficients while a deeper trap thus with a slower emission is in low order coefficients.

2.2.3.4 DLTS System

Biorad Digital DLTS system in EMAT's Electrical Characterization Lab (EMAT ECL) consists of a cryostat with APD He compressor, a bias supply, pulse generator, modified Boontoon capacitance meter, filter, A/D converter and a Biorad signal
processing unit. The FDLTS system is DOS-operated and run in Win95 on Pentium 75 PC. It is shown schematically in Figure 2-6.

![FDLTS System Components Schematic](image)

*Figure 2-7 FDLTS system components are schematically drawn.*

2.2.3.5 Measurements

2.2.3.5.1 Contact

After Schottky or asymmetric pn junction is formed, it is very important to form an Ohmic contact on the back of the sample. It is also crucial to fix the sample on a cryostat to secure both front and back contacts from any surrounding vibrations and stress due to temperature change from room temperature to 40 K. Ohmic contact on p type silicon can be formed by Al evaporation followed by sintering at 550°C. For n-type silicon, Al on n+ silicon makes an Ohmic contact. A simple alternative for an Ohmic contact for both types is scratching the sample backside with a diamond scribe until its native oxide is removed. Then, InGa is applied to wet the back surface after it is thoroughly cleaned with methanol. As a final step, silver paint is applied to the InGa-covered back surface to secure the sample on the cryostat from any other vibrations and thermal stress due to temperature cooling.
2.2.3.5.2 Operation

Before DLTS scan is run, a sample must meet sample requirements. To examine the qualifications of the sample, current-voltage (IV) and capacitance-voltage (CV) need to be made. Leakage current of 10μA is the maximum allowed for the FDLTS. CV provides Schottky junction built-in voltage, free carrier concentration profile and the range of capacitance meter to be set. For Biorad FDLTS, minimum range setting is very important after a \( V_r \) is chosen. This is practically the same as subtracting DC part of transient capacitance to optimize system sensitivity.

Main parameters for DLTS are \( V_r \), \( V_p \), \( T_w \), \( t_p \), and measurement time. \( V_r \) and \( V_p \) determine the DLTS scan region and \( T_w \) sets the emission rate of DLTS scan. \( T_w \) ranges from greater than 0.5ms to several seconds. Short \( T_w \) is necessary to detect a shallow trap while long \( T_w \) is needed for a deep trap. \( T_p \) is the time during which a trap is filled. \( T_p \) must be large enough to saturate a trap for profiling. Pulse width can distinguish a trap with large \( \sigma \) from other traps with small \( \sigma \). With a short pulse, only the trap with large \( \sigma \) will be filled and detected in transient capacitance. With all the parameters set, DLTS is ready for a temperature scan. Temperature scan must be slow enough to prevent temperature gradient between a temperature sensor and a sample. The reasonable scan rate is 0.01K/s. Otherwise a slight shift in temperature causes an error in trap energy level. Two \( T_w \) separated by at least one order of magnitude suffices to plot the Arrhenius for \( E_T \) and \( \sigma \). A library for traps is available to help identify the trap.

2.3 Summary

Junction capacitance measurement is a very powerful tool that facilitates the electrical and physical properties of electrically active defects in semiconductor. Defect energy levels in a semiconductor energy gap, its concentration and capture cross section are the main properties that can be measured by DLTS. A large signal to noise ratio results from extensive averaging during a DLTS signal process, and facilitates the measurement of trap concentration down to \( 10^{-4} \) or \( 10^{-5} \) of a doping concentration. These defect properties provide the basis to study the physical properties of defects such as diffusivity and solubility. Fourier Transform Digitized DLTS has made the DLTS data
acquisition process more efficient and shorter. The sensitivity and spectroscopic nature of DLTS sheds a light into the defects in semiconductor.
Chapter 3
Si:Er Light Emitter for Silicon Microphotonics

3.1 Introduction

As performance of a microchip is limited by resistance and capacitance in the integrated circuit, silicon-based optical interconnect is a promising solution to overcome the challenges in power consumption and clock distribution speed. Optical interconnection has inherent advantages over its electronic counterpart. The higher bandwidth of light facilitates a larger volume of information, and maintain the current level of the interconnect density. Its propagation delay on the chip level is negligible and power dissipation is low without capacitance and resistance. The charge neutrality of the photon eliminates concerns of cross talk. Above all, CMOS compatible Si-based optical interconnection will lead to higher yield than any other system, making it more economical. The ultimate proposed scheme of Si-based optical interconnects integrates a Si:Er Emitter, Si/SiO₂ waveguide/modulator/coupler/splitter and SiGe detector on a chip level. In Figure 3-1, a layout of Si-based optical signal routing system is schematically shown.
Figure 3-1  Si-based optical interconnect scheme: Si:Er system for light emitters, Si/SiO$_2$ for waveguides/switches/couplers, and SiGe for detectors.

![Diagram of Si-based optical interconnect scheme](image)

**Figure 3-2** Er$^{3+}$ ion luminescence spectra shows a main peak at $\lambda=1.537\mu$m with several satellite peaks which depend on the ligands.
3.2 Background

3.2.1 Er\(^{3+}\): Origin of 1.54\(\mu\)m Light Emission

The Er\(^{3+}\) ion emits light at the wavelength 1.54\(\mu\)m as the Er\(^{3+}\) ion makes a transition from the first excited state of 4f shell, \(^4I_{13/2}\), to the ground, \(^4I_{13/2}\) [10]. This transition of Er\(^{3+}\) that is not allowed in Er metal becomes possible in semiconductor matrix. It is generally accepted that ligand crystal field around Er is attributed to facilitating 1.54\(\mu\)m light emission. Unlike III-V semiconductor light emitters, Si:Er system employs an intra-center transition whose luminescence line width remains small and independent of temperature. The typical luminescence spectrum for Er\(^{3+}\) ion is shown in Figure 3-2.

3.2.2 Er Solubility and Diffusivity in Silicon

As a heavy and large rare earth element, Er solubility and diffusivity in Si is relatively small. Slow diffusion and strong Er oxidation tendency prevents Er from thermal diffusion into Si. In order to avoid Er oxidation, Er implantation is commonly used to incorporate Er into the system. Based on implantation of Er, Er solubility was found to be around mid 1\(\times\)10\(^{16}\)cm\(^{-3}\) at high temperature [16]. Er diffusivity ranges widely as shown in Figure 3-3. Er diffusivity derived from implanted Er shows higher diffusivity [16].

3.3 Electrical Study of Si:ErO

3.3.1 Motivation

The Si:Er system has received much attention since the sharp luminescence at a wavelength 1.54 \(\mu\)m from the 4f shell of the Si:Er\(^{3+}\) ion opens the possibility for Si-based optoelectronic applications. We have fabricated LED’s that operate at room temperature based on the Si:Er system [11], and we have
Figure 3- 3 Temperature dependence of the Er diffusion coefficient in Si (from Sobolev, 1995[12]). The plotted data are from Ageev et. al. [13], Nazyrov et. al. [14], Sobolev [15] and Ren [16].
Figure 3-4 PL intensity of Er/O implanted Si is plotted against temperature. Two regimes are observed [17].

Figure 3-5 PL intensity and decay time are plotted with respect to temperature for Er/O-implanted Si [17].
demonstrated that the LED can be used as part of an optical voice link [18]. Er is usually co-implanted with other impurities such as O, C, and F due to their luminescence enhancement effect [19,20]. The Si:Er system suffers from a decrease in luminescence intensity with increasing temperature in two distinct regimes as shown in Figure 3-4. Regime I shows a weak temperature dependence at temperatures from 4K to 100K while regime II reveals an activation energy of 160meV above 100K [21]. The temperature dependence of luminescence intensity is quite similar to that of excited Si:Er$^{3+}$ lifetime as demonstrated in Figure 3-5 [17]. We have concluded that a non-radiative energy back transfer mechanism from excited Si:Er$^{3+}$ ions is responsible for thermal quenching of the luminescence at high temperatures. Our observations revealed that the impurity Auger effect accounts for the moderate decrease in the luminescence intensity in the first regime while phonon-mediated processes are responsible for the second regime. It is very important to understand the electronic states introduced by Er/O co-implantation because the excitation and relaxation processes of the Si:Er system are mediated by recombination centers in the silicon band gap. In this chapter, we address the questions of the electrical activity of Er/O defect states, their structure, and energy levels and we present a model for the excitation and relaxation processes of Si:Er$^{3+}$ by correlating the electrical properties with the luminescence behavior of the Si:ErO system.

3.3.2 Experimental

3.3.2.1 CV, Spreading Resistance Profiling, Hall Effect, and DLTS

CZ Si wafers were singly implanted with Er at 320KeV, 400KeV, and 4.5MeV. Subsequently, oxygen implantation was implemented at beam energies that match the O peak with the Er peak. The projected range for peak concentrations of 5x10$^{17}$cm$^{-3}$ Er and 2x10$^{18}$cm$^{-3}$ O are located at 0.1μm, 0.14μm, and 1.5μm from the surface, respectively, according to Secondary Ion Mass Spectroscopy (SIMS) profiles. The samples were subsequently annealed in a conventional quartz tube furnace at temperatures between 600°C and 1000°C
Figure 3- 6 Free carrier concentration vs depth is plotted by CV on Er/O shallow implant CZ Si. The carrier increase in the Er/O implanted region indicates ErO is a donor.

Figure 3- 7 Donor distributions were determined from spreading resistance profiling in Cz Si that was Er/O- implanted and annealed at different temperatures. The Er SIMS profile is also shown as a reference.
under Ar ambient for 30 minutes. Spreading Resistance Profiling (SRP) measurements were made on p-type CZ Si (0.5-2Ωcm) that was Er/O implanted and annealed. CV measurements were carried out on n-type CZ Si (0.03-0.05Ωcm) after Au$_3$Pd Schottky contacts were evaporated on n-type CZ Si samples. Hall effect measurements were performed on implantation-induced n-type layer in a p-type substrate.

3.3.3 Results and Discussion

3.3.3.1 Donor Activity

CV profile of shallow Er/O-implant n-type CZ silicon shows a free carrier increase in the region where implant Er/O is distributed in Figure 3-6. The 900°C annealed sample indicates donors outdiffused to the surface. The Spreading Resistance Profile (SRP) in Figure 3-7 reveal that a pn junction has formed in the Er/O-implanted p-type CZ silicon, confirming that donors are created by Er/O implantation. Three notable features are observed. First, the SRP for the 600°C annealed sample reflects the compensation by implantation damage, and the sample annealed at 800°C shows donor activation with the highest donor concentration. Second, even though one takes into account the observation that the Er SIMS artificially extends the profile to greater depths, the donor profile does not overlap with the Er profile for all the anneals, suggesting that Er by itself cannot explain donor behavior. Third, the donor profile shrinks and moves toward the surface with higher annealing temperatures, again implying outdiffusion of donors.

3.3.3.2 ErO$_4$: Donor

To identify the defect structure of the donor associated with Er/O doping, several control experiments were carried out. The results are shown in Figure 3-8. Three 4.5MeV Er-implanted CZ Si samples were annealed at 900°C after
Figure 3-8 Distribution of donors in Cz Si by O implantation only, Er implantation only and Er/O coimplantation. Er/O coimplant results in donor increase.

Figure 3-9 Donor concentration increases linearly with [Er] in p-type CZ silicon that has been implanted with Er and annealed at 900°C for 30 minutes [23].
implantation with O only, Er only, and Er/O, respectively. As expected, oxygen by itself
does not generate donors since thermal donors by oxygen are annealed out at temperature
higher than 700°C [22]. Based on these observations, the excess donors are associated
with the Er implant and an oxygen implant increases the excess donors. Therefore, both
Er and O implants are needed to create donors. However, Er/O implants generate
abundant point defects such as Si interstitials and vacancies. These defects can also create
donors. In order to determine a defect structure for donors, one has to consider all other
possibilities and there are several possible defect structures for donors: (1) Er, (2) Er/Ox,
(3) Er/ points defects, (4) Er/O/point defects and (5) O/point defects. In Figure 3-9 [23],
the donor concentration linearly increases with increasing [Er] and becomes saturated at
5x10^{16} cm^{-3} for [Er]> 1x10^{17} cm^{-3} and drops beyond 10^{18} Er cm^{-3}, which is the threshold
for Er precipitation at high temperatures. After 900°C anneal, all the defects caused by
Ge implant that has the similar damage effect as Er implant were annealed out [23].
Therefore, the linear relationship between excess donors and Er shows that Er is directly
involved in the defect structure and the rapid drop in N_{donor} with Er precipitates clearly
confirms that excess donors are Er-related. Increased N_{donor} by an oxygen implant, thus,
makes ErOx a likely defect structure. The possibility that defects participate into the
donor structure can not be ruled.

To distinguish the donor structure among the rest of possible structures, we
analyze the effective diffusivity of donors based on annealing temperature dependence of
the donor profiles. Assuming complete activation of the donors at 800°C, one can make
a rough estimate of the effective diffusivity of donors by considering the profile at 800°C
as reference and taking D_{donor} (T) = (\Delta x)^2/t. D_{donor}, T, \Delta x and t are donor diffusivity,
annealing temperature, position difference between the reference and the profile at the
given temperature, and for the annealing time, respectively. However, a more complete
analysis should consider the continued activation of donors at higher temperatures and
evaluation of the complete donor profile. We
Figure 3- 10 Donor profiles of 4.5MeV Er co-implanted with O from spreading resistance measurements at different annealing temperatures.

<table>
<thead>
<tr>
<th></th>
<th>Donor</th>
<th>Er-trap limited oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{oxy}}$(cm$^2$/s)</td>
<td>---</td>
<td>0.13exp(-2.5eV/KT)</td>
</tr>
<tr>
<td>K</td>
<td>---</td>
<td>$10^{22}$exp(-1.5eV/KT)</td>
</tr>
<tr>
<td>[Er] (cm$^{-3}$)</td>
<td>---</td>
<td>5x10$^{17}$</td>
</tr>
<tr>
<td>$E_m$(eV)</td>
<td>4.1</td>
<td>4.0</td>
</tr>
<tr>
<td>$D(900^\circ\text{C})$(cm$^2$/s)</td>
<td>1.4x10$^{-14}$</td>
<td>1.1x10$^{-14}$</td>
</tr>
</tbody>
</table>

Table 3- 1 Calculation and comparison of donor diffusivity and Er-trap limited oxygen diffusivity. Both of the consistent values support that excess donors are Er-O complex.
analyzed annealing temperature dependent donor profiles from the 4.5MeV Er implanted samples, which maintain the shape of shape of donor profile at high temperatures as shown in Figure 3-10. The $\Delta x$ was measured from donor peak to peak. $D_{\text{donor}}$ at 900°C and 1000°C are $1.4 \times 10^{-14}$ cm$^2$/s, and $3.5 \times 10^{-13}$ cm$^2$/s, respectively.

The activation energy for donor diffusion is calculated from the data to be 4.1eV. To examine whether the donor outdiffusion is related to Er-trap limited motion of oxygen, we model the effective diffusivity of donors with the Er-trap limited diffusivity of oxygen, which can be expressed by the following equation [24]

$$D_{\text{oxy,Er}} = D_{\text{oxy}} \frac{K}{[\text{Er}]} \quad \text{Eq.3-1}$$

where $D_{\text{oxy,Er}}$, $D_{\text{oxy}}$, and $K$ are the Er-trap limited diffusivity of oxygen, oxygen diffusivity, and Er/O dissociation constant. The binding energy of the Er-O complex, $E_b$, can be reasonably approximated from the Coulombic interaction between the Er$^{3+}$ ion and oxygen in silicon. Assuming a singly charged oxygen and an interatomic distance of 2.5Å, one can estimate $E_b$ to be 1.5eV[25]. The calculation and comparison of $D_{\text{oxy,Er}}$ and $D_{\text{donor}}$ is presented in Table 3-1. The diffusivity values at 900°C and the migration energy values for Er trap-limited motion of the oxygen and donor are quite similar, indicating that the excess donors are related to Er-O complex. Furthermore, the activation energy for Er trap-limited motion of oxygen is close to the activation energy of the PL vs $1/T$ in the high temperature regime as shown in Figure 3-11. At temperatures greater than 1000°C, it is known that oxygen ligands become dissociated and outdiffuse. This is another confirmation that the outdiffusion of the donors is correlated to the Er trap-limited motion of oxygen. ErO$_x$ is related to optically active Er center as PL intensity falls together with ErO dissociation. Therefore, we conclude that [Si:ErO$_x$]$^{0+/+}$is the defect complex responsible for donors associated with Er/O doping.
Figure 3-11 PL intensity from Er/O implanted Cz Si as a function of the inverse of annealing temperature.

Figure 3-12 PL intensity is plotted with respect to integrated donors introduced by Er/O coimplantation.
We examined the correlation of PL intensity with total donors in the sample and found that the PL intensity is linearly proportional to the number of donors as shown in Figure 3-12. The linear relationship implies that the donor is directly related to the optically active center that involves Si:Er$^{3+}$. Therefore, Er$^{3+}$O$_x$ is likely to be a defect center that is associated with Er$^{3+}$ excitation.

3.3.3.3 ErO$_x$ Energy Level

We have measured carrier concentration by Hall effect to determine the donor energy position in the gap. Carrier concentration vs. 1/T from Hall effect measurements reveals two activated ionization levels of 40meV and 160meV as shown in Figure 3-13. For highly conductive n-type Si (N$_d$=3x10$^{17}$cm$^{-3}$) implanted with Er/O, most of excess donors in the Er implanted region still remain active at T=40K, indicating the majority of excess donors form shallow levels. DLTS on the sample could not detect the level at 0.16 eV below the conduction band. The high electric field of 1.2x10$^5$ V/cm in the junction region is attributed to the difficulties for DLTS measurement. The high field can enhance the emission rate from the trap by two orders of magnitude by Poole Frenkel effect [26]. This enhancement makes the rate window on the order of

![Figure 3-13 Carrier concentration by Hall effect measurement of n-region that was inverted by Er/O doping in p-type CZ Si is plotted with respect to 1/T.](image)

48
Figure 3-14 Capacitance vs T is plotted for the Er/O implanted sample that was annealed at 800°C for 30 minutes. The constant capacitance around 120K is due to a trap at $E_c - 0.15eV$.

10µs, which is shorter than the response time of Boontoon capacitance meter. Thus, it is possible that the deep level found by Hall effect measurement could not detected by DLTS since capacitance vs T on the same sample shown in Figure 3-14 indicated that there is a deep level around $E_c - 0.15eV$. Moreover, there has been a report that DLTS detected the level at $E_c - 0.15eV$ in Er-implanted n-type Si with its medium conductivity [27]. But the concentration of the reported level was only a small fraction of total donors, which can be activated up to 100% of the Er concentration [28]. ErO$_x$ forms a deep level roughly at $E_c - 0.16$ eV $\pm$ 0.01 eV and a shallow level.

3.3.3.4 Role of ErO$_x$ with $E_T = E_c - 0.160meV$ in Er Excitation

With two levels associated with ErO$_x$, it is likely that the excitation of Si:Er$^{3+}$ ions results from trap-mediated recombination which is much more efficient than band-to-band recombination [29]. The donors at 0.16 eV below the conduction band edge are most likely the gateway to Si:Er$^{3+}$ excitation. Because of indirect band gap of Si, the injected electrons and holes tend to form free excitons and bound excitons at [Si:ErO$_x$]$^{0/+}$centers. Both types of excitons can give their energy completely to electrons in the conduction band.
Figure 3-15 A model for the excitation and relaxation of Er$^{3+}$ in Si implanted with Er/O is schematically shown.

or phonons in the Si matrix. The e-h pairs bound to [Si:ErO$_x$]$^{0+/+}$centers can excite Si:Er$^{3+}$ ions if the excess energy difference between the resonant excitation energy of Si:Er$^{3+}$ and the recombination energy of a bound exciton can be transferred to nearby electrons or local phonons. Although free excitons can excite Si:Er$^{3+}$ ions, bound exciton recombination through the [Si:ErO$_x$]$^{0+/+}$ centers in the band gap will make the Er excitation process much more efficient. More [Si:ErO$_x$]$^{0+/+}$ centers will result in more excited Si:Er$^{3+}$, thus higher luminescence intensity. The excitation and relaxation processes of Si:Er$^{3+}$ ions are schematically illustrated in Figure 3-15. The de-excitation of Si:Er$^{3+}$ can occur either radiatively or nonradiatively. Figure 3-5 shows that the excited Si:Er$^{3+}$ lifetime decreases together with the luminescence intensity as temperature rises. To explain this observation, there must be internal nonradiative de-excitation paths that are faster than the radiative path for excited Si:Er$^{3+}$. If an inefficient excitation process was responsible for the luminescence quenching, the correlation between the luminescence intensity and the luminescence decay time would not exist. Consequently, nonradiative energy back transfer is responsible.
Figure 3- 16 Bias dependent EL intensity decay time for an Er/O LED. The luminescence decay time decreases with increasing current[21].

Figure 3- 17 Junction photocurrent dependence on temperature for an Er/O LED. The inset shows wavelength dependent junction photocurrent [21].
for the luminescence thermal quenching. Below 100K, the impurity Auger effect is dominant so that the back transfer energy flows to electrons as shown in Figure 3-15. Figure 3-16 shows the dependence of the excited state decay time on the LED bias state following injection. Under reverse bias, no carriers are present and the Si:Er$^{3+}$ decay is longest. As carrier density increases by zero and forward bias, the excited state decays become shorter and shorter. This Auger loss at low temperatures has a weak temperature dependence. Above 100K, the luminescence intensity decreases with increasing temperature with an activation energy of approximately 160meV. Junction photocurrent spectroscopy (JPCS) measurements were made on Er/O implanted LED. In the JPCS measurements, an Er/O implanted LED was illuminated with light of wavelengths around 1.54um and the corresponding photocurrent was measured. The JPCS signal reaches a maximum value at the excitation wavelength of 1.54um. Thus, excitation of the core 4f levels can result in valence electron excitation. The maximum junction photocurrent increases with temperature with the activation energy of 170meV as shown in Figure 3-17. Based on these observations, it was proposed that a phonon-mediated nonradiative energy back transfer mechanism in which a charge transfer occurs through the [Si:ErO$_x$]$^{0/+}$ center [21]. This nonradiative back transfer mechanism takes place in a series of two steps: unfilling the [Si:ErO$_x$]$^{0/+}$ centers by phonons and filling the [Si:ErO$_x$]$^{0/+}$ centers with electrons. Phonons provide the energy of about 150meV to the 0.8eV relaxation energy for Si:Er$^{3+}$ to excite an electron from the valence band to the empty [Si:ErO$_x$]$^{0/+}$ level at $E_c$-0.16eV. The electrons excited to the [Si:ErO$_x$]$^{0/+}$ level are further excited to the conduction band to yield a photocurrent. Phonon energies of about 160meV are required to fill and empty the [Si:ErO$_x$]$^{0/+}$ level. Further investigation is necessary to determine which step is rate limiting. Nonetheless, it is clear that this energy back transfer is only possible with the aid of phonons and that it becomes more efficient with increasing temperature.

3.3.4 Summary

CV and SRP measurements show that Er/O implantation introduces donor levels in the band gap. Donors outdiffuse at high annealing temperatures and the donor outdiffusion correlates to the Er-trap limited oxygen motion. [Si:ErO$_x$]$^{0/+}$ is proposed to
be the defect complex responsible for the donor activity. Hall effect and temperature dependent capacitance measurements show two energy levels are associated with ErOₓ at 40meV and 160meV below conduction band. The linear correlation between PL intensity and integrated donors further supports that the [Si:ErOₓ]⁰⁺ centers are the gateway to Si:Er³⁺ excitation. This model is consistent with the proposed phonon-mediated energy back transfer mechanism.
Chapter 4
Fe Gettering in p-type CZ Silicon for Photovoltaic Application

4.1 Introduction

Transition metals have adverse effects on electronic devices based on Si. Very often, they can be incorporated into the system easily and unintentionally since they are prevalent, fast, and fairly soluble in silicon at the processing temperatures. Most of processing equipment is made out of metals and it is inevitable to have a certain degree of wafer exposure to metal component during high temperature processing steps. Once incorporated into Si, they mostly form a deep level due to their electronic structure quite dissimilar to that of Si. These deep levels act as a recombination center, reducing minority carrier lifetime on which efficiency of pn junction devices such as solar cells or light emitter depends. It's quite important to understand the kinetics of metal in Si to remove them out of active device area. In this chapter, Fe, a notorious lifetime killer,
whose electronic properties have been well understood, will be investigated in its
gettering kinetics in p-type Si after its electronic and physical properties are reviewed.

4.2 Background

4.2.1 Electronic and Physical Properties of Fe

It is well known that Fe sits on the tetrahedral interstitial void in Si
lattice[30,31,32] and Fe\textsubscript{i} forms a donor level at E\textsubscript{v} + 0.38 eV [33,34,35]. In p-type Si, Fe\textsubscript{i}
tends to become positively charged with the Fermi level below its donor level and
Coulombically attracted to group III dopants which are usually negatively charged,
resulting in a Fe-acceptor pair [36,37]. Practically, all of Fe\textsubscript{i} pairs up with boron in p-
type Si, creating another donor level 0.1eV above the valence band edge. This FeB level
will be used as a fingerprint for dissolved Fe concentration in p-type Si. As an interstitial
impurity, Fe diffuses fairly fast. With its migration energy 0.68eV, Fe diffuses at a rate
of 4x10\textsuperscript{-6} cm\textsuperscript{2} sec\textsuperscript{-1} at 1100°C [38], which is equivalent of only 15 minutes for Fe to
contaminate through the thickness of wafer. Fe is readily dissolved up to 1x10\textsuperscript{14}cm\textsuperscript{-3} at
1000°C [39]. Its typical contamination level of mid 10\textsuperscript{12}cm\textsuperscript{-3} already degrades the device
minority carrier lifetime to tens of μs according to the following equation.

\[ \sigma v N_T = \frac{1}{\tau} \]  

Eq. 4-1

where \( \sigma, v, N_T, \) and \( \tau \) are capture cross section, free carrier thermal velocity, trap
concentration, and minority carrier life, respectively. The temperature dependent
diffusivity and solubility of Fe are plotted in Figure 4-1 and 4-2, respectively.

4.2.2 Transition Metal Gettering in Silicon

Gettering is keeping unwanted contaminants out cf the active device region.
Gettering mechanisms can be categorized into two: segregation gettering and relaxation
gettering.
Figure 4-1 Fe diffusivity vs T [39].

Figure 4-2 Fe Solubility vs T [39].
Segregation gettering takes advantage of the difference in solubility of contaminants in two regions adjacent to each other. The ratio of solubility of contaminant in an adjacent gettering layer with respect to Si is segregation coefficient, k.

\[ k = \frac{C_{s,Fe}^{Al}}{C_{s,Fe}^{Si}} \]  

Eq. 4-2

where \( C_{s,Fe}^{Al} \), \( C_{s,Fe}^{Si} \) are Fe solid solubility in Al and Si, respectively. Segregation coefficient is the most important parameter together with the diffusivity of contaminant in segregation gettering. Contaminants migrate out of Si region to the energetically favorable gettering region as shown in Figure 4-3. In principle, segregation gettering can be implemented by creating an adjacent region, which has the capability of holding high dissolved contaminants. The layers that employ segregation gettering include a phosphorous doped layer, backside damage, Al contact, and heavily B-doped p++ layer. Since these layers are located outside of the active device region, these are called external gettering sites.

![Figure 4-3 Gettering Mechanisms: segregation gettering and relaxation gettering.](image)

Relaxation gettering is driven by supersaturation of contaminants in an active region. Instead of contaminants diffusing out of an active device region and trapped outside, contaminants heterogeneously precipitate around gettering sites that are situated within the Si wafer but distant from the active device region. Relaxation gettering sites
provide heterogeneous nucleation sites so that contaminants prefer to precipitate around the relaxation gettering sites than other active region. Density and size of heterogeneous nucleation sites are important parameters and solubility limit of contaminants is the gettering limit. The relaxation gettering sites are called internal gettering sites.

4.3 Gettering Study of Fe in p-type silicon with Al Contact

4.3.1 Motivation

Al is the standard backside contact for Si solar cells due to three advantages. First, it makes a good Ohmic contact to p⁺ base material. Second, it alloys with Si at high processing temperatures to form a p⁺ layer, which generates backside field (BSF) effect to reduce minority carrier recombination velocity at the contact interface [40,41]. Third, it getters transition metals including Fe [42,43]. Even trace amounts of most transition metals, which are all too easily incorporated during solar cell processing, can degrade cell performance significantly by introducing carrier recombination centers into the silicon energy gap. The high diffusivity and moderate solubility of transition metals in silicon make silicon susceptible to transition metal contamination. The natural abundance of Fe makes it one of the most troublesome contaminants. It reduces the solar cell efficiency by pairing with boron in the p-type silicon base since the resultant FeB donor is an efficient recombination center. Gettering becomes quite important as contamination prevention is difficult and expensive. Fe segregation in molten Al with respect to Si is expected to be high, but it has never been measured in a physical system, and its effectiveness in the presence of other competing getters is unknown. Therefore, it is very important to understand the complexity of gettering reactions. Fe gettering by Al depends on the initial conditions. Al effectively getters Fe at contamination levels less than or equal to the Fe solubility in Si at the annealing temperature, in the absence of other Fe trapping mechanisms such as microdefects, dislocations or grain boundaries [44,45,46]. For Fe₁ at equilibrium with FeSi₂ precipitates in the bulk, which is most likely to be the case for solar grade Si as modeled by Tan [47], [Fe₁] is predicted to
remain at the solubility level until complete dissolution of Fe precipitates while Fe outdiffuses to the Si/Al interface. Our experimental study addresses what kinetic mechanisms dominate Fe gettering with Al contacts when initial [Fe_i] is above its solubility. We used an idealized system of evaporated Al and p-type CZ Si.

4.3.2 Experimental

P-type CZ silicon with N_B=1.3x10^{15} cm^{-3} was used for the following experiments. Clean p-type CZ samples were treated with organic cleaning: ultrasonic in trichloroethane, acetone, and methanol for 10 minutes, respectively. Then, the samples were etched for 2 to 3 minutes in a solution of HNO_3 and HF mixed in 20:1. Immediately before the samples were mounted into an evaporation chamber, they received 5% dilute HF dip. Fe was evaporatively deposited on both sides of the samples under the vacuum level of 7.5x10^{-7} mbar. The samples with Fe on both sides were put into quartz tubes, which were evacuated and sealed. The sample in the quartz ampoule was hung in a vertical furnace, annealed at 1000°C for 2 hours to introduce Fe at the solubility limit and finally quenched into oil to preserve the dissolved [Fe]. Samples with Al-contacts have been prepared. To prepare samples with Al contacts, Fe-deposited samples were stripped of Fe and iron silicide in a solution of HNO_3 and HF mixed in 10:1, and then, 0.4 μm thick Al was evaporated on both sides of stripped samples after the stripped samples received the cleaning steps listed above. The samples with Al contacts were annealed in ampoules under vacuum at 620°C, 700°C, and 800°C for various time lengths and quenched into oil. Al Schottky contacts were deposited on the samples after they were mechanically and/or chemically polished down to the center. For chemical etching, different ratios of HF:H_2NO_3:CH_3COOH were tried. The mixed solution of HF:H_2NO_3=1:3 was used for initial fast etching, and that of HF:H_2NO_3:CH_3CHOOH=1:5:12 was for final precise etching. The chemically polished surface was examined under an optical microscope for etch pit density. Biorad DL8000, Digitized Deep Level Transient Fourier Transform Spectroscopy, was used to measure [FeB]. The typical DLTS spectrum for FeB is shown in Figure 4-4. This concentration is equal to [Fe_i] since Fe_i pairs with boron within 24 hours at room temperature after the heat treatment. Minority carrier diffusion length, a key parameter for solar cell
performance, was measured by the EBIC technique. In Figure 4-5, all the experimental steps are schematically described.

\[ \text{DLTS Temperature Scan} \]

\[ \delta C (\text{pF}) \]

\[ T (\text{K}) \]

Fe after Indiffusion
In p-type CZ Si at 1000°C for 2 hrs

Figure 4-4 FeB forms a level at 0.1eV above valence band. A typical FeB DLTS spectra is shown for p type CZ Si that was indiffused with Fe at 1000°C for 2 hours.
annealed 2hrs at 1000°C & quenched in oil

Fe

Si:B:Fe

etching

Si:B:Fe

0.4 μm Al evap.
anneal & quench

Si:B:Fe

Al

Fe

Si:B:Fe

Si:B

Fe contact
anneal & quench

anneal & quench

polish down to the center &
deposit Al Schottky contact

Si:B:Fe

Si:B:Fe

Si:B

DLTS: [FeB]

EBIC: diffusion length

control sample

Figure 4-5 Sample Preparation for DLTS and EBIC.
4.3.3 Results and Discussion

The initial [FeB] in Fe-contaminated samples before annealing was $2.7 \times 10^{14} \text{cm}^{-3}$ by DLTS measurement. [FeB] vs. time in Figure 4-5 summarizes the time dependence of [Fe$_i$] with Si/Al interface at 800°C, 700°C, and 620°C. Three regimes were observed for the annealing time periods used: 1) initial fast decay, 2) slow decay with varying rates, 3) asymptotic decay. In the first regime, the decay rate was the fastest of all annealing time periods and became faster with increasing temperature. In the second regime, the decay rate decreased gradually with annealing time. This transition regime from the first to the third regime was shortened with increasing temperature. In the third regime, [FeB] asymptotically approached a concentration

![Graph showing the concentration of FeB over time for different temperatures.](image)

*Figure 4-6 [FeB] in Fe-contaminated p-type CZ Si with Al contacts is plotted against annealing time at 800°C, 700°C, & 620°C.*
that was higher with increasing temperature. At 800°C and 700°C, the residual [FeB] approached the solubility limit of Fe at the heat treatment temperature. The [FeB] at the surface after 60 minutes annealing at 700°C as shown in Figure 4-7 supports that [FeB] at the center would approach the [Fe₄] solubility limit. At 620°C, even though accurate evaluation requires longer annealing, the residual [FeB] seems to be reaching the solubility limit of Fe. In order to understand the mechanism controlling [Fe₄] in the initial fast decay regime, the exponential decay time constant, \( \tau \), was estimated from the initial slope of \( \log([\text{FeB}]) \) vs. annealing time at the heat treatment temperatures. The activation energy, \( E_a \) from a plot of \( \tau \) vs. \( 1/T \) was 0.65eV. Since the migration energy for Fe₄ is 0.68eV[39], an Fe diffusion-limited process is most likely responsible for the initial fast decay.
4.3.4 Model for Gettering Mechanisms

4.3.4.1 Si/Al contacts Gettering vs. Oxygen precipitates Gettering

Two Fe diffusion-limited mechanisms available are possible precipitate formation and outdiffusion, as schematically shown in Figure 4-8. The dissolved Fe can heterogeneously nucleate precipitates at preferred sites. Fast heterogeneous nucleation makes the process diffusion-limited. The process time constant is approximated to follow Ham’s law[48] as shown in Eq. 4-3, if heterogeneous nucleation by Fe is faster than Fe diffusion to Si/Al interface.

\[
\tau_{ppt} = \frac{1}{4\pi (nr)_{ppt} D_{Fe}}
\]

Eq.4- 3

where \(n_{ppt}, r_{ppt},\) and \(D_{Fe}\) are density and size of precipitates, and Fe diffusivity, respectively. Fick’s law controls the kinetics of outdiffusion. Considering only outdiffusion as the Fe gettering mechanism and the symmetric boundary conditions in Figure 4-7, one can analytically express [FeB] as an infinite series of the product of a Fourier cosine term and a time dependent exponential term. One needs the exact [Fe] at
the Si/Al interface, [Fe$_i$]$_l$, to express [FeB] accurately. However, [Fe$_i$]$_l$ decreases with time, approaching the solubility as shown in Figure 4-6. Consequently, setting [Fe] I to be the solubility of Fe, [Fe] sol, for short time, maximizes the rate estimated for Fe outdiffusion. We could reasonably assume [Fe$_i$]$_l$ was [Fe$_i$]$_{sol}$ for the purpose of comparing initial Fe gettering kinetics from the experimental data with that from Fick’s law. Except for the very beginning of Fe gettering kinetics, one can describe [FeB] quite reasonably with only the first cosine term until [FeB] at the center of sample gradually approaches the value at the boundary.

Figure 4-9 Both of [FeB]'s, experimental and Fick’s law-governed, are plotted against annealing time at 800°C, 700°C, & 620°C.

Then, the time constant can be approximated as shown in Eq. 4-4.
\[ \tau_d = \left[ D_{Fe} \left( \frac{2\pi}{t_{Si}} \right)^2 \right]^{-1} = \frac{\kappa \cdot (t_{Si}/2)^2}{D_{Fe}} \]  \hspace{1cm} \text{Eq. 4-4}

where \( \kappa \approx 0.41 \) and \( t_{Si} \) is sample thickness. The Fe gettering kinetics data were compared with the plots of \([FeB]\) vs. annealing time by numerical analysis of Fick’s law in Figure 4-8, which showed that the decay slope of experimental data was greater than that of the Fick’s law estimates for all three temperatures. This comparison indicates that initial fast decay is not due to outdiffusion. Both time constants for precipitates and outdiffusion are summarized in Table 4-1.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Experiment</th>
<th>Outdiffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>620°C</td>
<td>( \tau_{\text{meas}} &lt; 10 \text{ mins} )</td>
<td>( \tau_d = 22 \text{ mins} )</td>
</tr>
<tr>
<td>700°C</td>
<td>( \tau_{\text{meas}} &lt; 2.4 \text{ mins} )</td>
<td>( \tau_d = 10 \text{ mins} )</td>
</tr>
<tr>
<td>800°C</td>
<td>( \tau_{\text{meas}} &lt; 2.5 \text{ mins} )</td>
<td>( \tau_d = 5 \text{ mins} )</td>
</tr>
</tbody>
</table>

\textit{Table 4-1 Time constant Comparison: precipitate vs. outdiffusion.}

After Al gettering failed to explain Fe gettering kinetics, we model our kinetics by assuming that Fe precipitates heterogeneously around oxygen precipitate nuclei. The initial density and size of precipitates are estimated using fitted \( \tau_{\text{meas}} \) from \( \log \tau_{\text{meas}} \) vs. \( 1/T \), according to Ham’s law and the mass conservation in the spherical \( \text{FeSi}_2 \) precipitate formation around oxygen precipitate nuclei.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( (nr)^{\text{ppt}} \text{(cm}^2) )</th>
<th>( r^{\text{ppt}} \text{(nm)} )</th>
<th>( n^{\text{ppt}} \text{(cm}^{-3}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>620°C</td>
<td>870</td>
<td>13</td>
<td>6.6x10^8</td>
</tr>
<tr>
<td>700°C</td>
<td>910</td>
<td>16</td>
<td>5.7x10^8</td>
</tr>
<tr>
<td>800°C</td>
<td>790</td>
<td>17</td>
<td>4.6x10^8</td>
</tr>
</tbody>
</table>

\textit{Table 4-2 Initial precipitate size \& density at 620°C, 700°C, \& 800°C.}

The mass conservation equates the decrease in \([FeB]\) with the increase in \([\text{FeSi}_2]\). \( n_{\text{ppt}} \) and \( r_{\text{ppt}} \) were estimated and summarized in Table 4-2. The consistency of the values, \( n_{\text{ppt}} \) and \( r_{\text{ppt}} \), for three temperatures implies that the samples were identical and \( n_{\text{ppt}} \) was about
5x10^8 cm^-3. This value falls within the same orders of magnitude as the density of oxygen precipitate nuclei in single crystalline Cz Si. Therefore, heterogeneous Fe precipitate formation around oxygen nuclei reasonably accounts for the initial fast decay. The process is also consistent with the fact that [FeB] approaches the solubility limit of Fe at the heat treatment temperature for short term anneal. We also measured the precipitate density by etch pit counts. Initial count of etch pits was measured on the sample that was etched in a solution of HF:H_2NO_3:CH_3COOH=1:5:12 to the half thickness for DLTS measurement. The goal of sample etching for

![Figure 4-10](image)

**Figure 4-10** Under an optical microscope, etch pits were shown consistently for most of the samples that underwent the heat treatment of two hour anneal at 1000°C and subsequent anneal at 620°C, 700°C, or 800°C.

Schottky contact was to control the etching thickness with a slow etch rate and to get a smooth surface. However, it was consistently hard to get a macroscopically smooth surface after etching sample to its center for DLTS Schottky contact. After the heat treatments of two hour anneal at 1000°C and a subsequent anneal at 620°C, 800°C, and 900°C, most of samples had quite a number of precipitates nuclei. The reference sample that was annealed at 700°C for two hours in addition to two hour anneal at 1000°C showed etch pit density of 7x10^7 cm^-3 and the corresponding precipitate size is shown in
table 4-2. This estimate was made with an assumption that etch depth for etch pits is the height of the pyramidal etch pit. Little fast etching is likely to remove bulk and precipitates indiscriminately, resulting in underestimation of the etch pit density. The estimate can be improved with slower and selective etching. If etch pit counts are linearly proportional to the etched thickness, etch pit density can be calculated as etch pit counts divided by the etched thickness. The discrepancy between precipitate density calculation and etch pit density can also result from the assumption of a spherical shape of Fe precipitates. In fact, the punch out dislocation that can be as large as 1μm due to oxygen precipitates can be the internal gettering sites [49], decreasing the density of internal gettering sites. Nonetheless, this etch pit counts support that oxygen precipitates are present with a density close to what accounts for the short time Fe gettering.

### 4.3.5 Fe and Minority Carrier Diffusion Length

It is of great interest how much the minority carrier diffusion length is improved by Fe gettering with Al contacts. One can analytically correlate [FeB] with the minority carrier diffusion length in Eq. 4-5 assuming [FeB] is the dominant recombination center.

\[
[FeB] \approx \frac{D_e}{\sigma_e <v_e>} L_e^{-2} \tag{4-5}
\]

where \( \sigma_e, v_e, D_e, \) and \( L_e \) are capture cross-section, electron velocity, electron diffusivity, and diffusion length (μm).

\[\text{Figure 4-11 } \log[FeB] \text{ vs. } L_e. \text{ The dotted line is a plot for only FeB recombination centers with } \sigma_e = 5 \times 10^{15} \text{cm}^2 \text{ and } N_{\text{boron}} = 1.3 \times 10^{15} \text{cm}^{-3}.\]
and minority carrier diffusion length, respectively. Log \(L_c\) corresponds with log[FeB] with a negative two slope in the high [FeB] regime of Figure 4-11. It deviates from the correspondence in the low [FeB] regime with \(L_c\) being lower than that given by Eq. 4-6. \(L_c\) improvement with the reduction of [FeB] in the high [FeB] regime shows that FeB is the dominant carrier recombination center and that precipitated Fe is not so electrically active in the recombination process. In the low [FeB] regime, other recombination centers can be dominant or at least comparable with FeB since \(L_c\) is either independent of [FeB] or improves at a slower rate with decrease in [FeB].

4.3.6 Gettering Mechanism

Fe can begettered by two main mechanisms: precipitation and outdiffusion. These two mechanisms formulate a linear partial differential equation for Fe gettering by both internal gettering sites (oxygen precipitate nuclei) and Al/Si interface.

\[
\frac{\partial c}{\partial t} = D_{e0} \frac{\partial^2 c}{\partial x^2} + 4\pi r N_{pp}D_{e0}(c_{Fe,sol} - c(t)) \quad \text{Eq.4- 6}
\]

where \(c_{Fe,sol}\) is Fe solubility in Si. Depending on Fe contamination level, either mechanism can be dominant. To predict internal gettering by precipitates, \(N_{pp}, r_{pp}, D_{Fe}\), and \(c_{Fe,sol}\) in Si are necessary. Fe precipitates formation and dissolution processes are imbedded in the equation.

![Figure 4-12 Schematic of Fe gettering kinetics in p-type Cz Si with Al contacts: this study shows that the first regime is dominated by Fe precipitate formation around oxygen](image)

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Precipitate nuclei and the second regime is governed by both Fe precipitate formation and interface-limited outdiffusion.

Al/Si interface at a heat treatment above the Al-Si eutectic temperature has two gettering effects by forming a solid/liquid interface and doping the subsurface layer with Al to be $p^{++}$ type [50,51,52]. Liquid phase Al has practically no limit for holding Fe as long as its thickness is large enough to accommodate all Fe contamination. The $p^{++}$ layer formed by alloying Si with Al can not only increase gettering efficiency with higher Fe solubility in $p^{++}$ layer but also decrease the efficiency by deterring Fe diffusion. FeAl pairing is attributed to $p^{++}$ gettering. To quantify the Fe gettering by Al contact, more accurate $k_{Al/Si}$ is required and Fe solubility and diffusivity in a $p^{++}$ region need adjustment based on the solubility and stability of FeAl with temperature.

### 4.3.7 Summary

Fe gettering kinetics in intentionally Fe-contaminated p-type CZ single crystalline Si with Al contacts has been studied. When supersaturated, Fe precipitates heterogeneously at oxygen precipitate sites in the bulk during the initial stage of annealing. Once Fe concentration is close to its solubility, Fe precipitation kinetics slows down, and Fe outdiffuses to the Si/Al interface. The gettering kinetics is dependent on $N_{ppt}$, $r_{ppt}$, and the Fe gettering kinetics limit is set by the solubility of Fe. Mid $10^8$ cm$^{-3}$ oxide precipitates with a size of 15nm describes the diffusion-limited precipitates at the internal gettering sites according to our etch analysis. However, a defect such as a punch-out dislocation can also be the internal gettering sites according to the etch pit density analysis. The etch pit count favors these sites with a radius of 130nm. FeB is a dominant recombination centers in the high [FeB] regime and other recombination centers become significant in the low [FeB] regime. Finally, [Fe$_i$]-dependent Fe gettering kinetics with Al contacts are schematically summarized in Figure 4-12.
Chapter 5
Molybdenum in Silicon

5.1 Motivation

Mo unintentionally can contaminate a semiconductor system in different ways. The usual contamination level of $10^{12}$ Mo cm$^{-3}$ is found in the epitaxially grown layers[53,54]. The stainless gas transfer line in the epitaxial growth chamber is generally attributed to the source of Mo contamination [55]. HCl etching of the susceptor is also correlated with Mo contamination levels. Even during Si CMOS processing, Mo can be introduced to chips when BF$_2$ is ion implanted [56]. The similar charge to mass ratio of $^{98}$Mo$^{2+}$ ion to that of $^{11}$B$^{19}$F$_2^+$ makes the mass analyzer in an ion implanter unable to distinguish $^{11}$B$^{19}$F$_2^+$ from $^{98}$Mo$^{2+}$ ion [57]. When $^{11}$B$^{19}$F$_2^+$ is implanted, $^{98}$Mo$^{2+}$ ion is also impinged onto the target with twice as much energy. According to SIMS analyses of Mo profiles in wafers implanted with BF$_2$, Mo doses up to $2\times10^{12}$cm$^{-2}$ was detected.

It's important to study the effects of Mo on semiconductor devices. There is a report that Mo contamination during Si MOS processing would not affect device performance seriously[58]. However, another report suggested that Mo concentration on the level of
$10^{12}\text{cm}^{-3}$ starts to degrade the solar cell efficiency [59]. Nonetheless, the properties of Mo in silicon is relatively unknown and only limited data are available. Part of reasons is that oxidation tendency of Mo prevents thermal diffusion of Mo into silicon system. In this study, Mo was ion-implanted into Si. This chapter addresses the electrical and physical properties of implanted Mo in Si.

### 5.2 Mo properties in Silicon

Mo forms a hole trap in Si energy gap at 0.3eV above Si valence band (H0.3eV) [59,60,61]. Its capture cross section $\sigma_p$ and $\sigma_n$ are $5.5\times10^{-16}$ cm$^2$ and $1.6\times10^{-14}$ cm$^2$ respectively [59]. Solubility of Mo is on the level of $10^{12}$cm$^{-2}$ for both thermally diffused Mo [62] and melt-incorporated Mo [59]. All the Mo incorporated during Si melt growth becomes electrically active [59]. On the other hand, implanted Mo shows only part of Mo is electrically active. The maximum implanted Mo concentration measured by DLTS was $5\times10^{14}$cm$^{-3}$[57].

### 5.3 Experimental

Mo is ion implanted into p-type FZ with a hole concentration $2\times10^{15}$cm$^{-3}$ at an implant energy of 50KeV and 4.5MeV with doses of $1.3\times10^{10}$ cm$^{-2}$ and $1.3\times10^{11}$cm$^{-2}$. Some samples have been implanted with additional Si at an energy of 8MeV with various doses of $1\times10^{13}$, $1\times10^{14}$, and $1\times10^{15}$ cm$^{-2}$ to create separate vacancy-rich region and Si self interstitial-rich region. Implanted samples were annealed in a furnace at 750°C, 850°C, and 950°C for 30 minutes under Ar ambient. To observe initial diffusion behavior of Mo, some received rapid thermal anneal at 750°C for 1 s, 5 s, 10 s, 40 s, 160 s, and 640 s. Ti Schottky contacts were thermally evaporated. DLTS temperature scans and isothermal profiling scans were carried out to identify Mo signal and obtain Mo distribution.

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5.4 Results and Discussion

The typical DLTS signal for Mo is shown in Figure 5-1. Electrically active Mo concentration is calculated using Eq. 2-22.

![DLTS Temperature Scan](image)

Figure 5-1 DLTS spectra shows Mo peak occurs around 168K. The spectra was taken with \( V_r = 5 \text{V}, \ V_p = 0 \text{V}, \ T_w = 35 \text{ms}, \) and \( t_p = 10 \mu\text{m}. \)

Figure 5-2 shows that the evolution of implanted Mo concentration measured by DLTS after \( 1.3 \times 10^{10} \text{Mo cm}^{-2} \) was implanted at an energy of 4.5MeV. The profile is anomalous in a sense that Mo profile after annealing becomes asymmetric. Most implanted species maintain as-implanted profile in Gaussian shape but the peak of the Gaussian distribution falls with its width being either shrunk or expanded as the sample annealing proceeds. It is puzzling but interesting to note that Mo concentration steadily increases with the annealing time at a depth, \( x < R_p. \) This phenomenon becomes reasonable if the implant defects are taken into account. The Mo implant creates a vacancy-rich region at \( x < R_p \) and Si self interstitial-rich region at \( x \geq R_p. \) Once Mo is implanted, Mo can stay at a random position, either substitutionally or interstitially. Beyond its solubility, Mo may
even form clusters. However, once the annealing starts, Mo is likely to end up at a thermodynamically stable lattice site. If one assumes a substitutional Mo is the electrically active specie, which is also soluble and stable [59], the increase in Mo concentration in the vacancy-rich can be explained by Mo activation by its hopping to the vacancy region. The reason the Mo concentration at $x \geq R_p$ does not increase so fast as that in the region at $x < R_p$ can be that the excess Si interstitials prevent substitutional Mo from being formed by kicking-out substitutional Mo atoms.

![Graph showing Mo concentration vs depth](image)

**Figure 5-2 DLTS depth profiles of Mo, $H(0.30eV)$, were measured after the p-type FZ Si received 4.5MeV, 1.3x10^6 Mo/cm^2 ion-implantation and heat treatments at 830°C, for different time durations. Steady increase in Mo concentration is observed in a region $x < R_p$ and slight fluctuation of Mo concentration in a region $x > R_p$.**

To help understand the observation, TRIM simulation was employed. For 4.5 MeV Mo implant into Si, Mo has a Gaussian distribution with $R_p=1.86\mu m$ and $\Delta R_p=0.21\mu m$ according to a TRIM simulation. The as-implanted profile is shown in Figure 5-3. Mo peak concentration is approximately $2.5x10^{14}\text{cm}^{-3}$ and indeed roughly only 60% of implanted Mo becomes electrically active, confirming that more than one form of Mo exist in the Si. To understand Mo behaviors further, we examine the Mo diffusion at
different temperatures with a hypothesis that reasonably explained the annealing behavior of 4.5 MeV implanted Mo in p-type FZ Si.

![Graph showing Mo distribution](image)

**Figure 5-3** TRIM simulation of Mo distribution after 4.5 MeV Si at 1.3x10^10 cm^-2. Mo implantation creates a vacancy-rich region and a Si interstitial-rich region. Mo acts differently in these two regions.

### 5.4.1 Hypothesis

Based on the above observations, a model similar to that for Au [63, 64] and Pt [65, 66] is applied to Mo system since more substitutional Au would end up in a vacancy region and Si interstitials would kick out substitutional Au, keeping Au concentration from rising in the interstitial-rich region. We made several hypotheses such that a soluble and electrically active Mo sits on a substitutional lattice site and an interstitial Mo is not electrically active. Moreover, substitutional Mo is thermodynamically more stable and a predominant specie below its solubility. Beyond its solubility, Mo would cluster or precipitate. As with most cases, diffusivity of interterstitial Mo is faster than substitutional Mo. The following reaction equations summarize the hypotheses.

\[ V + Mo_i \rightarrow Mo_i \]

*Eq. 5-1*
\[
I + Mo_s \rightarrow Mo_i \quad Eq.5-2
\]

\[
C_{Mo_s} \gg C_{Mo_i} \quad Eq.5-3
\]

\[
D_{Mo_s} \ll D_{Mo_i} \quad Eq.5-4
\]

where \( I, \ V, \ C_x, \) and \( D_x \) denote Si interstitial, vacancy, concentration and diffusivity, respectively.

### 5.4.2 Mo Diffusion and Solubility

Mo diffusion distribution has been measured by DLTS for the samples that have been implanted with Mo only and annealed at 750°C, 850°C, and 950°C for 30 minutes. The profiles are shown in Figure 5-4. Mo profiles for 850°C and 950°C annealed samples can be fitted with a Gaussian profile. Source depletion is observed for 950°C annealed sample. The extrapolated surface concentration for 850°C annealed sample is \( 2.0 \times 10^{14} \text{ cm}^{-3} \), which can be the lower limit for the solubility limit for implanted Mo at 850°C. Due to the implant defects, the solubility seems to be increased quite higher than mid \( 10^{12} \text{ cm}^{-3} \), that for the thermally diffused Mo[59,62]. The concave Mo profile for 750°C annealed sample suggests that Mo possibly diffused by kick out mechanism. But it cannot be fitted with either Gaussian or a profile based on kick out mechanism because Mo concentration close to the surface is greater than what kick out mechanism would generate. It leads to the idea that both kick out and normal diffusion occurred for the implanted Mo. The combination of short time diffusion by kick out and subsequent normal diffusion reasonably fits the 750°C Mo diffusion profile. In order to verify the initial kick out mechanism, RTA was performed on Mo only implanted samples for 1 s, 5 s, 10 s, 40 s, 160 s, and 640 s at 750°C. Mo profiles after RTA are shown in Figure 5-5. Strikingly but expectedly, Mo diffused to 1μm depth even after 1 s, which is roughly how long it takes for most Si interstitials that are available to kick out substitutional Mo to diffuse out to the surface. In order to eliminate the possibility of channeling, DLTS on
Figure 5- 4 Mo diffusion profile is shown as a function of annealing temperature. Mo is implanted at 50keV with a dose of $1.3 \times 10^{13}$ cm$^{-2}$ and subsequently annealed for 30 minutes.

Figure 5- 5 Mo profiles are shown after RTA at 750°C for 1 s, 5 s, and 10 s. The samples were implanted with $1.3 \times 10^{11}$ Mo cm$^{-2}$ at 50keV.

as-implanted sample has been performed. No Mo level was detected. It is conclusive that short time fast Mo diffusion occurred during the heat treatments. Once implant-.
induced excess Si interstitials are consumed, normal diffusion also contributes to the overall Mo diffusion.

5.4.3 Model for Mo Diffusion

Based on the hypothesis and observations, we propose a model for Mo diffusion. Mo has the capability of diffusing by substitutionally and interstitially. Since Mo prefers to sit on substitutional sites, interstitial Mo diffuses by kick out mechanism. In the presence of excess Si interstitials, kick out mechanism can dominate Mo diffusion until excess Si interstitials are consumed by diffusing to the surface or replacing substitutional Mo as shown in Eq. 5-2. Once the concentration of Si interstitials that kick out substitutional Mo falls back to its equilibrium level, interstitial Mo concentration decreases to its thermodynamic equilibrium level. Normal diffusion by substitutional Mo becomes significant. Diffusion by kick out is not expected to be significant to overall Mo diffusion unless \( D_{Mo}C_{Mo} \geq \frac{D_{Mo}}{C_{Mo}} \). In the following section, we employ DOPDEES (Dial an Operator Partial Differential Equation Evaluator and Solver) which is developed at BU to examine the proposed model by making comparison of the experimental data with simulated data based on the model.

5.4.3.1 Mo Diffusion Simulation with DOPDEES

In order to simulate Mo diffusion, interstitial-substitutional exchange mechanism in addition to normal substitutional diffusion by Mo is considered. The code for Mo diffusion imbeds the following set of reactions: kick-out, and dissociative (Frank-Turnbull), silicon interstitial (I) and vacancy (V) recombination, and Fickian diffusion for Mo, Mo, I, and V. The detailed derivation of the subsequent equations are treated in Appendix A.

\[
\frac{\partial C_{Mo}}{\partial t} = \nabla \cdot D_{Mo} \nabla C_{Mo} - k_e^{K0} \left[ C_I C_{Mo} - K_{eq}^{K0-1} C_{Mo} \right] + k_e^{D5} \left[ C_V C_{Mo} - K_{eq}^{D5-1} C_{Mo} \right]
\]

Eq. 5-5
Figure 5-6 Point defect distributions by TRIM simulation are shown due to Mo implant at 50keV with a dose of $1.3 \times 10^{11} \text{cm}^{-2}$. A vacancy-rich region forms from surface to the projected range while a Si interstitial-rich region ranges from the projected range to slightly deeper than Mo profile.

Figure 5-7 The simulated results shows good fits with the experimental Mo profiles after RTA at 750°C for 40 s, 160 s, and 640 s. This simulation by DOPDEES is based on both diffusion by $Mo_i$ and $Mo_{i'}$.

\[
\frac{\partial C_{Mo}}{\partial t} = \nabla \cdot D_{Mo} \nabla C_{Mo} + k^{KO} \left[ C_i C_{Mo} - K^{-1} C_{Mo} \right] - k^{DS} \left[ C_i C_{Mo} - K^{-1} C_{Mo} \right]
\]  
Eq. 5-6
\[
\frac{\partial C_l}{\partial t} = \nabla \cdot D_l \nabla C_l - k_{KO}^{\text{C}_l \text{C}_{\text{Mo}_0}} - K_{eq}^{\text{C}_l \text{C}_{\text{Mo}_0}} \text{C}_{\text{Mo}_0} - k_{IV}^{\text{C}_l \text{C}_{\text{V}} - \text{C}_{\text{I}} \text{C}_{\text{V}}^*} 
\]  
Eq. 5-7

\[
\frac{\partial C_v}{\partial t} = \nabla \cdot D_v \nabla C_v - k_{DS}^{\text{C}_v \text{C}_{\text{Mo}_0}} - K_{eq}^{\text{C}_v \text{C}_{\text{Mo}_0}} \text{C}_{\text{Mo}_0} - k_{IV}^{\text{C}_v \text{C}_{\text{I}} - \text{C}_{\text{I}} \text{C}_{\text{V}}^*} 
\]  
Eq. 5-8

\[
D_{\text{eff}} = D_{\text{Mo}_0} \frac{C_{\text{Mo}_0}}{C_{\text{Mo}_0}} + D_{\text{Mo}_0} 
\]  
Eq. 5-9

where KO, DS, and IV denote that kick-out, dissociative, and I-V recombination. 

\[K_{eq}^{Y}, k_{+}^{Z}, D_x, \text{ and } C_x\] are equilibrium reaction constant, forward reaction rate constant, diffusivity, and concentration. Superscript Y and Z represent the reactions such as KO, DS, and IV while subscript x indicates defect species: Mo, Mo, V, and I respectively. The forward reaction rate constants are defined assuming the reactions are diffusion-limited processes.

\[
k_{KO} = 4\pi r_{KO} D_{\text{Mo}_0} 
\]  
Eq. 5-10

\[
k_{DS} = 4\pi r_{DS} (D_v + D_{\text{Mo}_0}) 
\]  
Eq. 5-11

\[
k_{IV} = 4\pi r_{IV} (D_I + D_V) 
\]  
Eq. 5-12

For simplicity, all the capture radii for kick-out, dissociative, and IV are set to a nearest neighbor distance, 2.35Å [67]. Surface boundaries act as an infinite source or sink for point defects. C_l and C_v are expected to go to the equilibrium values at the boundaries. Initial concentrations of I and V are given by TRIM simulation of point defect distributions induced by Mo implant as shown in Figure 5-6. One moment cluster model is also incorporated so that C_{Mo} beyond its solubility is set to its solubility. We used DOPDEES to solve the above set of nonlinear differential equations. The detailed code is attached to the appendix B. We used D_{eff} and C_{Mo,0}/C_{Mo,0} as the fitting parameters.

The choice of parameters is consistent with the proposed hypothesis. The parameters used to fit the 750°C annealed Mo profile are summarized table 5-1. The substitutional diffusivity and Mo solubility that were used are close to the published values for
implanted Mo[58]. Although the fit parameters by no means represent the actual values, they roughly estimate the physical variables. In Figure 5-7, simulation data are plotted on top of experimental data. Then, experimental Mo concentration for 60 s anneal at a depth around 0.8μm which deviated the concave profile by a sole kick-out mechanism is reasonably fitted with the simulation data. Mo profiles at two other anneal times seem to

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$D_{Mo}$ (cm$^2$/s)</th>
<th>$D_{Mo}$ (cm$^2$/s)</th>
<th>$C_{Mo} / C_{Mo_s}$</th>
<th>$C_{sol,Mo}$(cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>9.27x10$^{-13}$</td>
<td>1.86x10$^{-7}$</td>
<td>9x10$^{-6}$</td>
<td>2.1x10$^{14}$</td>
</tr>
</tbody>
</table>

Table 5-1 Parameters for DOPDEES simulation of Mo diffusion at 750°C.

Figure 5-8 The time evolution of $C_p$, $C_{Mo_s}$ and $C_{Mo}$ is plotted. $C_i$ diminishes quickly by outdiffusion to the surface, recombination with vacancy and Mo, kick-out. As a result, $C_{Mo_s}$ surges for short time, and Mo, diffuses fast, and decays, to form Mo$_s$ in the bulk.

follow the trend within experimental errors. In Figure 5-8, the time evolution of $C_i$, $C_{Mo_s}$ and $C_{Mo}$ is plotted, revealing the short time Mo diffusion kinetics. Si interstitial concentration decreases rapidly from the initial 10$^{17}$ cm$^{-3}$ level shown in Figure 5-6 to the 10$^{12}$ cm$^{-3}$ level after 1 s. Interstitials can be consumed in three ways: outdiffusion to the surface, recombination with vacancy and Mo$_s$ kick-out. Mo$_s$ kick-out by interstitials
generates excess Mo\textsubscript{i}, which diffused to the bulk 10µm deep only after 1 s as shown in Figure 5-8. Then, thermodynamically unstable excess Mo\textsubscript{i} ends up at substitutional lattice sites. The two orders of magnitude decrease in \( C_{\text{Mo}} \) without further diffusion to the bulk between 1 s and 40 s clearly shows this reaction. This is only way that more than \( 10^{12} \) cm\(^{-3} \) Mo\textsubscript{s} can be present at 1µm only after 1 s considering Mo is a slow diffuser. The time evolution of defects clearly illustrates that excess interstitial Mo created by Si interstitials dominates the short time diffusion and decays quickly as they become more stable substitutional Mo. The short time effective diffusion by interstitial Mo is enhanced

![Graph](image)

**Figure 5-9** Additional 8MeV Si at doses of \( 1 \times 10^{14} \text{ cm}^2 \) and \( 1 \times 10^{15} \text{ cm}^2 \) were implanted to p-type FZ Si which had been implanted with 50keV \( 1 \times 10^{11} \text{ Mo cm}^2 \). Samples were annealed for 30 minutes at 750°C and 850°C, respectively. Free carriers and Mo concentrations vs depth were plotted and increase in Mo concentration was observed where a vacancy-rich region was located.
Figure 5- 10 Diffusivity of Mo that is obtained from simulation fit of experimental Mo profiles is plotted with the diffusivity values available: Tobin[68], Hamaguchi [61] Dplot by Janet [58].

by a factor of greater than 500 over that by substitutional Mo. Once the short time TED is finished, normal substitutional diffusion also contributes to the overall Mo diffusion while the contribution by interstitial Mo diffusion decays to its equilibrium level. The Mo concentration shallower than 1μm cannot be fitted without substitutional diffusion in addition to the kick-out diffusion. The simulation verifies that Mo diffuses predominantly by the kick out mechanism for short time due to excess Si interstitials generated by Mo implant. Once Si interstitials are consumed, Mo interstitial diffusion becomes less dominant and substitutional normal diffusion also becomes significant.

5.4.3.2 Mo diffusion in vacancy-rich region

The presence of fast diffusing interstitial Mo is demonstrated in another independent experiment. In addition to 50keV Mo implant, 1x10^{14} Si cm^{-2} and 1x10^{15} Si cm^{-2} were implanted at an energy of 8 MeV to create a vacancy-rich region that is shallower than the projected range and a Si-interstitial rich region that ranges from the projected range to the deeper region. Then the samples were annealed for 30 minutes at 750°C and 850°C respectively. Free carrier and Mo profiles are shown in Figure 5-9.
Compared with the sample with Mo only implant and 750°C anneal, more Mo indiffused to the bulk and Mo accumulated where vacancy-rich region was located in both 850°C and 750°C annealed samples. For 850°C annealed sample, Mo filled up the vacancies around 3.25μm depth and diffused to the deeper region. For 750°C annealed sample, it seems that fast interstitial Mo was captured by the vacancies and piled up around 3.3μm, resulting in more substitutional Mo. Indeed, the total flux of interstitial Mo that would pass through the imaginary plane that is set slightly less than 2 μm in Figure 5-9 for the annealing time must be equal to the amount of Mo that has accumulated in the vacancy-rich region if the proposed hypothesis is correct. The calculation involves the following equation. The assumption is that the

\[
\int_0^{t_{\text{eq}}(x)} f_{\text{Mo}}(x) dt = \int_0^{t_{\text{eq}}(x)} D_{\text{Mo}}(x) \frac{\partial C_{\text{Mo}}(x)}{\partial x} dt = \int_{s_1}^{s_2} C_{\text{Mo}}(x) dx \quad \text{Eq. 5-13}
\]

vacancy-rich region is treated as a sink for interstitial Mo and only interstitial Mo is fast enough to reach the vacancy rich-region in 750°C annealed sample. The values that were used for fitting the experimental data were employed in this calculation: Then, 1.72x10^9 Mo cm^-2 have diffused through the plane at 2.0 μm. This is the lower limit for the amount of Mo that would pass through the plane since \( C_{\text{Mo}} \) at the surface is greater than the assumed equilibrium value of 1.8x10^9 m^-3 for short time. The amount of Mo in the accumulated region from 2.0μm to 3.5 μm is 1.0x10^9 cm^-2. In principle, the amount of Mo that pass through the plane should be greater than what has accumulated since some pass through the vacancy-rich region after it filled up most of vacancy traps. Nonetheless, both numbers are on the same of order of magnitude and supports that the idea that interstitial Mo diffuses fast and becomes substitutional Mo after recombining with vacancies.

5.5 Summary

The Mo diffusion kinetics and thermodynamics were studied using Mo implanted FZ Si. The Mo tendency to oxidize prevents Mo from diffusing from the surface into bulk. Implanted Mo interacts differently with vacancies and interstitials. This
observation led to the hypothesis that Mo can occupy substitutional and interstitial sites. The hypothesis also includes that substitutional Mo is electrically active and stable and unstable interstitial Mo diffuses faster. Short time TED of Mo at 750°C can be explained by the interstitial-substitutional exchange mechanism. Si interstitials generated by the Mo implant kick out substitutional Mo from the lattice sites, creating more interstitial Mo, which, in turn, diffuses quickly until it is trapped by a vacancy to become substitutional Mo. This idea was confirmed by DOPDEES simulation. Indeed, the effective interstitial diffusivity, \( D_{Mo_i} \left( \frac{C_{Mo_i}}{C_{Mo}} \right) \) becomes more than 500 times greater than that of \( D_{Mo} \) for a short time and decays soon to its equilibrium level. Once most of Si interstitials are consumed, diffusion by the kick out mechanism slows down and normal diffusion dominates the overall diffusion profile. At high temperatures, normal diffusion dominates and the extrapolation of Mo distribution to the surface for annealed sample allows us to estimate the lower limit of solubility of implanted Mo to be 2\( \times \)10^{14} cm\(^{-3} \) at 850°C. Further understanding in Mo diffusion at high temperature requires more information on the Mo profile near the end of its tail. This analysis can separate the normal diffusion mechanism from interstitial-substitutional exchange mechanism. The more comprehensive model requires additional analysis of temperature dependence of \( \frac{C_{Mo_i}}{C_{Mo}} \), and \( D_{Mo_i} \).
Chapter 6
Low K Dielectric Materials: Fluorosilicate Glass (FSG)

6.1 Introduction

In the current ULSI era, more than $10^7$ transistors are built on a single chip [1] and the device size shrinks below 0.25μm. The interconnection wire width in integrated circuit becomes narrower and narrower along with the spacing between the wires, resulting in increase both resistance and capacitance in integrated circuit. Higher resistance and capacitance requires more power to run the chip as well as delay its clock distribution speed since ever-decreasing device size makes the interconnection a bottleneck in clock distribution in spite of shorter intrinsic gate delay. As an imminent but marginal approach, a drive for low resistance and capacitance has been carried out. Copper has replaced aluminum wire on some of chips. Substitutes for SiO$_2$ were suggested including air, polymers and air-polymer combinations such as aerogels, xerogels, and foams in addition to fluorosilicate glass (FSG) [69], which has been already deployed on a Pentium chip [70]. This chapter investigates fluorinated SiO$_2$ grown by high
Figure 6-1 Polarizability has three components: dipolar, ionic, and electronic. Depending on the frequency, the magnitude of polarizability varies.

Figure 6-2 Schematic diagram illustrates how a crystal structure for SiO₂ changes when F is incorporated. Two F⁺ ions replace one O²⁻ ion, modifying the Si-O network.
plasma density chemical vapor deposition (HPD CVD). Electrical measurements of \( K \) and a model to correlate \( K \) and \( n \) with fluorine content will be presented.

### 6.2 Theory

Dielectric constant can be viewed as a measure of material response to external electric field to reduce the presence of electric field in the material. It is a function of frequency, density, composition, and short-range order among other parameters. A frequency dependent dielectric constant in Figure 6-1 shows dielectric constant consists of three components: dipolar, ionic, and electronic. Dielectric constant both at the electrical measurement (1MHz) and the current chip clock distribution frequency (<1GHz) falls in the first regime where the electric field frequency is slow enough for all of components to respond to it. However, dielectric constant at the optical frequency lies in the third regime where the electric field frequency is so fast that only electronic component can respond to the field. For this reason, \( K \) at the current clock distribution frequency has all of three components while \( n \), refractive index, has only electronic component.

Fluorine as a halogen element has the highest electronegativity on the periodic table and fluorine ion has its electronic polarizability that is more than three times less than that of oxygen [71]. According to Fourier Transform Infrared Spectroscopy analysis, as fluorine is incorporated into SiO\(_2\) system, a peak for Si-F stretching mode increases while the integrated IR strength for Si-O bond decreases [72]. It forms a single bond with a Si atom, replacing an oxygen ion with two fluorine ions as shown in Figure 6-2. This indicates that F-Si bond is stronger than Si-O bond. Fluorine modifies Si-O network, creating free volume, and changing the short-range order in the dielectric system. Electronic polarizability of \( F^+ \), stronger bond strength of Si-F, and free volume formation by F incorporation all contribute to the lowering of dielectric constant for fluorinated SiO\(_2\). The presence of F also has another K lowering effect by reducing the contribution to IR dielectric constant from Si-O bond by decreasing IR effective charge of Si-O bond [73]. However, the stability of fluorinated SiO\(_2\) becomes an important issue when fluorine content is greater than 10\%. The gap created by fluorine addition makes the dielectric material vulnerable to H\(_2\)O attack with high F content [74]. The dielectric
constant starts to increase with H$_2$O incorporation. Since careful FTIR study showed that no Si with two F ions has been observed up to 12 atomic F % [75], fluorinated SiO$_2$ can be viewed as a pseudo-alloy of SiO$_2$ and Si$_2$O$_3$F$_2$ as shown in Figure 6-2 up to 12 atomic F %, which falls within the range of practical interest. As F content increases, the composition of Si$_2$O$_3$F$_2$ increases along the tie line between SiO$_2$ and Si$_2$O$_3$F$_2$ in the ternary phase diagram of Si, O, and F. In order to calculate the dielectric constant of the heterogeneous structure, we consider two phases of SiO$_2$ and Si$_2$O$_3$F$_2$ to apply them to Clausius Mossotti relation. Assuming those two phases are randomly distributed on the cubic lattice, the overall dielectric constant takes the following form in terms of polarizability and density of each phase.

\[
\frac{K_T - 1}{K_T + 2} = \frac{4\pi}{3} \left( n_{SiO}^{\alpha} \alpha_{SiO} + n_{SiOF}^{\alpha} \alpha_{SiOF} \right)
\]

Eq. 6-1

where $K_T$, $n_x$, and $\alpha_x$ are the overall dielectric constant, density and polarizability. The overall dielectric constant can be also expressed in terms of dielectric constant of each phase [76].

\[
\frac{K_T - 1}{K_T + 2} = f_{SiO} \frac{K_{SiO} - 1}{K_{SiO} + 2} + f_{SiOF} \frac{K_{SiOF} - 1}{K_{SiOF} + 2}
\]

Eq. 6-2

where $K_x$ and $f_x$ are the dielectric constant and the fraction of each phase. The dielectric constant at optical frequency can also be obtained using $K=n^2$.

### 6.3 Experimental

About 400nm FSG was deposited on p-type (100) Si ($\rho=1\sim30\Omega\text{cm}$) by high density plasma chemical vapor deposition (HDP-CVD) that uses SiF$_4$/SiH$_4$/O$_2$/Ar chemistry. The fluorine has been incorporated between 5 atomic % to 7.5 atomic %.
Figure 6- 3 C-V on different types of dielectric materials were plotted. B-USG: SiO₂ on p type Si, USG: USG on 150Å thermal oxide/p-type Si, B-FSG9: 6.7 F % FSG on p-type Si, FSG9: 6.7 F % FSG on 150 Å/p-type Si.

Figure 6- 4 A typical free carrier concentration vs depletion depth is plotted. The flat region indicates the carrier concentration of bulk Si from 1.4 μm to 1.8 μm.

For comparison, SiO₂ film (USG) and some FSG were deposited on both bare and thermally grown oxide. FSG fluorine content was measured by a Nicolet Fourier Transform Infrared Spectroscopy (FT-IR). The ratio of the peak for Si-F stretching mode
that occurs at 937 cm\(^{-1}\) to the peak for Si-O stretching mode at 1095 cm\(^{-1}\) was measured by FTIR. The ratio was correlated with the corresponding fluorine concentration measured by secondary ion spectroscopy (SIMS). An ellipsometer measured the FSG thickness and refractive index at 633nm. To measure dielectric constant, Al metal contact was thermally evaporated under high vacuum to make a metal-insulator-semiconductor (MIS) structure. Boontoon capacitance meter measured the capacitance of the MIS sample at 1MHz frequency. The constant capacitance value in the accumulation regime of a capacitance-voltage (CV) plot was used to calculate the dielectric constant of FSG. K measurements on MIS were averaged over nine points across an 8" wafer.

6.4 Results and Discussion

Most of the MIS structure shows a leakage current of about hundred pA over wide range of voltages. The CV profile for USG films is typical, and the capacitance in the accumulation regime for FSG film is smaller than that for USG as expected due to the fluorine incorporation. The flat band voltage for USG on bare p-type Si, B-USG, is slightly shifted -4V from that for USG on the 150A thermally grown oxide,USG, indicating that the interface quality of thermally grown oxide on Si is better than that of the oxide film HDP-CVD-deposited. Flat band voltage for both of USG films is lower than that for FSG films while both of FSG films have practically the same flat band voltage. Fluorine incorporation is attributed to the greater flat band voltage, creating more positive charges near the FSG/p-type Si interface. The same flat band voltage for both FSG films indicates that fluorine must have reached the interface for FSG with thermal oxide. Moreover, a dip in CV profile that was observed for some FSG films suggests that F can degrade the interface. Some FSG films show unstable capacitance values that change with the measurement time.
Figure 6-1 Measured $K$ is plotted with respect to $F$ atomic %. Instability of capacitance, thus $K$ value was observed even around 6 F%. The stable and lowest $K$ was around 3.5. A model predicts $K$ value can be as low as 2.98 at 12 F%.

Figure 6-2 Refractive index vs atomic F % is plotted. Beyond 12%, instability is exerted. A model predicts $n$ can be as low as 1.395 while actual lowest $n$ measured is 1.423.
The plot of free carriers vs depletion depth shows a flat concentration region in the
depletion regime as expected from constant doping profile. The dielectric constant was
calculated with the following equation

\[ C_{\text{FSG}} = \frac{AK_{\text{FSG}}\epsilon_0}{t_{\text{FSG}}} \quad \text{Eq. 6-3} \]

where A, K and t are cross sectional area of MIS structure, dielectric constant, and
thickness of dielectric material. thickness of dielectric material. Measured K values are
plotted with respect to F % together with the calculated K using the Eq. 6-2 on Figure 6-5.
Although the reduction in K for FSG is clearly observed, the measured data scatter
around 6 F %, implying the actual instability of these films grown by HDP-CVD. The
lowest K is 3.53 at 6.5 F %. Measured refractive index values are also plotted against F
% with the calculated n. The n data show a decreasing trend with a better stability since
it only involves electronic polarizability at an optical measurement frequency. The
lowest refractive index is 1.423 at 6.6 F %.

6.5 Model for F content dependent n and K

The modeling is based on the fact that fluorinated SiO₂ can be treated as a pseudo
alloy of \((\text{SiO}_2)_{1-x}(\text{Si}_2\text{O}_3\text{F}_2)_{x}\) up to 12 F %, beyond which Si-F₂ bond makes it unstable.
Once F content is determined, the composition of \(\text{Si}_2\text{O}_3\text{F}_2\) can be determined. With the
known K and n values for SiO₂, those for \(\text{Si}_2\text{O}_3\text{F}_2\) can be obtained by the measured data
using Eq. 6-3. For refractive index, the relationship between n and K, \(n^2=K\), is used. The
K and n for FSG are plotted against F % in Figure 6-5,6. Our model predicts K can be as
low as 2.96 at 12 F % and the lowest n can be 1.395 at 12 F %. However, more accurate
estimate requires consideration of free volume created by F ions that modify the Si-O
network in the dielectric and H₂O incorporation by FSG. The free volume lowers the
dielectric constant and makes the dielectric susceptible to H₂O absorption, which
increases the dielectric constant.
6.6 Summary

We investigated fluorosilicate glass that was grown by HDP-CVD for low K dielectric material to reduce RC time delay. F incorporation degrades the FSG/p-type Si interface to a certain degree by shifting the flat band voltage of MIS structure -4V. Some FSG shows a dip, which indicates an interfacial qualities can be degraded by F ions. Based on pseudo alloy model and Clausius-Mossotti relation, K and n for FSG can be analytically expressed in terms of F % up to 12 F%. The model predicts the lowest K and n are 2.96 and 1.395 at 12 F%, respectively. However, the actual lowest K and n were 3.53 and 1.423 around 6.5 F%, respectively. K and n of FSG strongly depend on the processing technique since other IR active entities can be incorporated depending on the processes. The replacement of Si-O bonds with Si-F at high F% creates free volume in FSG. These free volumes and subsequent H₂O attack are attributed to the stability and K limit for HDP-CVD grown FSG.
Chapter 7  Summary and Future Work

7.1 Si:ErOₓ

Er forms its complexes with O as it is incorporated into Si. ErOₓ generates excess donors the levels of which were measured to be 40meV and 160meV below the conduction band in Si. The linear relationship between integrated Er photoluminescence intensity and integrated donor dose suggests that the donors are associated with optically active Er³⁺. The Er³⁺ excitation and energy back transfer processes are believed to occur via the charge transfer through the deep level. However, the concentration of the deep level is quite less than that of the shallow level. It is possible that an ensemble of ErOₓ exist that give a rise to the deep level as well as the shallow level. The relative stability of ErOₓ complexes determines the ratio of concentration of those levels. Within the same model, the possibility of a double donor by one of ErOₓ complex cannot be ruled out at this moment. Further study is required to determine which ErOₓ complex forms the deep level at Eₓ-160meV and then the thermodynamic stability of the ErOₓ with respect to other Er-O complexes will determine the optimal light intensity from Er³⁺.
7.2 Fe Gettering in p-type CZ Si

Internal gettering of Fe by oxygen precipitates in p-type CZ Si was investigated. Under high supersaturation of Fe, the precipitation mechanism is dominant until most of Fe precipitates. Subsequently, the outdiffusion of Fe to Al contact also contributes to the overall gettering of Fe. Precipitate density, size and Fe diffusivity determine the internal gettering kinetics and Fe solubility at an annealing temperature sets the gettering limit. A density of $5 \times 10^8 \text{cm}^{-3}$ with its size 15nm was estimated with an assumption of a spherical oxygen precipitate. However, the etch pit density analysis showed the density could be $7 \times 10^7 \text{cm}^{-3}$ with the size 130nm. The precise identification of the precipitate requires a further study on the microstructure of the precipitate. Moreover, a complete model of Fe gettering with Al contact needs a quantitative value of segregation coefficient of Fe in Al with respect to Si. The additional gettering effects by the Al-doped p$^{++}$ layer on Fe gettering also need to be investigated, including Fe segregation coefficient and diffusivity in Al-doped p$^{++}$ layer. Finally, with the appropriate boundary conditions at Al/Si, Fe gettering can be thoroughly modeled based on these mechanisms.

7.3 Molybdenum in Si

Mo diffusion mechanism and solubility were studied. Implanted Mo showed a higher solubility than thermally diffused Mo with the aid of implant damages. A low limit for Mo solubility at 850°C is measured to be around $2 \times 10^{14} \text{cm}^{-3}$. In the presence of implant-generated Si interstitials, Mo diffused rapidly by kick-out mechanism for short time at 750°C until Si interstitials were consumed to an equilibrium level. Then, substitutional Mo normal diffusion contributed to the overall diffusion. At higher temperatures, Mo shows a normal diffusion profile. DOPDEES simulation at 750°C was consistent with the experimental Mo profile, confirming our hypotheses: substitutional Mo is a thermodynamically stable, electrically active, and slower diffuser while interstitial Mo is a fast diffuser that exists at a lower concentration in Si. The diffusion mechanism at higher temperatures requires careful investigation since solubility and diffusivity of interstitial Mo changes with temperature and the near surface diffusion profile is not enough to distinguish Mo diffusion mechanisms. Mo diffusion over a larger
region is necessary to identify the diffusion mechanism. Moreover, in order to prove Mo sits on a substitutional site, a more sophisticated technique such as electron paramagnetic resonance (EPR) or optically detected magnetic resonance (ODMR) study will shed a light into the microstructure of Mo in Si.

7.4 Fluorinated SiO₂

Fluorinated SiO₂ (FSG) was considered as an alloy of SiO₂ and Si₂O₃F₂ up to 12 F%. The decreasing K with increasing F contents can be attributed to the smaller polarizability of F ion, stronger Si-F bond, and lowering of the Si-O infrared oscillation strength by F. The analytical expressions for dielectric constant and refractive index were developed in terms of fluorine content by applying the pseudo alloy model to Clausius Mossotti relation with measured data. According to the model, the lowest K and n are 2.96 and 1.395, respectively, at 12 F%. However, the instability of fluorinated FSG was observed around 6 F%. The lowest measured K and n were 3.53 and 1.423 at 6.5%. The increased free volume and the subsequent water attacks were believed to cause the instability. F ions modify the Si-O network in FSG, creating free volume, which, in turn, makes FSG vulnerable to H₂O. Thus a more accurate model should incorporate the influence of free volume and possible incorporation of other IR active entities such as water.
Appendix A

Derivation of non-linear partial differential equations for both interstitial-substitutional exchange and substitutional diffusion mechanisms.

A.1 Kick-out reaction

\[ I + Mo_s \xrightarrow{k_+^{KO}} Mo_i \]

*Forward reaction rate:*

\[ -\frac{\partial C_{Mo_s}}{\partial t} = k_+^{KO} C_I C_{Mo_s}, \]

*Backward reaction rate:*

\[ \frac{\partial C_{Mo_i}}{\partial t} = k_-^{KO} C_{Mo_i} \]

*At local equilibrium,*

\[ K_{eq}^{KO} = \frac{C_{Mo_i}}{C_I C_{Mo_s}}. \]

*Forward rate = backward reaction rate,*

\[ k_+^{KO} C_I C_{Mo_s} = k_-^{KO} C_{Mo_i}, \quad k_+^{KO} \frac{k_-^{KO}}{k_-^{KO}} = \frac{C_{Mo_i}}{C_I C_{Mo_s}} = K_{eq}^{KO} \]

However, \( K_{eq}^{KO}, k_+^{KO}, k_-^{KO} \) are constants, and the following relationship always holds true regardless of equilibrium.

\[ \frac{k_+^{KO}}{k_-^{KO}} = K_{eq}^{KO} \]

Then, the net rate of the change in \( Mo_s \) due to kick-out reaction is the following,
\[
\frac{\partial C_{Mo_s}}{\partial t} = -k^K_+ C_i C_{Mo_s} + k^K_- C_{Mo_i} \\
= -k^K_+ C_i C_{Mo_s} + \frac{k^K_+}{K^{eq}_i} C_{Mo_i} \\
= -k^K_+ \left[ C_i C_{Mo_s} - \frac{1}{K^{eq}_i} C_{Mo_i} \right]
\]

\[\therefore \frac{\partial C_{Mo_s}}{\partial t} = -k^K_+ \left[ C_i C_{Mo_s} - \frac{1}{K^{eq}_i} C_{Mo_i} \right] \quad \text{Eq. A-1}\]

\textbf{A.2 Dissociative reaction:}

\[V + Mo_i \xrightleftharpoons[^{k^{DS}_+}]{^ {k^{DS}_-}} Mo_s\]

\textit{Forward reaction:}
\[
\frac{\partial C_{Mo_s}}{\partial t} = k^{DS}_+ C_v C_{Mo_i}
\]

\textit{Backward reaction:}
\[
- \frac{\partial C_{Mo_i}}{\partial t} = k^{DS}_- C_{Mo_s}
\]

\textit{At local equilibrium,}
\[
K^{DS}_{eq} = \frac{C_{Mo_s}}{C_v C_{Mo_i}}
\]

\textit{Forward rate = backward rate:}
\[
k^{DS}_+ C_v C_{Mo_i} = k^{DS}_- C_{Mo_s}
\]

Then, the net rate of the change in \(C_{Mo_s}\) due to dissociative reaction is the following,

\[
\frac{k^{DS}_+}{k^{DS}_-} = \frac{C_{Mo_s}}{C_v C_{Mo_i}} = K^{DS}_{eq}
\]

\[
\frac{\partial C_{Mo_s}}{\partial t} = k^{DS}_+ C_v C_{Mo_i} - \frac{k^{DS}_+}{K^{DS}_{eq}} C_{Mo_i} \\
= k^{DS}_+ C_v C_{Mo_i} - \frac{k^{DS}_+}{K^{DS}_{eq}} C_{Mo_i}
\]

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\[ \therefore \frac{\partial C_{Mo_i}}{\partial t} = k^{DS}_+ \left[ C_v C_{Mo_i} - K^{-1}_{eq} C_{Mo_i} \right] \] \hspace{1cm} Eq.A-2

**A.3 I-V recombination reaction**

\[ I + V \leftrightharpoons k^{IV}_+ \rightarrow \phi \]

*Forward reaction rate:*

\[ -\frac{\partial C_I}{\partial t} = k^{IV}_+ C_I C_v \]

*Forward reaction rate in equilibrium:*

\[ -\frac{\partial C_I}{\partial t} = k^{IV}_+ C_I C_{v'} \]

*The net rate of change in \( I \):*

\[ \therefore \frac{\partial C_I}{\partial t} = -k^{IV}_+ \left[ C_I C_v - C_I C_{v'} \right] \] \hspace{1cm} Eq.A-3

Unless \( D_{Mo} \) is negligibly small, \( C_{Mo} \) can be changed by the Fickian diffusion by \( D_{Mo} \), in addition to interstitial-substitutional exchange diffusion by kick-out or dissociative mechanisms.

\[ \frac{\partial C_{Mo}}{\partial t} = \nabla \cdot D_{Mo} \nabla C_{Mo} - k^{KO}_+ \left[ C_I C_{Mo} - K^{-1}_{eq} C_{Mo} \right] + k^{DS}_+ \left[ C_v C_{Mo} - K^{-1}_{eq} C_{Mo} \right] \] \hspace{1cm} Eq.A-4

\( C_{Mo} \) can be changed by both its Fickian diffusion and interstitial-substitutional exchange diffusion.

\[ \frac{\partial C_{Mo}}{\partial t} = \nabla \cdot D_{Mo} \nabla C_{Mo} + k^{KO}_+ \left[ C_I C_{Mo} - K^{-1}_{eq} C_{Mo} \right] - k^{DS}_+ \left[ C_v C_{Mo} - K^{-1}_{eq} C_{Mo} \right] \] \hspace{1cm} Eq.A-5

I-V recombination, kick out, and Fickian diffusion contribute to \( C_I \).

\[ \frac{\partial C_I}{\partial t} = \nabla \cdot D_I \nabla C_I - k^{KO}_+ \left[ C_I C_{Mo} - K^{-1}_{eq} C_{Mo} \right] - k^{IV}_+ \left[ C_I C_v - C_I C_{v'} \right] \] \hspace{1cm} Eq.A-6

I-V recombination, dissociative, and Fickian diffusion contribute to \( C_v \)
\frac{\partial C_v}{\partial t} = \nabla \cdot D_v \nabla C_v - k^{DS}_+ \left[ C_v C_{M_0} - K_{eq}^{DS} C_{M_0} \right] - k^{IV}_+ \left[ C_j C_v - C_i, C_v \right] \quad Eq.A-7
Appendix B

DOPDEES codes for Mo diffusion simulation

After the point defect distributions are initialized by from their TRIM simulation profiles that result from Mo implant, the following main program calls two modules: “point-defect.tcl” and “metal-Mo.tcl.” Module “point-defect.tcl” governs the kinetics of vacancies and interstitials while module “metal-Mo.tcl” determines the kinetics of Mo diffusion. Kick out and dissociative mechanisms are embedded in “metal-Mo.tcl” in addition to substitutional Mo diffusion.

B.1 Main program

```tcl
#PMM: Moly diffusion
#
#------------------------------------------
# Uncomment following if you want to work in um-s unit system.
# unit-system um-s
set TEMP (750)
#enter depth in microns
set DEPTH(750) (250e-4)

#for each depth and temperature time to simulate
set TIME(250e-4,750) (40)
set TIME(250e-4,750) (160)
set TIME(250e-4,750) (640)

#read the parameter files
module params-BU
module params-metal-Mo

#Jaraiz and Gilmer
param Diff_0_I_887 [unit 1.2332e-06 cm2s-1]
param Diff_0_I_E [unit 0.9 eV]

#BU
param DCstar_V_887 [expr 0.1 *[unit 97726.1 cm-1s-1]]
param DCstar_V_E [unit 3.88 eV]
```
# Uncharged equilibrium concentrations

```c
foreach pd {I V}
    param Diff_0_$pd [arrh887 [param Diff_0_$($(pd)_887]
        [param Diff_0_$($(pd)_E)]
    param Cstar_i_$pd [func div [arrh887 [param DCstar_
        $(pd)_887] \n        [param DCstar_$(pd)_E]] [param Diff_0_$pd]]
    param Cstar_0_$pd [func div [param Cstar_i_$pd] \n        [func sum 1 [param Kchg_m_$pd] [param
        Kchg_p_$(pd)]]])
}
```

# Create the structure: First a region, then grids, then fields
region create Gas
field grid [list \n    -2e-7 1e-7 \n    0 1e-7]

# Create the structure: First a region, then grids, then fields
region create Si
field grid [list \n    0 1e-6 \n    1e-4 5e-5 \n    [expr $depth/2] 1e-2 \n    [expr $depth-1e-4] 5e-5 \n    $depth 1e-6]

# initialize vacancies and Si interstitials

```c
interpolate Vinit.pro Cv
interpolate Iinit.pro CI
field create CMos 1e6
field create CMoi [func prod CMos [param Moi_b_Mos]]
region select Si
module point-defect
module metal-Mo

puts "TEMP = [format "%.0f" [expr $TEMPK -273]] C"
#puts "DiCi= [param DiCi]"
puts "Di= [lindex [field tabulate x [param Diff_0_I] ] 11]"
puts "Ci= [lindex [field tabulate x [param Cstar_i_I] ] 11]"
solver engine lsode-nj
solver run 0 $TIME {
    region select Si
    writetofile plot[format "%.0f" $TEMPK]/cMo.[expr
        round($t)].prf [field
        tabulate x CMos]
    writetofile plot[format "%.0f" $TEMPK]/ci.[expr
        round($t)].prf [field tabulate x CI]
    writetofile plot[format "%.0f" $TEMPK]/cMotot.[expr
        round($t)].prf [field tabulate \n        [func div x $depth] [func div [func sum CMoi
```

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B.2 point-defect.tcl

#---------------------------------------------------------------
# PMM -- Process Modeling Modules (for DOPDEES and Alamode)
# (c) 1997 Alp H. Gencer alp@bu.edu
# $Id: point-defect.tcl,v 1.7 1997/07/23 13:16:41 alp Exp alp$
#---------------------------------------------------------------
# Equations governing point defects.
#---------------------------------------------------------------

module fields $ARGS

# Uncharged equilibrium concentrations
foreach pd (I V) {
    param Diff_0_$pd [arrh887 [param Diff_0_->pd]_887]
    [param Diff_0_->pd]_E]
    param Cstar_i_$pd [func div [arrh887 [param DCstar_-$pd]_887]
    \[param DCstar_-$pd]_E] [param Diff_0_->pd]]
    param Cstar_0_$pd [func div [param Cstar_i_$pd] \[func sum 1 [param Kchg_m_$pd] [param Kchg_p_$pd]]]
}

# IV-recombination
param kIV_0 [func prod [arrhenius [param pi4a] [param KR_E]] \[func sum [param Diff_0->I] [param Diff_0->V]]]

if [check_module carrierconc] {
    foreach pd $PD {
        set chi($pd) [func diffusivity $nmi 1 \[param Kchg_m_$pd] [param Kchg_p_$pd] 0]
        set DIFF($pd) [func prod [param Diff_0->PD] $chi($pd)]

    foreach DPT $FIELDS(DPT) {
        if {[string match $pd I]} {
            set F0 [param Fi_0->$DPT]
        } else {
            set F0 [expr 1-[param Fi_0->$DPT]]
        }
    }
}
set pi($pd,$DPT) [func div \n    [func prod [param Kpair_$pd_$DPT] $DIFF ($DPT,$pd)] \n    [func prod [param Diff_0_$DPT] $F0]]
if [check_arg debug] {
    puts "K_$DPT$pd=[field print [param Kpair_$pd_$DPT]]"
}
}

set Z($pd) $chi($pd)
if [check_arg full] {
    foreach DPT $FIELDS(DPT) {
        set Z($pd) [func sum $Z($pd) \n                      [func prod $pi($pd,$DPT) $NACT($DPT)]]
    }
}
# If a point defect doesn't exist, create it
if {1}[search $FIELDS(PD) $pd]<0} {
    field create $NAME($pd) [func prod [param Cstar_0_$pd]
    $Z($pd)]
} # Uncharged point defects
set C0($pd) [func div $NAME($pd) $Z($pd)]
# Equilibrium conc. depending on fermi level
param Cstar_$pd [func prod [param Cstar_0_$pd] $Z($pd)]
# Surface recombination rate
set SIGMA($pd) [func div $DIFF($pd) [param Surfrec_$pd]]
set FIELDS(PD) $PD
set kIV [func prod [param kIV_0] $Z(I) $Z(V)]
} else {
    # No dependence on fermi level, intrinsic material
    foreach pd $FIELDS(PD) {
        param Cstar_$pd [param Cstar_i_$pd]
        set SIGMA($pd) [func div [param Diff_0_$pd]
          [param Surfrec_$pd]]
        # Use a trick: assume all point defects are uncharged.
        param Cstar_0_$pd [param Cstar_i_$pd]
        set C0($pd) $NAME($pd)
        set DIFF($pd) [param Diff_0_$pd]
    }
    set kIV [param kIV_0]
}

foreach pd $FIELDS(PD) {
    if [check_arg debug] {
        puts "C${pd}0*=[field print [param Cstar_0_$pd]]	D${pd}0
        =[field print [param Diff_0_$pd]]"
    }
    op diff $NAME($pd) $DIFF($pd) $C0($pd)
    if {[!check_arg nosurfrec]} {
        foreach side [region neighbors] {
            op mixed $side $NAME($pd) $C0($pd) [param Cstar_0_$pd] $SIGMA($pd)
        }
    }
}
if [check_arg debug] {
    puts "SLAMBDA=$pd = [field print [param Surfrec_$pd]]"
}

if {llength $FIELDS(PD) == 2} {
    set KF [func prod $kIV [func sum [func prod $C0(I) $C0(V)] \ 
        [func prod -1 [param Cstar_0_I] [param Cstar_0_V]]]]
    op func $NAME(I) $KF -
    op func $NAME(V) $KF -
    if [check_arg debug] {
        puts "KR_0 = [field print [param kIV_0]]"
    }
}

B.3 metal-Mo.tcl

#------------------------------------------
# PMM -- Process Modeling Modules (for DOPDEES and Alamode)
#------------------------------------------
#This is a module for Metal/Mo diffusion
#
#------------------------------------------

set Moi_b_Mos [func div [arrhenius \ 
    [param Moi_b_Mos_T] [param Moiengy_b_Mos]] \ 
    [expr exp(-([param Moiengy_b_Mos] *300)/(0.0259 *T)) ] ]

set DMoi [func prod $Dmeff [func sum [func div 1 $Moi_b_Mos] 1]]
puts "Moi_b_Mos = [lindex [field tabulate x $Moi_b_Mos] 11]"
puts "DMoi = [lindex [field tabulate x $DMoi] 11]"

#diffuse pairs
op diff CMoi $DMoi CMoi
op diff CMos $DMos CMos
#
# Mos + I = Moi
set Keq_ko [func div $Moi_b_Mos [param Cstar_i_I]]
set kff [func prod \ 
    [arrhenius [param pi4a] [param Ebar_ko]] \ 
    [param Diff_0_I] ]
set rate [func prod $kff \ 
    [func subtract [func prod CMos CI] [func div CMoi $Keq_ko]]]
op func CMos $rate -
op func CI $rate -
op func CMoi $rate +
#
# Mos + V = Mos
set Keq_ds [func div 1 [func prod $Keq_ko \[param Cstar_i_V] [param Cstar_i_I]]]
set kff [func prod \[arrhenius [param pi4a] [param Ebar_ds]] \[func sum [param Diff_0_V] $DMoi] ]
set rate [func prod $kff \[func subtract [func prod CMoi CV] [func div CMos $Keq_ds]]]
op func CMos $rate +
op func CV $rate -
op func CMoi $rate -

#Boundary conditions

set SIGMAMo [func div $DMoi [param Surfrec_Mo]]
set CMoi_eq [func prod $Moi_b_Mos [param Css_Mo] ]
#use a '-noboundary' switch to your module call if you dont like #this boundary condition and something else to your script
if {[!check_arg noboundary]} {
    foreach side [region neighbors] {
        op mixed $side CMoi CMoi $CMoi_eq $SIGMAMo
        #op mixed $side CMos CMos [param Css_Mo] $SIGMAMo
    }
}

B.4 param.metal-Mo.tcl: parameters for Mo diffusion

param Css_Mo 2e14

#Mo measured diffusivity
set Dmeff [arrhenius 7e-3 2.21 ]

#other fitting parameters
param Moiengy_b_Mos 0 ;#gives energy dependence to Moi/Mos
param Moi_b_Mos_750 [expr 9e-6] ;# some small value

#Just a high enough value
param Surfrec_Mo [param Surfrec_I]

#parameters add a barrier to diffusion limited reaction
param Ebar_ko 0 ;#added to ko reaction
param Ebar_ds 0 ;#added to dissociative reaction
[22] Discussion with J. Michel.
[25] Discussion with L.C. Kimerling
[39] G. Klaus, Metal Impurities in Silicon-Device Fabrication, Springer Series in
applied to solar cells,” 10th IEEE Photovoltaic Specialists Conf., Palo Alto, California,
[52] Aimee Smith, she is working on Fe gettering simulation by p+ layer and Al in her Ph.D. thesis.
[70] Private communication with Dr. Hichem M' Saad from Applied Materials (1999).
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