DESIGN PRINCIPLES FOR HIGH PERFORMANCE, LOW ENVIRONMENTAL IMPACT SILICON CLEANS

By

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ABSTRACT
The production of future generation integrated circuit devices requires precise control of impurities on the silicon surface. Cleaning of silicon wafers has historically involved the use of concentrated chemicals, large amounts of rinse water, and elevated temperatures to remove particles, metals, and organic matter from the surface. Poor understanding of the mechanisms of contamination has necessitated large margins of error in cleaning processes and has made cleaning the largest consumer of resources in an IC process line. Explosive growth within the semiconductor sector coupled with the increased need for cleaning in device manufacturing presents an enormous burden for the natural environment. By better understanding the relevant parameters in a cleaning step, future process will continue meet performance specifications while simultaneously reducing their impact on the environment.

The environmental performance of the manufacturer is limited by the available technologies for wafer cleaning. Design changes occurring at the tool, chemical, and system level all affect the overall environmental impact of a fab. A modified Cost of Ownership (CoO) expression based on the tool consumable cost (CC), footprint (F), yield (Y), throughput (T), and utilization (U) is presented as a guideline for identifying the next generation of 'green' technologies. Barriers to the implementation of an ideal wetbench are also discussed.

The intrinsic silicon-HF interface provides a baseline for understanding the impact of contamination on the electronic quality of the surface. Minority carrier lifetime measurements made by Radio-Frequency Photoconductance Decay (RF-PCD) show that defects on this surface are not described by any known models for a single mid-gap, electronic state. A model is presented in which each physical defect introduces two coupled mid-gap states. By analogy with P_n-centers observed at the Si-SiO_2 interface, these states correspond to the three physical states of a dangling bond. The doubly-occupied state may play a role in native oxide growth and metal deposition; the unoccupied state is a likely site for attack during fluoride etching.

Metal contaminants at the silicon-liquid interface have also been studied using RF-PCD. The deposition of part per trillion (ppt) levels of Cu is shown to increase by a factor of 17.5 by using a 500:1 solution of HF instead of a 100:1 solution. This strong dependence arises from a shift in the electrochemical potential at the wafer surface. With the reduction in [H^+], the potential shifts to more cathodic values and causes the Cu deposition rate to increase. To prevent unacceptable levels of contamination from dilute HF solutions, the purity of a D:J HF bath must scale as D^{-0.78}. 

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CHAPTER 1 - INTRODUCTION

WAFER CLEANING

The production of contamination-free silicon surfaces has long been an interest for the fabrication of semiconductor devices\(^1\). Surface quality becomes increasingly important as device dimensions continue to shrink: thinner gate oxides, shallower implanted regions, smaller contact holes. The addition of new materials in the fabrication process, notably high dielectric materials for gate stacks, further necessitates a fundamental understanding of electrochemical processes involved in silicon processing.

To guide the manufacture of future semiconductor devices and continue the steady progress embodied in Moore’s Law, the Semiconductor Industry Association has established guidelines for wafer surface cleanliness. Their International Technology Roadmap for Semiconductors\(^2\) defines allowable levels of particle, organic, and metallic contamination for front-end processes. Table 1-1 shows these values for the next few technology generations.

Table 1-1. Surface cleanliness requirements specified by the SIA Roadmap for the next two technology generations.

<table>
<thead>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td>Critical Metals: Fe, Ni, Zn, Cu, Zn, Na (cm(^{-2}))</td>
<td>7e9</td>
<td>2.9e9</td>
<td>2.1e9</td>
<td>1.8e9</td>
<td>1.7e9</td>
</tr>
<tr>
<td>Organics (cm(^{-2}))</td>
<td>6.6e13</td>
<td>4.5e13</td>
<td>2.8e13</td>
<td>2.0e13</td>
<td>1.4e13</td>
</tr>
<tr>
<td>Surface Oxygen (cm(^{-2}))</td>
<td>1e14</td>
<td>1e14</td>
<td>1e12</td>
<td>1e12</td>
<td>1e12</td>
</tr>
<tr>
<td>RMS roughness (Å)</td>
<td>1.4</td>
<td>1.0</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

15
Meeting these goals has driven the understanding and development of new cleaning processes. The undesired potential for yield drops has simultaneously led to the use of very aggressive cleaning chemistries, continuous advancement in the purity of process chemicals, and an increased frequency of cleaning steps. These three trends have made wafer cleaning the largest consumer of chemicals in a semiconductor fab.

ENVIRONMENTAL CONCERNS

The semiconductor industry has long promoted itself as a ‘clean industry’. In many ways, this characterization is appropriate. When compared to the ‘big six’ most polluting American industries – paper, chemicals, automotive, steel, petroleum, and transportation – the overall environmental impacts of semiconductor processing are quite small. But this comparison itself is a bit misleading: while semiconductor manufacturing accounted for only 0.2% of greenhouse gas emissions by U. S. industries in 1990, that level soared to 1.4% by 1996.

Continuing growth within the industry, while maintaining current emission levels per device, would quickly drastically alter these figures. Diversification within the industry, from basic devices and robust processors toward powerful application specific integrated circuits (ASICs), has resulted in an enormous increase in the annual volume of silicon processed. In anticipation that environmental concerns may soon limit industry growth, semiconductor manufacturers have begun to show interest in making their process lines more ‘green.’
Wafer cleaning processes are particularly hard hit by industry growth. Not only is the total volume of processed silicon increasing, but the devices are also becoming more complex. Since wafers are routinely cleaned both before and after a fabrication step, the increased resource use for cleaning is enormous. For current state-of-the-art process lines, wafer cleaning steps account for roughly 25% of all processing steps and 30% of all process time. The widespread use of cleans results in enormous consumption of not only cleaning chemicals but also rinse water. Even the electricity required by heating, ventilation and air conditioning (HVAC) is directly attributed to the demand for wafer cleanliness.

**OVERVIEW**

The design of environmentally sound cleaning processes requires knowledge of current technology as well as a fundamental understanding of how surface contamination occurs. Chapter 3 analyzes current trends in wafer cleaning technology. A modified version of the cost of ownership (CoO) that includes facility-level environmental impacts is used as a preliminary metric for identifying environmentally sound, cost effective solutions to future cleaning needs. While not an exact metric, this approach highlights the importance of 5 parameters in designing a cleaning process: consumable cost, fab footprint, throughput, utilization, and yield. From the analysis of tool designs, chemical cleaning recipes, and system-wide issues, a future vision of the ideal 'green' wetbench is developed. Technology barriers to the implementation of such a tool are briefly discussed.
The intrinsic silicon-liquid interface is studied in Chapter 4 as a baseline for understanding the impact of surface contaminants. Minority carrier lifetime measurements present a unique insight into the electronic nature of dangling bond defects that are present when a silicon wafer is in contact with HF solutions. These measurements show that each defect introduces two coupled mid-gap states instead of a single recombination level. Physically, these two states correspond to three distinct occupancies for the dangling bond. The significance of each of these states is discussed with respect to the processes of native oxidation, silicon etching, and metal deposition.

Chapter 5 shows how part per trillion levels of metallic contaminants behave in contact with this intrinsic surface. A model is presented in which the metal, as a minority species, is driven by the etching and hydrogen evolution reactions occurring in the silicon-HF system. In this context, metal deposition is studied as a function of the HF bath concentration. The strong dependence, measured experimentally with RF-PCD, is explained in terms of a shift in the electrochemical potential at the wafer surface. Based on this model, a semi-empirical relation is developed for metal purity requirements in dilute HF solutions. For the case of the Cu, this relation requires that the purity of a $D:1$ solution of HF scales as $D^{1.78}$. Similar measurements for other metals of interest, such as Ag and Au, could be established with the same approach.

Metal contamination of the silicon surface may also occur without direct electron transfer from the substrate to the metal. Chapter 6 shows how Pourbaix (E-pH) diagrams are used to calculate the solubility of metal contaminants. This broad thermodynamic approach provides a simple framework for simultaneously studying the impacts of alkalinity, oxidizing strength, anion complexing, and metal silicate formation. From
these results, predictions are made on how to design an SC-2 bath that can operate with less acid and yet still clean surfaces as effectively as the standard RCA process.

Chapter 7 presents an application of the knowledge gained about metal deposition from HF solutions. Using minority carrier lifetime as a probe of surface contamination, an *in-situ* monitor for metal in HF is shown. Detection of 20 parts per trillion of Cu in a 500:1 HF bath is demonstrated with this device. Since this monitor is based solely on the use of a silicon wafer as a bath probe, there is no risk of contamination and this system is a viable option for clean processing conditions. The benefits of this monitor, for use in a point-of-use recycling system or simply to limit contamination spikes, are discussed.

Finally Chapter 8 summarizes achievements and makes suggestions for potential future work.
CHAPTER 2 – EXPERIMENTAL PROCEDURES

RADIO-FREQUENCY PHOTOCONDUCTANCE DECAY

Radio Frequency Photoconductance Decay (RF-PCD) falls under the category of minority carrier lifetime measurement techniques. Other minority carrier characterization tools, including conventional photoconductance, Microwave Photoconductance Decay ($\mu$-PCD) and Surface Photovoltage (SPV) measurements, have been widely used to evaluate bulk defects in semiconductors$^{4,5,6}$ and, particularly, metal defects$^7$. With a passivating solid film, such as SiO$_2$, the PCD techniques are also used to study surface defects$^8$. RF-PCD is unique in its ability to measure wafers in the presence of wet chemical passivants.

As with other photoconductance techniques, RF-PCD is based on observing decay transients following the injection of excess carriers. Figure 2-1 shows a schematic of the RF-PCD measurement system. A strobe lamp, emitting a broad range of above-bandgap light, is used as a carrier injection source. An RF coil is used as a contactless probe of the wafer conductivity. With the wafer positioned near the coil, free carriers produce eddy-currents in response to the generated AC magnetic field. The power contained in these eddy currents is$^9$:

$$P = \frac{E_T^2}{8\pi n^2 \sigma} \tau$$
where $E_T$ is the rms RF voltage, $n$ is the number of turns on the coil, $t$ is the wafer thickness, and $\sigma$ is the wafer conductivity. By measuring this power loss, the RF coil probes the wafer conductivity without requiring any physical contact.

![Diagram of the measurement system](image)

**Figure 2-1. Schematic of the Radio-Frequency Photoconductance Decay measurement system.** The rf coil positioned outside the cleaning tank probes the wafer conductivity while the strobe lamp injects excess carriers from the front surface.

Other lifetime measurement systems, such as $\mu$-PCD, also make use of the principle of eddy current absorption. Microwave PCD uses probe frequencies of 8-40 GHz\(^{10}\) where water is strongly absorbing. RF-PCD, though, uses probing frequencies of 20-60 MHz and can therefore be used on a silicon wafer that is immersed in a cleaning solution. It has been shown that various chemical species, including HF\(^{37}\), iodine dissolved in methanol\(^{11}\), and ammonium fluoride (NH\(_4\)F)\(^{12}\) produce different terminations of the silicon surface. Such widely varying states of the silicon surface elucidate the distinction between recombination at surface sites and recombination at defects in the wafer bulk.
In general, the dynamics of excess carriers (in the absence of an external electric field) are determined by two processes: diffusion and recombination. The differential equation that incorporates these two processes is (assuming planar symmetry):

\[
\frac{\partial \Delta n}{\partial t} = D \frac{\partial^2 \Delta n}{\partial x^2} - \Delta n \frac{1}{\tau_{\text{bulk}}}
\]

where \( D \) is the minority carrier diffusion constant and \( \tau_{\text{bulk}} \) is the bulk recombination lifetime. We require that excess carriers cannot leave the wafer, so the flux of carriers to the surface must be identical to the recombination rate at each surface. The recombination activity of the surface is characterized by the surface recombination velocity (SRV), \( S \),

\[
S = N_i \sigma v_{th}
\]

where \( N_i \) is the areal density of surface defects, \( \sigma \) is the minority carrier capture cross-section, and \( v_{th} \) is the carrier thermal velocity. With this definition, the boundary conditions we need are:

\[
S \Delta n \bigg|_{x=d/2} = \mp D \frac{\partial \Delta n}{\partial x} \bigg|_{x=d/2}
\]

The general solution to this system of equations can be written as the sum of one odd and one even function:

\[
\Delta n(x,t) = \Delta n^e(x,t) + \Delta n^o(x,t)
\]

where

\[
\Delta n^e(x,t) = \sum_i A_i^e \cos(k_i^e x) \exp(-t/\tau_i^e)
\]

\[
\Delta n^o(x,t) = \sum_i A_i^o \sin(k_i^o x) \exp(-t/\tau_i^o)
\]

For each of the modes to satisfy our original equation, we require
\[
\frac{1}{\tau_i} = D k_i^2 + \frac{1}{\tau_{bulk}}
\]

for all terms in both the even and odd solutions. The allowed \(k_i\) values are determined by the boundary conditions:

\[
k_i^e \tan \left( \frac{k_i^e d}{2} \right) = \frac{S}{D} \\
k_i^o \cot \left( \frac{k_i^o d}{2} \right) = -\frac{S}{D}
\]

The amplitude of each of these allowed modes is determined by the initial carrier concentration. This analysis is greatly simplified, though, by noting that all values for \(k\), except for \(k_0^e\), are larger than \(\pi/d\). Each of these modes, therefore, decays with a timeconstant smaller than \(d^2/(\pi^2 D)\), the 1-D transit time. For a thickness of 750 \(\mu\)m, typical transit times are 50 \(\mu\)s for n-type wafers and 16 \(\mu\)s for p-type. At times much longer than this transit time, the recombination behavior is dominated by the fundamental decay mode associated with \(k_0^e\).

In this region of the decay, the recombination rate is given by

\[
\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surf}}
\]

where surface lifetime is defined as the smallest solution to

\[
\sqrt{\frac{D}{\tau_{surf}}} \tan \left( \frac{d}{2\sqrt{D \tau_{surf}}} \right) = s
\]
Figure 2-2. Measured minority carrier lifetime shown for a range of surface recombination velocities (SRV). For high bulk lifetimes (>1ms) there is a large domain where the measured lifetime varies inversely with the surface defect density.

Figure 2-2 shows how this measured lifetime varies with the $s$, assuming that the bulk lifetime is reasonably high (>1ms). The three regions of the graph correspond to three physically distinct recombination pathways. For very highly defective (and hence, high $s$) surfaces, recombination is limited by diffusion of minority carriers to the surface. The measured lifetime is thus the diffusion time:

$$\tau_{\text{meas}} = \frac{d^2}{\pi^2 D}$$

For the other extreme, where the surface is nearly defect-free and $s$ nears 0, recombination is limited by the defect sites in the wafer bulk. In this regime, the measured lifetime is precisely the bulk lifetime:

$$\tau_{\text{meas}} = \tau_{\text{bulk}}$$
In between these two extremes, the lifetime is limited by recombination at the surface defect sites. Only in this regime is the lifetime a direct measure of \( s \):

\[
\tau_{\text{eff}} = \frac{d}{2s}
\]

Substituting the previous expression for \( s \) yields a direct correspondence between the surface defect density, \( N_t \), and the measured lifetime:

\[
N_t = \frac{1}{\sigma v_{\text{th}} \tau_{\text{meas}}}
\]

Thus, for real-time monitoring of surface defects, changes in inverse lifetime correlate directly with changes in the defect density.

**SAMPLE PREPARATION**

Unless otherwise noted, all silicon samples used were prepared with the ‘MIT Clean’.

This process consists of:

- 2 min. immersion in a .5% HF bath
- 15 s water DI water rinse
- 4 min. immersion in a 4:1 solution of \( \text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 \) at 90°C
- 2 min. DI rinse
- 2 min. immersion in a .5% HF bath

The first step of this procedure strips any native oxide present on the wafer surface. The following rinse is necessary to remove any residual fluorine on the surface and facilitate wetting by the sulfuric/peroxide mixture. This mixture produces Caro’s acid, \( \text{H}_2\text{SO}_5 \), which aggressively oxidizes the silicon surface. The 4 minute immersion results in an oxide that is roughly 20 Å thick. The final HF immersion strips away this oxide.
removing any contaminants present on the surface. The silicon surface produced by this procedure is terminated predominantly (>99%) by hydrogen, with some residual fluorine\textsuperscript{13}. 
CHAPTER 3 – METRICS AND APPROACHES FOR ENVIRONMENTALLY BENIGN WAFER CLEANING

INTRODUCTION

In the current design methodologies for semiconductor device fabrication, unit operations are chosen based mainly on their ability to perform a single given function. Environmental impacts are not heavily weighed in the decision making process and are usually treated only at the 'end of pipe', where effluent from the fab is treated to make it safe for disposal or emission. This emphasis on pollution control instead of pollution prevention has fostered the notion that addressing environmental, safety, and health (ESH) issues opposes efforts to increase profitability.

Addressing ESH issues during process design can generate cost savings two ways. First, the incorporation of ESH considerations into process design necessarily leads to cost savings through reduced resource consumption. As resource use, notably water and electricity consumption, constitute significant fractions of fab operating expenses, these savings alone may justify switching to ESH-friendly processes. Second, costs of complying with environmental regulations may make current processes unaffordable in the near future. Changes in water use permits, energy taxes, or chemical handling requirements can all lead to increased fab operating costs, as well as increased costs for input materials. Including ESH impacts into the design process protects against the enormous costs of modifying process flows that have already been transferred to full-scale production.
The ESH issues that require the most attention vary greatly from fab to fab. Since growth in the semiconductor industry occurs on a global scale, there are many issues that can enter in the decision making process. For island nations, the cost of water may be a large fraction of operating cost, while in a less developed country, electricity scarcity may limit some processes. For U.S.-based companies with operations abroad, considering these issues will facilitate transfer of process flows.

The difficulty facing process engineers is how to design future processes which reduce environmental impact without compromising device yield. In this paper, we outline a number of instances in wafer cleaning where addressing ESH concerns may increase productivity. We begin with a discussion of metrics for evaluating process alternatives and follow with a discussion of relevant issues on the chemical, tool, and system-wide levels.
BACKGROUND

Cost of Ownership

Tools for decision making are becoming more important as the industry continues to grow and as process lines become more diverse. Whereas performance alone was long the main driving force in decision making, cost is growing in importance. Cost of Ownership (CoO) is a means of calculating the contribution of one tool to the total cost of processing a single wafer. It is defined as:

\[
CoO = \frac{FC+OC}{Y \times T \times U}
\]

where FC is the fixed cost of equipment, OC is the operating cost (including chemicals, water, and electricity), Y is the total yield, T is wafer throughput, and U is tool utilization. Conventional treatment of ESH concerns leads mostly to increases in fixed costs, through cost of acquiring permits and ESH resources, as well as increased operating costs for ESH support staff. In considering ESH issues in the design of cleaning processes, there is a large potential for direct reduction of operating costs, as well a possibility of finding processes which lead to increased tool utilization, throughput, or even yield.

Of these terms, only FC has no direct environmental consequences (apart from the upstream environmental costs associated with tool production). The Operating Costs for wet cleans are composed largely of the cost of consumables – water, chemicals, and electricity – for both the tool and the facility, but also includes some costs for routine maintenance. Yield drops represent a loss of all the resources that contributed to wafer
production. Wafer throughput is directly tied to facility-related environmental impacts; tools that can process wafers more rapidly reduce the fabspace required and, consequently, reduce the costs associated with maintaining the cleanroom environment. Similarly, tools that have low utilization are not making the efficient use of the clean environment.

To make these dependencies more clear, we can split the OC into two components: the cost of consumables per wafer (CC) and the facility cost (FaC) of maintaining the cleanroom environment. Other operating costs, such as routine service needs, are, for our purposes, incorporated into the amortized FC. For a given tool design, the first term scales directly with the number of wafers processed. Expressed in the units of $/(unit time), this term is CC×T×U. The facility cost is independent of the number of wafers processed, but depends directly on the footprint (F) of the tool. For FaC expressed in units of $/(unit area)/(unit time), the second term of our OC is F×FaC. Substituting these expressions, we get our modified Cost of Ownership expression:

\[ CoO = \frac{FC+T×U×CC+F×FaC}{Y×T×U} \]

This formulation of the CoO makes explicit the important factors in our environmental impact analysis: consumable cost, footprint, throughput, yield, and utilization.

Other Figures of Merit

While there are numerous opportunities for ESH and productivity improvements, identification of one optimal solution for future technologies is very difficult. Though this
optimal solution may certainly vary for individual fabs depending on production goals and facility location, there is still some need to quantify all possible alternatives. Numerous methods of life cycle analysis (LCA) are currently being developed to fill this void.

One such method, the Sustainable Process Index (SPI), assigns to each consumptive activity an area of land required to perform that activity sustainably. Water use, for example, would be divided by the local average rainfall value to determine an area from which that water could be harvested. Electricity requirements are included by calculating the area required by the most efficient, commercially available solar cells to produce the same amount of energy. In this way, processes that have the smallest 'ecological footprint' are deemed the most sustainable. One large advantage of this method is its ability to account for local factors, such as water scarcity in the southwestern U.S. While this method is valuable for its ideological significance, the lack of any monetary equivalence makes it unlikely to play a large role in decision making.

Another promising method that attempts to assess the actual damage to valued environmental qualities is the Swedish Environmental Priority System (EPS). This method assigns monetary costs to damages incurred in the areas of human health, biodiversity, land fertility, resources and aesthetic values. The costs calculated are those borne by society at large, and are thus likely to play a large role in defining future environmental policies. By using this as a guide in decision making, future industrial
processes are more likely to be in line with policies of the time, and thus less susceptible to modification from environmental regulation.

Cleaning Requirements

Cleaning processes are currently the largest consumers of chemicals and energy in the fab, largely due to the frequency with which cleans are performed. In current state of the art process lines, cleans account for roughly 25% of all steps. For a typical 8" production facility which starts 5,000 wafers per week, these numbers translate into 5 GWh of electricity, 240 millions gallons of water, and 300 tons of hazardous chemicals consumed each year.

Cleans are required to prevent contamination of three types: organic compounds, metals, and particles. The presence of organics on the wafer surface can cause incomplete removal of native oxides and metals in subsequent cleaning steps and micromasking effects during reactive ion etching (RIE). Organics are particularly harmful at high temperatures where reaction with the silicon substrate can form silicon carbide precipitates at the Si/SiO₂ interface, reducing gate oxide integrity (GOI). Metal contamination can cause interfacial structural defects, stacking faults during high temperature or epitaxial processing, increased leakage currents, and reduced minority carrier lifetimes. Particulate contamination is an issue throughout the process line. Killer defects, defined as one-tenth the size of the minimum feature or larger, may block vias, create shorts between metal lines, threaten GOI, exacerbate electromigration, or otherwise lead to failure.
**CHEMISTRY LEVEL CONCERNS**

A typical front-end-of-line wet cleaning chemistry sequence is shown in Figure 3-1. The cleaning process is divided into two main sections: residual photoresist removal and pre-gate cleaning.

**RESIDUAL PHOTORESIST REMOVAL**

H$_2$SO$_4$-H$_2$O$_2$ of composition 3:1 to 4:1 at 120-130°C is used for residual photoresist removal. The residual photoresist is removed from the wafer surface through oxidation. As the residual photoresist is oxidized, the H$_2$O$_2$ decomposes into CO$_2$ and water slowly diluting the bath. In addition, H$_2$O$_2$ readily decomposes at high temperatures, causing further concentration drifts. In order to maintain desired bath concentrations, the bath must be periodically spiked with more H$_2$O$_2$.\textsuperscript{17} Precise process control of current chemistry is difficult and chemical consumption is high. Energy consumption is also high. In order to maintain bath temperatures of 120-130°C, constant heating is required and the use of concentrated chemicals makes exhaust handling and abatement necessary. Furthermore, sulfuric residues from H$_2$SO$_4$ are difficult to remove, therefore a high volume of rinse water is used following this clean step.\textsuperscript{18} As demonstrated, current residual photoresist removal chemistry is less than desirable.
An alternative to the current inorganic stripper chemistry is ozonated water. Ozonated water is a strong oxidizing agent. H_2O-O_3 rapidly oxidizes and removes residual photoresist on the surface of the wafer without high temperature processing or concentrated chemicals. ⑨
## Typical Front End of Line Wet Cleaning Process

<table>
<thead>
<tr>
<th>Type of Clean</th>
<th>Chemistry</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ 4:1</td>
<td>Organic Carboxylic Acid</td>
</tr>
<tr>
<td></td>
<td>120-130°C</td>
<td>Metal</td>
</tr>
<tr>
<td>Residual Photoresist Removal</td>
<td>DI Water Rinse Room Temperature</td>
<td>Chemical Residue Removal</td>
</tr>
<tr>
<td></td>
<td>Diluted HF 0.5% Room Temperature</td>
<td>Chemical Oxide</td>
</tr>
<tr>
<td></td>
<td>DI Water Rinse Room Temperature</td>
<td>Chemical Residue Removal</td>
</tr>
<tr>
<td></td>
<td>NH$_4$OH/\text{H}_2\text{O}/\text{H}_2\text{O} 0.05:1:5</td>
<td>Particle</td>
</tr>
<tr>
<td></td>
<td>80-90°C</td>
<td></td>
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<tr>
<td>Pre-gate Clean</td>
<td>DI Water Rinse Room Temperature</td>
<td>Chemical Residue Removal</td>
</tr>
<tr>
<td></td>
<td>Hot DI Water Rinse 80-90°C</td>
<td>Chemical Residue Removal</td>
</tr>
<tr>
<td></td>
<td>DI Water Rinse Room Temperature</td>
<td>Chemical Residue Removal</td>
</tr>
<tr>
<td></td>
<td>HCl/\text{H}_2\text{O}/\text{H}_2\text{O} 1:1:5</td>
<td>Metal</td>
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<td></td>
<td>80-90°C</td>
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<td></td>
<td>DI Water Rinse Room Temperature</td>
<td>Chemical Residue Removal</td>
</tr>
</tbody>
</table>

Figure 3-1. Typical recipes for residual resist removal and pre-gate cleaning.

**Pre-gate Cleaning**

The basis of conventional pre-gate chemistry was developed at RCA by Kern and Puotinen in 1965. The RCA clean involves two steps: SC-1 (standard cleaning 1), a NH$_4$OH-H$_2$O$_2$-H$_2$O of composition 1:1:5 to 1:2:7 at 70-80°C and SC-2 (standard cleaning...
2), a HCl-H$_2$O$_2$-H$_2$O of composition 1:1:5 to 1:2:8 at 70-80°C. SC-1 uses oxidation and dissolution to remove organics and particles from the surface of the wafer, where as SC-2 uses dissolution and ion-exchange to remove metal contamination. One or more DI water rinses follow each clean step. Several variations of the RCA clean are used in industry today. As shown in figure 2, an additional HF-last clean step, HF-H$_2$O at a concentration of 0.5% HF, is frequently used to H-terminate the wafer surface following the SC-2 step. H-termination hinders native oxide growth between process steps. The HF-last clean may also be followed by a short, DI water rinse.

Like the residual photo resist removal process, the RCA clean uses large volumes of highly concentrated chemicals and is prone to concentration drifts. Changes in bath concentrations can be particularly harmful in the SC-1 cleaning step where high concentrations of NH$_4$OH can actually etch into the silicon wafer, damaging the substrate surface. Once again, precise process control is difficult. The use of concentrated chemicals creates exhaust handling and abatement issues that lead to high energy consumption. NH$_3$ vapors from SC-1 and HCl vapors from SC-2 can form NH$_4$Cl particles that can introduce particle contamination to clean wafers. There are significant opportunities for ESH improvements of the RCA pre-gate cleaning process.

The chemical consumption of the RCA clean can be easily reduced by diluting current SC-1 and SC-2 chemistries. A team from IBM Microelectronics has shown that the use of megasonics allows an 85% dilution of the SC-1 solution without a loss in cleaning performance. The chemical energy lost through dilution is compensated by megasonic
energy. The same group of scientists showed that a 90-95% dilution of the SC-2 solution without megasonics is possible without losses in cleaning performance. An even greater reduction in chemical consumption and energy use can be achieved by lowering bath temperatures. The research at IBM Microelectronics showed that a 10% reduction in SC-1 bath temperature and a 50% reduction in SC-2 bath temperature are achievable without affecting cleaning capabilities. Lower bath temperatures also help to reduce exhaust, as well as increase process control by reducing the need for H_2O_2 bath spiking. Together, diluted bath chemistries and reduced bath temperatures drastically lower the overall volume of chemicals consumed in the pre-gate cleaning process. H_2O_2 use is reduced by 88%, NH_4OH use is reduced by 92%, and HCl use is reduced by 96%. Although overall chemical consumption is reduced, diluted RCA chemistry still uses several concentrated chemicals.

The Interuniversity Microelectronic Center (IMEC) has developed a self-limiting cleaning chemistry which eliminates NH_4OH and HCl use in pre-gate cleaning. The IMEC chemistry separates the cleaning process into two steps: oxidation and etch. In the first cleaning step, a thin layer of oxide is grown on the wafer surface trapping contaminants. In the second cleaning step, the oxide is etched removing the embedded impurities and passivating the wafer surface. Because oxidation and etch are separated, greater process control is possible: oxide film growth can be monitored and oxide etch is self-limiting. IMEC chemistry achieves in two bathes, what the RCA does in three baths. By reducing the number of baths, chemical consumption is significantly reduced. Furthermore, the number of rinses is also reduced. The capabilities of the IMEC cleaning
process have been proven using $\text{H}_2\text{SO}_4$ of composition 4:1 at 90°C for the oxidation step and 0.5% HF-0.1% IPA in $\text{H}_2\text{O}$ mixture at room temperature for the etch step.

Ohmi presents another alternative pre-gate cleaning chemistry. Like the IMEC clean, Ohmi's cleaning chemistry reduces the number of baths by separating oxidation and etch, however Ohmi also uses room temperature chemistry and limits concentrated chemical use to HF. Because the Ohmi clean is at room temperature, evaporation and exhaust issues are minimal. The first step of the clean uses room temperature ozonated water to remove organics and metal contaminants. The second step of the clean uses megasonic assisted (0.5%)HF-(0.1-1%)$\text{H}_2\text{O}_2$-$\text{H}_2\text{O}$-surfactant to remove particles and metal contaminants. The Ohmi two step RCA clean replacement is followed by a megasonics-assisted ozonated water rinse and a diluted 0.1% HF clean. The additional process steps help to improve contaminant removal and maximize H-termination of the wafer surface. The main difference between the IMEC clean and Ohmi's clean is the use of ionic surfactant and megasonics in the second step. Surfactants used in conjunction with megasonics help to remove particles more efficiently from the wafer surface.
Figure 3-2. Schematic and process recipe for the SCROD tool. Ozonized water and dilute HF completely replace the traditional RCA clean.

Another simplification of the RCA cleaning process has been demonstrated by Hattori.\textsuperscript{25} This process is also preformed entirely at room temperature and uses only ozonated DI water and dilute HF. Similar to the Piranha, each portion of this sequence is self-limiting, so that roughening is reduced. Each pulse of ozonated water creates a thin chemical oxide. The subsequent HF pulse strips this oxide and leaves a hydrogen-terminated silicon surface. When the ozonated water and HF used simultaneously, roughening of the surface is reported. With chemicals delivered by a single-wafer spray tool, this process consumes as little as 5% as much HF as a standard immersion RCA process.

DI Water Rinse

As shown in figure 2, several DI water rinses are used in wet cleaning. In front end of line rinses nearly 265 gallons of DI water, room temperature or heated, are used per 150 mm wafer to remove chemical residues between wet chemical cleaning steps.\textsuperscript{26} In
general, rinse processes have not been optimized to minimize water use, however recent
interest in DI water use reduction has prompted several studies of rinse processes.
Among the factors found to influence rinse efficiency are bath volume, water flow, wafer
spacing, bleed flow, and megasonics.

A group of researchers from Hewlett-Packard demonstrated that by reducing the volume
of the dump-rinser by a factor of two, the volume of water used per rinse was reduced by
a factor of 3 and the cycle time was reduced by over 60%. The same group of
researchers showed that doubling the flow rate of the dump-rinser, reduces cycle time by
1/2 without losses in performance. In addition, it was found that slightly increased drain
times result in shorter overall cycle time. A group of researchers at Motorola determined
that the efficiency of the rinse can be increased with decreased wafer spacing.\textsuperscript{27} The
increase in efficiency has been linked to increased flow rates between the wafers.
Controlled parallel downward flow of rinse water can remove chemicals from the wafer
surface twice as fast as the uncontrolled flow of traditional dump-rinser. Rinse
efficiency can also be increase by pulsing the water stream or using megasonics.\textsuperscript{27,24}
Optimization of the bleed flow rate for each dump-rinser can greatly reduce water
consumption. A bleed flow rate in a single dump-rinser of just 1 gpm greater than
necessary wastes 0.5 million gallons of DI water/year.\textsuperscript{28}

\textbf{Tool level issues}

In addition to chemistry, tool choice is also important in reducing the environmental
impact of the cleaning process. The conventional wet bench tool has multiple open, static
baths. Wafers are moved from bath to bath during the cleaning process. Because the baths are open, exhaust handling is necessary. The fumes from the baths must be drawn out of the cleanroom environment and scrubbed to meet OSHA's stringent exhaust standards. The static baths allow only one chemistry to be used per bench. Limited versatility, batch processing, and queuing between cleaning baths reduces utilization to 20-30% for the conventional wet bench. Furthermore, high temperature processes consume an unnecessary amount of energy.

**Figure 3-3. Schematic of Verteq's single-bath overflow system.** The single chamber saves greatly on the wetbench footprint.

The overflow tool design is a slight ESH improvement on the conventional wet bench design. As shown in figure 3, the overflow tool allows sequential cleaning steps to be performed in a single open bath. Although the high flow rates of the overflow tool permit more dilute chemistries, chemical savings are not substantial. Furthermore, the
single bath design reduces the cleanroom footprint of the wet-bench and improves tool versatility, however exhaust handling and high chemical consumption are still concerns.

![Diagram of the CFM 'Full-Flow' wafer cleaning system.](image)

**Figure 3-4.** Schematic of the CFM ‘Full-Flow’ wafer cleaning system. The fully enclosed, flowing system allows for more effective removal of contaminants from the surface.

As shown in figure 4, the full-flow tool design is also a single chamber tool that can be used for sequential cleaning steps, however its process chamber is sealed. The sealed chamber is purged with nitrogen, then filled with ultrapure water. The cleaning chemicals are bled into the water flow that enters near the floor of the chamber and is expelled near the top of the chamber. As a result, the full-flow design has all the advantages of the overflow design (reduced cleanroom footprint, improved tool versatility, and dilute chemistries), without the exhaust handling issues associated with the overflow design. In addition, the wafers are not exposed to the cleanroom environment between cleaning steps, thus contaminants cannot be introduced between
cleaning steps. The full-flow tool also has drying and passivation capabilities such that the entire cleaning process can be completed without any exposure to the cleanroom environment. The sealed chamber also increases process control by preventing bath composition drift caused by evaporation. The flow of chemicals over the wafer is controlled, the wafers can be placed closer together increasing the throughput of the tool.

As shown in figure 5, the spray tool design is a single, chamber tool that uses a fine spray of chemicals for cleaning. The fine spray speeds the motion of chemicals to the wafer surface, increasing reaction efficiency and allowing more dilute chemistries. The motion of the spray produces a megasonic effect within the chamber, helping to remove particles and contaminants more efficiently. As in the full-flow design, multiple cleaning steps can be completed in the same closed chamber, therefore wafers are not exposed to the cleanroom environment between cleaning steps. No environmental contaminants are introduced during cleaning. In addition, cleanroom footprint is reduced and tool versatility is improved. Also like the full-flow design, the spray tool's sealed chamber prevents composition drifts of cleaning chemicals, increasing process control.

Beyond wet cleaning there are several options for more ESH friendly cleaning processes. Perhaps the most similar alternative cleaning process to wet cleaning is vapor phase cleaning. A vapor phase tool uses the previously mentioned aqueous chemistries in a gaseous state to clean the wafer surface. Wafer cleaning occurs at ambient temperatures and pressures. An inert carrier gas such as N₂ is used to introduce the reactant species to the process chamber. The gaseous chemicals are extremely reactive, therefore a vapor
phase cleaning tool can use as little as 1/100 of the volume of concentrated chemicals that is used in wet cleaning processes. The effectiveness of vapor phase cleaning can be enhanced by evacuating the process chamber prior to cleaning or by irradiating the process chamber with UV light. Vapor phase cleaning is currently used for some specialized applications, however it has yet to be accepted for wide scale use.

**SYSTEM-WIDE ISSUES**

Apart from changes that occur on the cleaning tool scale or changes in chemistry which can easily be substituted into current process lines, there are system-wide changes which may drastically change the way wafers are processed. While these changes are have the highest associated capital costs, the opportunities for decreasing cost of ownership (CoO) through decreased consumption and increased utilization are also large.

**Mini-environments**

In a typical cleanroom environment, wafers are completely exposed during transfer between unit operations. To prevent contamination by airborne organics and particulates during this exposure, all air flowing in the ambient must be constantly filtered and recirculated. The energy cost of maintaining a cleanroom is significant, as roughly 30% of fab-wide energy use goes for heating, ventilation and air conditioning (HVAC)
An alternative approach to keeping wafers contamination-free is to maintain only small Class 1 environments around each tool in a Class 10 or 10,000 cleanroom\textsuperscript{31} and use transfer pods to maintain cleanliness between steps. For 200 mm such pods, the standard mechanical interface (SMIF), are already in use. Another standard, the front opening universal pod (FOUP), has also been developed for 300 mm process tools. A 7500-m\textsuperscript{2} Taiwan Semiconductor fab which is currently using mini-environments reports a 1500 kW power savings, which translates into $1 million per year\textsuperscript{30}.

In addition to reducing demand on HVAC systems, mini-environments also hold potential to reduce the number of cleaning steps in a process flow. In many operations, cleaning occurs as a first step, to prepare the wafer surface, and also as a final step, to remove any residues. In a patterning sequence, for example, the wafer is cleaned both prior to applying photoresist and following resist ashing. In this 'clean-process-clean' sequencing, there are roughly twice as many cleans as necessary. By ensuring that the wafer is kept completely contamination free (and oxygen-free, in cases where a native oxide is detrimental), a sequence of just 'process-clean' is possible.

Cluster tools

Processes which often follow one another in process flows provide an opportunity to consolidate multiple tools into one single cluster tool. Formation of interconnects and vias, for example, involves deposition of Al preceded by deposition of a diffusion barrier and/or followed by deposition of an anti-reflective coating (ARC). Since these
operations are quite similar, they can easily be integrated into a single tool which performs both functions.

The main advantage of this system is the reduction in queuing time. As a wafer moves from the process 1 to process 2, another wafer can begin process 1, increasing overall throughput by nearly a factor of two. When multiple metal deposition steps are required for a single level of metallization, this factor becomes even larger. Another advantage of cluster tools is the reduced cleanroom footprint, as loadlocks previously required between the steps can be eliminated. Also, as was the case with mini-environments, the cleaning step required between the processes can be eliminated since the wafers are not exposed to cleanroom air.

Trends in front-of-end-line processing are currently creating an opportunity for clustering of gate definition and source-drain implant steps. Shallow junction depths required by forthcoming technologies preclude implantation through a screen oxide. This necessitates implantation directly into a bare silicon surface, which is much more susceptible to particle adhesion than the oxidized surface. Therefore these implants will almost certainly require a controlled ambient to protect against particle contamination. Since the poly-Si etch step which defines the gate already requires such an atmosphere, significant throughput gains are likely with clustering. The largest barrier to integration is development of single wafer cleans for etch residue, most likely dry processes, which are compatible with current vacuum technology.
Single wafer vs. Batch processing

The mode in which wafers are processed, i.e. wafer by wafer or in batches, has a great impact on both wafer throughput and tool utilization. When batch and single wafer processes are intermixed in a single process line, there is the additional impact of queuing time. One large cost issue with wet benches is this issue of queuing. As wet cleans, and immersion cleans especially, are particularly ill suited to operating in a single wafer mode, reliance on wet cleaning creates bottlenecks in process lines that are increasingly becoming filled with single wafer steps.

One area of interest is the pre-furnace clean. As long as batch furnaces continue to be used for high temperature treatments, batch cleaning will not represent a significant utilization bottleneck. Concerns about temperature uniformity for 300 mm wafers, though, indicate rapid thermal processing (RTP) furnaces as a likely alternative to conventional batch furnaces for the growth of ultra-thin (<40A) gate oxides. In this case, development of a single wafer clean would yield great saving by eliminating the time required to queue wafers for cleaning and de-queue them for oxidation.

In the area of resist residue removal, this issue is already of practical importance. Bulk films of photoresist are already removed in single wafer O₂ ashing steps. Subsequent patterning is also performed on a wafer by wafer basis. Between these two steps, though, the wafers must be queued for cleaning to remove the resist residue, and dequeued again
for patterning. Thus, the use of a piranha bath for residue removal greatly limits throughput.

Point-of-use recycling

Recycling chemicals and water used in current cleaning processes, instead of completely re-designing the processes, is another approach to reducing ESH impact. The potential is especially large for wet cleaning since reaction by-products make up only a very small part of the effluent stream. While reprocessing is common today only for the most heavily used chemicals, like sulfuric acid, point-of-use (POU) purification makes recycling feasible for many others.

Point-of-use recycling is already an option for some chemicals. For HF solutions, a point-of-use filter now exists which removes metallic impurities using an ion-exchange resin\textsuperscript{37}. Since the actual amount of HF consumed during a dilute HF dip is quite small, it may be possible to use an HF bath for up to 20 times as long as current industry practice. Membrane systems are also available for the purification of isopropyl alcohol (IPA) used in drying processes\textsuperscript{39}. The membranes remove the bulk of the water from the IPA and molecular sieves are used to achieve purity of 50 ppm water.

The high cost of producing ultrapure water (UPW) and large volumes in which it is used make it attractive for POU recycling\textsuperscript{34}. In dump rinsing, the majority of the chemical residue is removed during the first rinse. Subsequent rinse stages result in very little
contamination of the rinse water. These very dilute solutions are readily purified by currently available catalytic filters.

Implementation of any point-of-use recycling system is currently limited by the availability of real-time sensors which can monitor filter performance. Development of one such monitor for HF solutions has already been demonstrated for low parts per billion of Cu contamination\textsuperscript{76}. A monitor capable of detecting parts per billion of organic contaminants in water is also under development\textsuperscript{53}.

**THE IDEAL ESH CLEANING TOOL**

Taken together, the observations of the previous sections define requirements for the ideal, environmentally friendly ‘wetbench’. The enormous utilization and throughput advantages of single-wafer processing necessitate that cleans also be adapted to handle one wafer at a time. The limited effectiveness of immersion cleaning requires that new tools use an alternate form of chemical delivery. The chemistry for this tool should be as simple as possible. The simplified recipe of the SCROD tool is very strong candidate, but others may also exist. The enclosed nature of this single-wafer tool automatically reduces on chemical vapors and eliminates the need for tool exhaust. To make this system truly a ‘closed loop’, the chemicals in use need to be purified at the point of use. By making a tool that can attach to cluster tools or fit inside a mini-environment, this single-wafer module will reduce demands on cleanroom air and limit the need for redundant cleaning steps.
Figure 3-5. Schematic of an ideal wet cleaning tool that incorporates individual findings of the tool, chemical, and system-level issues in wafer cleaning.

To realize this picture of the future wet-bench, many issues need to be addressed. Further studies on the range of use and effectiveness of simplified recipes are needed before RCA replacements gain wide acceptance. The method of chemical delivery (flowing, spray, or spin-on) must be investigated to determine which can clean most efficiently. Point-of-use filters exist for some chemicals, but other will need to be developed to suit the needs of replacement chemistries. To ensure the effectiveness of these recycled chemicals, *in-situ* monitors for both contamination and chemical composition need to be developed.

**Conclusions**

Increased productivity at the level of cleaning chemistry can be achieved by reducing chemical usage and designing efficient cleaning processes. By reducing the volume of concentrated chemicals per bath and reducing the number of baths, the total chemical consumption, and thus operating cost, can be reduced. Furthermore, cleaning processes that involve fewer steps require less time, and thus result in higher throughput.
Tool designs impact productivity by determining footprint, utilization, and cleaning efficiency. Tools which can use multiple chemistries in a single bath require less cleanroom floorspace and have higher utilization. Tool designs which increase delivery of chemicals to the wafer surface reduce the amount of chemicals required for cleaning.

Changes on the system-wide level can lead to increases in throughput and utilization and decreases in chemical and energy consumption. Single wafer processing eliminates the time required to queue wafers in a batch. Mini-environments reduce the demand on HVAC systems. Cluster tools and mini-environments reduce the number of times a wafer needs to be cleaned. Point-of-use recycling reduces the amount of chemicals consumed.

While the design recommendations presented above show numerous ‘win-win’ situations for the manufacturer as well as the environment, implementation of these changes is still quite limited. Although barriers presented by capital costs certainly play some role, this stagnation is due in large part to the industry's resistance to change. While the paradigm of continuous improvement has helped chip performance keep pace with Moore’s Law, process design, particularly in wet cleaning, is decades behind. In the future, emphasis should be placed on implementing process changes which increase productivity and reduce ESH impact.
CHAPTER 4 – THE INTRINSIC SILICON-LIQUID INTERFACE

INTRODUCTION

Silicon surfaces have been widely studied throughout the evolution of semiconductor device technology. The highly reactive nature of bare silicon wafers necessitates a foreign species to passivate the dangling bonds that arise at the surface. Early on, silicon dioxide (SiO$_2$) was found to render a surface with relatively few electrically active defects. Electron Paramagnetic Resonance (EPR) studies of the Si (111)/SiO$_2$ interface identified the dominant surface defect, the P$_b$-center, as a silicon dangling bond.$^{35}$ Further EPR studies on the Si (100)/SiO$_2$ interface have identified the presence of two distinct defects, P$_{b0}$ and P$_{b1}$, though the physical significance of these defects has yet to be identified.$^{36}$

Liquid-phase passivation of the silicon surface with concentrated hydrofluoric acid (HF) was first demonstrated by Yablonsitch et al.$^{37}$ Infrared absorption measurements of these surfaces$^{13}$ have shown that the dominant species is Si-H. The stability of this hydrogen-passivated surface has led to the prevalence of ‘HF-last’ cleaning sequences, where immersion in and HF solution is used as the final chemical step prior to gate oxidation or epitaxial layer growth.
Numerous other models were also studied as possible explanations for the observed non-exponential decay curves. Among these are: transient surface recombination modes, trapping/de-trapping modes for bulk defects, and band-bending-induced changes in the surface recombination rate. Brief analyses of each of these models are presented along with abbreviated explanations of their shortcomings. The failure of each of these models emphasizes the importance of injection-level dependence measurements to identify the source of non-exponential carrier decays.

**BACKGROUND**

The kinetics of defect-mediated carrier recombination in semiconductors were originally investigated concurrently by Shockley and Read\textsuperscript{41} and Hall\textsuperscript{42}. The resulting Shockley-Read-Hall (SRH) theory of recombination is based on the following set of assumptions:

- Carrier capture rates are first-order with respect to both the carrier concentration and the availability of defect sites.
- Carrier emission is first-order with respect to the defect occupation and exponentially dependent on the energy required.
- Defects are in quasi-equilibrium with both bands, so that electron and hole capture rates must always balance.

These assumptions define an expression for the carrier lifetime that is a function of the electron and hole capture coefficients, the density of defects, the defect energy level, and the injection-level dependence of the recombination lifetime.
Based on the electron capture cross-section, $\sigma_e$, of $10^{-16}$ cm$^{-2}$ for the P$b$-center, surface coverage by dangling bonds in a 100:1 HF solution has been estimated at 30 part per million$^{38}$. The exact origin of these dangling bonds is not known. They may occur at boundaries between reconstructed 2×1 regions of the Si (100) surface$^{39}$. They may be spontaneously generated for entropic reasons, like Schottky (vacancy) defects in the crystal bulk. Additionally, Wade and Chidsey$^{40}$ have shown that oxygen dissolved in solution scavenges hydrogen from the surface and generates dangling bonds.

Minority carrier lifetime measurements of these surfaces are presented. A bias light is used to change the background carrier concentration and probe the injection-level dependence of the recombination rate. The observed dependence is not consistent with any known models for recombination through a single electronic defect level. A model is presented in which the physical defect contributes two coupled mid-gap states. The presence of two states, and hence two more capture parameters, yields an injection-level dependence that varies much more rapidly than known models for a single state.

The presence of two defect levels defines three physical states of the defect: unoccupied, singly-occupied, and doubly-occupied. By analogy with the P$b$-center, these three states correspond to three states of a dangling bond defect. The doubly-occupied state is an electron source and may be instrumental in native oxide formation as well as electroless plating of metals on the surface. The unoccupied state represents a likely site for fluoride attack and may play a role in the etching of the silicon surface.
Figure 4-1. Rate expressions used in the Shockley-Reed-Hall (SRH) model for recombination via a single defect level.

Figure 4-1 is a representation of recombination in the SRH model. The four processes shown are: (1) electron capture from the conduction band to an empty defect level, (2) electron emission from a filled defect to the conduction band, (3) hole capture by a filled defect level, and (4) hole emission from an empty defect level to the valence band.

Under equilibrium conditions, the principle of detailed balance requires that capture and emission rates are equal for both carriers:

\[ R_1 = R_2 \]
\[ c_e N_0 N_T (1 - f_0) = e_e N_T f_0 \]
\[ e_e = c_e n_0 \frac{(1 - f_0)}{f_0} \]

\[ R_3 = R_4 \]
\[ c_h p_0 N_T f_0 = e_h N_T (1 - f_0) \]
\[ e_h = c_h p_0 \frac{f_0}{(1 - f_0)} \]
The equilibrium occupation, $f_0$, is determined directly from the Fermi level and the defect trap level:

$$f_0 = \frac{1}{1 + \exp\left(\frac{E_F - E_T}{kT}\right)}$$

$$\frac{1 - f_0}{f_0} = \exp\left(\frac{E_F - E_T}{kT}\right)$$

Using the definitions

$$n_1 = n_0 \times \exp\left(\frac{E_F - E_T}{kT}\right)$$

$$p_1 = p_0 \times \exp\left(-\frac{E_F - E_T}{kT}\right)$$

the emission coefficients are written as

$$e_e = c_e n_1$$

$$e_h = c_h p_1$$

The constants $n_1$ and $p_1$, by virtue of their definitions, are the electron and hole concentrations when the Fermi level is equal to the defect energy level. With these definitions, the net recombination rates for each carrier are

$$R_e = R_1 - R_2 = c_e (n N_T (1 - f) - n_1 N_T f)$$

$$R_h = R_3 - R_4 = c_h (p N_T f - p_1 N_T (1 - f))$$

If the defect level occupation changes slowly with time, the rates for electron and hole capture, must be nearly equal. With this constraint, the above expressions determine the steady-state occupation of the defect level:

$$f = \frac{c_e n + c_h p_1}{c_e (n + n_1) + c_h (p + p_1)}$$
Substituting into earlier expressions for the recombination rate, and rewriting $n = n_0 + \Delta n$ and $p = p_0 + \Delta p$, yields

$$R = c_e c_h N_T \frac{(p_0 + n_0 + \Delta n)}{(c_e (n_0 + n_1 + \Delta n) + c_h (p_0 + p_1 + \Delta n))} \Delta n$$

$$= \frac{\Delta n}{\tau_{SRH}}$$

where

$$\tau_{SRH} = \frac{1}{N_T c_e c_h} \frac{c_e (n_0 + n_1 + \Delta n) + c_h (p_0 + p_1 + \Delta n)}{p_0 + n_0 + \Delta n}$$

$$= \frac{\tau_h (n_0 + n_1 + \Delta n) + \tau_e (p_0 + p_1 + \Delta n)}{(p_0 + n_0 + \Delta n)}$$

is the familiar expression for the SRH lifetime. Substitutions have been made for the electron and hole capture rate constants: $\tau_e = (N_T c_e)^{-1}$, $\tau_h = (N_T c_h)^{-1}$. To make the injection-level dependence clear, this expression is re-written as

$$\tau_{SRH} = \frac{[\tau_h (n_0 + n_1) + \tau_e (p_0 + p_1)] + (\tau_h + \tau_e) \Delta n}{(p_0 + n_0 + \Delta n)}$$

$$= \frac{\tau_0 + \tau_1 \left( \frac{\Delta n}{(p_0 + n_0)} \right)}{1 + \Delta n / (p_0 + n_0)}$$

where the values for $\tau_0$ and $\tau_1$ are now the only variables in the lifetime expression.

Thus, while the defect has four characteristics of interest ($N_T$, $c_e$, $c_h$, and $E_T$), the lifetime measurement is capable of determining at most two of these.

Lifetime measurements at low injection levels are widely used to probe the minority carrier properties of defects\textsuperscript{4,5,6,7,8}. At low injection levels, this expression
reduces to the time constant for minority carrier capture. For a mid-gap defect in p-type material, for example, \( n_0 \ll n_I \), \( p_I \ll p_0 \), so that,

\[
\tau_{SRH} = \tau_0 = \frac{\left[ \tau_h (n_0 + n_i) + \tau_e (p_0 + p_i) \right]}{p_0 + n_0} \approx \tau_e.
\]

Physically, this limiting case is understood in terms of the defect-level occupancy. Since holes far out number electrons near equilibrium, the defects will be predominantly empty and electron capture is the rate-limiting step in recombination.

This approximation is valid for \( \Delta n < 0.05 \times p_0 \), a condition which is known as low level injection (LLI). Within this regime, the lifetime is nearly constant, meaning that the carrier decay will be described well by a single exponential. In the SRH theory, the decay shape deviates significantly from the single exponential only when \( \Delta n \sim p_0 \). The observation of non-exponential decays in the LLI regime, therefore, indicates the presence of physical effects that lie outside the bounds of the SRH model.

**RECOMBINATION VIA A TWO-LEVEL DEFECT**

The two-level defect system may be analyzed in much the same was as the SRH approach to a single-level defect. Instead of each defect site being either 'full' or 'empty', though, there are now three possibilities: 0, 1, or 2 electrons localized about the defect center. For all three states to be involved in the recombination process, the singly-occupied species must be capable of capturing either electrons or holes. Since any significant degree of charge would strongly repel one of the carriers, this state must be electrically neutral, and the states may be labeled as follows:
0 electrons $\rightarrow D^+$
1 electron $\rightarrow D^0$
2 electrons $\rightarrow D^-$

\[
\begin{align*}
R_1 &= c^+_e n[D^+] \\
R_2 &= e^+_h [D^+] \\
R_3 &= c^0_e n[D^0] \\
R_4 &= e^0_h [D^0] \\
R_5 &= c^0_h p[D^0] \\
R_6 &= e^0_e [D^0] \\
R_7 &= c^-_h p[D^-] \\
R_8 &= e^-_e [D^-]
\end{align*}
\]

**Figure 4-2.** Transitions possible between charge states of the defect center. Each transition may occur either by capture of a carrier or emission of the opposite type of carrier.

As shown in Figure 4-2, any transition between two states of the defect may occur by either of two processes: capture of one type of carrier or emission of the opposite type of carrier. The transitions $D^+\rightarrow D^0$ and $D^0\rightarrow D^-$ occur through either electron capture from the conduction band or hole emission into the valence band; $D^-\rightarrow D^0$ and $D^0\rightarrow D^+$ occur through hole capture or electron emission.

As was done for the single-level defect, the emission coefficients are expressed in terms of capture coefficients and equilibrium defect level occupations. Figure 4-3
summarizes how emission coefficients can be re-written in terms of a corresponding
capture coefficient and equilibrium values for carrier concentrations and defect level
occupations. To simplify further expressions, four new constants have been introduced:

\[
\begin{align*}
    n_1 &= n_0 \times \frac{[D^+]^eq}{[D^0]^eq} \\
    n_2 &= n_0 \times \frac{[D^0]^eq}{[D^-]^eq} \\
    p_1 &= p_0 \times \frac{[D^0]^eq}{[D^+]^eq} \\
    p_2 &= p_0 \times \frac{[D^-]^eq}{[D^0]^eq}
\end{align*}
\]

As with the single-level defect, the equilibrium concentrations of the defect states can be
calculated directly from the energies of the defect levels. Since the two levels are
coupled (i.e., the second level cannot be occupied unless the first level is already full), the
calculation is slightly more complicated than the earlier case. Defects for which the
lower level is not occupied correspond to the D\(^+\) species. If the fraction of defects in the
D\(^+\), D\(^0\), and D\(^-\) states are denoted as \(f_+\), \(f_0\), and \(f\) (with the implicit constraint that \(f_+ + f_0 + f = 1\)), the occupation of D\(^+\) is

\[
f_+^eq = 1 - \frac{1}{\exp(E_{f_1,E_F}/kT) + 1} = \frac{\exp(E_{f_1,E_F}/kT)}{\exp(E_{f_1,E_F}/kT) + 1}.
\]

By the 'coupling' condition, the second level is occupied only when the first level is full,
so the D\(^-\) defects are exactly those for which the 2\(^{nd}\) level is occupied:

\[
f_-^eq = \frac{1}{\exp(E_{f_2,E_F}/kT) + 1}.
\]

The fraction of neutral D\(^0\) sites is then the remainder of the defects:

\[
f_0^eq = 1 - f_-^eq - f_+^eq = 1 - \frac{1}{\exp(E_{f_1,E_F}/kT) + 1} - \frac{\exp(E_{f_1,E_F}/kT)}{\exp(E_{f_1,E_F}/kT) + 1}.
\]
These expressions are rather cumbersome and do lend themselves to easy simplification, but suffice for the calculation of the constants \( n_1, n_2, p_1, \) and \( p_2. \)

<table>
<thead>
<tr>
<th>Capture term</th>
<th>Emission term</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 = c_e^+ n[D^+] )</td>
<td>( R_6 = e_e^0 [D^0] )</td>
</tr>
<tr>
<td>( R_3 = c_e^0 n[D^0] )</td>
<td>( R_8 = e_e^- [D^-] )</td>
</tr>
<tr>
<td>( R_5 = c_h^0 p[D^0] )</td>
<td>( R_2 = e_h^+ [D^+] )</td>
</tr>
<tr>
<td>( R_7 = c_h^- p[D^-] )</td>
<td>( R_4 = e_h^0 [D^0] )</td>
</tr>
</tbody>
</table>

Figure 4-3. Calculation of emission coefficients based on the principle of detailed balance. The values \( n_1, n_2, p_1, \) and \( p_2 \) are all defined from the equilibrium occupation of the defect levels.

In the single-level model, the condition of steady-state recombination (i.e., that the defect state did not charge up) placed a constraint on \( f \), the occupation of the defect level.

Equivalently, this condition represents a balance between occupied and unoccupied sites, such that the net capture rate of electrons by unoccupied defects is equal to the net capture rate of holes by occupied sites. For a defect with three states, this ‘steady-state’ condition imposes two parallel constraints on the relative concentrations of each defect charge state: equilibrium between \( D^+ \) and \( D^0 \), and equilibrium between \( D^0 \) and \( D^- \).

The \( D^+ \) and \( D^0 \) equilibrium requires that
\[ R_1 + R_2 = R_3 + R_4 \\
\]
\[ c^+_e n[D^+] + e^+_h[D^+] = c^+_e p[D^0] + e^+_e[D^0] \]
\[ (c^+_e n + c^+_h p_1)[D^+] = (c^+_e p + c^+_e n_1)[D^0] \]
\[ r_+ = \frac{[D^+]}{[D^0]} = \frac{c^+_e p + c^+_e n_1}{c^+_e n + c^+_h p_1} \]

Similarly, the equilibrium between \( D^0 \) and \( D^- \) requires

\[ R_3 + R_4 = R_7 + R_8 \]
\[ c^-_e n[D^0] + e^-_h[D^0] = c^-_e p[D^-] + e^-_e[D^-] \]
\[ (c^-_e n + c^-_h p_2)[D^0] = (c^-_e p + c^-_e n_2)[D^-] \]
\[ r_- = \frac{[D^-]}{[D^0]} = \frac{c^-_e n + c^-_h p_2}{c^-_e p + c^-_e n_2} \]

These two conditions wholly determine the concentration of each defect species as a function of the carrier concentrations.

The decay of excess carriers is made up of four terms (capture and emission terms for each of the defect levels):

\[ \frac{dn}{dt} = -c^+_e n[D^+] + c^+_e n_1[D^0] - c^-_e n[D^0] + c^-_e n_2[D^-] \]
\[ = -[D^0]\left(c^+_e (r_+ n - n_1) + c^-_e (n - r_+ n_2)\right) \]

Each defect site is in one of the three states, \( D^- + D^0 + D^+ = N_R \), so \( D^0 \) can be written in terms of \( r_+ \) and \( r_- \), yielding the rate expression:

\[ \frac{dn}{dt} = -\frac{N_R}{r_- + 1 + r_+} \left(c^+_e (r_+ n - n_1) + c^-_e (n - r_+ n_2)\right) \]

From this rate equation for carrier recombination (see Appendix A), we see that the lifetime has the general form

\[ \tau(\Delta n) = -\frac{\Delta n}{\frac{dn}{dt}} = \tau_0 \left(\frac{1 + \tau_{n1} \Delta n + \tau_{n2} \Delta n^2}{(1 + \tau_d \Delta n)\left(1 + \frac{\Delta n}{(p_0 + n_0)}\right)}\right) \]
so that there are now 4 adjustable parameters ($\tau_0$, $\tau_{nl}$, $\tau_{n2}$, and $\tau_d$) in the expression for the lifetime.

Figure 4-4 demonstrates how such an injection-level dependence differs distinctly from the single-level defect. All curves shown are constrained to have the same low-level injection lifetime of 1ms. The three curves for single-level defects have different values for the high-injection lifetime, but all are very similar in that they change most rapidly when the injection level nears the doping level. The curve for the two-level defect shows very different behavior. The lifetime changes significantly for relative injection levels as low as 1%.

![Figure 4-4](image)

Figure 4-4. Comparison of injection level dependence of the carrier lifetime. The curves all have the same low-level injection lifetime of 1ms. All the curves corresponding to single-level defects change most rapidly for $\eta=1$, while the only the two-level defect varies significantly for $\eta\sim0.01$. 
The unique behavior for the two-level defect alters lifetime measurements in two ways: the shape of the individual decay curves and the physical meaning of the lifetime. Even if the injection level for the lifetime measurement is about 1% of the doping level, the recombination lifetime may change during the decay. This change leads to decay shapes that differ from the ideal single exponential.

Since the carrier decay does not obey a single exponential, any calculated value for the ‘lifetime’ depends on which region of the decay is used. Therefore, no one region of a single decay curve can be used to extract a true minority carrier lifetime. Only the asymptotic value for an infinitesimally small injection level has physical meaning. Accurate measurement and identification of the defect center, as we will show, is only accomplished with injection-level dependent lifetime measurements.

In spite of these complications, there are still conditions under which single lifetime measurements may be used with two-level defects. Since the decay rate is still directly proportional to the density of defect centers, a simple single exponential fit is still appropriate as a relative measure of defect density. For example, if two samples have the same dominant defect, then the ratio of the single-exponential ‘lifetimes’ is given by the ratio of the defect densities (assuming that both decay curves have been fit over the same amplitude range). Time-dependent lifetime measurements (for in-situ monitoring or other kinetic studies) are therefore still possible, as long as the injection level is fixed and the background carrier concentration does not change.
LIFETIME MEASUREMENTS FOR DILUTE HF-PASSIVATED Si (100)

Lifetime measurements on silicon (100) wafers immersed in hydrofluoric acid (HF) solutions have been made using RF-PCD. Samples for this study were cut from a 200 mm, p-type silicon wafer with a resistivity of 10 Ω-cm. The standard MIT cleaning process was performed prior to immersion into a 100:1 HF solution. A quartz halogen lamp was used as a bias source to change the background carrier concentration.

Quantification of the injection-level has been performed by two methods. A unity-gain photocell was used to provide a direct measure of the incident photon flux. Additionally, the amplitude of the decay curve is used as an indicator of the background carrier concentration. Since the instrument itself measures a fractional change in the wafer conductivity, the amplitude of the decay curve changes even though the injection pulse is kept constant. As the background carrier concentration is increased, the effect of the injection pulse is less pronounced, and the amplitude of the decay curve decreases. The 30% change in the amplitude thus corresponds to a roughly 7% change in the background carrier concentration (after accounting for the mobility difference between electrons and holes).

Figure 4-5 shows a series of lifetime measurements performed on one p-type silicon sample. The unbiased decay curve is clearly not a single exponential. The data can be fit well by a two exponential decay where the 'slow' component has a lifetime roughly 4 times larger than the 'fast' component. With the application of the bias light, the curves tend toward a single exponential decay that is comparable in rate to the
original 'fast' component. This observation points toward an injection-level dependent lifetime in which the lifetime decreases for higher injection level.

The two-level model discussed earlier is capable of producing such a dependence. In a p-type wafer at equilibrium, defects are predominantly in the D⁺ state. Recombination for low levels of injection will occur predominantly between D₀ and D⁺ states. As the injection level increases, the fraction of D₀ and D⁺ defects will increase, so that transitions between these two states become more likely. If these transitions are much faster than the D₀/D⁺ transitions, the overall recombination rate will be faster at these higher injection levels.
Figure 4-5. Excess carrier decay curves for a p-type silicon (100) wafer immersed in a 100:1 aqueous solution of HF. The background carrier concentration is changed using a quartz lamp as a bias source. The lifetime decreases dramatically even though the maximum bias level is only ≈5% of the doping level.

Since the decay shape defined by the two-level defect model does not have a closed form solution, fitting of this data could only be accomplished using a decay simulator. Such a simulator was written in C++ to produce a series of decay curves from the following set of parameters:

- Amp – Amplitude of the unbiased decay curve. (Amplitudes for biased decays are determined by how much the illumination changes the background wafer conductivity.)
- \( N_T \) – Density of defects sites.
- \( c_e^+, c_e^0, c_h^0, c_h^- \) – coefficients for carrier capture
- $E_{t1}, E_{t2}$ - energy levels for the defect

Of these eight parameters, seven (all except the decay amplitude) are characteristics of the defect centers. From the expression derived earlier for the injection-dependence of the lifetime, we know that the recombination lifetime alone can determine at most 4 of these uniquely. For the purposes of this study, the capture cross-sections were deemed to be of the most interest, and reasonable values for $N_T$, $E_{t1}$, and $E_{t2}$ were choosen. To keep the average capture cross-section near $10^{-16}\, \text{cm}^2$ (the value previously reported for P$_b$-centers at the Si/SiO$_2$ interface$^{43}$), $N_T$ was chosen to be $10^{10}\, \text{cm}^{-2}$. The energy levels were arbitrarily chosen to both be near mid-gap at values of 0.4 eV and 0.6 eV above the valence band.

The remaining 5 parameters were allowed to vary. A 'method of steepest ascent'-type approach was used to find the parameter set that minimized the total sum of squares deviation for the entire data set. The results of this fitting process are shown in Figure 4-8. These fits show very good agreement with data for all decay curves in the data set.
Figure 4-6. Decay curves for the dilute HF-passivated wafer overlaid with fitting results from the two-level defect simulator. All the decay curves were fit simultaneously with one parameter set. Since the injection-level dependent lifetime has only 4 degrees of freedom, the density of defect sites and values for the energy levels were fixed, while the 4 capture parameters were all allowed to vary.

The capture cross-sections calculated by this fitting procedure are summarized in Figure 4-8. These calculated values are in general agreement with the earlier hypothesis that recombination through the 2nd level must be much faster than recombination through the 1st. The only unsettling result of this fitting process is the relative sizes of $\sigma_e^1$ and $\sigma_e^2$. Since $\sigma_e^1$ represents capture of electrons by a positively-charged defect, we would expect it to be large compared with $\sigma_e^2$, the capture coefficient for electrons at a neutral site. The calculated values, though, indicate that $\sigma_e^2$ is more than 40× larger than $\sigma_e^1$. This calculated disparity may result from the arbitrary choices for the defect energy levels. Measurements on n-type wafers should elucidate this issue, assuming that the defects formed on n-type are the same as those observed on p-type.
\[ \sigma_e^1 = 3.0 \times 10^{-17} \text{ cm}^2 \]
\[ \sigma_h^1 = 1.3 \times 10^{-17} \text{ cm}^2 \]
\[ \sigma_e^2 = 1.4 \times 10^{-15} \text{ cm}^2 \]
\[ \sigma_h^2 = 4.8 \times 10^{-15} \text{ cm}^2 \]

**Figure 4-7.** Capture cross-sections calculated for p-type silicon (100) passivated with dilute HF. The surface defect density was fixed at $10^{10} \text{ cm}^{-2}$ so that the geometric mean of the cross-sections would lie near $10^{-16} \text{ cm}^2$, the value reported for $P_b$ centers at the Si/SiO$_2$ interface.

**OTHER ATTEMPTED MODELS**

Prior to the formulation of this theory for recombination via two defect levels, many other models were considered as possible explanations for our experimental observations. Transient modes arising from transport of carriers to the wafer surface have been shown to produce decay curves that have two exponential components$^{44}$. Capture and emission of minority carriers from temporary trap sites are known to produce non-exponential decays$^{45}$. A band-bending potential at the wafer surface, resulting from an accumulation of surface charge, also alters the recombination rate$^{76,46}$. Each of these models has been carefully examined and none is capable of fully explaining the measurements shown for HF-passivated surfaces.
Surface Diffusion Transients

In the surface transient model, the measured lifetime changes during the carrier decay because of the presence of higher order decay modes. Immediately after the injection pulse, there is a relatively large concentration of carriers near the surface. These near-surface carriers recombine rapidly and produce an initial steep region of the decay curve. As the surface concentration drops, recombination slows until it reaches a rate that represents a balance between diffusion of carriers to the surface and recombination of those carriers.

As discussed under the 'Experimental' section, each of the these higher modes has a time constant that is below the 'transit time' for carriers to diffuse to the surface. For the p-type wafers used in this study, this lifetime is roughly 16 μs. The decay curves obtained under room-lighting conditions are well fit by a sum of two exponentials, but the values obtained from such a fitting are $\tau_1=2.6\text{ms}$ and $\tau_2=700\mu\text{s}$. The 'steeper' part of the decay is, thus, well over one order of magnitude slower than is required by the surface transient model. In addition to this failure, the surface transient model is also in capable of explaining the strong change in lifetime that we have observed with the introduction of the bias light. With the addition of background carriers, the transient effects of a changing carrier distribution should become less pronounced, while the data indicates that this initial mode appears to become dominant for higher injection levels.
Capture and Emission from Trap Sites

The presence of 'temporary traps' is another common interpretation for the observation of non-exponential decays. In this model, there are two types of mid-gap states: recombination centers, which have a reasonable probability for capturing either carrier type, and trap sites, which will capture minority carriers but have only a negligible capture cross-section for majority carriers. The presence of these two centers results in carrier decays that have two physically distinct regions.

![Diagram of carrier decay](image)

Figure 4-8. Schematic of the two regimes of carrier decay for temporary traps in p-type silicon. The traps will capture minority carriers (electrons, in this case) immediately following carrier injection, but will re-emit those carriers as the system nears equilibrium.

For the case of p-type material, the trap sites capture and re-emit electrons from the conduction band. Under equilibrium conditions, these traps will be mostly empty (assuming that they are not positioned very near to the valence band). Immediately after the carrier injection pulse, the traps will capture electrons rapidly. This capture rate drops gradually for two reasons: (1) filling of trap sites and (2) drop in the electron concentration due to recombination. As the capture rate drops, electron re-emission
becomes the dominant process. The traps then continue to emit electrons until equilibrium is reached.

With the presence of these two regimes, the carrier decays will look roughly like the sum of two exponentials. At short times, the measured decay constant is determined by capture at recombination sites and capture at traps. At longer times, the decay curve is a combination of electron emission from traps and capture at recombination centers.

There temporary traps can be identified through the use of a bias light source. In p-type material, the presence of even a small amount of background electrons will ensure that the electron traps are occupied at all stages of the lifetime measurement. Since they are neither capturing nor emitting electrons, they will have no impact on the carrier decay curves. The curves taken in the presence of bias light, therefore, consist only of a single exponential mode with a decay constant equal to the recombination lifetime. In these basic respects, the data as shown is consistent with a trapping/de-trapping model.

The amplitude of the second exponential term is a measure of the density of trap states. For the data shown, this amplitude is one half of the amplitude of the entire decay. For an injection level of $2 \times 10^{14}$ cm$^{-3}$, this amplitude corresponds to a trap density of $10^{14}$ cm$^{-3}$ in the bulk (or, equivalently, $3.75 \times 10^{12}$ cm$^{-2}$ on the surface). At this concentration, the filling of traps states constitutes a large fraction of the initial carrier decay rate. So, if these traps states are indeed filled by the presence of a bias light, the initial decay rate should be much slower than the unbiased case. The data clearly shows, though, the initial portion of the decay is actually somewhat faster when the bias light is used. For this reason, the observed non-linearities are not explained by the presence of temporary trap states.
Surface Band-bending

Bending of energy bands near the wafer surface, due to the presence of surface charge, has been shown elsewhere\textsuperscript{46} to modify the kinetics of surface recombination. In the case of low surface recombination velocity, where diffusion of carriers to the surface does not limit the recombination rate, the band-bending alters the recombination rate by changing the concentration of carriers at the surface. An attractive surface potential will increase the surface carrier concentration and hence increase the rate of surface recombination. A repulsive potential will drive carriers away from the surface and slow the recombination rate.

From the unbiased decay curve, the recombination rate is fastest immediately after the injection pulse. In terms of a band-bending model, this feature implies that even a relatively small injection level ($\sim 2\times10^{14}\text{cm}^{-3}$) will generate a surface potential that is attractive to minority carriers. At this level of injection, the majority carrier concentration is not changing significantly, so excess minority carriers alone must generate a potential that attracts further minority carriers to the surface. Without any viable explanation of how this may occur, the observations cannot be attributed to the presence of a band-bending surface potential.

**Physical Significance**

The precise nature of the defects on the H-passivated surface are not known. In analogy with P$_b$-centers observed at the Si-SiO$_2$ interface, it is assumed that these defects
are dangling bonds. Figure 4-9 represents the three physical states for this defect. As was stated in establishing the model, the unoccupied defect state would have a net charge of \( +q \). Simply on electrostatic grounds, this site should be very attractive for dissociated \( F^- \) ions in solution. Further measurements could establish whether or not these defect states are correlated with the rate of silicon etching.

![Diagram of possible physical states](image)

**Figure 4-9.** Possible physical states corresponding to the three electronic states of the surface defect. The unoccupied dangling bond states (left) would be most susceptible to \( F^- \) attack and may be an activated state in the etching of silicon.

The doubly-occupied state, similarly, will serve as a source for electrons. In the process of native oxidation, electrons are transferred from the silicon surface to an adsorbed \( O_2 \) molecule. The density of doubly-occupied sites may therefore be the limiting species in the degradation of the Si-H passivation. Metal deposition is another reduction reaction that is known to occur at the silicon surface. Illumination levels and wafer doping type have already been shown to influence the rate of metal deposition. Electron donation from a doubly-occupied dangling bond may prove to be physical mechanism by which electrons are transferred from the silicon substrate to the metal ion in solution.
CONCLUSIONS

Based on the fundamental framework for defect-assisted recombination laid down by Shockley, Read, and Hall, a modeled had been developed for carrier recombination in a two-level defect system. This analysis shows that the two-level lifetime may change significantly within the regime of low-level injection, where the lifetime of a single-level defect is nearly constant. Because of this injection level dependence, carrier decay curves will not obey a single exponential shape and the calculated lifetime will depend on which region of the decay curve is used for the fitting. The observed decay curves will also change with time if the background carrier concentration is not kept constant.

Experimental measurements show that silicon (100) wafers immersed in dilute HF solutions are an example of a two-level defect system. Decay curves obtained without background light deviate greatly from a single exponential. Measurements taken under low levels of bias illumination show that the lifetime changes noticeably for injection levels well below the doping level. By using a decay simulator and assuming values for the defect density and energy levels, values have been extracted for all 4 carrier capture coefficients.

Other well-known models have been tested as possible explanations for the observed behavior. Transient surface decays require initial lifetimes that are an order of magnitude below what is observed. Trapping and de-trapping effects are also not adequate for describing the initial regions of the decays. Finally, a surface band-bending model was found to require the existence of an improbable surface potential. With the failure of each of these models, the two-level defect is the simplest explanation to describe the HF-passivated silicon (100) system.
CHAPTER 5 – CONTAMINATION FROM SURFACE REACTIONS

INTRODUCTION

The deposition of metal ions onto silicon surfaces has received much attention since the advent of HF-last wafer cleaning sequences. The thermodynamics driving electron transfer between silicon and ionic species was first established by Morrison. Further understanding of the thermodynamics metal precipitate formation, including the roles of wafer doping and illumination, has been advanced by Norga et al. and Oskam et al. From their work, it is known that precipitates on n-type silicon are smaller but more numerous, while those on p-type tend to be few and large.

Due to the difficulty in measuring small levels of surface species, most kinetic studies of metal deposition use levels of contamination far in excess of industry standards. Many published studies use levels of Cu in excess of 10 ppb. At this level, metal deposition is the dominant cathodic reaction, and the corrosion potential at the wafer surface is determined by balancing this reaction with the rate of silicon etching. When the metal is truly in the trace regime, below 100 ppt, hydrogen evolution dominates the cathodic current. The resulting potential is then a result of the intrinsic reactions at the silicon surface. In this regime, metal deposition is driven by changes in this surface chemistry.

In-situ metal deposition measurements are made in this work using RF-PCD. With a sensitivity for surface metals of $10^8 \text{cm}^{-2}$, this device provides a unique opportunity to study the kinetics of metal deposition in the sub-ppb range. Measurements are
performed to determine the role of HF concentration in the metal deposition rate. The results show a 17.5× enhancement in the deposition rate in moving from a 100:1 to a 500:1 solution. These results are discussed in terms of the rate equations for electron transfer reactions and the shift in the surface potential due to HF dilution. Generalization of these results leads to a semi-empirical expression for Cu purity constraints in dilute HF solutions. Similar expressions for other metals may be determined by measurement of the required transfer coefficient, $\alpha$.

**Dilute HF Cleaning**

In the semiconductor industry, wafer cleaning processes are rapidly incorporating the use of dilute chemistries. Hydrofluoric acid has commonly been used in a 50:1 or 100:1 dilution, but even solutions of 500:1 or 1000:1 are now being introduced in the fab line. Moving to these new processes simultaneously satisfies two goals: reduced chemical consumption and increased process control.

As device dimensions continue to shrink, the tolerances on each fabrication step also become smaller. For wet chemical oxide removal, etch rates need to be carefully controlled to guarantee complete oxide removal on the source and drain regions without under-cutting the gate. For wet chemical systems, the time to immerse the wafers in the bath introduces some device-to-device variation in effective etching time. Using dilute chemistries reduces the resulting variation in oxide removal.

These new chemistries will continue to be used only if they can produce surfaces that meet the requirements for particle, organic, and metal contaminants specified by the
Semiconductor Industry Association's National Technology Roadmap for Semiconductors².

EXPERIMENTAL

Metal deposition rates are measured by the minority carrier lifetime technique, RF-PCD. HF from a 20 liter tank is pumped through a PFA flowcell, where it flows across the surface of a 1"×1" piece of silicon. Any reducible metals present in the HF will deposit on the surface of this wafer and create electrically active defect sites. These metal adsorbates are then detected through their influence on the minority carrier lifetime, which is measured by RF-PCD. The time constant for the decay of these excess carriers provides information about the density of surface defects on the monitor wafer.

To calibrate this measurement, silicon wafers have been analyzed with Total-reflection X-Ray Fluorescence (TXRF) to provide and independent measure of the surface metal coverage. This calibration has shown that in the regime of low surface coverage there is a direct correspondence between the concentration of metal adsorbates and the measured lifetime⁷⁶. To use this technique for measuring metal deposition rates, small changes in the lifetime of the silicon monitor wafer are observed as a function of time. In a system with flowing HF, the static boundary layer near the wafer surface leads to both transient and steady-state behaviors⁵³. Care was taken to insure that all the data used in this study was taken in the steady-state regime.

The concentration of metals in the HF bath is controlled by adding precisely measured quantities of an Atomic Absorption Spectroscopy standard (Alfa Aesar Spectrapure™, 10,005 μg/ml in 3% HNO₃) directly to the 20 liter HF bath. To achieve a
single ppt metal background, the HF bath is processed through an ion-exchange purifier, 
provided by Millipore Corporation.

Silicon pieces used for these experiments were cut from 8-inch n-type wafers 
(\(\rho=10-40\Omega\cdot\text{cm}\)) provided by Mitsubishi Silicon America. The pieces are cleaned for 2 
min. in 100:1 HF, 4 min. in a 4:1 \(\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2\) solution at 90°C, 2 min. DI water rinse, 
and a final 5 min. immersion in another dilute HF bath. Ashland Gigabit chemicals and 
18 M\(\Omega\)-cm DI water are used for all cleaning steps to produce contamination-free 
surfaces. The 20 liter tank and all PFA tubing used in the circulating system are soaked 
in a 5% H\(\text{NO}_3\) solution prior to measurements to dissolve adsorbed metals.

**Dependence of Cu deposition on HF concentration**

The results of deposition rate measurements for 100:1 and 500:1 solutions of HF 
are shown in Figure 5-1. Both sets of data show a strong linear correlation between the 
deposition rate and the concentration of metal in solution, indicating that the Cu reduction 
reaction:

\[
\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0
\]  
(1)
Figure 5-1. Cu deposition rates from 100:1 and 500:1 HF solutions. The deposition rate is calculated as the rate of change of the surface coverage. The strong linear correlation between deposition rate and Cu concentration is consistent with our model of first order reaction kinetics.

is first-order with respect to [Cu] at this low contamination level. The deposition rates for the 500:1 solution, though, are roughly 17.5 times larger than the values for 100:1 HF. To understand how Cu deposition is affected by dilution of the HF, all the reactions occurring at the wafer surface need to be considered. It is widely agreed\textsuperscript{54,55,56} that the dominant anodic reaction is silicon oxidation and dissolution:

\[ Si + 6F^- \rightarrow SiF_6^{2-} + 4e^- \]  \hspace{1cm} (2)

When Cu is present in solution, there are two competing cathodic reactions: the Cu reduction reaction shown above, as well as hydrogen evolution

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (3)
Figure 5-2 shows how the redox levels of each of these half-reactions compares to the energy bands of an n-type silicon wafer. The Cu$^{2+}$ and H$^-$ have reduction potentials that lie below the Fermi level and will thus accept electrons from the silicon wafer. Silicon, on the other hand, has an oxidation potential which lies above E$_F$, and will therefore donate its electrons and form the SiF$_6^{2-}$ species.

![Diagram of redox levels and energy bands](image)

**Figure 5-2.** Band diagram for n-type silicon and redox levels for electrochemical surface reactions, referred to the same vacuum scale. The positions of the redox levels show that electron transfer required for silicon dissolution, hydrogen evolution, and Cu reduction can all be mediated by the Fermi level.

Schematically, this system may be represented with the circuit diagram shown in Figure 5-3. The oxidation and dissolution of the silicon acts as a source of electrons. These electrons can be consumed by two parallel pathways: hydrogen evolution or Cu reduction. If the hydrogen evolution reaction becomes less favorable due to reduction of [H$^+$], electrons will be more likely to follow the Cu reduction pathway.
Figure 5-3. Circuit schematic for metal deposition from dilute HF. The reduction in H₂ evolution with chemical dilution results in a higher Cu deposition current.

The role of pH in the rate of Cu reduction is determined quantitatively by analyzing the kinetics of each surface reaction. All of the reactions in this system can be thought of as irreversible, since the concentration of each reaction product is negligible compared to the reactants. All the back reactions can then be neglected, and the currents associated with each reaction can be written as a function of E, the potential on the silicon:

\[ j_{si} = j_{0si} \exp(n_{si}(1 - \alpha_{si})(E - E_1)/\phi) \]  \hspace{1cm} (4)

\[ j_H = j_{0H} \exp(-n_H\alpha_H(E - E_2)/\phi) \]  \hspace{1cm} (5)

\[ j_{Cu} = j_{0Cu} \exp(-n_{Cu}\alpha_{Cu}(E - E_3)/\phi) \]  \hspace{1cm} (6)

where \( \phi \) is the thermal potential (equal to \( k_B T/e \)) and \( j_{0x}, n_x, \alpha_x \), and \( E_x \) for each half-reaction are the exchange current, number of electrons transferred in the rate determining step, cathodic transfer coefficient, and equilibrium potential. An exchange current, \( j_0 \),
can be thought of as an ‘attempt frequency’ that contains information about the collision rate of the reactant species. The transfer coefficient, $\alpha$, depends on the shape of the potential energy barrier between reactants and products and can vary between 0 and 1. The form of $j_0$ and the value for $n$ are dependent on the rate-determining step of the reaction mechanism. Hydrogen evolution is known to occur by reaction of two hydrogen radicals$^{56}$, so that the reaction is second order with respect to both $[H^+]$ and electron transfer:

$$j_{OH} = [H^+]^2 k_H ; \ n_H = 2$$  \(7\)

The silicon oxidation reaction is much more complex. While the net reaction commonly agreed to be the one given in equation 2, there is some uncertainty on the rate-limiting step. Since the Si-F bond is very polar, any surface silicon atom with one bond to a fluorine atom will have weak backbonds and will be more susceptible to further etching$^{58}$. It is likely, then, that replacement of one surface hydrogen atom by fluorine is the rate-limiting step and hence, the reaction is first order with respect to $[F^-]$ and dependent on the transfer of one electron:

$$j_{0Si} = [F^-] k_{Si} ; \ n_{Si} = 1$$  \(8\)

These assumptions, determine how dilution changes the potential at the surface and, hence, the Cu deposition rate. Figure 5-4 shows schematically how these dependencies cause the rest potential to shift to more cathodic values. Under steady-state conditions, the silicon wafer is not accumulating charge and must reach a rest potential, $E_r$, where the anodic and cathodic currents are equal in magnitude. In diluting the HF bath from 100:1 down to 500:1, the hydrogen-evolution current is reduced by a factor of 25, while silicon dissolution drops by only a factor of 5. Under these conditions, the potential must
become more cathodic to reach steady-state. The shift in the potential is determined by equating \( j_{Si} = j_H \) and substituting the expressions in equations 4, 5, 7 and 8:

\[
[F^-] k_{Si} e^{\frac{n_{Si}(1-\alpha_{Si})(E_r-E_1)}{\phi}} = [H^+]^2 k_H e^{\frac{-n_{H}\alpha_{H}(E_r-E_2)}{\phi}}
\]  

(9)

Since \([F^-] = [H^+]\) for HF solutions near the concentrations of interest, this expression allows us to write \( E_r \) directly as a function of \([H^+]\)

\[
E_r = \frac{n_{Si}(1-\alpha_{Si})E_1 + n_{H}\alpha_{H}E_2 + \phi(ln\left(\frac{\alpha_{Si}}{k_H}\right) + ln([H^+]))}{n_{Si}(1-\alpha_{Si}) + n_{H}\alpha_{H}}
\]

(10)

Substituting this value for \( E \) in equation 6 provides an expression for \( j_{Cu} \) in terms of \([H^+]\).

Only the last term in the numerator has a dependence on \([H^+]\), so the resulting \( Cu \) deposition current, \( j_{Cu} \), depends on \([H^+]\) according to:

\[
j_{Cu} = j_{1Cu} [H^+] \frac{n_{Cu}\alpha_{Cu}}{n_{Si}(1-\alpha_{Si}) + n_{H}\alpha_{H}}
\]

(11)

where the prefactor \( j_{1Cu} \) is independent of \([H^+]\). Bertagna et al.\(^{54}\) have estimated values of \( n_{Si}(1-\alpha_{Si}) = 0.12 \) and \( n_{H}\alpha_{H} = 0.35 \).
Figure 5-4. Schematic Tafel plot showing anodic and cathodic currents during silicon etching in 100:1 and 500:1 HF solutions. The rest potential, $E_r$, for each solution is determined by the intersection of the two currents. The second-order dependence of $j_H$ on $[H^+]$ causes this potential to shift to a higher (more cathodic) value.

The experimental data shows a 17.5 times increase in deposition rate with a 5 times change in the HF concentration. For the power law dependence shown above to explain this increase, the exponent of $[H^+]$ must be 1.78. Using the values above and $n_{Cu}=2$, the value for $\alpha_{Cu}$ of 0.42 is determined. This value falls well within the range of reasonable values for a transfer coefficient.

This numerical analysis shows that this electrochemical model is consistent with the observed dependence of Cu deposition rate on HF concentration. Since the hydrogen evolution reaction is second order with respect to $H^+$, while silicon etching is only first
order with respect to \( F \), diluting the HF causes the potential at the silicon surface to shift to more cathodic values. This change in the potential increases the rate of the Cu deposition reaction. Based on this model, and the observation that the deposition rate is first order with respect to [Cu], the following formula for the deposition rate of Cu from a D:1 solution of (DI water) : (49% HF) is established:

\[
F_{Cu} = 0.55[\text{Cu}]D^{1.78}
\]  

(12)

where \( F_{Cu} \) has the units of atoms/(cm\(^2\cdot\text{s})\) and Cu is given in parts per trillion.

Equation 12 provides a quantitative evaluation of the trade-off between chemical consumption and bath purity. For new, more dilute HF cleans to prevent metal contamination as effectively as current recipes, the level of metal contamination in the bath must scale with \( D^{1.78} \). To maintain this higher level of purity without decreasing bath lifetime, processes may need to be modified to prevent build-up of contaminants in the bath. Reduction of bath-to-bath cross-contamination and point-of-use recycling are two potential solutions.

**CONCLUSIONS**

Metal contamination in cleaning baths is of great importance for manufacturers of state of the art electronic devices. Decreasing device dimensions and increasing process complexity tighten constraints on the allowable levels of surface metal contamination. Other processing trends, such as the use of increasingly dilute chemistries, place added importance on controlling metallic contamination in cleaning baths.
Measurements are presented showing that Cu deposition from a 500:1 bath of HF proceeds 17.5 times faster than deposition from 100:1 HF. This observation is explained as a change in the rest potential at the wafer surface due to reduced rates of hydrogen evolution and silicon dissolution. Based on this theory, the cathodic transfer coefficient $\alpha=0.42$ for the Cu reduction reaction is calculated. These results establish a semi-empirical relationship between the Cu deposition rate and the dilution ratio, $D$, of the bath. This relation predicts that bath purity must scale with $D^{1.78}$ to prevent increased metal contamination of process wafers.

While the results shown are for Cu deposition, this model is equally applicable to the deposition of other metals. Depending on the their respective cathodic transfer coefficients, they may or may not exhibit a similarly strong dependence on the concentration of the HF bath. Techniques to control bath purity will be required for more dilute chemistries to further reduce the Cost of Ownership.
CHAPTER 6 – CONTAMINATION FROM BULK CHEMICAL REACTIONS

Metal contamination has long been a concern in the processing of silicon devices. Metal-induced defect levels in the wafer bulk are known increase junction leakage. Surface metals present during gate oxidation have been shown to form precipitates at the Si-SiO₂ interface and degrade Gate Oxide Integrity (GOI). Metals also commonly decorate dislocations and lead to junction shorting. All these effects have driven interest in ultrapure chemicals to prevent metal contamination during wet processing.

The solubility of a metal in a cleaning solution is a key metric for predicting the tendency for that metal to deposit on the wafer surface. Previous attempts to calculate metal solubilities in RCA cleans⁵⁹,⁶⁰ have focused on the impact of pH on the tendency toward metal deposition. With a Pourbaix-based thermodynamic approach, the roles of not only pH, but also oxidizing strength, complexing agents, and the oxidized silicon substrate can simultaneously be studied. Many of these issues have previously been addressed on a qualitative level⁶¹,⁶². This work expands on their multidimensional approach to produce quantitative analysis of metal solubilities in these oxidizing solutions.

POURBAIX DIAGRAMS FOR METAL CORROSION

The use of E-pH diagrams to study corrosion of metals in aqueous solutions was pioneered by Marcel Pourbaix⁶³ in the 1940’s. In these diagrams, the most stable metal
species is mapped as a function of the oxidizing strength (E) and alkalinity (pH) of the aqueous environment. For the purposes of corrosion prediction, regions of solid phase stability correspond to a passivated surface. While the surface region of the metal will react to form this stable second phase, the underlying metal will remain intact. When an aqueous species is most stable, though, the metal is subjected to constant attack from the surrounding solution and gradually dissolves.

For the purposes of wafer cleaning, these diagrams have very different interpretations. When a metal is highly soluble in the surrounding aqueous environment, it will not deposit on the surface of a silicon wafer. Thus, the areas on the diagram which are designated by aqueous species represent chemistries that will prevent metal contamination. Conversely, if a solid is the most stable species, metal ions present in solutions have a driving force to precipitate. Since the silicon surface is a site for heterogeneous nucleation, these chemistries will result in contamination of the wafer.

Figure 6-1 shows the Pourbaix diagram for the Fe-H\textsubscript{2}O system. The three sets of boundary lines correspond to solutions which have 10\textsuperscript{0}, 10\textsuperscript{-3}, and 10\textsuperscript{-6} molar concentrations of Fe. Under conditions of high pH (basic solutions), the solid Fe\textsubscript{2}O\textsubscript{3} is the most stable phase. Qualitatively, the stability of this phase explains why Fe contamination is so common from the SC-1 clean, which has a pH of about 10. For very acidic solutions, the aqueous species Fe\textsuperscript{2+} and Fe\textsuperscript{3+} dominate, thus explaining why the acidic SC-2 clean is so effective at removing Fe contamination.
Figure 6-1. Pourbaix diagram for the Fe-H₂O system showing phase boundaries for 10⁶, 10⁻³, and 10⁻⁶ molar solutions of Fe. In corrosion science, the regions of solid phase stability indicate passivation of the metal surface. For our application, these regions correspond to contamination of the silicon surface.

Figure 6-2 shows the Pourbaix diagram of the Cu-H₂O system. The behavior on the acidic end of the map is in general agreement with the Fe diagram, where the presence of the aqueous species indicates high solubility in acidic solutions. For high pH's, though, the Cu system exhibits a soluble hydroxide. The presence of this hydroxide species greatly increases the solubility of Cu in basic solutions and explains why Cu is generally not a problematic contaminant from the basic SC-1 clean.
Figure 6-2. Pourbaix diagram for the Cu-H₂O system with phase boundaries for solutions of 10⁰, 10⁻³, and 10⁻⁶ molar Cu. Unlike the Fe-H₂O system, Cu exhibits a soluble hydroxide that increases the Cu solubility in basic solutions.

QUANTITATIVE SOLUBILITY CALCULATIONS

The approach for quantifying metal solubilities in cleaning baths is summarized in Figure 6-3. Since equilibrium between a solid and a solution necessarily involves equilibria with all possible aqueous species, one ion is arbitrarily chosen as the ‘reference ion’. The solubility of this one ion is calculated by considering formation reactions for all possible solid phases. The aqueous-aqueous equilibria are then used to determine the concentrations of other aqueous species for the saturated solution. The sum of all these dissolved forms of the ion represents the total metallic solubility.
Equilibrate each solid with reference ion  
Reference ion solubility is minimum of individual solubilities  
Pick E, pH, T  
Equilibrate reference ion with other aqueous species  
Sum of individual solubilities represents total metallic solubility

Figure 6-3. Flow chart of the process used to calculate total metal ion solubilities. Any ion may be chosen as the reference ion, since the equilibria between ionic species are used to determine the total solubility.

Metal ions in aqueous solutions can form a number of species: metal ions, metal-anion complexes, pure metal precipitates, metal oxide precipitates, and metal silicates. The relative stability of each of these species is determined by the Gibbs free energy of formation, $G_f$. For current purposes, each of the solid species (pure metals, oxides, and silicates) is assumed to be pure, so that

$$G(solid) = G'(solid)$$

The free energy of the solids, thus, do not depend on the amount of the metal present. Dissolved species (metal ions and metal-anion complexes), though, are in solution and their free energies depend strongly on their concentrations. Since we are interested in studying low levels of metal contamination, it is most convenient to use the Henrian (infinitely dilute) reference state. The free energy of a dissolved species is then
\[ G(\text{aquaes}) = G^\text{st}\ (\text{aquaes}) + RT \ln([\text{aquaes}]) \]

where and \( G^\text{st} \) is the free energy in the Henrian standard state. The free energy of the dissolved substance, thus, increases as the concentration of the substance increases. The metal solubility is determined as the concentration above which solid phase formation becomes thermodynamically favorable.

These simple assumptions about the free energies of the various species allow for calculation of the free energy change for any solid-forming reaction. In the most general form, the dissolved substance consists of the metal ion complexed with either a hydroxide ion (\( \text{OH}^- \)) or an extrinsic complexing agent (\( \text{A} \)), \( M(\text{OH})_x\text{A}_y(\text{aq}) \). This aqueous species reacts with \( \text{OH}^- \), \( \text{A} \), or \( \text{SiO}_2 \) or transfers electrons to form a solid, \( M(\text{OH})_x\text{A}_y\cdot(\text{SiO}_2)_z \):

\[
\text{Aqueous Ion} + \{\text{A}, \text{OH}^-, \text{SiO}_2, \text{e}^-\} \rightleftharpoons \text{Solid}
\]

In this reaction, the solid species are written in bold to emphasize the distinction between aqueous and solid forms of the metal. To make the dependence on pH (as opposed to pOH) more explicit, these equilibria may be rewritten as

\[
\text{Aqueous Ion} + \{\text{A}, \text{SiO}_2, \text{e}^-\} \rightleftharpoons \text{Solid} + \{\text{H}^+\}
\]

This one reaction, at fixed E and pH, determines a concentration of the aqueous species for which there is equilibrium with the solid. This is the partial solubility of the aqueous species with respect to the given solid phase. Figure 6-4 shows schematically how these free energies are used to determine a partial solubility.
Figure 6-4. Free energy curves for one pair of solid and aqueous phases as a function of metal concentration. When the two free energies are equal, the species are in equilibrium. This condition determines the partial solubility of the metal species for this one reaction.

In the most general form, the free energy change for any reaction, per mole of the reference ion, is written as:

$$\Delta G_r (E, pH) = \Delta G^0 + RT(\alpha \cdot pH + \beta \cdot E + \gamma \cdot pA + \log[M])$$

where $pA = \log_{10}[A]$. Since the surface is assumed to be oxidized, $SiO_2$ is abundant and does not vary with $E$ or $pH$. Equilibrium requires that this free energy vanish, giving the partial solubility as

$$[M] = \exp(-\Delta G^0 / RT - \alpha \cdot pH - \beta \cdot E - \gamma \cdot pA).$$

From this expression, it is clear that all the reactions of interest can be characterized by four quantities:

- $\Delta G^0$, the free energy change for the pure substances
• $\alpha$, the number of hydrogen ions evolved per mole of metal ion
• $\beta$, the number of electrons evolved per mole of metal ion
• $\gamma$, the number of atoms/molecules of the extrinsic complexing agent involved.

There are many equilibria of this form, but the calculations are simplified by focusing on one of the aqueous species, called the reference ion. When one solid phase is in equilibrium with this reference ion, it is simultaneously in equilibrium with all the other aqueous species. The equilibria between the solids and the reference ion are sufficient to describe the system. Once the solubility of the reference species has been calculated, the equilibria between the aqueous species are used to determine the overall metal solubility.

This approach leads to some equilibria which may seem unnecessarily complicated. For example, if $M^{++}$ is chosen as the reference ion, the $M(OH)_3$ oxide would be defined by the reaction

$$M^{++} + 3H_2O \rightarrow M(OH)_3 + 3H^+ + e^-$$

instead of the simple precipitation reaction

$$2M^{+++} + 3H_2O \rightarrow M_2O_3 + 6H^+$$

While the first reaction is clearly more complicated, and 'unphysical' from a kinetic perspective, the two reactions are equivalent for the purposes of equilibrium calculations.

Tables of the values used for calculations in this work are shown in Table 6-1 (Fe), Table 6-2 (Cu), and Table 6-3 (Al).
Table 6-1. Summary of Fe species formation reactions relative to the Fe$^{2+}$ ionic state. Only states with reasonable free energies of formation have been considered. Information about chlorides has been provided for SC-2 calculations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Phase</th>
<th>$\Delta G^0_r$ (eV)</th>
<th>$H^+$ evolved</th>
<th>$e^-$ consumed</th>
<th>Dep. on anion conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>solid</td>
<td>0.818</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>FeO</td>
<td>solid</td>
<td>0.688</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>solid</td>
<td>0.588</td>
<td>2.66</td>
<td>-0.66</td>
<td>0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>solid</td>
<td>0.659</td>
<td>3</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>FeCl$_2$</td>
<td>solid</td>
<td>1.28</td>
<td>0</td>
<td>-1</td>
<td>3</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>solid</td>
<td>0.308</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Fe(OH)$_3$-$</td>
<td>aq.</td>
<td>1.82</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>aq.</td>
<td>0.769</td>
<td>0</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>Fe(OH)$_2$$^{2+}$</td>
<td>aq.</td>
<td>0.898</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>Fe(OH)$_2$$^+</td>
<td>aq.</td>
<td>1.19</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>FeCl$^{2+}$</td>
<td>aq.</td>
<td>0.6375</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6-2. Summary of relevant Cu-species formation reactions. Cu$^{2+}$ is the reference ionic state.

<table>
<thead>
<tr>
<th>Species</th>
<th>Phase</th>
<th>$\Delta G^0_r$ (eV)</th>
<th>$H^+$ evolved</th>
<th>$e^-$ consumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>solid</td>
<td>-0.673</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>solid</td>
<td>0.136</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CuO</td>
<td>solid</td>
<td>0.467</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>aq.</td>
<td>0.132</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Cu(OH)$_3$-$</td>
<td>aq.</td>
<td>1.58</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Cu(OH)$_4$$^{2-}$</td>
<td>aq.</td>
<td>2.36</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6-3. Summary of relevant Al-species formation reactions. Al$^{3+}$ is the reference ionic state.

<table>
<thead>
<tr>
<th>Species</th>
<th>Phase</th>
<th>$\Delta G^0_r$ (eV)</th>
<th>$H^+$ evolved</th>
<th>$e^-$ consumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>solid</td>
<td>0.423</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (Gibbsite)</td>
<td>solid</td>
<td>5.026</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Al$_2$Si$_2$O$_5$ (kaolinite)</td>
<td>solid</td>
<td>0.29</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Al(OH)$_4$$^-$</td>
<td>aq.</td>
<td>1.328</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>
For each solid-forming reaction, there is a critical concentration of the reference ion below which the reaction cannot proceed. For formation of the n-th solid phase, this value is denoted $S_n$, the partial solubility with respect to the n-th solid. The minimum of all these $S_i$ is the concentration of the reference ion below which no solid will form, thus the true solubility of the reference ion. Based on the solubility of this reference species, the total metallic solubility is calculated by considering all equilibria between the reference ion and other aqueous species.

Ion-ion equilibria are analyzed in much the same way as the ion-solid equilibria above. In general, these reactions take the form:

$$\text{Reference Ion} + \{A, SiO}_2, e^-\} \Leftrightarrow \text{Ion2} + \{H^+\}$$

Again, by writing the free energy change as:

$$\Delta G, (E, pH) = \Delta G^0 + RT(\alpha \cdot pH + \beta \cdot E + \gamma \cdot pA + \log[M_{ref}] - \log(Ion2))$$

The concentration of the second ionic species is then related to the concentration of the reference ion by:

$$[Ion2] = [M_{ref}] \exp(-\Delta G^0 / RT - \alpha \cdot pH - \beta \cdot E - \gamma \cdot pA)$$

By summing contributions from all ions, the total metal solubility is established.

The approach as outlined above requires only thermodynamic data for all possible species, solid and aqueous, that may be present when a metal contaminant is present in the cleaning chemistry of interest. Much of this data is contained in Pourbaix's "Atlas of Electrochemical Equilibria in Aqueous Solutions". Since his work, intended for the study of metal corrosion, dealt only with high concentrations of metals, some additional species need to be included for our model to be accurate for the treatment of trace levels of contamination. In addition, species created by reactions with foreign chelating agents
or the silica substrate are not tabulated by Pourbaix. Thermodynamic data for these species may be found in the "NBS Tables of Thermodynamic Data" or other similar thermodynamic database.

**DETERMINATION OF CLEANING COORDINATES**

The following results are presented, in the Pourbaix framework, as functions of the solutions oxidizing strength and pH. Determination of the pH of a cleaning bath is relatively straightforward. For strong acids, complete dissociation is assumed and

\[ pH = -\log_{10}[H^+] = -\log_{10}[\text{Acid Content}] \]

For weaker acids, the \( K_a \) must be used to determine the exact solution pH.

The oxidizing strength of the solution is a bit more complicated. The dominant reduction reaction is determined by the chemistry used. For conventional RCA processes, peroxide is the oxidizing agent, so the relevant redox reaction is

\[ H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O \]

The redox potential resulting from this equilibrium, referenced against the standard hydrogen electrode, is

\[ E = 1.776 - 2.3 \frac{kT}{e} pH + \frac{kT}{2e} \ln[H_2O_2] \]

In this way, the oxidizing strength depends on both the acidic/base content as well as the addition of peroxide. Changing the peroxide content is the most direct means of controlling \( E \) without effecting the pH, but does not allow for a wide range of \( E \) values. From the dependence shown above, the oxidizing strength changes only 30 mV per
decade change in peroxide content. Further control over \( E \) must be accomplished by using other oxidizing agents, such as \( O_3, HNO_3 \), or \( I_2 \).

The decomposition of ozone in acidic media proceeds as

\[
O_3 + 2H^+ + 2e^- \leftrightarrow H_2O + O_2
\]

The resulting oxidizing potential is similar in form to the case of peroxide, as both reactions consume two hydrogen ions and two electrons:

\[
E = 2.26 - 2.3 \frac{kT}{e} pH + \frac{kT}{2e} \ln\left(\frac{O_3}{O_2}\right)
\]

The use of ozone as a peroxide replacement thus results in a more strongly oxidizing potential.

Nitric acid has long been a candidate for wafer cleaning due to its strongly oxidizing and acidic nature\(^{29}\). The nitrate ion decomposes in acidic solutions through the formation of nitrous acid:

\[
NO_3^- + 3H^+ + 2e^- \leftrightarrow H_2O + HNO_2
\]

The corresponding oxidizing potential,

\[
E = 0.94 - 3.5 \frac{kT}{e} pH + \frac{kT}{2e} \ln\left(\frac{NO_3^-}{HNO_2}\right)
\]

depends on concentration of the acid used, but is generally positioned near 0.94 V, significantly weaker than the potential of peroxide solutions.

Iodine addition to cleaning solutions has been briefly studied, specifically for the rapid etching of Ge surfaces. Under conditions of low iodide content (\(<10^{-3} \text{ M}\)), the reduction of iodine proceeds by

\[
I_2 + 2e^- \leftrightarrow 2I^-,
\]
resulting in an oxidizing strength of

\[ E = 0.5535 + \frac{kT}{2e} \ln\left(\frac{I_2}{(I^-)^2}\right) \]

These are merely a few of the many options available as oxidizing agents. The following calculations will look explicitly at the role of oxidizing strength in metal solubility, on the assumption that a chemistry can be found to produce that value of \( E \).

**DILUTION OF STANDARD RECIPES: SC-1**

Metal contamination is ubiquitous from SC-1 solutions. Previous work\(^6\) has shown that the conventional chemistry used for SC-1, 1:1:5 NH\(_4\)OH:H\(_2\)O\(_2\):DI at 80°C, produces a strong driving force for the formation of metal oxide precipitates. It has been shown that the driving force is so large that the level of contamination is limited only by diffusion of metal ions to the surface\(^6\). In this chemistry, the only means of preventing contamination is to use ultrapure starting chemicals, with total metal concentrations below hundreds of parts per trillion (ppt).

SC-1 recipes dilute in NH\(_4\)OH have been seen to reduce the roughening effects of hydroxide etching of silicon\(^6\). These recipes may have 10-25% as much ammonium hydroxide as the standard solution. The particle removal capability of these cleans have proven comparable to the original clean\(^6\), but metal deposition has not been widely studied.

Solubility calculations for Cu and Fe in basic solutions with the oxidizing strength of peroxide are shown in Figure 6-5. With increasing pH, the Cu solubility first drops due to hydroxide formation:

\[ \text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 \]
As the pH increases further, though, the formation of a soluble hydroxide results in a higher solubility:

$$\text{Cu(OH)}_2 + OH^- \rightarrow \text{Cu(OH)}_3^-$$

These two competing reactions result in a minimum solubility Cu of roughly 1 ppb at a pH near 9 (or a 100:1 dilution of the standard NH$_4$OH concentration).

The Fe solubility, quite conversely, is constant at a value near 20 ppt. Throughout this region, solubility of Fe is limited by the precipitation reaction

$$\text{Fe(OH)}_3 \leftrightarrow \text{Fe(OH)}_3$$

Since this reaction does not require either H$^+$ or e$^-$, this is 'plateau' on an E-pH map where this reaction results in a constant value for the Fe solubility. Small changes in the bath composition have no effect on solubility in this region. Further calculations for this region show that only very weakly oxidizing solutions can yield significant increases in the Fe solubility.
Figure 6-5. Solubilities for Cu in Fe in basic peroxide solutions. The Cu concentration drops due to Cu(OH)$_2$ formation, but increases again as the soluble hydroxide, Cu(OH)$_2$-$^-$ becomes dominant. The Fe concentration is constant and is entirely attributed to equilibrium between aqueous Fe(OH)$_3$ and solid Fe$_2$O$_3$.

Dilute versions of SC-1, therefore, do not have a strong impact on the tendency for metal contamination. A decrease in alkalinity from the pH of 11 does lead to gradual reductions of the Cu solubility, but even the minimum value (roughly 1 ppb) is above the value for today’s state-of-the-art cleaning chemicals. The Fe solubility is constantly low, and Fe contamination can only be inhibited, thermodynamically, by purifying below the level of 20 ppt.

**Dilution of Standard Recipes: SC-2**

In the second step of the RCA process, SC-2, metals are removed by an acidic clean consisting of hydrochloric acid (HCl), hydrogen peroxide (H$_2$O$_2$) and de-ionized water in a ratio of 1:1:6 maintained at a temperature of 70°C. The works of Antilla and Tilli$^{69}$ as
well as Ouimet et. al\textsuperscript{20} have shown empirically that dilute versions of SC-2, with as little as $10^{-6}$ as much HCl, remove metals as effectively as the original recipe, but a full understanding of why such dilutions work has not yet been presented.

Figure 6-6 shows Fe solubilities as a function of pH for solutions of three different oxidizing strengths (where chloride species have been allowed to properly reflect the SC-2 chemistry). Most applications of dilute SC-2 solutions retain the standard H$_2$O$_2$ concentration, and would therefore lie along the line shown for $E^0=1.7$ V. Along this line, switching from a standard solution, near pH=1, to a 10:1 dilution, at pH=2, the Fe solubility drops by roughly 4 orders of magnitude.

In spite of this dramatic reduction in solubility, the solution is still quite capable of removing Fe deposits. Even at a dilution of 100:1 (for a pH of 3), the solubility of the peroxide solution is near 1 ppb. While chemicals of this purity level were not common when W. Kern developed the RCA clean\textsuperscript{70} in the 1960’s, they have been widely available since the early nineties. In this way, an increase in the purity of starting chemicals actually enables the use of less of that chemical.
Though the solubility at pH=2 is still 100 ppb, well above purity levels in current chemicals, there are two potential downsides to this chemistry. First, the rate of metal removal should be strongly determined by the undersaturation of the metal in solution, so this dilute chemistry is likely much slower at redissolving Fe deposits. Second, for immersion cleaning baths that are used for multiple batches of wafers, the Fe that is removed from wafers will accumulate in solution. Reducing the metal solubility reduces the time over which the cleaning bath will be effective.

![Graph showing Fe solubility vs pH](image)

**Figure 6-6.** Fe solubility as function of pH for different solution oxidizing strengths. The solubility increases greatly for less oxidizing solutions as the formation of $\text{Fe}^{3+}$, and hence $\text{Fe(OH)}_3$, is retarded.

Figure 6-6 defines another approach to acid dilution that will not compromise the metal solubility at all. The two lines shown for $E^0=0.7 \text{ V}$ and $E^0=0.8 \text{ V}$ correspond to solutions that are significantly less oxidizing than peroxide, and lie between the values
given earlier for nitric acid and iodine. For these weak oxidizers, the iron solubility is seen to be much higher than the case of peroxide. This effect is understood in terms of the dominant solid-forming reaction for this region:

\[ Fe^{2+} + 3H_2O \leftrightarrow Fe(OH)_3 + e^- \]

By reducing the solution oxidizing strength, the oxidization of Fe\(^{2+}\) to Fe\(^{3+}\) is retarded, and formation of the iron (III) hydroxide is similarly limited. These diluted oxidizing solutions can maintain the same Fe solubility with 10% as much HCl (for \(E^0 = 0.8\) V) or even 0.1% as much of the acid (for \(E^0 = 0.7\) V).

**ROLE OF ANION COMPLEXING**

The ability of SC-2 to remove deposits of iron oxides has long been attributed not only to the low pH, but also to role of chloride as a complexing agent. By including iron chlorides in the list of allowed species, the solubility enhancement gained by using HCl instead of another acid is easily quantified.
Figure 6-7. Fe solubility as a function of pH at the standard oxidizing strength of peroxide, either with or without chlorides. The solubility enhancement, due to FeCl\textsuperscript{2+} formation, is strongest for concentrated solutions, but greatly decreases for higher pH.

Figure 6-7 shows Fe solubility when iron chlorides are allowed in the calculations and when they are excluded. Indeed, at a pH of 1, the Cl\textsuperscript{-} serves to raise the Fe solubility by over one order of magnitude, and presumably speeds dissolution of iron oxide deposits. For more dilute versions of SC-2, though, this advantage is rapidly lost. Near a pH of 2, roughly a 10:1 dilution of the standard chemistry, the two solubilities are nearly identical.
Figure 6-8. Solubilities of the dominant iron species in acidic peroxide solutions. The iron (III) chloride ion dominates for extremely low pHS, but drops rapidly as the H\(^+\) and Cl\(^-\) concentrations are reduced.

Figure 6-8 shows the solubilities of the three most dominant species, FeCl\(^{2+}\), Fe\(^{3+}\), and Fe\(^{2+}\) for peroxide solutions. In very acidic solutions, FeCl\(^{2+}\) is the most dominant species, but Fe\(^{3+}\) becomes dominant near a pH of 2.2. These differing dependencies are understood by writing the equilibrium between the two ions:

\[
Fe^{3+} + Cl^- \leftrightarrow FeCl^{2+}
\]

With the use of more dilute solutions, the Cl\(^-\) concentration decreases, and thus the concentration of FeCl\(^{2+}\) also drops in proportion to Fe\(^{3+}\).

This result establishes a regime of cleans for which the use of HCl is advantageous. For acid concentrations near the standard recipe and down to a 10:1
dilution, Cl- complexing provides a noticeable solubility enhancement. For solutions more dilute than 10:1, the effects of Cl- are negligible and other acids may be equally or more effective.

**Metal Silicate Formation**

The basic SC-1 chemistry has long been known as a source for surface metal contamination. One of the most ubiquitous and problem metal contaminants is aluminum\(^1\). Recent results have shown that low levels of Al contamination greatly accelerate the initial stages of oxide growth\(^2\). For the growth of ultrathin (<30A) oxides, this effect greatly complicates any attempts at process control. For this reason, understanding of Al contamination is of great interest.

Figure 6-9 shows calculated Al solubilities as a function of pH for a standard oxidizing strength of 1 V. Two lines are shown: one for which only formation of alumina is allowed, and a second where the formation of an aluminum silicate is included. When the silicate is neglected, the solubility of Al seems quite high for the SC-1 solution, well above 1 ppm. The strong tendency to form the silicate, though, results in a solubility that is roughly 3 orders of magnitude smaller. To reduce the tendency for this silicate to form, more basic or more strongly oxidizing solutions may be effective as an alternative to continued purification of the starting chemicals.
Figure 6-9. Aluminum solubility as a function of pH with respect to the formation of Gibbsite and Kaolinite at the standard oxidizing strength of 1V. The two curves are similar in shape because the two formation reactions evolve the same amount of H\(^+\) per mole of Al\(^{3+}\).

**CONCLUSIONS**

We have presented a broad thermodynamic model for the calculation of metal solubilities in aqueous solutions. Our model is based on Pourbaix’s E-pH diagrams, but has been extended to include the impacts of the silica substrate and extrinsic complexing agents. We have used this model to analyze a number of issues in wafer cleaning.

We have performed calculations to study the impact of dilute SC-1 and SC-2 chemistries on the solubilities of Fe and Cu. Our results show that Cu is soluble in a wide range of SC-1 concentrations, but that Fe solubility is quite low. In addition, this Fe solubility is constant across a large range of compositions near the standard recipe. For
SC-2, the Fe is shown to be greatly reduced by dilutions which change only the acid concentration. This solubility drop can be prevented by using solutions that are dilute in not only HCl, but also H$_2$O$_2$.

The specific role of Cl$^-$ in increasing Fe SC-2 solubility has been studied by disallowing the formation of all chloride species. Our results show that the presence of Cl$^-$ in a standard SC-2 increases the Fe solubility by over a factor of 10. For dilute versions of SC-2, though, this enhancement is dramatically reduced. The use of more dilute SC-2 type solutions, therefore, need not be constrained to the use of HCl.

Finally, the thermodynamic role for the silica substrate has been modeled for the case of aluminum silicate formation. By including the silicate species in our calculations, the Al solubility drops by nearly 3 orders of magnitude compared to the oxide-only case. This tendency for silicate formation necessitates more basic or more oxidizing solutions to prevent Al contamination during SC-1 cleaning.
CHAPTER 7 – IN-SITU MONITORING OF METAL CONTAMINATION IN HF BATHS

INTRODUCTION

The allowable levels of metallic surface contamination, as specified by the SIA Roadmap, are rapidly decreasing to meet the performance needs of advanced semiconductor devices. By the year 2009, cleaning processes need to produce surfaces with fewer than $1 \times 10^9$ atoms/cm$^2$ of each of the most critical heavy metals, including Cu, Au, Ag, Hg, Ti, Cr, Ni, and Fe$^2$. To attain these levels of surface cleanliness, the Roadmap specifies starting purity levels for all chemicals used in silicon processing. For concentrated hydrofluoric acid (HF), this requirement is currently 250 parts per trillion (ppt), and will reach 50 ppt by the year 2009.

This level of purity must be maintained throughout the life of the cleaning bath in order to guarantee high yields. Current methods for evaluating bath contamination use off-line analytical techniques, such as Inductively-Coupled Plasma Mass Spectroscopy (ICP-MS) and Total X-Ray Reflection Fluorescence (TXRF), to measure the contamination levels of cleaning baths and monitor wafers. Such methods are both expensive and time-consuming. As an alternative to bath monitoring, some manufacturers change cleaning solutions based on fixed schedules, independent of the actual degree of contamination. This approach eliminates problems arising from gradual contamination of the bath, but can not prevent yield excursions that result from unpredictable spikes in contamination levels.
In-situ monitors for bath contamination provide real-time information on the concentration of metals present in cleaning baths. Since metals are detected directly in the cleaning bath, contamination spikes can be observed before any process wafers actually become contaminated. To be compatible with current ultra-clean processes, a monitor must have very limited contact with the chemical bath to prevent introduction of foreign species. Today’s state of the art processes require a monitor capable of detecting tens of parts per trillion of metal contamination within a few minutes.

The open-circuit potential (OCP) of the silicon wafer has been proposed as a means of monitoring the surface condition\textsuperscript{73}. This technique has also been applied to in-situ monitoring of metal contamination in cleaning baths\textsuperscript{74}. Drawbacks of this technique include the need to have a contact to the silicon wafer and a reference electrode immersed in the solution.

The monitor we have developed is based on the contactless measurement of minority carrier lifetime. We have previously demonstrated in-situ detection of 1-5 parts per billion (ppb) Cu in a 100:1 HF bath\textsuperscript{75}. Currently, many manufacturers are using more dilute HF solutions to achieve better control over the oxide etching process. In this work, we evaluate the sensitivity of our monitor when used with a 500:1 HF solution and report a detection limit for Cu below 20 ppt.

**EXPERIMENTAL**

A schematic of our point-of-use recycling system is shown in Figure 7-1. The HF solution is pumped through a per-fluoro-alkoxy (PFA) flowcell, where it contacts a 25 mm × 25 mm piece of a 200 mm silicon wafer. The minority carrier lifetime of this
wafer is measured by Radio-Frequency Photoconductance Decay (RF-PCD). In this measurement, a radio-frequency (RF) coil is positioned near the back side of the cell to monitor changes in the wafer conductance. The time constant for the decay of these excess carriers provides information about the density of surface defects on the monitor wafer. A linear least-squares fit is used to extract a time constant from the exponential conductance decay. Since the entire system is computer-driven, measurements can be made every 3 seconds.

![Diagram](image)

**Figure 7-1.** Schematic of our point-of-use HF reprocessing system, including a metal purifier based on macrocycle ligand chemistry and an *in-situ* monitor based on the measurement of minority carrier lifetime. Any metals which pass the purifier deposit on a silicon wafer housed in the flowcell and are detected as a change in the surface recombination velocity of the wafer.

To calibrate this measurement, silicon wafers have been analyzed with TXRF to provide and independent measure of the surface metal coverage. This calibration has shown that in the regime of low surface coverage there is a direct correspondence between the concentration of metal adsorbates and the measured lifetime\(^{76,77}\). To use this
technique for measuring metal deposition rates, we observe changes in the lifetime of the silicon monitor wafer as a function of time.

Silicon pieces used for these experiments were cut from 200 mm n-type wafers (ρ=10-40Ω-cm) provided by Mitsubishi Silicon America. The pieces are cleaned for 2 min. in 100:1 HF, 4 min. in a 4:1 H₂SO₄:H₂O₂ solution at 90°C, 2 min. de-ionized (DI) water rinse, and a final 5 min. immersion in another dilute HF bath.

Ashland Gigabit chemicals and 18 MΩ-cm DI water are used for all cleaning steps to guarantee contamination-free surfaces. The 20 liter tank and all PFA tubing used in the recycling system are soaked in a 5% HNO₃ solution to dissolve adsorbed metals. To achieve a single ppt metal background, the HF bath is processed through an ion-exchange purifier, provided by Millipore Corporation. The solution used for spiking the HF bath was prepared using Alfa Aesar’s Spectrapure™ AAS Cu standard (10,005 μg/ml in 3% HNO₃). Spiking of the bath is performed by adding precisely measured quantities of the spike solution into the 20 liter bath.

DETECTION OF PPT LEVEL Cu CONTAMINATION

The RF-PCD measurement technique detects contaminants on the silicon surface as a change in the minority carrier recombination lifetime. When surface recombination is the dominant pathway for recombination, the measured lifetime varies with the surface condition according to

\[ \tau_{\text{meas}} = \frac{d}{2S} \]  \hspace{1cm} (13)

where \( d \) is the wafer thickness and \( S \), the surface recombination velocity, is given by
\[ S = N_s \sigma v_{th}. \]  \hspace{1cm} (14)

\( N_s \) is the areal density of surface defects, \( \sigma \) is the capture cross-section for minority carriers, and \( v_{th} \) is the thermal velocity of minority carriers\(^77\). A calibration between lifetime measurements and TXRF data has determined a capture cross-section for holes of \( \sigma_h = 9.6 \times 10^{-17} \text{cm}^2 \) per atomic Cu adsorbate\(^76\).

A clean wafer in 100:1 HF has a recombination lifetime of 1 ms. While the system is acquiring lifetime data, the scatter is routinely as low as \( \pm 1/4 \% \). A 1\% change in the measured lifetime is then easily detected above the noise. From equations 1 and 2, we see that this 1\% change in lifetime is equivalent to adding \( 3.8 \times 10^8 \) Cu atoms/cm\(^2\) to the surface of a 750 \( \mu \text{m} \) thick wafer.

Based on this sensitivity to surface defects, we can calculate a time required to detect contamination in the HF bath

\[ t = 3.8 \times 10^8 \text{ cm}^{-2} / r \]  \hspace{1cm} (15)

where \( r \) is the metal deposition rate in atoms/(cm\(^2\)-s). The rate of metal deposition is determined by the concentration of metal ions, the concentration of HF in the cleaning bath\(^78\), and the doping level of the monitor wafer\(^79\). In the manufacturing environment, the maximum time allowed for detecting contamination determines the lowest metal concentrations that can be observed.
Figure 7-2. Representation of the wafer/solution interface when the HF is flowing. The static boundary layer gives rise to transient and steady-states regimes of metal deposition.

Since the wafer we use as a monitor is immersed in a stream of HF, fluid flow across the wafer will affect transport of the metals to the surface. Figure 7-2 shows how a boundary layer forms near the wafer surface under conditions of laminar flow. Since this boundary layer is stagnant and does not mix with the rest of the solution, the concentration of Cu at the wafer surface, $[Cu]^*$, may differ significantly from the Cu concentration in the well-mixed regions of the cleaning bath. The steady-state value of $[Cu]^*$ is determined by two processes: mass transport of Cu through the boundary layer and electrochemical reduction at the wafer/solution interface.

For very low levels of surface coverage ($<10^{-5}$ monolayer), atomic adsorption is the dominant pathway for metals to deposit on the silicon surface. In this regime, the surface reaction rate will depend linearly on the Cu concentration in solution near the surface ($[Cu]^*$):

$$J_{\text{reaction}} = k[Cu]^*$$  \hspace{1cm} (16)
If we approximate the boundary layer thickness as being roughly uniform over the measurement area, transport of metal ions to the wafer surface will be governed by the 1-dimensional diffusion equation. The solution is then given by:

\[ J_{\text{diff}} = \frac{D([Cu]_{\text{bath}} - [Cu]^*)}{\delta} \]  

(17)

where \( D \) is the metal ion diffusion constant and \( \delta \) is the boundary layer thickness. When these two fluxes are not equal, the value of \([Cu]^*\) will change with time. This is observed when there are contaminants in the bath as circulation begins or when contaminants are added to the bath.

![Boundary layer edge diagram](image)

Figure 7-3. Cu concentration profile near the monitor wafer surface under steady-state conditions. The uniform concentration gradient drives diffusion across the boundary layer.
Under steady-state conditions, the two fluxes are equal and \([Cu]^*\) does not vary with time. Figure 7-3 shows the Cu profile near the wafer surface in this situation. There is a Cu concentration gradient extending to the edge of the boundary layer, at which point \([Cu]\) is equal to that in the bulk of the bath. The steady-state value of \([Cu]^*\) results in a steady-state metal deposition rate of

$$\frac{dN_{surf}}{dt} = k[Cu]^* = [Cu]_{bath} \frac{k}{1 + k\delta/D}$$

(18)

For our detector, this constant reaction rate is observed as a constant increase of the Cu coverage over time. Figure 7-4 shows data acquired for the addition of 20-150 ppt Cu to a 500:1 bath of dilute HF. Prior to spiking with Cu, metals were removed from the HF bath using an ion-exchange membrane filter. The data set corresponding to ‘No Spike’ shows that the initial metal level is below the detection limit of our monitor. For each subsequent data set, Cu was added to the HF bath and the system was run until the steady-state deposition behavior had been observed for roughly 1000 seconds. The line corresponding to 20 ppt Cu can be clearly seen above the background noise within 400-600s of operation.
Figure 7-4. Steady-state deposition rate measurements for a 500:1 dilute HF bath contaminated with 20-150 ppt Cu. The surface coverage is calculated from the minority carrier lifetime of a 25 mm x 25 mm monitor piece of silicon. The linear increase of Cu coverage with time indicates a constant deposition rate.

Metal deposition rates can be calculated from the slopes of these lines by first converting the lifetime data to surface coverages, according to equation 2. Figure 5-1 plots this calculated deposition flux as a function of Cu concentration for a bath of 500:1 HF. The data shows a strong linear correlation between deposition rate and Cu concentration, in agreement with the proposed model.
Figure 7-5. Cu deposition rates from a 500:1 HF solution. The deposition rate is calculated as the rate of change of the surface coverage. The strong linear correlation between deposition rate and Cu concentration is consistent with our model of first order reaction kinetics and one-dimensional diffusion across a boundary layer.

CONCLUSIONS

Monitoring metal contamination in cleaning baths is of great importance for manufacturers of state of the art electronic devices. Decreasing device dimensions and increasing process complexity tighten constraints on the allowable levels of surface metal contamination. Other processing trends, such as the use of increasingly dilute chemistries, place added importance on controlling metallic contamination in cleaning baths.

We have developed an in-situ monitor for metal contamination based on the measurement of minority carrier lifetime by Radio-Frequency Photoconductance Decay.
(RF-PCD). For a 500:1 dilute HF bath, we demonstrate *in-situ* detection of 20 parts per trillion of Cu. Based on the response we have observed for this level of contamination, we estimate a lower detection limit of 10 ppt. At this level of sensitivity, our monitor is appropriate for current state of the art manufacturing environments.
CHAPTER 8 – CONCLUSIONS AND FUTURE WORK

Upcoming technologies for the cleaning of silicon wafers provide numerous opportunities to improve the industry's environmental performance. The trends toward the use of simplified cleaning recipes and single-wafer processing reduce both chemical consumption at the tool and resource consumption by the fab as a whole. With throughput as an additional driver, these processes are being optimized to use process chemicals more efficiently than immersion wet benches. Chemical reuse is not currently being implemented, but better understanding of the effectiveness of dilute chemistries and new technologies for in-situ monitoring and point-of-use purification should make this a viable option in the near future.

The industry standard for clean silicon is the hydrogen-passivated surface. Detailed analysis of hydrogen-passivated surfaces has shown that defects on these surfaces behave differently from any known bulk defects. The injection-level dependent lifetime, as measured by RF-PCD is explained well by a model in which each defect produces two mid-gap electronic states. By analogy with dangling bonds, these two-level defects may play a role in a number of silicon surface reactions.

Contamination reactions on this intrinsic surface has also been measured with RF-PCD. The sensitivity of this technique rivals the best known tools for surface analysis, and has the advantage of measuring in-situ. This technique allows for precise measurement at trace levels of contamination, where the factors controlling the reaction rate become strongly dependent on intrinsic surface reactions. In this trace regime, metal deposition measurements show that the deposition rate is strongly dependent on the
concentration of the HF solution. Combining the electrochemical model with experimental data produces a semi-empirical relation, in which the purity of a $D:l$ HF bath must scale as $D^{-1.78}$.

Metal contamination in oxidizing solutions has been modeled, quantitatively, using Pourbaix diagrams. These diagrams, based on simple thermodynamics data, provide a simple framework for calculating the metal solubility as a function of pH, oxidizing strength, complexing agents, and the silica substrate. Calculations show that deposition from the SC-1 clean is mostly independent of bath composition. The effectiveness of Cl$^-$ in SC-2 vanishes above a pH of 3. Dilute versions of SC-2 based on less strongly oxidizing chemistries show great potential as environmentally benign metal removing solutions.

Finally, a monitor for metal contamination in HF has been demonstrated. Such a monitor, used alone, would guarantee the cleanliness of the HF and extend the useful bath lifetime. As part of a point-of-use recycling system, this monitor would serve to ensure proper operation of the metal filter. The monitor is based on the measurement of minority carrier lifetime and is fully compatible with ultraclean processing. This device has demonstrate in-situ detection of 20 parts per trillion (ppt) in 500:1 HF, and further design improvements could drive this sensitivity down to single ppts.
FUTURE WORK

The implementation of environmentally benign cleaning processes, and design for environment (DFE) more generally, has been limited by the availability of metrics for environmental performance. Without a means of quantifying the benefits of an alternative chemistry, little change is likely. While a modified cost of ownership expression has been used in this work as a rough guideline, the CoO alone is clearly not adequate for evaluating the environmental impact of new processes. While some metrics, such as the Sustainability Process Index (SPI) are being developed, further work is warranted to develop a metric that can be easily applied to the semiconductor industry. With this measure as a guide, the evaluation and implementation of new processes should process much more quickly.

This work has focused largely on the prevention of metallic contamination. The main purpose of the SC-1 clean, though, is the removal of particles. Better understanding of the processes of particle deposition, or further development of existing particle prevention technologies (such as mini-environments) may completely eliminate the need for SC-1, and hence the metal contamination that is known to come with it. Furthermore, better understanding of the particle removal capabilities of dilute SC-1 solutions will aid in developing more complete models for wafer cleaning.

Even within the area of metal deposition there are many interesting questions remaining. Preliminary work has shown that the rate of metal deposition is strongly impacted by dissolved gases in solution. Dissolved oxygen is already known to roughen the silicon surface and further deleterious effects of oxygen may necessitate the use of oxygen-free solutions. Furthermore, the deposition of one metal has been seen to
increase with trace levels of another metal, most notably for iron and copper in HF. Understanding these 'co-deposition' effects is essential for an accurate understanding of how contamination occurs in an industrial setting.

Finally, the fundamental investigation of the hydrogen-terminated silicon surface points toward a number of future studies. Minority-carrier lifetime measurements are unique in their sensitivity to these defects and provide a very versatile tool for understanding a wide range of surface reactions. Lifetime measurements taken during exposure to air will determine whether the doubly-occupied dangling bond is a reactive site for oxygen attack. For wafers in contact with dilute HF, this same doubly-occupied species may limit the transfer of electrons from the substrate to metal ions in solution. The unoccupied species, conversely, may limit the rate of attack by fluoride ions. All of these phenomena are important for understanding the effectiveness of hydrogen passivation, and RF-PCD presents a unique opportunity to study them.
APPENDIX A - CALCULATION OF THE INJECTION-LEVEL DEPENDENCE OF THE TWO-LEVEL SYSTEM

In Chapter 4, an expression was derived for carrier recombination through a two-level defect:

\[
\frac{dn}{dt} = - \frac{N_T}{r_- + 1 + r_+} \left( c_e^n (r_e n - n_1) + c_e^0 (n - r_e n_2) \right)
\]

The ratios \( r_- \) and \( r_+ \) were determined to be

\[
\begin{align*}
    r_- & \equiv \frac{[D^-]}{[D^0]} = \frac{c_e^n n + c_e^0 p_2}{c_e^- p + c_e^0 n_2} \\
    r_+ & \equiv \frac{[D^+]}{[D^0]} = \frac{c_e^0 p + c_e^+ n_1}{c_e^+ n + c_e^0 p_1}
\end{align*}
\]

and the constants \( n_1 \) and \( n_2 \) were defined

\[
\begin{align*}
    n_1 &= n_0 \times \frac{[D^+]_{eq}}{[D^0]_{eq}} \\
    n_2 &= n_0 \times \frac{[D^0]_{eq}}{[D^-]_{eq}}
\end{align*}
\]

Each of the ratios can be separated into numerator and denominator,

\[
\begin{align*}
    r_- & \equiv \frac{n_-}{d_-} \\
    r_+ & \equiv \frac{n_+}{d_+}
\end{align*}
\]

where each of the four terms, \( n_- \), \( n_+ \), \( d_- \), and \( d_+ \) are linear functions of the injection level, \( \Delta n \). The rate equation is re-written as
\[
\frac{dn}{dt} = -\frac{N_T(d_+d_-)}{n_-d_+ + d_+d_- + n_+d_-} \left( c_e^+ \frac{n_-n - d_+n_1}{d_+} + c_e^- \frac{d_-n - n_+n_2}{d_-} \right).
\]

Each numerator of the terms in parentheses can be simplified:

\[
n_-n - d_+n_1 = (c_h^0 p + c_e^+n_1)n - (c_e^+n + c_h^0 p_1)n_1
\]
\[
= c_e^+(np - n_1p_1)
\]
\[
= c_e^+(p_0 + n_0 + \Delta n)\Delta n
\]

where the substitutions \( p = p_0 + \Delta n \) and \( n = n_0 + \Delta n \) have been made and the identity \( n_0p_0 = n_1p_1 = n_t^2 \) has been used. Similarly,

\[
d_-n - n_+n_2 = (c_h^0 n_2 + c_e^-p)n - (c_e^-n + c_h^- p_2)n_2
\]
\[
= c_e^-(np - n_2p_2)
\]
\[
= c_e^-(p_0 + n_0 + \Delta n)\Delta n
\]

The recombination rate equation is now

\[
\frac{dn}{dt} = -\frac{N_T(d_+d_-)}{n_-d_+ + d_+d_- + n_+d_-} \left( c_e^+ c_h^0 + c_e^- c_h^- \right) \left( p_0 + n_0 + \Delta n \right) \Delta n
\]

\[
= -\frac{N_T(d_+c_e^+c_h^0 + d_-c_e^-c_h^-)}{n_-d_+ + d_+d_- + n_+d_-} \left( p_0 + n_0 + \Delta n \right) \Delta n
\]

The recombination lifetime is then

\[
\tau = \frac{\Delta n}{-\frac{dn}{dt}}
\]

\[
= \frac{n_-d_+ + d_+d_- + n_+d_-}{N_T(d_+c_e^+c_h^0 + d_-c_e^-c_h^-) \left( p_0 + n_0 + \Delta n \right)}
\]

Since each of \( n_-, n_+, d_+, \) and \( d_- \) is linear in \( \Delta n \), the resulting expression (assuming factorization is not possible) will have the form given earlier:
\[
\tau(\Delta n) \equiv \tau_0 \left( \frac{1 + \tau_{n1} \Delta n + \tau_{n2} \Delta n^2}{(1 + \tau_d \Delta n) \left(1 + \Delta n/(p_0 + n_0)\right)} \right)
\]

Each of the four coefficients can now be expressed in terms of physical parameters of the defect system:

\[
\tau_0 = \frac{(c_n^0 p_0 c_n^0 n_2 + c_k^0 c_n^- p_0^2 + c_n^0 n_2 c_n^+ n_1 + c_n^+ n_1 c_n^- p_0) + (c_n^0 n_0 c_k^0 p_1 + c_n^0 c_n^+ n_0 + c_n^- p_2 c_n^0 p_1 + c_n^- p_2 c_n^+ n_0)}{N_T(\tau_0 + n_0)(c_n^0 c_n^- (c_n^0 n_2 + c_n^- p_0) + c_n^0 c_n^- (c_n^0 p_1 + c_n^+ n_0))}
\]

\[
\tau_{n1} = \frac{c_n^0 c_n^0 (p_0 n_2 + n_0 p_1 + p_1 n_2) + c_n^- (p_0^2 + p_1^2 + p_1 p_0) + c_n^0 c_n^- (n_2 n_1 + n_0^2 + n_2 n_0) + c_n^+ c_n^- (n_1 p_0 + p_2 n_0 + p_0 n_0)}{N_T(\tau_0 + n_0)(c_n^0 c_n^- (c_n^0 n_2 + c_n^- p_0) + c_n^0 c_n^- (c_n^0 p_1 + c_n^+ n_0))}
\]

\[
\tau_{n2} = \frac{c_n^0 c_n^0 (p_0 n_2 + n_0 p_1 + p_1 n_2) + c_n^- (p_0^2 + p_1^2 + p_1 p_0) + c_n^0 c_n^- (n_2 n_1 + n_0^2 + n_2 n_0) + c_n^+ c_n^- (n_1 p_0 + p_2 n_0 + p_0 n_0)}{c_n^0 c_n^- (n_2 + p_1) + c_n^- (2p_0 + p_1) + c_n^0 c_n^- (2n_0 + n_1) + c_n^+ c_n^- (n_1 + p_2 + p_0 + n_0)}
\]

\[
\tau_d = \frac{c_n^0 c_n^- (c_n^0 n_2 + c_n^- p_0) + c_n^- c_n^+ (c_n^0 p_1 + c_n^+ n_0)}{c_n^0 c_n^- (c_n^0 n_2 + c_n^- p_0) + c_n^- c_n^+ (c_n^0 p_1 + c_n^+ n_0)}
\]
NOTES

14 Laurie Beu, Oral Presentation at Stanford University, August 13, 1997.
22 C. Y. Chang and S. M. Sze, ULSI Technology, 1996, p. 86.
67 Reduced roughness for dilute SC-1


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