Alternative Passivation for Silicon (100), Environmentally Benign Manufacturing, and Cooperative Strategy in Semiconductor Industry

By

Julia Kam Chu Chan

B.S., University of California, Berkeley (1995)

Submitted to the Technology and Policy and the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degrees of

Master of Science in Technology and Policy

and

Master of Science in Materials Science and Engineering

at the
Massachusetts Institute of Technology
September 2000

Signature of Author..
Technology Policy Program
August 18, 2000

Certified by..
Lionel C. Kimerling
Thomas Lord Professor of Materials Science and Engineering
Thesis Supervisor

Certified by..
Robert Rose
Professor of Materials Science and Engineering
Thesis Committee

Accepted by..
Dan Hastings
Chairman, Department Head of Technology Policy Program

Accepted by..
Carl V. Thompson II
Starros Salapatas Professor of Materials Science and Engineering
Chairman, Departmental Committee on Graduate Students

Alternative Passivation for Silicon (100), Environmentally Benign Manufacturing, and Cooperative Strategy in Semiconductor Industry

by

Julia Kam Chu Chan

Submitted to the Engineering System Division and the
Department of Materials Science and Engineering
on August 18, 2000 in Partial Fulfillment of the Requirements for the Degrees of
Master of Science in Technology Policy Program
And
Master of Science in Materials Science and Engineering

Abstract

My personal involvement, as a research graduate student, sponsored by Engineering Research Center, a center created by National Science Foundation and Semiconductor Research Corporation demonstrates that, through industrial research staffs' mentoring, university research can bring innovative environmentally benign manufacturing methods to the U.S. semiconductor industry. Our group has used methoxy to protect the bare silicon surface, because we have identified that the industrial standard, hydrogen passivation of silicon (H-Si) degrades rapidly when exposes to air. In this thesis, two new processing steps are added to make this methoxy passivation compatible to industrial practice. In addition, a preliminary gate oxide test demonstrated that this methoxy terminated silicon (MeO-Si) yielded a thinner ultra thin gate oxide than those wafers cleaned by IBM's conventional RCA and dilute hydrofluoric acid last clean without compromising its reliability. Furthermore, particle count results shown that this MeO-Si has the same particle resistance as H-Si. Further mechanistic and thermodynamic studies are performed such that this process is optimized. As a result, MeO-Si is 49 times more stable than H-Si against air degradation. Through this center, an Environmental Safety and Health incorporated Cost of Ownership is developed in this thesis. This is done by using in vitro studies to evaluate the toxicity of new chemicals used, and by using lifecycle analysis to calculate the amount of untreated chemical, which leaks to the environment. Both of these will give rise to an environmental figure of merit to modify the conventional cost of ownership. In the last section, a strategic analysis of this Engineering Research Center is performed to demonstrated that students are a very important media to (1) facilitating technology transfer to industry, (2) enhancing collaboration along the chain of semiconductor industrial participants.

Thesis Supervisor: Lionel C. Kimerling
Title: Thomas Lord Professor of Materials Science

Table of Contents

1. Introduction

List of Figures

List of Tables

Acknowledgments

I would like to thank my home department, Technology Policy Program (TPP), which offers board and flexible education curriculum so that I can explore the opportunity that MIT offers and to develop this dual masters thesis with the Department of Materials Science and Engineering of MIT.

I would like to thank Prof. Rose, who has been a great thesis committee in helping me with both the content and the grammar for my thesis development. Personally, I enjoy being a teaching assistance in his class because he made awesome thermo jokes! Honestly, when I was the student, I don't quit get them.

I would like to thank Dr. Harald Okorn Schmidt for many things. First, it was such a great opportunity to work with him at IBM. I have learnt so much from him about research style in industry as well as how to write papers. I particular enjoy others scientific conversation about organic food and hormone contaminated milk!

I need to thank Anand for being helpful when I really needed his expertise, and I also enjoy teaching with him in Thermo as well.

I want to thank Minghao, who has been so kind hearted to help me to get deionized water during the weekend from MTL.

I would like to thank students from Prof. Rubner's group, who have kindly let me use their equipment for weekdays as well as weekend. They are great!

I want to thank Kanto Chemical and Ashland chemical, both has donate chemical for my research!

I would like to thank everyone in the group, who has been charming in many ways, and be helpful every now and then, which has colored the laboratory life.

Save the best for the last: I would like to thank my advisor Prof. Kimerling. First, he has introduced me to the semiconductor industry. Secondly, he has taught me to work and think like an engineer. And he even gives me lecture in English—Environmentally benign instead of environmental benign. Most importantly, he always gave me challenging questions to solve by myself. This allows me to really know my interests, my ability, and myself.

Chapter 1

Introduction

1.1 Motivation

The motivation behind my thesis is to enhance the leadership position of the microelectronics industry in this boundary less global economy. Two strategies are proposed here to ensure success in this competition. The first one is innovation by strategic alliance with research teams at universities. This is because, often, innovation is not the main stream of research in the semiconductor industry. Therefore, it is a disruptive technology and will be cost effectively carried out by outsiders. In addition, innovation strengthens global competitive positions as international patent laws such as the Paris convention and the Berne convention have been reinforced. Added to this, patent itself is a legal monopoly, which will violate neither the anti-trust law of the United State nor the competitive law of the European Union. The second recommended strategy is the well-known principle low cost of manufacturing.

Environmental safety and health concerns have been increasing both internationally and locally beginning with the discovery of the ozone hole caused by fluorocarbons. International markets like Germany and Switzerland have prohibited microelectronic imports if they contain non-environmental components [1]. Since both of these countries are active participants of the European Union (EU), there is a threat that the whole EU may adapt the same policy. Within the U.S., the Environmental

Protection Agency (EPA) has imposed the total life cycle responsibility on cars, monitors, etc. A similar life cycle responsibility may be imposed on the microelectronic industry.

To reach the global market, it is often cost effective for a company to set up manufacturing facilities in other countries. However, European nations always have stricter environmental regulations than the U.S. For example, when AMD attempted to set up a manufacturing facility (fab) in Germany, a new fab plan was needed in order to pass the Germany's environmental standard. This imposed extra fixed costs for operation. Therefore, it is cost effective for a company to design a universal model environmentally benign fab to reduce cost and time for globalization.

1.2 Thesis Organization

In this thesis, three case studies are involved. The first case study, alkoxy passivation on Si (100), demonstrates that innovative scientific research developed from a university can directly benefit industry. In addition, innovation may bring in unexpected processing advantages. This is explored in chapter 2. The second case study shows that interdisciplinary education involving the understanding of toxicity of chemical use, the biological impacts on human beings, and new environmentally incorporated cost of ownership is needed to cultivate the future work force of microelectronic industry as well as immediate implementation. In this case study a new environmental figure of merit through the use of (1) life cycle analysis (LCA), (2) and in vitro studies and computer simulation to evaluation the toxicity of chemical. These topics are covered in Chapter 3 and 4. The third case study demonstrates that through proper management policy, collaboration among microelectronic industry, and universities will enhance U.S. microelectronic industry to be a global market leader. This will be covered in Chapter 5.

Chapter 2

Alkoxy passivation on Silicon (100)

2.1 Introduction

Current wet processing is a sequence of 1) RCA clean, 2) DHF clean, 3) a water rinse, and 4) a Marangoni drying step. This processing sequence will yield a hydrogen terminated (H-Si) surface.

Conventional RCA clean includes a Standard Cleaning 1 (SC1) and a SC2 bath. SC1 is a mixture of ammonia, hydrogen peroxide, and water for removing organic and particulate contamination by oxidation, while SC2 is a mixture of hydrochloric acid, hydrogen peroxide, and water to desorb metal contamination by forming metal complexes. The DHF last clean is used to 1) further remove metal contamination and 2) to form a hydrogen-terminated silicon (H-Si)[2].

This H-Si surface will protect the underlying reactive bare silicon against air degradation. This surface is hydrophobic in nature, which resists moisture. However, cleaning the surface with DHF clean will form some polar fluorine terminated silicon sites (F-Si), which are hydrophilic in nature. The amount of F-Si formed strongly depends on the concentration of HF used, and higher the concentraction of HF used, the more the F-Si sites are formed [3]. When this surface is rinsed by the other ultrapure water step, F-Si sites, and some of the H-Si sites will react with water to form polar Si-OH sites. These polar sites will decrease the hydrophobicity of the wafers. And it is well know that hydrophilic sites facilitate native oxide formation [4], [5] and particle deposition [6]. Both of which will jeopardize the quality of gate oxide formed in the subsequence processing steps. Therefore, the Marangoni drying step is employed to dry the wafers after this water rinse step to reduce moisture assisted air degradation.

Despite the effectiveness of Marangoni drying, the left over polar sites, such as F-Si and Si-OH are hydrophilic. In addition, H-Si itself also degrades in air. Therefore, industry tends to reduce the time window of exposure by taking these sensitive wafers to further process immediately. This can be done by increasing the ratio of the number of furnaces to the number of wet-benches. This is because a typical wet-bench clean requires only 1 hour, while a typical gate oxide growing step varies from 3-6 hours [7]. However, this process requires extra space to house the furnace. In addition, this process reduces the time window between transferring from the wet process station to the furnace. If the wet bench break down, the utilization of the related furnace will decrease dramatically.

The other method is to grow a protective oxide, called a sacrificial oxide, after this complete wet processing sequence. This sacrificial oxide will protect the bare silicon surface against air degradation for an extended period of time, i.e. one day. When these wafers are needed for further processing, then either a DHF etch, or another complete wet processing sequence will be performed before the subsequence processing steps. However, this re-cleaning process increases the cost of production and decreases the yield. Equation 2.1 states the mathematical formula explaining why additional steps will reduce yield.

$$\text{Final yield}=\prod_{X=1}^{X=\text{the total number of steps}} \text{yield of each step} \qquad \text{(Equation 2.1)}$$

To overcome the above problems, we need a new passivation technique to protect the bare silicon surface, so as to 1) avoid re-clean, 2) increase time window for processing, and 3) and increase yield. The essence of this chapter is to present an innovation—alkoxy passivation, which was initiated and developed in M.I.T. Previously, this novel passivation has demonstrated high air stability as compare to conventional H-Si. However, it was not compatible with current practice. Through a strategic alliance with an industrial partner, IBM research staff Harald Okorn Schmidt, two new processing steps had been invented so that this new passivation technique was tested in Yorktown Heights. In addition, this process has been further optimized such that this methoxy- passivated surface is 49 times more stable than H-passivated surface.

2.2 Summary of previous work and present work

2.2.1 Summary of previous work

M'saad investigated new ways of alternative passivation by using different halogens such as chlorine, bromine, iodine, in methanol to create what was then believed to be halogen passivated silicon. He also verified that iodine was the best passivant. In addition, he has identified the optimized amount of concentration of iodine used [8], [9], [10].

Burr and Mo have evaluated this alkoxy passivation [11]. They identified that methoxy (MeO) not iodine, was the chemical species passivating the silicon surface (MeO-Si). This finding was verified by both experiment and theory. In addition, they also found that this iodine MeOH passivation followed a two steps reaction mechanism. Futhermore, after 10 min of immersion of this wafer in this solution, the amount of iodine passivated site (Si-I) is approximately 10%, and its concentration remained constant. This surface was then subjected to air degradation test assessed by ATR-FTIR and XPS synchrotron technique. The results shown that this surface (90% MeO-Si and 10% I-Si) is more robust against air oxidation than H-Si and isopropoxy passivated silicon (IPA-Si). [11].

2.2.2 Summary of this thesis work

This work involves a systematic evaluation of the advantages of alkoxy passivation over H- passivation. In addition, a new and consistent reaction mechanism is proposed. Through a collaboration with IBM research staff Harald Okorn Schmidt, we added a novel reaction step to make this reaction process compatible with industrial practice (The detail of this process will be discussed in Section 2.8). Then, a preliminary gate oxide integrity testing was performed. The results indicated that this MeO- passivated silicon surface yielded a thinner ultra thin gate oxide than those wafers, which were cleaned by conventional RCA and HF type cleans. In addition, the reliability of MeO- passivated silicon is the same as those conventional cleaned wafers. Meanwhile, I have optimized this process through understanding the thermodynamic and the kinetics of this surface reaction mechanism. As of today, air stability of this surface is about 49 times more stable that H- Si.

2.3 Measurement Technique

2.3.1 Radiofrequency conductance decay

Radiofrequency conductance decay (RFPCD) measurement is used to investigate the surface condition of the silicon wafers. This technique records the decay of minority carriers generated by a strobe light pulse. A radio frequency coil records the change in conductance when the conductance of the silicon wafer reaches the resonance frequency generated by the coil. This change in conductance of the wafer is due to the change in minority carriers' lifetime (τ). This lifetime of minority carriers recorded by RFPCD is related to the bulk lifetime (τ_b) and the surface minority carrier lifetime (τ_s), the thickness of the wafer (d), and the surface recombination velocity (S) as shown in equation 2.2. Since we have used wafers with high bulk lifetime, thus, the lifetime measured by RFPCD is equivalent to the surface minority carrier lifetime. Lifetime recorded by RFPCD is therefore related to the number of trap states (N_t) in the surface of silicon wafer if we assume that the presence of the mid-level traps are due to formation of native oxide. This relationship is indicated in equations 2.3 and 2.4. Capture cross section for oxygen (σ) used is equal to 10^{-16} cm^{-2} [11]. The thermal velocity (v_{th}) of the electron at 300 K is equal to 1.17 $*10^7$ cm/s. In short, higher lifetime (better surface quality) implies lower numbers of trap states (vice versa).

$$S = \frac{d}{2 * \tau_{measure}} \qquad \text{(Equation 2.2)}$$

$$\frac{1}{\tau_{measure}} = \frac{1}{\tau_b} + \frac{1}{\tau_s}$$ (Equation 2.3)

$$N_t = \frac{d}{2\sigma v_{th} \tau}$$ (Equation 2.4)

From the above equations, we can infer that N_t or inverse minority carrier's lifetime vs time gives the same information about the surface condition of the wafer in a given time. The important difference is that number of traps calculation assume only one type of degradation effect—native oxide formation. Therefore, it does not account for other types degradation effect such as metal deposition. Yet, in all situations, since native oxide degradation dominate over other effect, therefore, we can approximate these two terms as interchangeable. Some of the data shown in this thesis utilizes inverse lifetime vs time to represent in-situ measurement because those data can be actually seen in the computer screen of RFPCD.

As for data fitting, Y=MX+C is used to evaluate the linear part of the passivation curve as well as degradation curve in air or in solution. The speed for this passivation or degradation is called the rate of passivation or degradation, which is the slope (M) of this linear approximately. C is the intercept, which is used in the air degradation experiment to find out the initial number of traps on the wafers' surface when they first degraded at time zero.

2.3.2 Charge to Breakdown (Qbd) and Time to Fail (tbd)

IBM research staff Harald O'korn Schmidt used the above techniques to evaluate the reliability of the gate oxide grown . In measuring Qbd, a fixed current in the Fowler-Nordheim

(F-N) tunneling region is forced through the oxide while the voltage is monitored. When is voltage across the oxide suddenly decreases, then the oxide is classified to be failed. The time taken to fail is called the tbd, and Qbd is the product of the fixed current used and the corresponding tbd measured.

2.3.2 Contact angle measurement

This measurement is widely used to measure the wetability of a surface. A liquid droplet, in this case, water is added to the surface of interested, then, a picture is taken, and the computer will estimate the contact angle between the water and air interface of the sample. Figure 2-1 shows the vector diagram of wetting. σlg is the vector representing the surface tension between the liquid and gas interface, σsg is the surface tension between the solid and gas, and σsl is the surface tension between the liquid and solid. The contact angle measured is (θ)[12].

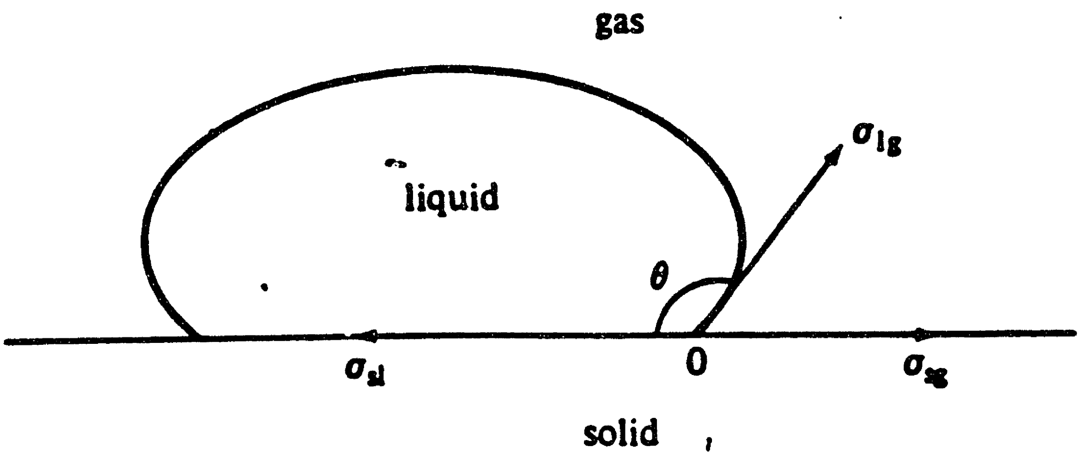


Figure 2-1 Interfacial forces of a water droplet.

2.4 Experimental procedure

Procedure A

Wafer used were CZ wafers, p-typed, Boron doped, with resistivity 20-40 ohm-cm, and thickness of 725 um, with (100) orientation. Methanol (MeOH) used was of cleanroom grade, and hydrofluoric acid (49%) (HF) used contain 0.1 ppb metal impurity (Gigabit Chemical). Both were donated by Ashland chemical. The final dilute hydrofluoric acid (0.5%)DHF last cleansing step as well as of the organic solution were subjected to an hour research grade argon (Grade 5 Argon from BOC gas) bubbling to remove all the dissolved oxygen (Degas).

Conventional MIT HF cleaning was performed, which contained 5 steps. First, the silicon wafer was immersed in dilute hydrofluoric acid (DHF) for 2 min. This is followed by a 10 seconds deionized water rinse. Then, these wafers were immersed in a Piranha bath containing a 4 to 1 ratio of concentrated sulphuric acid and hydrogen peroxide. This step was followed with a 2 min DHF immersion. This last step will be referred to as DHF last in the rest of the chapter. After this step, the silicon surface is terminated by hydrogen (Si-H).

MeO-Si is formed by the DHF sequence with a final immersion of this Si-H wafer into a solution of MeOH with $5*10^{-4}$ M of iodine. This complete DHF and MeOH:iodine sequence is referred as procedure A in the rest of the chapter.

Procedure B

Unless specified, everything is the same as procedure A except that 1) Kanto grade ultrapure organic solvent is used, 2) no degas is required, and 3) another pure MeOH immersion step is added.

Procedure C

It is essentially same as procedure B except that another new step are added after this. This new step is to dip the wafer into a water flow bath.

2.5 Alkoxy passivation mechanism[1]

2.5.1 Passivation mechanism proposed by Burr [11]

Experiment A of Figure 2-1 summarizes the procedure leads to the generation of a methoxy terminated silicon surface (MeO-Si) in solution. First, a conventional hydrogen terminated silicon (Si-H) is needed. This can be achieved by immersing an oxidized silicon wafer into 40% ammonia fluoride solution for 15 min. Subsequence immersion of this Si-H wafer into a methanol solution with $5*10^{-4}$ M of iodine will yield MeO-Si.

To demonstrate that iodine is a necessary species to form MeO-Si, the Si-H was immersed in pure MeOH (Experiment C in Figure 2-1). No passivation was recorded in ATR-FTIR measurement and XPS measurement.

In experiment B, the bare silicon surface was exposed to iodine gas to form iodine-terminated silicon (Si-I). This Si-I would then be immersed in MeOH solution.[2] MeO-Si surface was generated. This proves that MeO can replace I-Si. Thermodynamic calculations in Burr's thesis also supported this[11]. It was concluded that MeO-Si termination is a two step

---

[1] Alkoxy is represented by RO- where R is alkyl group, and O is oxygen. Alkoxy with H, i.e. RO-H is alcohol, which is a stable compound.

mechanism. The first step is the formation of Si-I, the intermediate specie. The second step involves the replacement of Si-I with MeO-Si. As for the first step, Burr believed that Si-I formation is achieved by: (Step 1) light initiation to form iodine radicals (Equation 2.5), (Step 2) I radicals replacement H of Si-H (Equation 2.6), (Step 3) nucleophilic substitution of MeO- for I- in Si-I surface (Equation 2.7) [11].[3]

$I_2 \rightarrow 2\,I\bullet$ $\Delta H_{BD} = 151$ kJ/mol (Equation2.5) [13] [4]

$I\bullet + Si\text{-}H \rightarrow H\bullet + Si\text{-}I$ $\Delta H = 6.2$ kJ/mol (Equation 2.6)[13][5]

$Si\text{-}I + EtOH \rightarrow EtO\text{-}Si + HI$ $\Delta H_f = -378$ kJ/mol (Equation 2.7) [13][6]

---

[2] All the organic solution used by Burr and Mo is subjected to oxygen removal by 45 min argon gas saturation. The data were collected by XPS and ATR-FTIR measurement.

[3] Nucleophilic substitution describes a reaction, which involves a negatively charged species that will react with a positive site (the nucleus) by replacing its negative partner.

[4] ΔH_{BD} = Bond dissociation enthalpy; I•is iodine radical. All the enthalpy data are obtained from CRC Handbook of Chemistry and Physics. Edited by David R. Lide., 72nd (1991-1992).

[5] ΔH= Change in enthalpy.

[6] ΔH_f =Change in enthalpy of formation, which is equal to the sum of enthalpy of formation of the right hand side substracting the sum of enthalpy of the left hand side.

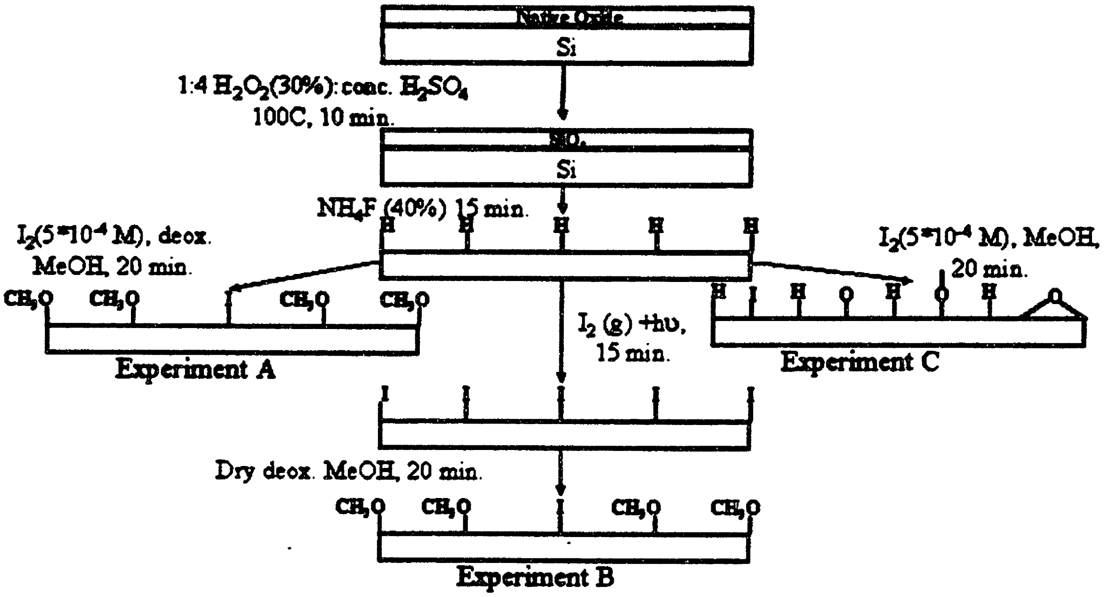


Figure 2-2 Experiment flowchart by Burr [11] to verify that MeO- passivation is a two steps process.

2.5.2 Elucidate the initiating step for alkoxy passivation

To verify whether iodine radical or iodine ion (I^-) was responsible for the formation of Si-I, potassium iodide (KI) was used to replace iodine to see whether this MeO-Si passivation will take place or not. If KI in MeOH accelerates this process, then, I^- is responsible for catalysis of this process. MeOH and iodine is not used as a reference for this experiment because in-situ measurement from former students [8] [11], as well as in Figure 2-4 shown that this solution always shows passivation effect (reducing the number of traps). By running methanol as a reference, we can directly investigate exactly what KI will do to a surface.

Experimental Procedure

To generate the MeOH reference, procedure A is followed without the use of iodine. As for KI in Methanol, 10^{-3} mole of KI is used, which is twice of that of iodine. This is because each mole of iodine will yield two moles of iodide radical. [7]

Results and discussion

Table 2.1 indicates the rate of degradation of Si-H in these two different solutions[8], and Figure 2-2 summarizes the results obtained. This data shows that the N_t of Si-H in pure MeOH increases at a slower rate than Si-H in MeOH:KI. This indicates that degradation occurs in both solutions, and KI: MeOH solution degrades the wafer surface much faster than pure MeOH.

Solution used	KI: MeOH	MeOH
Rate of degradation in solution (N_t/sec)	$1.109*10^7$	$7.731*10^6$

Table 2.1 The rate of degradation of Si-H in KI: MeOH and MeOH

---

[7] Unless specified, oxygen was removed from all the organic solution used, and in the DHF last step as well.

[8] Y= MX+C. M is the fitted slope of the data, which is the rate of degradation in this case. C is the intercept, which represents the potential initial number of traps presented at time zero.

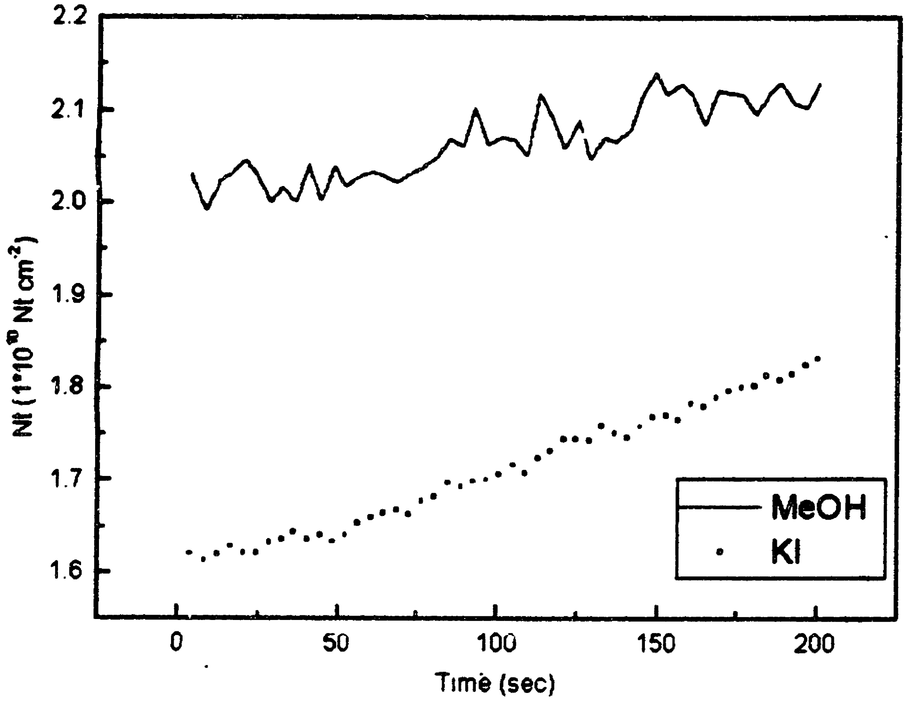


Figure 2-3 In –situ measurement of Si-H degradation in MeOH and KI:MeOH

Figure 2-2 indicates that the initial number of traps is difference between the wafers immersed in MeOH and KI: MeOH solution. This difference is due to the difference surface preparation. However, this does not affect the validity of the data to evaluate the degradation effect of those solutions on the wafers' surface, as rate of degradation (the change in the number of traps per cm^2 per second) is the measurement employed.

This degradation can be explained by metal deposition onto weak unpassivated polar Si-F sites and dangling bonds (Si•) formation (See equations 2.8-2.10). This is because, a HPLC grade solvent contains 5 ppm of residue, which is most likely the left over metal catalyst.

This proposed explanation is further supported by the recorded increase in rate of degradation in MeOH:KI solution, which has a higher ionic strength than pure MeOH. Higher ionic strength solutions facilitate metal degradation because these reactions involve electron transfer.

The following equations illustrate how metal ions compete with the passivant to degrade the silicon wafers. There are two types of metal degradation. One is physisorbed from solution [12]:

$$M^{z+}\text{ (solution)} \rightarrow M^{z+}\text{ (Silicon)} \qquad \text{(Equation 2.8)}$$

The second type of degradation involved reduction on M^{z+} to form M^0. The electrons needed are provided by silicon oxidation, which result in dissolution of surface silicon [13], and therefore, causing surface defect formation.

$$M^{z+}\text{ (solution)} + ze^- \rightarrow M^0\text{ (solution)} \qquad \text{(Equation 2.9)}$$

$$Si \rightarrow Si^{X+} + Xe^- \qquad \text{(Equation 2.10)}$$

From this experiment, we also conclude that iodide ion is not the very first chemical species to initiate this reaction. This observation can be explained by some fundamental chemistry. Iodine molecule is a well-known oxidant. Therefore, it oxidizes the Si-H bonds (See equations 2.11A to 2.11B). This facilitates nucleophilic substitution of silicon with iodine[12]. This is because electronic deficient iodine which is of higher Pauli electronegativity (0.7) can replace a lower Pauli electronegative H (0.3) to form a stronger polar bond with silicon. The iodine for this reaction can be electronic (Equation 2.12 B) or radical (Equation 2.12C) in character when this replacement take place [13].

Step 1. Active iodine radical or iodine ion generation:

$I_2 \xrightarrow{\text{Room Temp.}} 2I\bullet$ $\Delta H_{BD} = 151$ kJ/mol [13] (Equation 2.11)

$I_2 + 2e^- \rightarrow 2I^-$ $\Delta H = -113.56$kJ/mol [13] (Equation 2.12A)

$SiH \longrightarrow Si\bullet + H\bullet$ $\Delta H = 299.2$kJ/mol [13] (Equation 2.12 B)

$H\bullet \rightarrow H^+ + e^-$ (Equation 2.12 C)

Step 2. Si-I bond formation.

$Si\bullet \rightarrow Si^+ + e^-$ (Equation 2.13 A)

$Si^+ + I^- \dashrightarrow Si\text{-}I$ (Equation 2.13 B)

$Si\bullet + I\bullet \dashrightarrow Si\text{-}I$ $\Delta H = -293$ kJ/mol [13] (Equation 2.13 C)

2.6 Alkoxy increases the extent of solution passivation

In this set of experiments, the goal is to answer the following questions:

1. Is alkoxy passivation better than Si-H formed after HF (49%) last?
2. Is alkoxy passivation better than Si-H formed after DHF last?
3. Does different size of alkyl group (R-) affect the extent of alkoxy (RO-) passivation?

Experimental Procedure

Experimental procedure was the same as procedure A. HPLC grade of m ethanol (MeOH), ethanol (EtOH), and isopropanol (IPA) were used to prepare $5*10^{-4}$ molar of iodine.

Results and discussion

Figure 2-3 shows a typical passivation curve collected from the in-situ measurement of RFPCD for alkoxy (RO-) passivation. Each datapoint represents one lifetime measurement. Table 2.2 shows the average N_t remaining after each passivation process has reached equilibrium (The flat part of the passivation curve.). The resulting surface formed from different alcohols had similar final N_t, which is less than DHF passivation and also less than 49% HF passivation. This is because alcohol and iodine solution will increase the extent of passivation by reacting with the unpassivated sites in additional to replacing H-Si as observed by Burr [11]. This increase in extent of passivation will be discussed in Section 2.9.

As shown in the data, the final number of traps in 49% HF is 0.69 10^{10} $N_t\,cm^{-2}$, which is less than DHF (N_t=10^{10} $N_t\,cm^{-2}$). The difference between 49% HF and DHF can be explained by the fact that 49% HF is a strong etching chemical, it continuously reacts with the silicon to provide apparently good surfaces passivation in the time scale of RFPCD measurement. Yet, the surface is in fact terminated largely by fluorine [3], which is an undesirable species for air stability as described in the introduction. In addition, concentrated HF will increase surface roughening, therefore, it is not useful for manufacturing high quality devices.

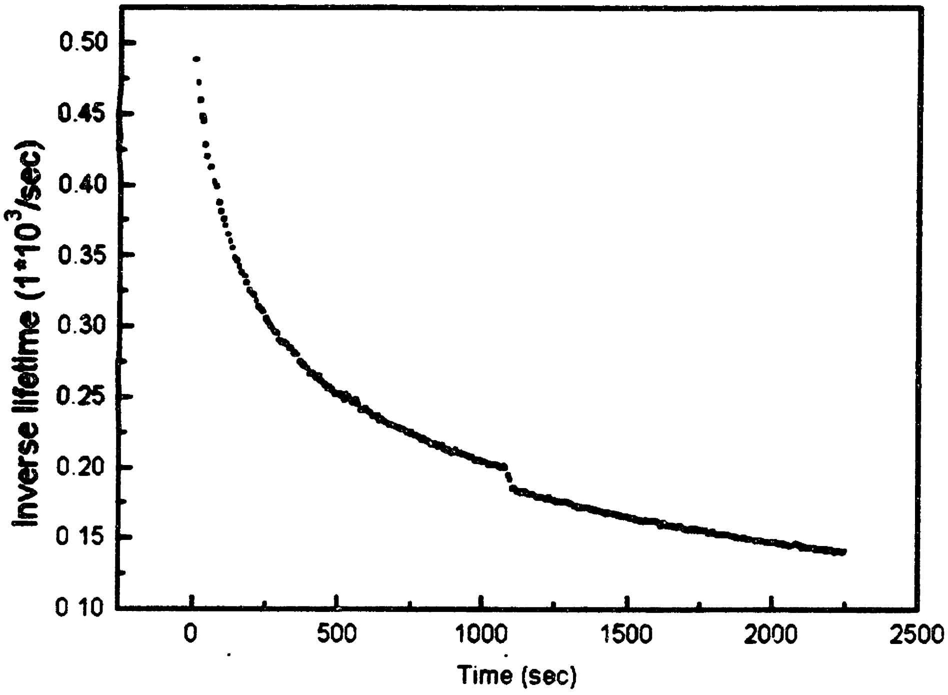


Figure 2-4 In-situ continuous inverse lifetime measurement of Si-H converting to MeO-Si in an argon saturated MeOH iodine solution.[9]

Solution	DHF	49% HF	Isopropanol :I_2	Ethanol : I_2	MeOH : I_2
Extent of Passivation (10^{10}Nt/cm^2)	1.0+/-0.2	0.69+/-0.02	0.66+/-0.0+2	0.79+/-0.08	0.65+/-0.04

Table 2.2 Summary of the equilibrium N_t presence on the wafers in different passivating solution.

---

[9] The discontinuity is due to relocation of the beaker containing the wafer. This figure can be directly observed from the computer screen.

2.7 Temperature Dependence of EtOH Passivation

The motivation behind this experiment is to elucidate the activation energy barrier (E_A) for this reaction. In this experiment, not only the E_A has been found, but the kinetic dynamic of this passivation mechanism is also identified.

Experimental procedure

Experimental procedure was the same as procedure A except that HPLC grade ethanol (EtOH) and iodine solution is immersed in a hot water bath. The bath temperature was around 43 C. The reference experiment is performed at room temperature.

Results and discussion

Table 2.3 summarizes the rate of EtOH passivation. High temperature results in higher passivation rate. In addition, the number of traps formed per centimeter square in a 43 C bath is only 0.56, which is lower than the number of traps formed per centimeter square in a 23 C bath (0.79). Base on these data, the activation energy (E_A) of this reaction is calculated to be approximately 300 kJ per mole.[10]

Temperature	23 C	43 C
Rate of passivation	$9.7 +/-2 *10^{-4}$	$1.2+/-0.1 *10^{-3}$
Extent of passivation (10^{10} traps/cm^2)	0.79+/-0.08	0.56+/-0.04

Table 2.3 The rate and extent of MeO-passivated silicon in MEOH:I_2 at different temperature.

---

[10] Rate of passivation (dNt/dt) = $A*e(-E_A/RT)$, where R=8.314KJ/mole, and T is in Kelvin, and the exact E_A = 280.9 kJ/mol.

These data also indicates that the extent of passivation increases with increasing in temperature. This is because the heat applied allows either weakening of the Si-H bond or breaking some of them as shown in equation 2.11 B. This effect facilitates subsequent reaction of this silicon with iodine ion as well as the iodine radical. In addition, increase in temperature will established a new equilibrium. Since EtO-Si is about –378 kJ/mol more stable than that of Si-I (see equation 2.14), [11]thus according to the Le-Chatelier principle, we can infer that the equilibrium favors the formation of Si-I. [12] Therefore, at higher temperature the surface coverage of Si-I increases, which is a undesirable passivant in air, and the detail will be discussed in Section 2.9.

Si-I +EtOH→ EtO-Si + HI ΔH_f= -378 kJ/mol (Equation 2.14)[13]

2.8 Investigate solution quality

This section is dedicated to evaluate how the quality of the solution, and its oxygen content influence the alkoxy passivation technique. These experiments are of manufacturing importance as high quality solvents and degassing.

2.8.1. Metal content of solvent used

In this section, the alkoxy passivation effect is investigated by using two different quality of commonly used cleanroom solvent. One of them is the standard CMOS grade

---

[11] Formation of this exothermic Si-O bond drives this reaction.

[12] RFPCD cannot distinguish the difference between Si-I, MeO-Si, or H-Si. The primary function of RFPCD is to detect weak bonds, i.e. mid level traps. The detail will be discussed in 2.13.

[13] ΔH_f =Enthalpy of formation.

provided by Ashland, while the other one is the Ultrapure grade from Kanto, which is of lower metal content.

Experimental procedure

The experimental procedure was the same as that stated as Procedure A except that two different quality of organic solvent are used. In addition, there was no pre-degassing, i.e. the solution used was atmospheric saturated. One of them is Ashland CMOS grade MeOH, which has less than 100 ppb of metals with no particles specification.[14] The other one is ultra-high purity MeOH provided by Kanto. This is of extra high purity with most of the metals content less that 1 ppb, but it contains less than 5 ppb of sodium and zinc. The particles in this solution are 0.5 μm in diameter with less than 60 particles per ml.

Result and discussion

Table 2.4 summarizes the results. From this data, we can conclude that higher quality solvent yields lesser numbers of surface trap states. This is consistent with the discussion in Section 2.3.2 , where metallic impurities degrades silicon wafers.

Chemical Quality	Ashland CMOS Metals< 100ppb	Ultra pure Kanto Na, Zn < 5ppb Others Metal < 1ppb
N_t (10^{10}/cm^2)	1.57	0.10+/- 0.01

Table 2.4 In-situ N_t recorded from different quality of organic solvents used.

2.8.2 Use of atmospheric saturated solution

---

[14] Data sited from M'saad's thesis, and the wafer thickness is 500 um [8].

Wafer processing requires particle free environments, thus, ultra-pure and low particle argon gas was used for removing the oxygen from the solution. This is a cost ineffective process. However, some companies in the U.S. employ this technique to improve their wet cleaning process. Therefore, it is worthwhile to investigate how methoxy passivation performs under regular low cost atmosphere and costly degas atmosphere.

Experimental procedure was basically the same as A, with the degas step eliminated for the non-degas experiment. The organic solvent used was Kanto Ultra pure MeOH, and the HF used was Ashland Gigabit.

Results and discussion

Solution	Degas DHF	Non-degas DHF	Degas MeOH :I_2	Non-degas MeOH :I_2
10^{10}Nt/cm^{2}	1.0+/-0.2	2.8+/-0.3	0.65+/-0.04	1.0+/-0.1

Table 2.5 N_t of silicon wafers in degas solution and non-degas DHF and MeOH:I_2.

From Table 2.5, we can conclude that the degassed solution will yield higher quality silicon surfaces. This is because oxygen competes with the passivants such as H or I to react with the silicon surface. Once a Si-O bond is formed, further passivation with H or I is impossible as Si-O is a very strong bond, which is of the order of 799.6 kJ/mol. Si-H and Si-I are much weaker bonds, which have enthalpies of formation of 299.2 and 293 kJ/mol respectively. The other conclusion one can draw from this experiment is that we can use high quality solvents such as Kanto Ultrapure organic solvent to avoid using the degas environment for alkoxy passivation. This is because the improvement of using degas environment for alkoxy passivation is about 1.5 better than the non-degas situation vs. in the situation with using degas

DHF, almost three times improvement is possible. Of course, detail financial calculation will justify if degas is necessary when this process is used by the industry. As for convinience, the experiments for the rest of the chapter do not use degas environment.

2.9 How alkoxy passivation reduces surface traps

To observe how alkoxy passivation takes place, in-situ RFPCD provides the answer. Figure 2-4 shows an in-situ measurement of a passivation of silicon in non-degassed DHF and its subsequent transferral to a non-degassed MeOH iodine solution. In DHF, a equilibrium N_t of $0.31 *10^{11}/cm^2$ is recorded. [15] This number is reduced to $0.018*10^{11}/cm^2$ within 3 min when this Si-H wafer was immersed in MeOH:iodine solution.[16] However, there is a sudden increase in inverse lifetime during the transfer process. This is because, during transfer in air, Si-H is exposed. This degrades the wafer quality. Hence, an increased in surface-trapped states are recorded by RFPCD. Yet, there are left over active sites (unpassivated sites such as Si• and poorly passivated sites such as Si-F) to allow MeOH passivation to take place besides site exchange, i.e. changing from Si-H to MeO-Si as described in Section 2.9) This leads to an increase in the extent of passivation. The following equations describe the reactions involved.

Reactions with polar Si-F:

Si-F+ MeOH$\rightarrow$ MeO-Si + HF ΔH = -389.6 kJ/mol (Equation 2.15)

Reaction with dangling bond:

Si• + I•$\rightarrow$ Si-I ΔH= -293 kJ/mol (Equation 2.16)

Si-I + MeOH$\rightarrow$ MeO-Si + HI ΔH= -378 kJ/mol (Equation 2.17)

---

[15] The flat part of the curve in Figure 2.4 is corresponds to the equilibrium lifetime.

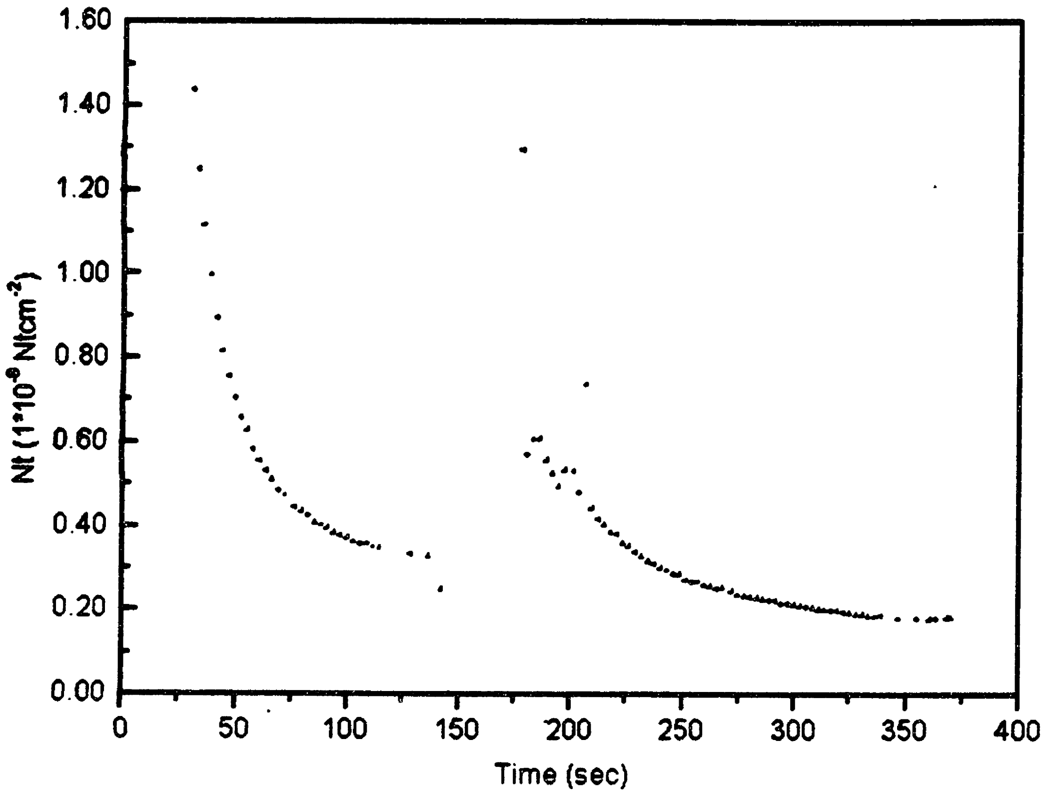


Figure 2-4 In-situ passivation in atmospheric saturated DHF and subsequent immersion in atmospheric saturated MeOH:iodine.

---

[16] A normal MeOH:iodine immersion required a 45 min to one hour 20 min immersion.

2-10 New Processing steps remove iodine and particles for gate oxide integrity testing

From previous experiment and results, we conclude that alkoxy passivation increases the extent of passivation in solution as well as resisting oxidation in air. The next step is to test the reliability of this new technology.

A. Process modification

Procedure A gives rise to a MeO- termination with 10 percent of Si-I remaining on the surface after MeOH/iodine immersion. Burr demonstrated that subsequent MeOH rinses removed iodide sites and reduced Si-I coverage to 5% [11]. In order to bring this technology to the cleanroom facility at IBM-Yorktown Heights, further reduction in iodine coverage is needed. Therefore, a MeOH bath is added after procedure A to improve the extent of MeO- passivation. The immersion time of this bath was between 3 to 5 min. (This new procedure will be referred to procedure B.)

At Yorktown Heights, another problem arose. Particle counts test on the MeO- surface demonstrated that this surface attracts particles. An additional water rinse was suggested. With this additional step after procedure B, a particle free surface was formed (The sequence of these new processing steps is referred as procedure C). The particle counts data is illustrated in Figure 2-6 and 2-7. The number of particles deposited on the silicon wafer after a Marangoni dry with subsequence spin drying has a similar number of particles as the wafer cleaned by procedure C. Therefore, a preliminary conclusion is that MeOH passivation does not attract particles onto the surface of silicon.

B. Gate oxide Integrity Testing

Experimental procedures

IBM provided 8-inch wafers to be used. There are two types of wafers. One was used for gate oxide evaluation, and the others were tested wafers for RFPCD measurement. These wafers were cleaned by the state of the art pre-clean procedure with hydrophilic last cleaning step. These wafers were then divided up for the three different types of cleaning procedure: (1) RCA clean followed with hydrophilic last step, (2) DHF clean followed with Marangoni drying technique, and (3) MeOH clean.

The procedure for MIT's methanol passivation performed on a pre-cleaned oxidized silicon wafer was: (1) 2 min immersion in dilute hydrofluoric acid bath (0.5%); (2) 1hour and 20 min immersion into a $5*10^{-4}$ M of iodine in MeOH; (3) immersion into MeOH bath for 3 min, (4) 2 dips into a water flow bath (Procedure C).[17]

Wafers from three different types of passivation were then transferred to the furnace immediately. They were subjected to the same oxidation process and a subsequent poly-gate deposition to form N+ on P capacitor structure (Capacitor and FET N+ gate structure). All wafers were processed to M1 level. They were then tested for charge to breakdown (Q_{bd}) by constant voltage stress, and quantum mechanical/electrical oxide thickness was determined by Capacitance/Voltage (CV) measurement [16].

Results and discussion

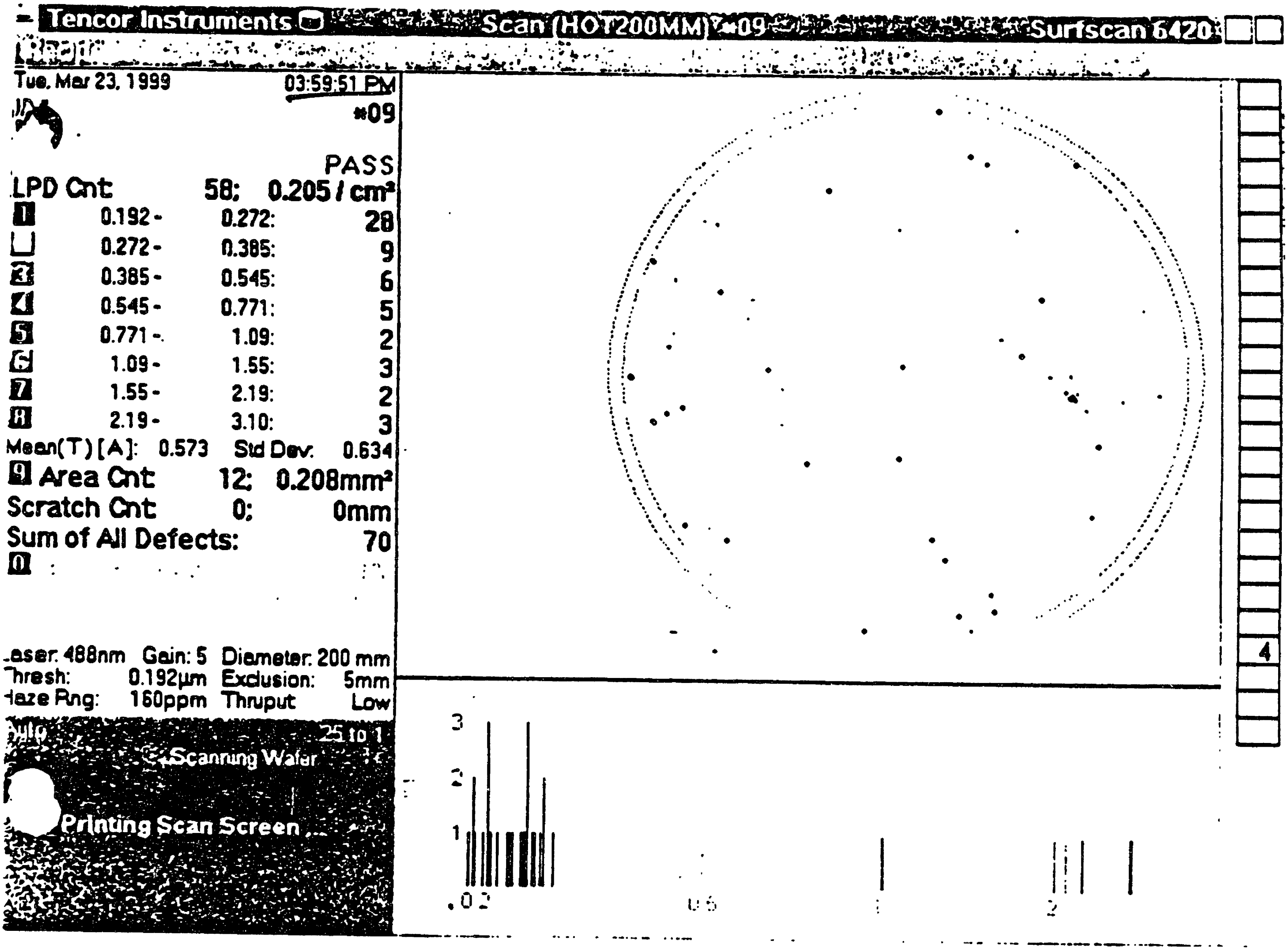
The results collected from Q_{bd} and Time to breakdown (T_{bd}) are shown in Figures 2-8 and 2-9 respectively. A summary of different oxide thickness is shown in Table 2.6. There is a significant reduction in thickness achieved by MeOH clean. This is most likely due to delay in burning off the methoxy group. In Figure 2-8 and 2-9, despite methoxy passivation appear to have the lowest reliability among other types of passivation, when the thickness were being taken into an account for these Qbd and Tbd tests, IBM researchers conclude that the reliability of the thinner dielectrics grown on MeOH/Iodine is equivalent to a RCA type or HF last cleaning processes. In short, MeOH passivation yielded a thinner ultra thin gate oxide with the same reliability as industrial standard cleans as RCA and HF methods. In addition, a high interfacial lifetime for gate oxide grown on MeO-Si substrate of 1.4+/-0.2 $(ms)^{-1}$ was recorded with RFPCD. This indicates a smooth interface. This smooth interface is most likely due to consistent rates of heterogeneous nucleation onto almost homogeneous MeO-passivated surface.

Type of clean use	MeOH Clean	DHF-last Clean	RCA-type Clean
Thickness (A)	21.04	21.66	22.13

Table 2.6 Difference in thickness of gate oxide formed from different surface preparated silicon.

---

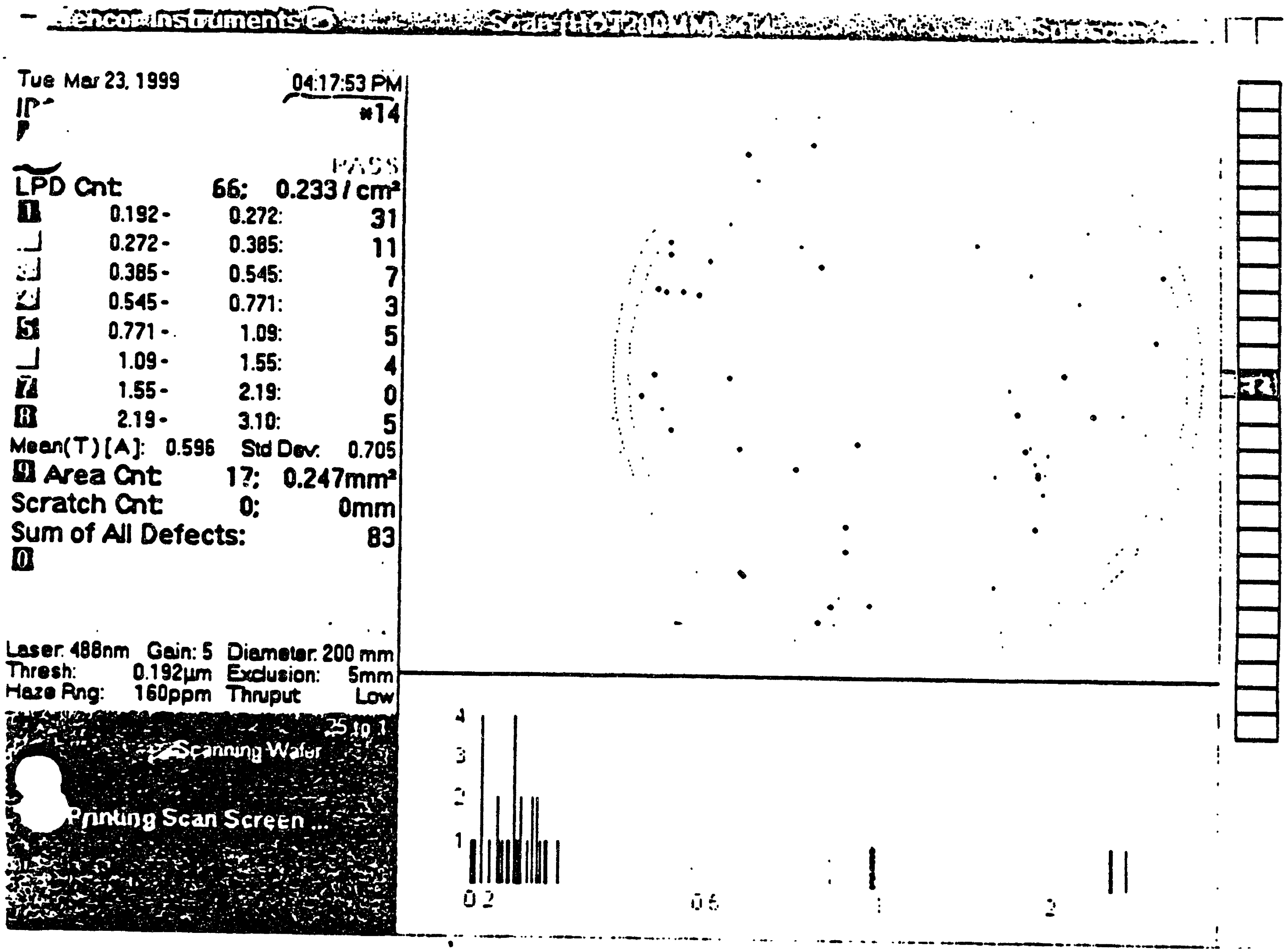
[17] No degas for this procedure C.



```
Tencor Instruments  Scan (HOT200MM) #09  Surfscan 6420
Tue, Mar 23, 1999            03:59:51 PM
                                     #09
                                    PASS
LPD Cnt              58;   0.205 / cm²
1       0.192 -    0.272:             28
2       0.272 -    0.385:              9
3       0.385 -    0.545:              6
4       0.545 -    0.771:              5
5       0.771 -     1.09:              2
6        1.09 -     1.55:              3
7        1.55 -     2.19:              2
8        2.19 -     3.10:              3
Mean(T) [A]:  0.573   Std Dev:     0.634
9 Area Cnt          12;   0.208mm²
Scratch Cnt          0;          0mm
Sum of All Defects:                   70
0

aser: 488nm   Gain: 5    Diameter: 200 mm
Thresh:       0.192µm    Exclusion:  5mm
Haze Rng:     160ppm     Thruput     Low
                                 25 to 1
Scanning Wafer
Printing Scan Screen
```

Figure 2-6 Particle count data for MeO-passivation after spin-drying.



Tue Mar 23, 1999 04:17:53 PM

#14

PASS

LPD Cnt 66: 0.233 / cm²

1	0.192 -	0.272:	31
2	0.272 -	0.385:	11
3	0.385 -	0.545:	7
4	0.545 -	0.771:	3
5	0.771 -	1.09:	5
6	1.09 -	1.55:	4
7	1.55 -	2.19:	0
8	2.19 -	3.10:	5

Mean(T) [A]: 0.596 Std Dev: 0.705

9 Area Cnt 17: 0.247mm²

Scratch Cnt 0: 0mm

Sum of All Defects: 83

0

Laser: 488nm Gain: 5 Diameter: 200 mm

Thresh: 0.192µm Exclusion: 5mm

Haze Rng: 160ppm Thruput Low

25 to 1

Scanning Wafer

Printing Scan Screen ...

Figure 2-7 Particle count data for H-passivated silicon after spin-drying.

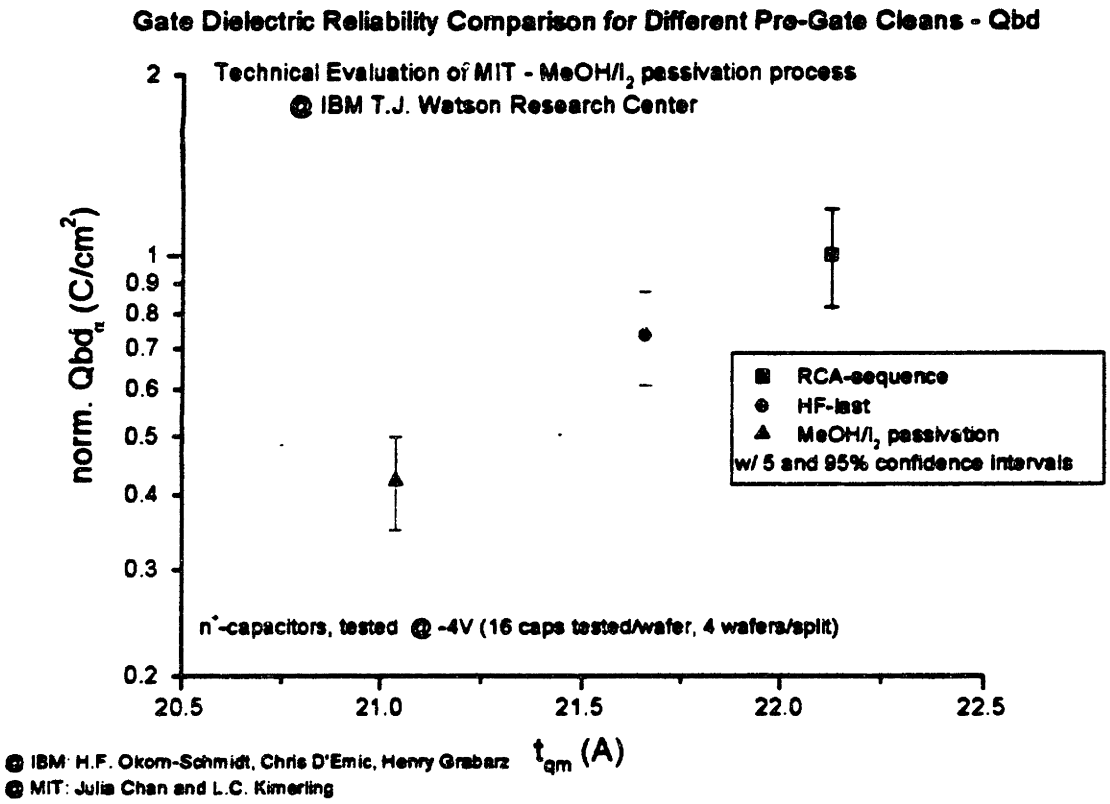
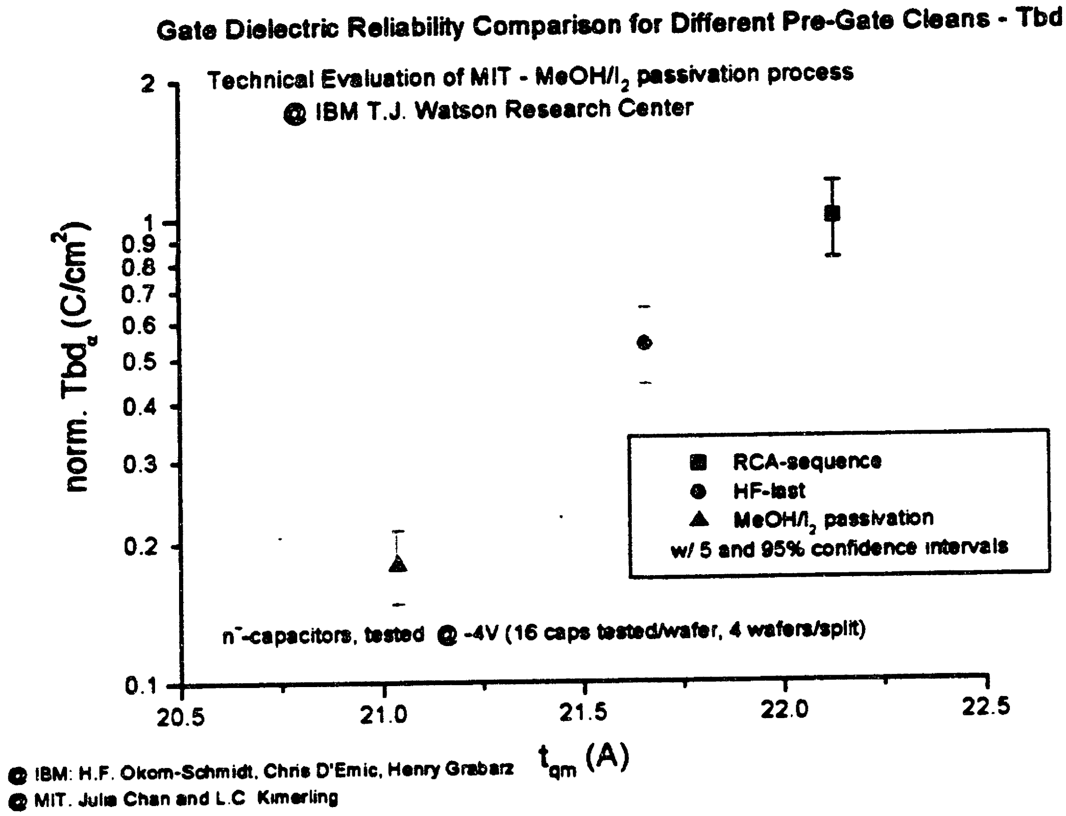


Figure 2-8 Qbd for different pre-gate cleansing processes.



@ IBM: H.F. Okom-Schmidt, Chris D'Emic, Henry Grabarz

@ MIT. Julie Chan and L.C Kimerling

Figure 2-9 Tbd for different pre-gate cleansing processes.

2.11 Process Optimization

2.11.1 New processing steps to remove weak Si-I sites

In order to optimize this process, we should first identify whether MeO-Si, or I-Si provides a better passivation against air degradation. Therefore, in this section, a saturated iodine MeOH solution is used to generate a 0.6 monolayer (ML) of iodine on the bare silicon surface [11]. Then, a in-situ RFPCD measurement is performed in air to observed how robust this surface is against air degradation.

Results and discussion

Figure 2-10 displays an in-situ degradation of 0.6 monolayer covered Si-I surface. The rate of degradation of this surface is 5 $*10^9$ $N_t/cm^2/sec$, which is 13 times faster than an Si-H surface (Summary of degradation rate is shown in Table 2.7).

This observation can be explained by the fact that, not only Si-I is a polar site, which facilitate water deposition (hydrophilic), and hence native oxide formation [17], but it also weakens the back bond like that of polar Si-F sites.[18]

---

[18] The mechanism will be discussed later.

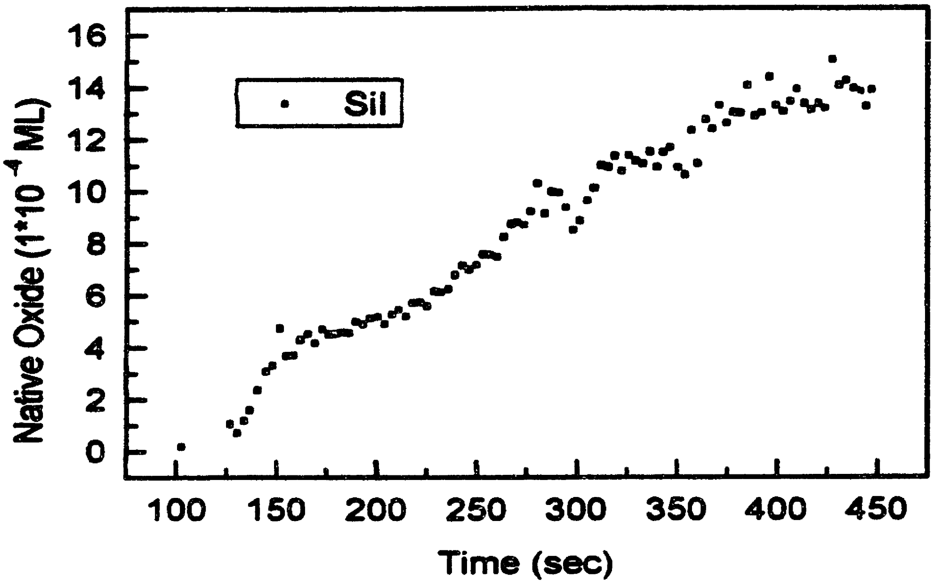


Figure 2-10 Air degradation of 0.6 ML of Si-I.

2.11.2 Thermodynamic effect

Since formation of MeO-Si is favored by equilibrium thermodynamics, thus, increasing the time of immersion of the wafer in pure MeOH bath will allow the silicon surface to reach a new equilibrium covering with more MeO-. Figure 2-11 shows the in-situ measurement of silicon wafer coming out of MeOH iodine solution with subsequent transfer to a pure MeOH bath.

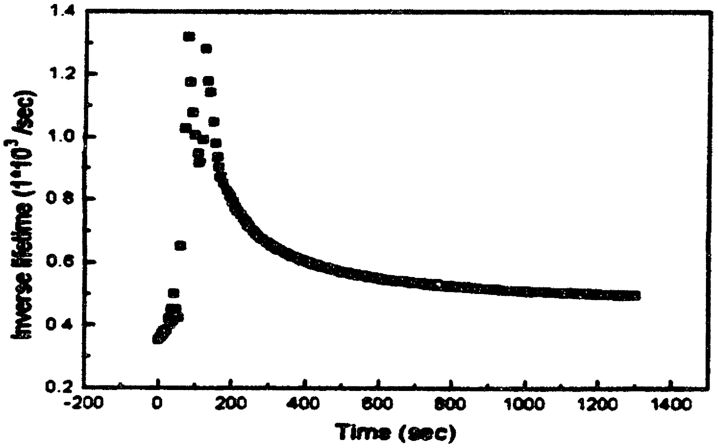


Figure 2-11 In-situ measurement of silicon wafer transfer from MeOH:iodine to MeOH.

Results and discussion

This result demonstrates the power of RFPCD to capture in-situ surface quality. At time zero, where the wafer was still in MeOH:iodine solution, a 0.3 $(ms)^{-1}$ equilibrium lifetime was observed. As demonstrated in Burr thesis [11], approximately 10% of Si-I was covered on the surface and the rest of the surface was covered with MeO-Si. This wafer was then transfer in air to another solution of pure MeOH. During exposure to air, the unpassivated dangling bond Si• will be oxidized by air directly because of its reactive nature (See equation 2.18). Polar bonds such as Si-I and Si-F (if present) will first be oxidized (Relative rate of air degradation of different passivation is shown in Table 2.7, where 0.6 ML of Si-I degrades 658 times faster than MeO-Si covered surface.). Some MeO-Si may be oxidized as well. The mechanism for native oxide formation is believed to be moisture assisted back bonding attack of reactive oxygen atom and hydroxy group as shown in Figure 2-12. [17]. After the silicon atom in this surface layer has been completely bonded with oxygen, SiX_2 will fall off (X stands for I, F, or MeO species.). Thus, the underlying native oxide is exposed. Since the air exposure time is less than a second, only a small number of these sites are being oxidized. Therefore, during re-immersion in MeOH, a lot of Si-I and may be some Si-F sites are still available for reacting with MeOH to form MeO-Si. Therefore, the final inverse lifetime in pure MeOH is only 0.5 $(ms)^{-1}$, and cannot re-reach the low value ($0.3\ ms^{-1}$) in MeOH: iodine solution because some of those weak sites are lost to air oxidation.

$$\bullet Si\text{--}Si\bullet + \frac{1}{2} O_2 \rightarrow Si\text{-}O\text{-}Si \qquad \text{(Equation 2.17)}$$

In short, by monitoring the immersion time of the silicon wafer in pure MeOH bath before equilibrium, the amount of Si-I and potentially Si-F on the surface can be controlled. Figure 2-11 shows the in-situ measurement of the number of traps form of all these MeO-passivated wafers and a Si-H passivated wafer when they were exposed to air. The linear part of this slope is fitted with the linear regression formula as stated in the experimental section. These results are summarized in Table 2.7. In addition, using this linear regression technique, the initial number of traps at time zero of different passivation is identified as well. Note that in Table 2.7, for an optimized MeOH passivation, where the sample is immersed in MeOH for 30 min., has comparable amount of initial number of traps as that of Si-H passivated surface. This indicates that this additional pure MeOH bath allows complete removal of Si-I sites left behind from the former MeOH: iodine bath. The main result of this finding is that this optimized MeO-passivated silicon is 48.7 times more stable than convention H-Si passivation against air degradation. (Note: The observation for the first 500 sec will be discussed in the following section.)

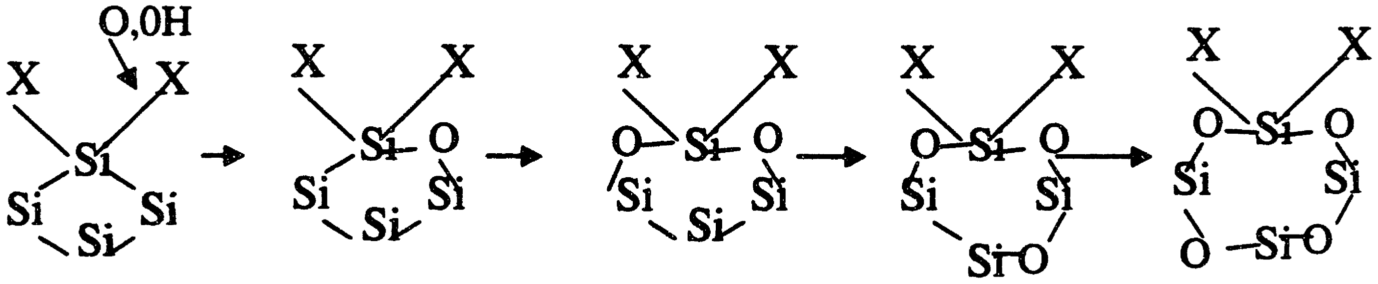


Figure 2-12 the mechanism for air degradation (X-Stands for F, I, MeO)

Surface	Si-H	MeOH 5 min	MeOH 8 min	MeOH 30 min	Si-I
Rate of degradation ($1*10^7 N_t/cm^2/sec$)	37	3.64	1.16	0.76	500+/-200
Initial N_t ($1*10^{10} N_t/cm^2$)	9.7	11.6	10.0	9.2	N/A

Table 2.7. Summary of air degradation rate and initial number of traps formed from different surface preparation.

To understand this effect, one should look at the chemical structure of this methoxy passivated silicon surface. As shown in Figure 2-12, oxygen, being an electron donor, is able to partially donate its lone pair to the neighboring dangling bonds. This electronic donation effect is even stronger for iodine since iodine is less electronegative than oxygen. However, this donation results in weakening the O-Si bond of MeO-Si. Thus, RFPCD will pick up this signal as weak sites as the primary function of RFPCD is to detect the presence of mid level traps due to weak bond formation.

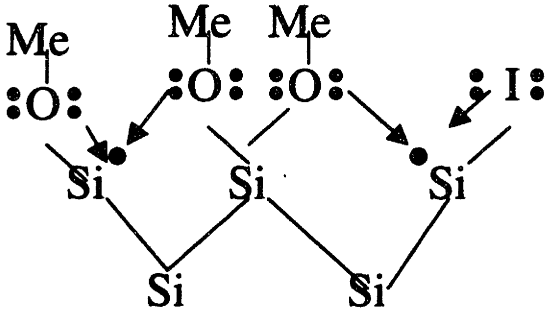


Figure 2-13 Lone pair effect which accounts for the initial observation in air degradation for the first 500 seconds of MeO-Si.

This bond weakening effect disappears graduately as the wafers expose to oxygen (Conformational relaxation of surface). This is because those dangling bonds react with oxygen, thus, the lone pair effect disappears, and allows a complete recovery of O-Si of MeO-Si.

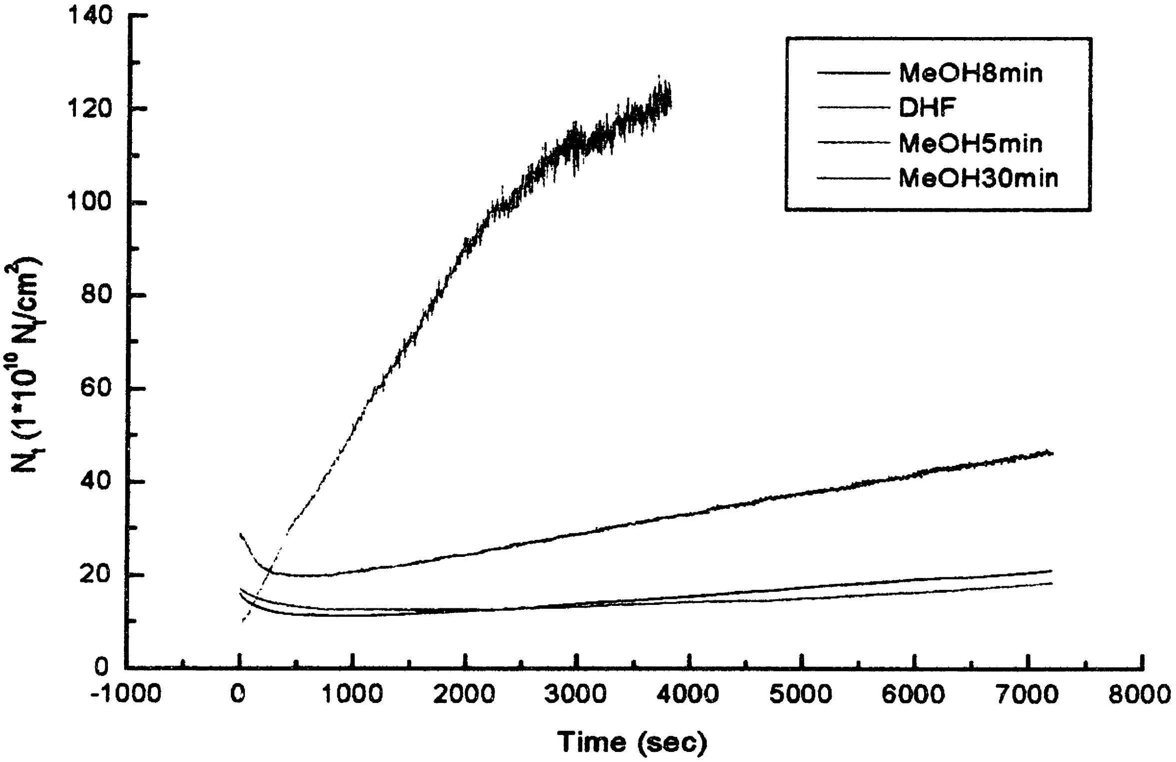


Figure 2-13 Complete in-situ air degradation of different type and different extent of passivation.

2.12 Initial degradation effect

During the first 500 seconds of in-situ measurement of air degradation of MeO-passivated surface shown in Figure 2-11, the initial number of traps at time zero recorded is very high, then, the number of traps for these MeO-Si surface decreases in air, i.e. recovery.

2.13 Moisture Effect of oxygen degradation on H-Si surface

Moisture facilitates silicon surface degradation in air has been well studied. Using RFPCD technique, we are able to record the sub-monolayer kinetic of air degradation during the first 100 min.[19] Figure 2-15 shows the in-situ measurement, and rate of air degradation onto these wafers are summarized in Table 2.8.

Atmosphere	Dry Oxygen	Wet Oxygen
Rate of native oxide formation (10^{-8}ML/sec)	1.63	3.55
Initial number of traps (10^{-4} Nt/cm^2)	1.31	1.37

Table 2.8 Degradation rate of H-Si in dry and wet oxygen.

---

[19]

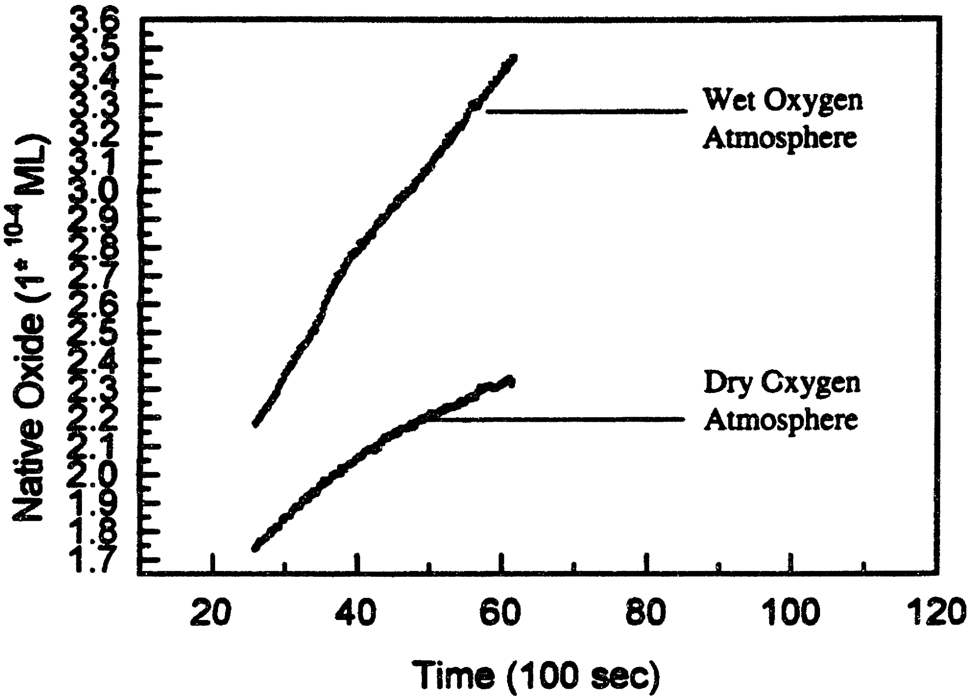


Figure 2-15 Moisture effect on native oxide formation on H-Si

Results and Discussion

As indicated by the above data, moist atmosphere degrades the wafers about two times faster than dry cxygen. Therefore, two ways of reducing air degradation effect are suggested. One is to avoid moisture from the cleanroom, while the other one is to make the silicon surface protective, i.e. passive, or hydrophobic. Therefore, in the following section, hydrophobicity of this alkoxy-passivated wafer will be investigated.

2-15 Hydrophobicity of MeO-Si

A hydrophobic wafer surface is important for several reasons. A hydrophobic surface reduces physisorption water onto the wafer surfaces, which (1) retards native oxide formation [4],[5], and (2) prevents particle deposition by capillary action [6].

Experiment procedure

Procedures were the same as procedure C. Before passivation occurred, contact angles were measured on this oxide. Contact angles of subsequent processes are being measured. Table 2.9 summarizes the results. And Figure 2-16 displays the contact angle captured on MeO-Si.

States of Silicon	Thermo-oxide	Oxide formed after Piranha bath	H-terminated Silicon	MeO-terminated Silicon	Isopropanol-terminated Silicon
Contact angle	25.5	~0	80+/-2	73.5+/-5.5	90

Table 2.9 Contact angle measurement on different type of surface passivated silicon

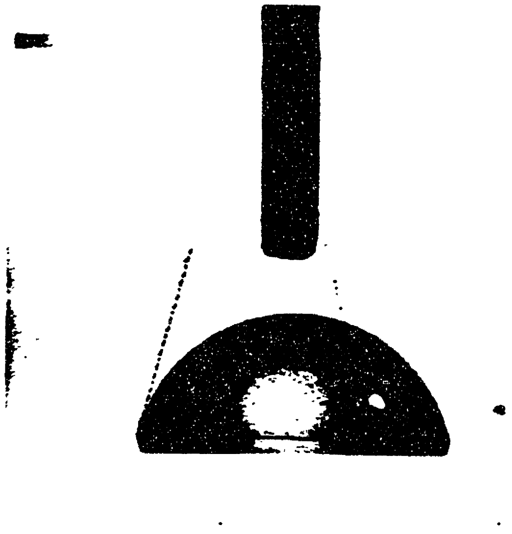


Figure 2-16 Contact angle of a water droplet forming on MeO-Si. A contact angle of 73 is recorded.

Results and Discussion

Contact angle measurement will determine the hydrophobicity of a surface. A contact angle larger than 40 degrees indicates that the surface is hydrophobic. From Table 2.9, one can concluded that an oxidized silicon surfaces are hydrophilic surfaces because their contact angle is smaller than 40 degrees. However, such a surface is stable towards air degradation. Thus, the silicon underneath is well protected.

The current HF-last cleans, used in the semiconductor industry, yield contact angles around 60-80 degrees [6]. Our HF-last clean yields a hydrogen-terminated surface with a contact angle of about 82 degrees, and a methoxy-terminated surface has a contact angle of about 70 degrees, and isopropoxyl-terminated surface has a contact angle of 90 degree. From this data, an increasing contact angle, i.e. hydrophobicity, was observed with using alcohol with bigger organic head groups.

This observation can be explained by understanding what causes hydrophobicity. A hydrophobic surface simply means that water does not spread on it. This effect can be evaluated by the geometric mean technique based on summation of dispersion force. Some of the forces contributing to this interfacial interaction (surface tension) are metallic bonding, hydrogen bonding, and London dispersion forces (dipole-dipole attraction) [19]. The resultant of these forces can be displaced in the vector diagram shown in Figure 2-1.

Large contact angle was observed in the H-termination because hydrogen and silicon have similar electronegativity. As a result, a non-polar surface is formed. This surface will naturally repel the polar water molecules.

On the other hand, the hydrophobicity in alkoxy termination is dominated by a permanent dipole. The oxygen atom carries a partial negative charge, and the organic head groups of the alkoxy molecules are therefore positively charged. This dipole interacts with water molecules, which have strong permanent dipole moment. However, unlike Coulomb interaction, which falls as $(1/R)$, dipole interaction falls sharply with distance $(1/R^3)$, where R is the intermolecular distance between the surface and the moisture. Therefore, when the organic groups increase in size, not only the charge density of each organic head groups decrease, but most importantly, the distance of interaction increases. This accounts for the increasing hydrophobicity with bigger organic head groups [20].

2.16 Cost of ownership concerning MeO- passivation vs. H-passivation.

A cost estimate is performed between conventional H-passivation with re-cleaning and MeO-passivation. The numbers used here are estimated in order to illustrate this concept. As stated earlier, a conventional H-passivation with re-cleaning will include RCA clean with DHF last, sacrificial oxide, and DHF last cleaning or another RCA clean with DHF last. This additional sacrificial oxide step is estimated to reduce the yield to 93%. On the other hand, methoxy passivation is a complete wet bench process, i.e., no sacrificial oxide is needed, therefore, no lost in yield for this process. Since we defined cost of ownership as

CoO=(fixed costs +operating costs)/(yield (Y)*throughput(T) *utilization (U)) (Equation 2.18)

The corresponding trade off positions between those terms are as follow:
1) Fixed costs:
  A) MeO passivation requires 1) a new system to deliver MeOH, 2) a complete set of new tools. An extra cost of this tool as compared to conventional wet bench tools is around $0.2 million per line.
  B) MeO- passivation does not require a furnace for sacrificial oxide. Therefore a fixed cost of $100,000 for furnace purchase can be saved.
2) Operating costs:
MeO passivation has lower operating costs because
A) It does not require any sacrificial oxide. This will save approximately $ 6000 US worth of electricity per month.
B) The deposition cost of MeOH and HF is assumed to be the same.
3) Yield
It is assumed that both processes will give the same yield. This is consistent with the prelimary results collected from IBM on a non-optimized process.
4) Utilization
Since MeO-passivation will not require sacrificial oxide formation and re-clean, therefore, the utilization of wet branch and furnace increase. An estimate of two times improvement will occur.
5) Throughput
This will increased because less time is waste for re-clean.

Calculation

A) The change in CoO of using MeO- passivation for a year:

  - (0.2million-100,000-6000*12)/2 U*Y*T =14000/U*Y*T

B) Breakeven occur when the change in fix cost is balanced by the energy saved term:

  - 0.2 million-100,000=6000*12* number of year needs to reach breakeven
  - Breakeven= 1.38 years.

2.17 Conclusion

An optimized methanol passivation yields a MeO- terminated surface that is 49 times more resistance to air degradation than H-Si. This hydrophobic surface resists water film condensation. And therefore, it reduces moisture assisted particle deposition and organic contamination, and oxygen degradation. A preliminary gate oxides integrity test on a non-optimized methoxy passivation process has shown that a thinner ultra-thin gate oxide is formed on this surface, which has similar reliability as those wafers that are cleaned by RCA and HF type cleans. An estimated cost of implementation is performed, which illustrates that the breakeven year is around 1.4, which demonstrates that this passivation is worthwhile to investigate in. However, there are environmental concerns of using MeOH and iodine. MeOH itself has a flashpoint of 11 C. Thus, it is flammable in air. Special containers are needed to incorporate in the conventional wet bench process [21]. In addition, iodine may cause birth defects. Besides, the current manufacturing end of pipe abatement system is not designed to trap small organic molecules like MeOH [22]. However, the novel stability of this consistence surface yields a processing advantage. With further manufacturing investigation, there is a possibility to use this process to benefit the next generation high performance device.

Chapter 3

Two Approaches for Environmental Safety and Health (ESH) in Microelectronic Industry

3.1 Introduction

Conventional engineering focuses on optimization by lowering the cost of production and maximizing the profit. Cost of ownership (CoO) is widely used in evaluating new technology in the microelectronic industry (Figure 3.1) [23].

$$\text{Cost of Ownership} = \frac{(\text{Fixed costs} + \text{Operation costs})}{\text{Throughput} * \text{Yield} * \text{Utilization}} \qquad \text{(Equation 3.1)}$$

However, this CoO does not incorporate risk factors such as probability of accident, cost of compensation, etc. associated with the process of interest. Therefore, it does not match with the need of ESH manufacturing. In this chapter, therefore, the importance of toxicity and life cycle analysis of chemicals are illustrated with the use of arsenic implantation. In addition, a cost comparison between environmentally benign alternatives to conventional equipment for arsenic implantation is done to demonstrate the limitation of this formation. This calculation foreshadows the need of new environmental figures of merit to incorporate employee health and environmental impact. The content of this chapter has been used in the Microelectronic Processing Technology class (3.155J/6.152 J/10.480J) at MIT and the Engineering Research Center (ERC) to raise the awareness of future engineers and scientists.

3.2 Toxicity in Manufacturing Processes

3.2.1 Background

In this chapter, a well-known and widely used toxic compound, arsine (AsH_3) is studied. This compound contains Arsenic (As), a group V element, which serves as an important dopant for making n-type silicon. This n-type structure appears in many electronic devices.

This section is sub-divided into three parts. First, a description of As implantation will be given (Engineering). Then its impact on human health will be discussed (toxicology, followed by a life cycle analysis of As within the fab will be illustrated. Then an ESH engineering design solution based on using the results from lifecycle analysis is suggested, followed by a discussion which demonstrates that an ESH incorporated cost of ownership is needed to evaluate the impact of chemicals on human beings as well as on the environment.

Ion implantation takes up approximately 10 % of the total processing space in a fabrication factory [18]. A typical As doping equipment set up is shown in Figure 3-1.

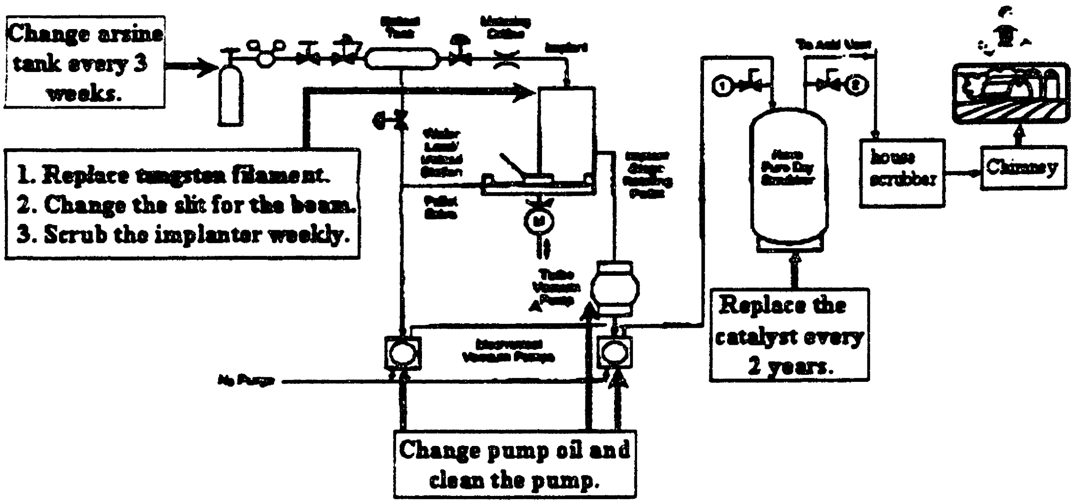


Figure 3-1 Point and frequency of exposure of arsenic compounds in arsenic implantation.

In this figure, point and frequency of exposure are illustrated. This figure defines the life cycle analysis of chemicals used within the fab. The starting point is on the left hand side of the figure where arsine is delivered in gaseous form in a high-pressure cylinder. The arsine tank is located on the production floor. It has to be replaced every 3 weeks. During implantation, arsine goes through the implanter where actual implantation of As into the silicon wafer takes place. The circulation of As into the implanter is achieved by the mechanical pumps. 95% of arsine going through the implanter is unused and, consequently, is removed by the mechanical pump. The exhaust of this pump will pass through the scrubber. Finally, this un-used gas will be further purified by the house scrubber, which contains solution that dissolves most of the remaining chemical. This house scrubber is connected to the chimney to release all the purified gas to the atmosphere [24]. According to the dry scrubber provider, Novapure, no more then 5 ppb of Arsine gas will be able to escape the chimney, and this is below the threshold limit value (TLV). [1]

Maintenance such as replacing the tungsten filaments will expose the workers to solid arsenic waste. Other maintenance steps include changing the slits for the As beam and scrubbing the ion implanters on a weekly basis. Moreover, the oil in the pump may trap some arsenic compound. Therefore, it has to be changed as well. Generally speaking, it is more cost effective for the company to let the pump run down rather than to dispose of the oil as required [25]. The ultimate arsenic trap in this system is a dry scrubber, which contains catalyst that can react with As gas to form solid arsenic oxide. Although arsenic oxide is toxic, it is solid at room temperature and pressure. Therefore, it is safer for the workers to handle. In addition, this catalyst only needs to be replaced every 2 years; therefore, it has dramatically reduced the frequency of exposure of workers to arsenic compounds [24].

Besides using dry scrubbers to remove As, some companies use burn boxes to oxidized As gas into solid form, or to use wet scrubbers, which contain permanganate to oxidize the As gas into As (VI) oxide. The equations of all the reactions are summarized in Table 3.1

---

[1] TLV stands for threshold limited value, and will be discussed in chapter 4.

***Burn Box*:**	$2AsH_3 + 3O_2 --> As_2O_3 + 3H_2O$
	$4AsH_3 + 3O_2 ---> 4As^0 + 6H_2O$
***Dry Scrubbing*:**	$2AsH_3 + 3CuO ---> Cu_3As + As^0 + 3H_2O$
	$Cu_3As + As^0 + 3O_2 --> 3CuO + As_2O_3$
***Wet Scrubbing*:**	$4MnO_4^- + 2AsH_3 --> As_2O_3 + H_2O + 4 MnO_2 + 4OH^-$
	$32MnO4^- + 12AsH_3 --> 3As_4O_{10} + 2H_2O + 32OH^- + 32MnO_2$

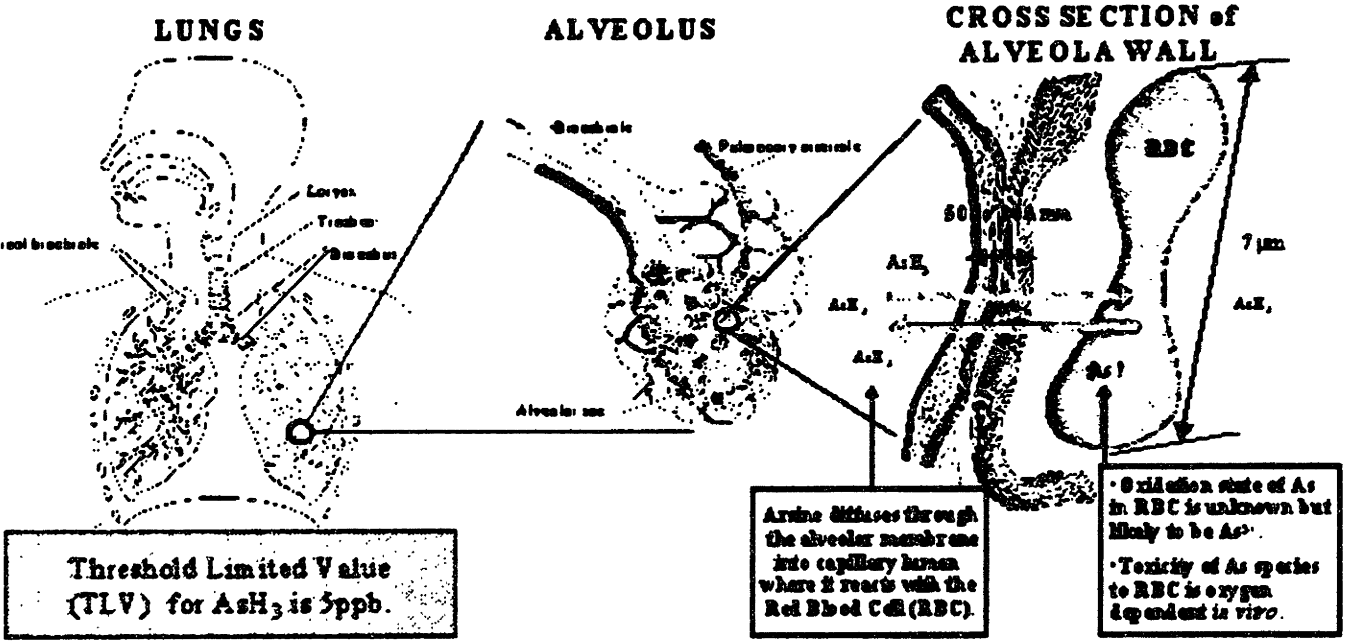
Table 3.1 Equations for removing arsine down stream.

3.2.2 How does As intoxicate human beings?

Most engineers I have interviewed are aware of the toxicity of As, but they do not know how As intoxicates human beings. It is therefore very important to describe the toxic pathway: Entrance, metabolism, and excretion of toxin. This is of great importance because by understanding when and where the toxin is within the patients' body, an appropriate treatment can be delivered to them.

3.2.2.1. Common exposure

The main route of exposure to arsine is inhalation. Figure 3-2 shows the pathway. First, arsine is inhaled through the nostril to reach the respiration system. Then, it diffuses through the alveolus membrane into the blood stream and reaches the red blood cells (RBC). RBC's contains millions of hemoglobin molecules. Each hemoglobin contains 4 Heme groups, which are the only units used for carrying fresh oxygen to our body. Arsine reacts with the Heme group to form methemoglobin, which is a higher oxidized form than the useful oxyhemoglobin. Thus, this reaction reduces the oxygen carrying capacity of RBC. Arsine reacts with other sites of the hemoglobin. This will result in protein denaturing to form insoluble precipitates called Heinz bodies. All of these reactions will lead to the rupture of hemoglobin. And thus, it reduces the oxygen carrying capacity of the blood stream. In a serious situation, this can result in death [23].



Threshold Limited Value (TLV) for AsH_3 is 5ppb.

Arsine diffuses through the alveolar membrane into capillary lumen where it reacts with the Red Blood Cell (RBC).

- Oxidation state of As in RBC is unknown but likely to be As^{3+}.
- Toxicity of As species to RBC is oxygen dependent *in vivo*.

Figure 3-2 Diffusion of arsine gas through the human respiration system

Besides the above pathway, there are a couple other pathways that may cause the rupture of Hemoglobin. First, arsine may undergo redox chemistry to produce hydrogen peroxide, which will lead to the rupture of RBC. The other suggests that arsine may inhibit catalase and the Na/K-ATP ase. Both of these catalysts are important enzymes within RBC. Their damage may cause cell rupture. Both of these events lead to acute poisoning [26]. (Figure 3-3 shows the structure of healthy hemoglobin.)

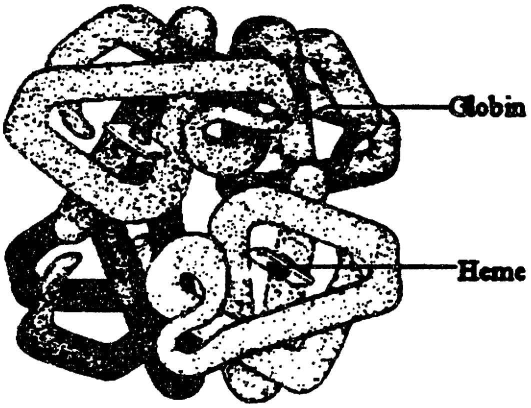


Figure 3-3 The structure of a healthy hemoglobin.

3.2.2.2 Common causes of fatalities: Kidney Failure

Kidney failure is the most common symptom for arsenic poisoning. Figure 3.4 shows a cross section of the human kidney. A human kidney contains thousands of nephurons, one of which is shown in Figure 3.5. Each nephuron is a filtration unit, which filters the unwanted substances from the blood. Arsine intoxicates the tubule cells of nephuron, as a results, dead tubule cells accumulate in the tubular lumen, resulting in renal failure [27].

Kidney

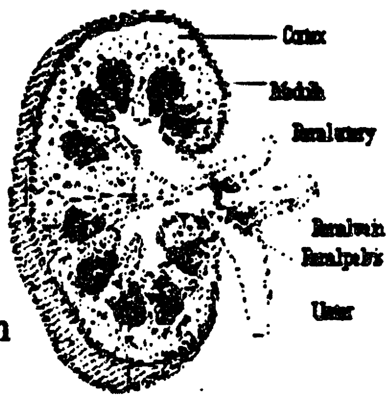


Figure 3-4 Cross Section of human kidney

Nephuron

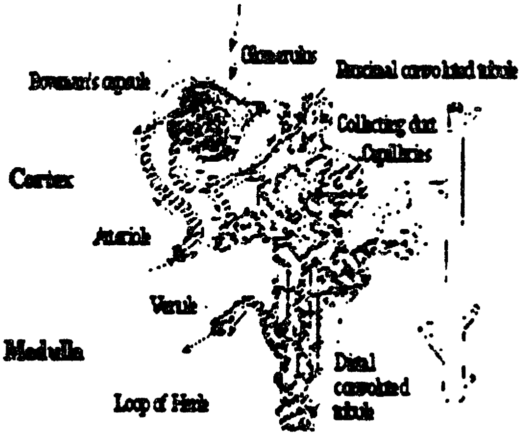


Figure 3-5 Nephuron, the fundamental filtration unit of the kidney.

Other studies in human beings have shown that arsenic poisoning will lead to glomerular damage as well as necrosis damage (Both are the cells of Nephuron). This will results in ineffective filtration. Thus, some RBC may excrete out in the urine. This is called red urine. In addition, other blood proteins are also found in the urine as well.

In fact, this is a typical exposure symptom for workers. In severe cases, permanent kidney damage may result. However, dialysis can restore proper kidney functioning [23].

3.2.2.3 Toxicity associates with chronic exposure

Chronic exposure of workers often happens during handling of arsenic oxide from waste or solid arsenic [25]. This chronic exposure to arsenic compound has cumulative damaging effects. Inorganic arsenic is a skin and lung carcinogen; chronic loss of RBC will lead to anemia. Moreover, the patients will have a higher risk of diabetes and cardiovascular disease. In addition, the peripheral and central nervous system will be affected [26].

3.2.3 Life cycle analysis for the environment

This section is dedicated to discussion of the importance of life cycle analysis (LCA) for estimating the possible environmental cost of waste disposal. Arsenic waste is trapped by pump oil, by the slurry from scrubbing the implanters, and in the wet and dry scrubbers. This waste is then delivered to the waste handling companies. Therefore, this handling cost is incorporated in the operation cost of conventional CoO. Since this waste will be properly handled, it will not be counted as an environmental cost from the prospective of microelectronic industry. Through careful mass balance calculation, waste that escapes to the environment can be assessed through the use of this LCA. Thus, a new cost term, Environmental Safety and Health Factor (ESHF), can be developed. This term will be incorporated into the operation cost term of this conventional CoO to account for environmental cost imposed by the fab. Details will be discussed in the following chapter.

3.3 ESH Engineering

ESH engineering is defined as an alternative means of development, which will increase operational and environmental safety. Since acute toxicity imposes major financial burdens, which are caused by down time for inspection, clean up, and monetary compensation for injured employees, it should always be avoided. According to LCA of Figure 3-1, acute toxicity on the employee will most likely occur during tank changing, therefore, this is the area that ESH engineering shall take place.

3.3.1 Engineering Question: What can be done to avoid arsine gas leakage?

Conventional systems utilize high-pressure arsine containing tanks to store arsine molecules. Yet, with the use of a high surface area catalyst, a lot of arsine molecules can be stored at negative pressure with respect to the atmosphere. This source of arsine is called the Safety Delivery Sources (SDS), in which arsine is delivered to the implanters by concentration and pressure difference [28].

Implementation of this technology requires that the CoO will not be too high to reduce the competitiveness of the fab. Therefore, a relative cost of ownership as shown in Table 3.2 to demonstrate whether this technology is worthwhile for implementation.

F=fixed costs; *P*= operation costs; *T*=throughput, *Y*=yield, *U*=utilization
Fc=fixed cost for conventional high pressure arsine tank; Fs=fixed cost of SDS, etc.
SDS estimate

- Fixed costs (increase)
    - **Equal to *F* + the cost of delivery system hardware and software + some other components**
- Operation costs (similar)
    - **Function of total time of workers , cost of materials, *e.g.*, wafers, cost of arsine, electricity, etc.**
    - **Reduction in loss of workers time in changing AsH_3 because the lifetime of SDS increased approximately by a factor of 2.**
    - **Cost of AsH_3 per atom in SDS is 2 to 3 times higher then high pressure tank.**
    - **Other functions of operation costs remain unchanged.**
- Utilization (increase)
    - **More utilization of ion implanters as well as other machines because less time is spent on changing the AsH_3 cylinder.**
- Throughput and yield are estimated to be the same as regular AsH_3

Table 3.2 CoO of SDS vs. convention high pressure arsine used for arsenic implantation.

Based on the above information, we have performed the following estimation of SDS vs. conventional arsine tank. First, we assume that the throughput and the yield do not change. From the information in Table 3.2, the operation cost of SDS is approximately 3 times more than the operation cost of conventional arsine tank (Ops(tank)). Yet, we estimate an improvement of utilization of SDS by a factor of 2, i.e. utilization of SDS is equal to 2U(tank). If we further assume that in the lifetime of an implanter, the fixed cost become very much less than the operation cost, then, we can approximate that the CoO of SDS is equal to 1.5 times the CoO of conventional arsine tank.

Despite the increase in CoO for using SDS, many fabs have decided to use SDS because safety is the most important criteria for manufacturing. This example indicates the insufficient information provided by this simple CoO. However, in the following chapter, a new ESH CoO will be defined such that the safety of a technology or chemical to both the environment and human beings can be quantified.

3.4 Conclusion

This chapter delivers 4 important concepts. First, life cycle analysis is an effective means to identify point and frequency of exposure and to trace the environmental impact of chemicals used. This will lead to a new operation cost to be incorporated in the ESH CoO in the following chapter. Secondly, environmentally benign manufacturing is an interdisciplinary subject that needs to be incorporated in academic curricula to educate future scientists and engineers to be aware of implementing and designing ESH processes. Thirdly, cost of implementing safer technology may bring some manufacturing benefits such as increase in utilization and decision-makers cannot ignore the significance of these factors. Most importantly, conventional CoO does not incorporate the ESH factors, and therefore, in the following chapter, a new ESH CoO will be developed for a conclusive evaluation of new technology.

Chapter 4

Risk Assessment: New Strategy for Rapid Chemical Evaluation (RCE) and Environmental Responsibility

4.1 Introduction

There are 100 newly made chemicals being used in the manufacturing facility (fab) each year [29], and significant amounts of these chemicals are made to test for the possibility of creating the perfect lithography. However, the toxicity of these chemicals is not known.

In the conventional sequence for researching new chemicals, the R & D process takes approximately 7 to 10 years. This is followed by a 1-4 year period to set up new tools for this new chemistry. During this period, the ESH solution will also be integrated. Another two more years will be spent for manufacturing optimization. However, if EPA identifies that this new chemical is toxic, this chemical will not be allowed in use. Thus, 10-12 years of human resources, time, and money will be wasted. Therefore, new ways of early screening of chemicals is of urgent need. The biggest problem is that there is no data for assessment of the toxicity of new chemicals [30].

4.2 Regulation for Existing Chemical

Toxicity limits for exposure in the US are set up by three agencies. The Occupational Safety and Health Administration (OSHA) has set up Permissible Exposure Limits (PELs). As of today, it has set up 470 PELs for various forms of approximately 300 chemical substances. The majority of these limits were established in 1971 when OSHA was first created. The data are based on literature studies of many different toxicology experiments in the 50's and the early 60's. Since 1996, OSHA has been attempting to revise those old standards. Yet, no particular systematic experimental strategy is proposed [31].

National Institute for Occupational Safety and Health (NIOSH) defines its Recommended Exposure Limit (REL) of exposure to chemicals by conducting field studies. These studies are called the Health Hazard Evaluations (HHEs). These HHEs investigate possible health hazards in the workplace. Evaluations are brought on by requisitions submitted by employers and or employees. Much of the REL were done under the authority of Occupational Safety and Health Act in 1970 [32].

The Procedure of NIOSH is listed as follows:

This NIOSH Project Officer will contact the requestors, the employers, and the local union representatives, if they exist, to discuss the request in order to plan for a visit to the workplace. Yet, not all requests will lead to a site visit.

If a site visit is warranted, the following procedure will take place.

1. Direct observation and evaluation of production processes and employee work practices.
2. Measurements of air contamination levels and extent of employees' exposure.

3. Medical tests or physical examinations of employees.

4. Review and evaluations of the employer's records of injuries and illnesses (OSHA logs), employee exposures, medical tests, and job histories. Sometimes one or more site visits may be needed to complete an evaluation.

The third agency is the American Conference of Governmental Industrial Hygienists (ACGIH), which was set up in 1936. It focused on addressing many issues in relationships with industry, labor, the medical profession, and other agencies, technical standards, educations, uniform reporting, illnesses among workers, etc. In short, it focuses on industrial atmospheres and industry and government relationships [33].

Among the many activities ACGIH performs, setting the Threshold Limit Values (TLV) of Chemical Substances is its most well known accomplishment. The earlier form of TLV was called Maximum Allowable Concentrations. TLV was introduced in 1956, and it referred to Time Weighted Average (TWA) for an eight-hour work shift. The first documentation of the TLVs was published in 1962. As of today, there are more than 700 chemical substances and physical agents as well as 50 Biological Exposure Indices for the selected chemicals [34].

4.3 Evaluation of New Chemicals

According to the Toxic Substances Control Act (TSCA) under federal law, the chemical identity, production volume, proposed users, estimates of exposure and release, and any available health and environmental test data of all newly made chemicals for industrial manufacturing and usage have to be reported to the Environmental Protection

Agency (EPA) 90 days before their production. Although there is no requirement for the manufacturers to conduct testing for any newly made chemical before its entry into the market, EPA uses its own Structure Activity Teams (SAT) to evaluate those chemicals. If these teams of chemists, toxicologists, and environmental scientists conclude that there is insufficient information for the chemical or they suspect that chemical may present risk to the environment and human health, then, under section 4 of TSCA, EPA has the authority to request the manufacturer or processors of chemicals to run toxicity testing on those chemicals, or EPA may prohibit or limit the production of those chemicals [34].

As essential minerals such as iron supplements have their limit of intake, the chemicals used in a manufacturing environment have their own limits of exposure. The current standards, as stated in the last section, are Threshold Limit Values, Permissible Exposure Limit, and Recommended Exposure Limit. These limits were developed in the 70's based on the data collected on the 50's and 60's. This data consists mostly of animal testing and historical records on human health. In general, this toxicity data is collected from many different experiments. Over time, those experiments do not run on large numbers of human samples. Because of this, an extrapolation factor is developed to map those data to human relevance. Table 4.1 summarizes the rank of human relevance of those data. The higher the relevance of those data to humans, the lower the extrapolation factors [35].

Table 4.1 Human relevance ranking

Relevant ranking	Experiment
1 (Highest relevant)	Large scale human chronic exposure data.
2	Acute human exposure data.
3	Large scale, long term, multi-species animal data.
4	Long-term, single species animal data.
5 (Lowest relevant)	Acute animal exposure data.

4.4 Recommended Rapid Chemical Evaluation (RCE)

For modern semiconductor manufacturing environments, these toxicity tests are not quite necessary. First, cleanroom environments stress non-contact automation to reduce contamination. All operators wear bunny suits with goggles and gloves to prevent contamination. Many of the machines are operated by Program Logic Controllers, in which, the well-protected operators only need to work with the computer. In addition, individual tools have their own built-in exhausts [30]. As the microelectronic industry moves toward smaller device dimensions, minienvironments are gaining increasing popularity. The minienvironment contains wafers and chemicals completely isolated from the operators to reduce contamination. Based on the characteristics of clean-room manufacturing environment, toxicity testing are unnecessary and beyond affordable cost for the current semiconductor manufacturing environment, where the success of a manufacturing facility is a strong function of (1) short time to market and (2) low manufacturing cost.

4.5 Standard tests recommended for the IC industry to validate human factors

In vitro study, in fact, is very suitable for evaluating chemical exposure limits for today semiconductor manufacturing environment. Not only do the tools in use minimize the contact between users and the chemicals, but also accidental spills are confined to skin and inhalation only. Besides, in-vitro studies can provide rapid turnaround time for test results. This is equivalent to rapid use of new chemicals in the manufacturing facilities, and rapid new products to the market. The other experimental advantages of using in-vitro tests are summarized in Table 4.2.

Table 4.2 Advantages of using in vitro toxicity testing system [36]

- Allow for control of environmental conditions
- Eliminate interactive systemic effects
- Utilize large number of test organisms (cells) per dose level
- Reduce variability between experiments
- Allow for simultaneous and/or repeated sampling over time. Make feasible complex interactive toxicity experiments
- Are often quicker and cheaper
- Require smaller quantities of test chemicals
- Produce smaller quantities of toxic waste
- Utilize human cells
- Reduce intact animal usage

Based on the information generated from in-vitro testing, a new standard is therefore proposed here for rapid chemical screening for semiconductor manufacturing industry. This method involves the use of in vitro toxicology testing, in-vitro toxicokinetic studies, Structure-Activity Relationships (SAR)[1], tier strategy[2], computer simulations of toxicokinetics, and computer simulation of physical conditions to generate in vitro toxicity limit as a function of exposure time. Then, an extrapolation factor is determined to set the limit of exposure to human relevance. In addition, based on the Toxicity impact on human health, the cost of medication and compensation can be evaluated. We name this cost term as "Human Factor (HuF)".

This Human Factor can be incorporated in the operation cost term in the cost of ownership by multiplying it by the probability of an undesirable accident that might happen in a given period of operation. This term is named "Human Operation Cost (HOC)" (See Equation 4.1). To account for environmental cost of those chemicals, which are not accounted for by proper waste disposal, we used the "Environmental Safety and Health Factor (ESHF)". This cost term comes from detailed mass balance with the aid of life cycle analysis (LCA). Both of these can be added to the conventional operation cost as described in Equation 4.2. The new ESH incorporated CoO is displaced in Equation 4.3.

Human operation cost (HOC)= P(HuF)*HuF (Equation 4.1)

Total operation cost in a defined period of time=
conventional operation cost term + ESHF+HOC (Equation 4.2)

---

[1] SARS has been using recently for predicting toxic potentials for chemicals. The relationship is determined principally by either the physicochemical or electronics properties of the chemicals,. Mathematical expressions can be formulated such that toxicity can be predicted without testing in any biological system [34].

[2] Tier Strategy is widely used in cosmetic industry, in which products are variations in formulations of previously marked products. Step 1 is to used the historical database of former products. Step 2. Run small Battery of in vitro testing Step 3. If results from step 2 is consistent with historical base. This is followed by human volunteer testing. This strategy avoids unnecessary animal testing [34].

$$\text{ESH CoO}=\frac{(\text{Fix cost} + \text{Conventional operation cost}+ \text{ESHF}+ \text{HOC})}{(\text{Yield}^{*}\text{Throughput}^{*}\text{Utilization})} \quad \text{(Equation 4.3)}$$

$$\text{ESH CoO}= \text{CoO} + \frac{\text{ESHF} + \text{HOC}}{(\text{Yield}^{*}\text{Throughput}^{*}\text{Utilization})}$$

$$\text{Environmental Figure of Merit} = \frac{\text{ESHF} + \text{HOC}}{(\text{Yield}^{*}\text{Throughput}^{*}\text{Utilization})}$$

P(HuF)=Probability of exposure over a defined period of time
HuF=Human Factors (cost of exposure)
ESHF=Environmental Safety and Health Factor

4.6 In vitro toxicity tests

In vitro testing, a human cellular based test is used to identify cytotoxicity. Its current application involves determination of corrosivity to human skin. For example, if the transcutaneous electrical resistance (TER) measured across human skin is below 11 ohm/disc, then, the chemical is considered to be corrosive. Table 4.3 states other uses of in-vitro testing to predict toxicity.

Table 4.3 Examples of Applications of Cells In Vitro in Toxicology [36]

- General cytotoxicity, mainly related to acute toxicity, including lethality, skin and eye damage
- Organ-specific toxicity
- Mechanisms of toxicity
- Biotransformation to toxic metabolites
- Genotoxicity (e.g., unscheduled DNA synthesis.)
- Reproductive toxicity
- Mixture toxicity
- Comparative toxicity
- Photosensitivity

A scheme of the toxicological process is display in Figure 4-1. This process includes many interacting processes such as toxicokinetics, initiation, and toxicodynamics. Toxin is absorbed into the body after initial exposure. These toxins can be excreted, stored, or distributed to intoxicate the subjects. The active form of the toxin is labeled as T in this diagram. The formation of T is controlled by toxicokinetic process. Once T is formed, it will interact with molecular targets M (Initiation). This interaction results in altemations in cellular macromolecules, M*. These macromolecules initiate the cascade of biological events level called toxicodynamics. These events begin at the molecular, cellular, and eventually extend to higher levels of biological organization. In-vitro study can evaluate events happening in the molecular and cellular level as indicated in the box [37].

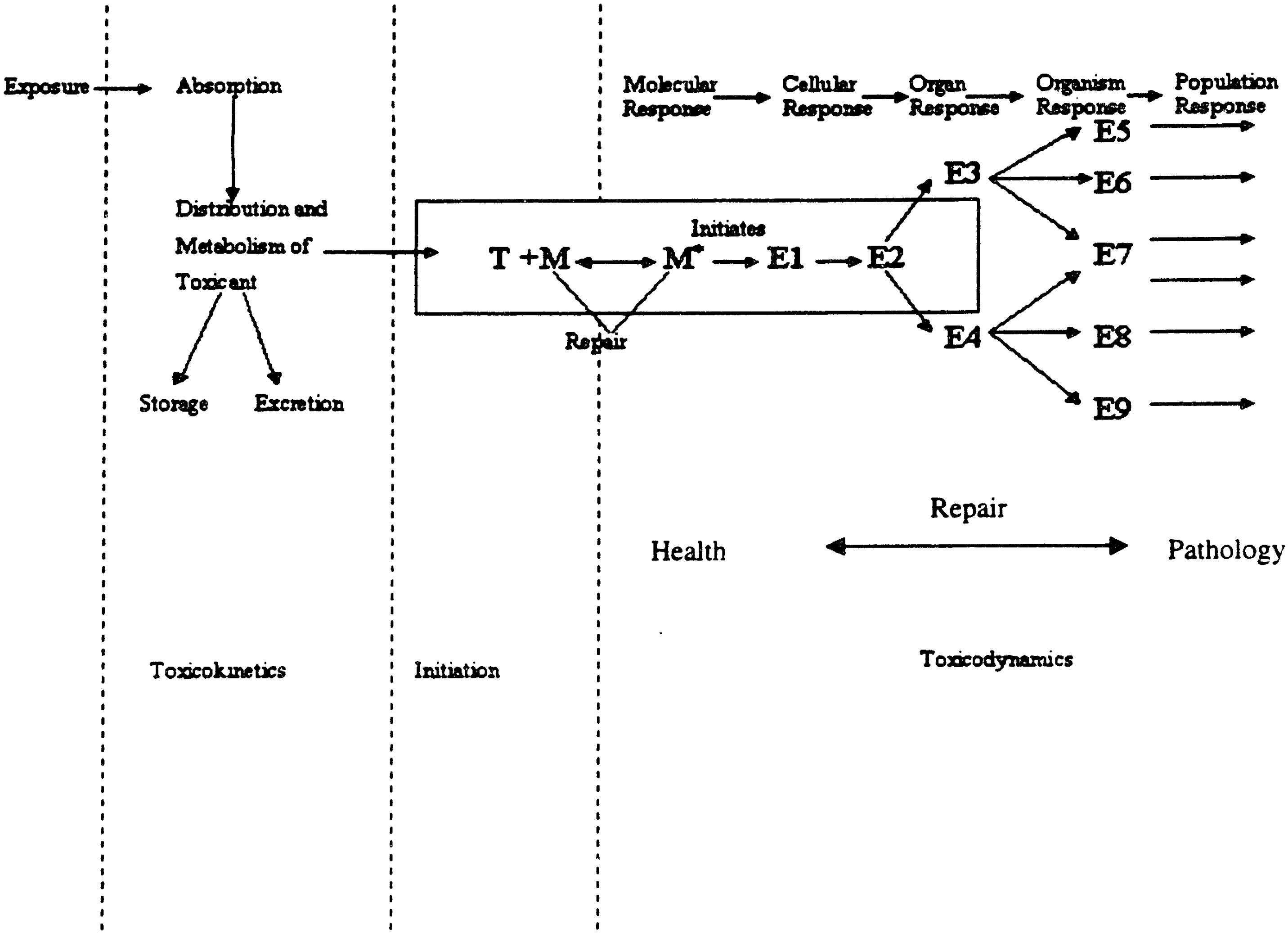


Figure 4-1 Diagram of the toxicological process [37].

Table 4.4 Examples of Cells In vitro that have been used in toxicological studies [38]

- Fibroblasts from various species
- Lymphoblastoid
- Ascites sarcoma
- Lymphocytes
- Keratinocytes
- Liver cells, mainly hepatocytes
- Hepatoma
- Kidney, medullary and cortical cells
- Lung, various types
- Brain-derived cell types
- Dorsal root ganglia cell cultures
- Testicular cell cultures
- Sertoli cells
- Bladder cells
- Heart cells
- Cells from cerebral microvessels
- Adipocytes

Table 4.5 Biological Endpoints for detecting cytotoxicity [39].

Endpoint	Endpoints measurement
Cell morphology	Cell size and shape
	Cell-cell contacts
	Nuclear size, shape, and inclusions
	Nuclear number, size, shape, and inclusions
Cell viability	Cytoplasmic vacuolation
	Vital dye uptake
	Tyypan blie exclusion
	Cell number
	Replating efficiency
Cell adhesion	Attachment to culture surface
	Cell-cell adhesion
Cell proliferation	Increase in cell number
	Increase in total DNA
	Increase in total RNA
	Increase in total protein
	Colony formation
Membrane damage	Loss of enzymes (e.g. LDH)
	Loss of ions or cofactors (e.g. Ca2+, NADPH)
	Leakage from preloaded cells
Membrane damage	Thymidine and DNA synthesis
	Uridine and RNA synthesis
	Amino Acids and Protein synthesis
Metabolic effects	Inhibition of metabolism cooperation
	Cofactors depletion (e.g. ATP)
	Mitochondrial function

To define Human Factors, first the chemical entrance pathway to the operators must be identified. For example, in a manufacturing facility, the most common exposure pathways are inhalation and skin contact. Based on SAR, one can identify the biological pathway after the chemical enters the human body. If SAR does not exist for this particular toxin, one can use a spectrum of cell types from various organs (hepatocytes, proximal tubular cells, neurons, cardiac myocytes, etc.) to identify which cell types are more sensitive to the toxin of interest (See Table 4.4). If this toxin then triggers other metabolic activities, those cells will be cultured in the presence or absence of that metabolizing system [36]. From this experiment, cellular toxicity can be identified by measuring the biological endpoints. Table 4.5 shows a list of biological end points.

To obtain an extrapolation factor to human relevance, we have to overcome some of the difficulties of in vitro toxicity testing with computer simulation. First, the fundamental problem of in vitro tests is that it focuses only on initiation, and cellular and molecular response [36], therefore, the biological pathways of the toxins cannot be evaluated directly. However, this situation can be relieved by computer simulation. For example, if a new compound A is closely related to compounds B, C, and D[3] which has extrapolation factors developed, then, one can use computer simulation to assess the extrapolation factor of compound A. For example, one can use the SAR strategy with computer simulation to generate weighted factors (in percentage) for each of the extrapolation factors of B, C, and D respectively, then, multiply them with the extrapolation factors of B, C, and D respectively. The accuracy of these extrapolation factors increases if B, C, and D, are closely related to A, or if there are more terms contribute to this linear combination formula.

$$E(A) = W(B) * E(B) + W(C) * E(C) + \ldots\ldots\ldots \qquad (1)^4$$

$$W(B) + W(C) + \ldots\ldots\ldots = 1 \qquad (2)$$

E(A)= Extrapolation factor of A, etc.
W(B)= Weight factor of B for compound A.

---

[3] Closely related means that they have similar toxicity effect base on same sets of in vitro studies and they also have related functional groups.

[4] W(B) etc, is the weight factor of chemical B. And E(A) etc. is the extrapolation factor of A.

The second problem of in vitro testing is that it cannot measure how a toxin triggers the immune response, which results in affecting other cell types. However, this can be overcome with the advancement of toxicology studies of cellular mechanism. In addition, if some biological markers such as cytokines are identified, then, corresponding interactive biological processes can be obtained [36].

Even better, one can use computer simulation to simulate the physical and the biological environment (Toxicokinetic). Both of these will increase the accuracy of in vitro testing, and therefore it also increases the accuracy of Human Factor. For example, if a tank of arsine leaks in an open space, it will cause less harm on humans and cost less for the companies to compensate the workers and for cleaning up than a leak in confined environment. In the case of simulating the biological environment, one can use the existing toxicokinetic information as well as other physical information to overcome the lack of in vitro studies. For example, we can use Fick's law of diffusion[5] to estimate the time needed for arsine or other gases to permeate the inhalation system. This translates to how fast a toxin will intoxicate human beings, therefore, an accurate limit of exposure can be determined.

Another limitation of the vitro toxicity study is that it cannot predict chronic exposure limit because a lot of pathological pathways are still poorly understand [36]. However, in cleanroom environments where tools are equipped with their own exhausts, and for the microelectronic industry using minienvironment tools, in vitro studies are good assessments for evaluating the toxicity impact of chemical use.

4.7 Using LCA to evaluate ESHF

The cost of disposal of waste generated from any process is incorporated into the conventional operation cost. Yet, with the use of LCA discussed in Chapter 3, a detailed environmental cost can be assessed. This term is referred to ESHF and will be incorporated into the operation cost. Using arsine as an example, the used dry scrubbers are collected by a waste handling company. The mass difference between the unused dry scrubber and the used scrubber allows manufacturers to calculate the amount of arsenic waste generated.[6] If we subtract what is collected by the dry scrubber by the amount of incoming arsenic compound, then, we can estimate how much waste ends up in the slurry and pump oil.[7] If the amount measured in the slurry and pump oil does not match up with the calculated value, then, significant amounts of arsenic compounds have been leaked to the environment, and this can give rise to the true environmental cost of a process, what we called the ESHF, which is a function of penalty from the corresponding government agency, and its unit is in US dollars.

---

[5] $\text{Rate} = K\,\Delta\,PA*s/d/(MW)\wedge^{0.5}$ (Where K=constant, P= pressure, A= surface area, d= distance of diffusion, mw= molecular weight.)

[6] The scrubber provider can give the exact number of efficiency, thus allowing an exact weight of Arsenic to be calculated.

4.8 Environmental Safety and Health Cost of Ownership

By using the LCA, one can identify the most risky operation. In ion implantation, the most risky operation is the sudden leakage of arsine gas. This implies that an ESH technology is needed for this part of the system. To assess the feasibility of using a new ESH technology, we can perform the following calculation. Table 4.6 shows the assumed number for illustration of the proposed concept. In short, ESH CoO added an environmental figure of merits to the conventional CoO. Let us assume that HuF for exposure of 5 ppb of As in 5 min without explosion is a million dollars US,[8] and should be the same for both gas sources since they deliver the same gas. But the probability factor, i.e., the risk of exposure between two sources can be very different. We can define the probability of exposure as a multiple of probability of making a mistake * relative leak rate. [9] Assume for both SDS and conventional arsine sources the same probability of making a mistake. Then, the probability of exposure is equal to the relative leaking rate. Therefore, the probability of exposure, P(HuF), of SDS then can be estimated to 0.0001, and the P(HuF) of arsine tank is 0.1. To be consistence with Chapter 3, we assume 1) the yield and throughput are the same, 2) the fix cost is much smaller than the operation cost in the lifetime of the implanter, and 3) the utilization of SDS is two times that of the conventional tank.

---

[7] Pump oil and slurry are also collected by waste handling company. Only those waste not collected by the waste company are considered as environmental hazard.

[8] This cost come is a function of downtime, medication, and explosion if there is any.

[9] (The rate of leaking in an ESH source/the rate of leaking in a conventional source)

Table 4.6 ESH CoO item's cost displace for SDS and conventional arsine source (tank)

Items	SDS	Tank
Relative Utilization	2*U	U
Probability for in accident to occur over a period of a year	0.0001	0.1
Human Factor (Cost for compensation, down time, etc.)	1 million	1 million
Environmental Figure of Merits/ Y*U*T	500	100,000

From this table, we can conclude that the environmental figure of merit of the conventional tank is $100, 000 and $ 500 for using SDS. This implies, approximately, the relative cost of ownership of SDS will be only 1.5 CoO (tank)[10]-100,000/Y*U*T. Because of this ESH term, the cost of implementing a safer technology is justified. Therefore, ESH CoO is the cost of ownership to be used in today semiconductor manufacturing sites.

4.9 Conclusion

To match with global competition, and the demand of EPA, a cost effective and rapid way to evaluate newly made chemicals is of urgent need. This chapter demonstrates that in vitro studies can assess toxicity efficiently for cleanroom operations. In addition, this term can be converted into dollar costs by multiplying the probability of risk of operation of a particular tool in a defined operated period of term. In addition, the amount of untreated chemical can be assessed through the use of LCA such that a

---

[10] CoO (SDS)=1.5 CoO (Tank) was derived in Chapter 3.

corresponding environmental cost (ESHF) can be obtained. Both of these terms can be added to the operation cost such that an ESH CoO can be obtained for decision makers to justify whether it is cost efficient to implement a safer technology.

Chapter 5

Policy Analysis of Engineering Research Center (ERC): A strategy for environmentally benign manufacturing

5.1 Introduction

Environmental issues have become global concerns among government, citizens, and many industries. To achieve this common good, cooperation in both international levels to national level among industries is required. Yet, industrial collaboration has been a difficult subject because of global and national competition among players who share the same market. To facilitate cooperative effort in achieving environmentally benign manufacturing so as to revolutionize the current manufacturing methods in semiconductor industry, the Engineering Research Center (ERC) was set up by the National Science Foundation (NSF) and the Semiconductor Research Cooperation (SRC). This center aims to enhance research development at the university level, which is well known as a creative source for industry.

In the semiconductor industry, innovation and low cost are the key elements for success of the individual company. Cooperation, therefore, is hindered. Learning from difficulties in sharing industrial research, ERC has adapted the neutral middleman strategy to facilitate collaboration between semiconductor industry participants. This is achieved by using the University of Arizona as the center of collaboration. Moreover, students are the primary tools to connect the industries' players along the food chain of semiconductor industries to enhance communication and facilitate technology transfer from university to industry.

In this chapter, a brief summary of environmental policy background is given. Then, focus will be shifted towards the history of cooperative effort in semiconductor industries in the US. In the last sections, a strategic analysis of the ERC is presented.

5.2 A History of Environmental Policy

5.2.1 Brief Summary of the Environmental Policy in the US

Before the 70's, there was no centralized agency to tackle environmental issues such as carbon dioxide issues. Therefore, in the 70's, President Nixon appointed former senator Edward Muskie to be the head of the EPA. EPA, organizationally, has collected a set of US environmental agencies. The goal of EPA is to perform R&D, to monitor, to set standards, to enforce, and to set a good public relation image. The work EPA had achieved in the 70's was to abate obvious pollutants such as soot and smoke from cars and smoke stacks, raw sewage, and chemicals from municipal and industrial wastewater.

In the 80's, the EPA recognized there was obvious "unfinished business" in this area. In addition, it "discovered" new problems such as carbon dioxide problems, acid precipitation, and hazardous waste. These new problems proved difficult to measure. Therefore, a more quantitative and scientific effort was required [40].

In the late 80's, the EPA recognized that its effort in control and implementation in environmental policy as a Federal agency was fragmented in three incoherent ways.

The first fragmentation concerned implementation of new laws when there was a new problem to control. Secondly, the EPA always initiated a new program as a tool to deal with each new specific federal law. Thirdly, the tools used were primarily "end of pipe" equipment to capture pollutants. In the late 80's, the EPA was acting as "a reactive agency." [40]

5.2.2 Brief Summary of Environmental Policy in Europe

During this period of time, the European countries had experienced acid rain and ozone depletion. They were concerned that if there were delayed actions, those expensive consequences would hit them by the 90's. Therefore, in the 80's, the European countries initiated the "precautionary principle." [1] [41].

5.2.3 Cultural difference between Europe and the US affected their policy strategy

The environmental policy in North America in the 80's was still in the regulatory phase. The different between European and the US policy strategy can be summarized in Vogel's statement:

The Culture

Business executives in America continue to view government officials in much the same terms that they view their competitors: the challenges to profitability pose by each should be met as aggressively as possible. British businessmen are both less competitive with each other and more willing to cooperate with government offices [42].

5.2.4 New Strategy of EPA in the 90's

The EPA had learnt well from its past experience as well as the success of Europe and refined its strategy. First, environmental control has shifted towards the state level [39]. Secondly, it has adapted the pollution prevention methods [40] achieve these goals, EPA used techniques like: goal and standard setting, design and implementation, monitoring, funding, R&D [38].

5.3 Introduction of Voluntary Initiative

Technically, the pollution prevention methods that EPA adapted are called Voluntary Initiative (VI). It has two definitions. Prof. V. Norberg-Bohm has defined it as any non-statutory initiative that aims at improving corporate environmental performance. This is further divided into two categories:1) collective initiatives where the level of operations are within the industry and trade association, and 2) individual initiatives, where environmentally benign work is done by individual company.

The second definition of VI is characterized by the nature of partnership between industries and government. The first category is self-regulation. This is done by setting

---

[1] This includes limit carbon dioxide emission. Detail is included in the European Commission White Paper on Competitiveness and Employment, Luxembourg: EC, 1993.

one's own environmental target. The driving force behind individual or groups of individuals to perform this self-regulation is rarely a decision of conscience but rather motivated by the threat of government regulation [45]. This type of operation is good for industry with a few powerful players. For example, the American Petroleum Institute (API) has a voluntary program for its members known as Strategies for Today's Environmental Partnerships (STEP) program. This program includes a mission statement and set of guiding principles. Yet, the drawback is that there is no well-defined responsibility because no governing agency is involved.

The second type is voluntary agreement. This is an agreement signed between the government agency and corresponding industry. This co-operation is good for industry, containing both large and small players who share the same environmental responsibility. For example, in the Canadian memoranda of understanding (MOUs), an agreement was signed between industries and government such that those industries could achieve the government goals of environmental protection in the ways that they prefer [46].

Another advantage of voluntary agreement is demonstrated in the Canadian Automobile Parts Manufacturing Association (APMA) in MOU. APMA had 25 chemical targets, yet it was focused on training and providing technical assistance to the smaller players within the industries and, thus the big players bare the responsibility [44].

Allowing flexibility among operators is another important advantage. For example, it reduces the time for regulatory approval [45]. In addition, a feed back mechanism exists because government will monitor its progress. Furthermore, a clear and unique responsibility is well defined. Last but not least, it raises awareness among companies of all sizes.

The third type is Voluntary Challenge. In this category, the regulatory agency or the government sets a target to invite industries to participate. For example, in the US EPA 33/50 program, a challenge called for voluntary reduction of releases of 17 toxic chemicals by the industry by 33% (relative to 1988 levels) at the end of 1992, and 50% by the end of 1995 was set. There were 7500 companies invited to participate ion the program, of which only 1300 of them accepted the invitation, but pledged to reduce the target. By 1992, toxic releases reduced to 60% of the base year level, and 50% was reached by 1994 [47]. The advantage of this approach is very much similar to voluntary agreement. Yet, it is only good for targeting common pollutants released by varieties of industries.

5.4 Voluntary initiative in the semiconductor industry in the US

5.4.1 Global Effort of US lags behind Europe

The semiconductor Industries Association (SIA) is responsible for maintaining US leadership worldwide. It has approached global ESH issues by using the self-regulatory approach. For example, in 1990, there was an annual bilateral discussion between SIA and the Electronic industries Association of Japan (EIAJ) about environmental safety and health (ESH) aspects of worldwide semiconductor manufacturing processes [48].

In the early 90's, the EU semiconductor industry was the global leader in ESH manufacturing. The European Electronic Component Manufacturers Association hosted the first ESH international conference in Brussels. The title was "The World's

Environment: Where the Electronics Industry wants to be in the Year 2000". This conference is aiming to eliminate hazardous substances used in the fab, to discuss the possibility of using chemical alternatives, to reduce industrial wastes, to employ recycling and re-use programs, and to take advantage of achievable control technologies and to implement an environmental-management system. This conference has attracted participants like as SIA, EIAJ, and the Korean Semiconductor Industry Association. During the conference, several issues were addressed:

1.National regulations, policy and law
2.Projects or standards at national or association levels
3.Environmental management programs
4.Influence of chemical substances on environment, safety and health
5.Industry case studies on various subjects such as recycling or recovery of chemical wastes, scarp recycling, total quality management applied to the environment, ergonomics, equipment safety, and product take back strategies [49].

5.4.2 National Effort of the US Environmental Policy

EPA adapted voluntary agreement and voluntary challenge to regulate ESH issues in the microelectronic industry. A voluntary agreement, MOU, was signed between SIA and EPA in 1995 to reduce global warming gases [48]. In addition, a voluntary challenge and voluntary agreement were signed with individual microelectronic industries. For example, IBM adopted the voluntary challenge by joining the 33/50 EPA program, and had achieved a 84% reduction chemical releases and transfers between the year 1988 and 1995. Moreover, IBM microelectronics division also signed a voluntary agreement, which was called a memorandum with the EPA to focus on minimizing emission of six perfluorocompounds [48].

5.5 ESH manufacturing is a disruptive technology in IC industry

In order to achieve global leadership in environmentally benign manufacturing in timely manner, innovative solutions are needed. Innovative solutions are better done in smaller units. Since ESH manufacturing is a new concept, oftentimes, it deviates from mainstream research. Therefore, university research teams are ideal subsidiaries to provide ESH solution.

University research on ESH microelectronic was funded by SEMATECH, a joint agent between semiconductor representatives and the Department of Defense through the Semiconductor Research Corporation (SRC). In addition, EPA has also funded universities to perform ESH related research directly. However, most of these programs suffer some drawbacks.

First, universities will do what SEMATECH, SRC or EPA wants, but those research works were not always matched with industrial need. This is because the companies of the microelectronic industry will not always tell SRC their research directions explicitly as, oftentimes, they were being considered as trade secrets. Sometimes, SRC will even fund research that industries have already performed [48].

Secondly, the time taken for conventional technology transfer between university and industries has not been minimized. An ideal technology transfer is achieved by having the inventors to work with manufacturing people to develop this technology. To implement of new technology in operation effectively, the developers should work directly with the operators. Yet, employees of different specialties can hardly work well with workers, who are skillful in other ways. Sometimes different levels of education adds another barrier for collaboration. These problems are often solved by well-trained managers. From this, we can infer that there exists a higher level of difficulty for technology transfer from the university level to the industry passing through SRC. This technology transfer is mostly done by written reports or some conversation between management. The person who developed this technology, mostly the students, will not work with either SRC or the companies directly. Thus, not only is this loop of technology transfer is longer than the one mentioned within the technology chain of companies, but also this loop of technology transfer is not over seen by any manager [45].

5.6 Why is it important for the US to gain international leadership in environmentally benign research semiconductor industry?

The US had lost its DRAM market place to Japan in the 80's and to Korea in the 90's. It has been losing its market place in applied electronics to Asia. To regain a global leading position in the IC industry, the most opportunistic niche for the industry is that of an environmentally benign manufacturing leader. In recognizing this, the US is hosting the 3rd international conference in year 2000 to raise issues about the importance of environmentally benign manufacturing [50].

The US government and industries had recognized the importance of being a technology leader back in the early 90's when dealing with the international treaty on carbon dioxide emissions. The US is well known as the biggest consumer in the world, emitting 25% of carbon dioxide in the globe [41]. By establishing themselves as the scientific leader in the environmental policy negotiation through the creation of IPCC, the US has a significant influential power in the Kyoto Protocol negotiation [41].

In parallel to the recognition of scientific methods, there is an advancement of enforcing the international patent laws. The Paris convention and Berne convention have covered intellectual property rights with regard to inventions, copyright etc. Yet, there was no real international enforcement effort before 1996. In 1996, US entrepreneurs, the victims of international property right (IPR) abuse, had pushed forward a GATT agreement on Trade-Related Aspects of Intellectual Property Rights (TRIPS). This agreement attempts to enforce both the Paris convention and the Berne Convention, and all members of world trade organization have to obey it [1]. The significance of advancement in patentable science has proven to be an effective and important tool in international environmental negotiation. For example, the US signed the Montreal Protocol since Du Pont has developed an environmental benign alternative.

An additional characteristic of the US legal system is that the patent is given to the first inventors [50]. Therefore, if the US leads in environmentally benign semiconductor manufacturing, it can control competition through the use of TRIPS with the US patents. The US companies can dominate the world market by collecting licensing fees parallel with new international clean manufacturing policies to impede competitors in the global market. Most importantly, this strategy will not violate the anti-trust law because the Rule of Reason encourages the advancement of science and engineering [50]. Not to mentioned that ESH research is a common good to the society, and the keen academic participation makes patenting ESH research results far away from infringing anti-trust law.

5.7 Engineering Research Center (ERC) –The New Strategy

5.7.1 Background

A focused subsidiary such as ERC will facilitate collaboration along the technology chain in semiconductor industry for the following reason: unlike other cutting-edge technology, environmental research is a common concern, therefore, players are more open to communication with each other. This concern enhances collaboration. Secondly, environmental manufacturing is still a new concept for the industry. New ideas from external participants are needed.

In the following paragraphs, I will address (1) why SEMATECH and SRC will not perform the function of ERC. (2) A historic background of ERC is provided to demonstrate that its unique organization has attracted players from the whole food chain of semiconductor industry. (3) A strategic analysis of ERC is presented in the last section.

5.7.2 What is the focus of SEMATECH?

SEMATECH was originally composed of 14 big companies as its started in 1987. It is now shrunken in size. As of 1999, before merging into International SEMATECH, it was left with only 9 members. After merging with 4 international companies, the International SEMATECH was formed and it contains 13 companies (Table 5.1).

Table 5.1 Member companies of SEMATECH

AMD
Conexant
Hewlett-Packard
Hyundai
Infineon Technologies
IBM
Intel
Lucent Technologies
Motorola
Philips
STMicoelectronics
TSMC
Texas Instrument

SEMATECH is transformed from being a research consortium in the 80's intended to improve the US manufacturing technology to compete with Japanese low cost manufacturing into a global observer to oversee international competition. As cited from its 1999 annual report, which stated that "With this consolidation the consortium has grown from nine to 13 full members. Such growth and diversity increases our influence among other worldwide consortia and strengthens our ability to leverage our resources and leadership into directions that shape the industry. [49]" However, Semiconductor International Association (SIA) considered SEMATECH as an Austin Texas based consortium performing advanced and critical research to improve the American competitive position [48].

In summary, the primary function of SEMATECH has shifted from being a pure research consortium to overseeing international semiconductor research and development. This will improve the American competitive position, yet, to oversee academic research, SRC is the primary operator.

5.7.3 Why did NSF/SRC create the ERC?

In 1982, the Semiconductor Research Consortium (SRC) was established by SIA. Table 5.2 shows the member companies involved in year 2000. This is a research consortium focussed on long-term, pre-competitive research in semiconductor technology at the US university level [51].

Table 5.2 Member lists of SRC

SRC Full Members
Advanced Micro Devices, Inc.
Compaq Computer Corp
Conexant System Inc.
Eastman Kodak Company
Hewlett-Packard Company
IBM Corporation
Intersil Corporation
LSI Logic Corporation
Lucent Technologies
Motorola, Incorporated
National Semiconductor Corporation
Northrop Grumman
Texas Instruments Incorporated
United Microelectronics Corp. Group

SRC Science Members

Cadence Design Systems
Eaton Corporation
Etec Systems, Inc.
Mentor Graphic Corporation
Novellus Systems, Inc.
Shipley Company, Inc.
Synopsys, Inc.
ULTRATECH Stepper

SRC Associate Members

The MITRE Corporation

SRC Affiliate Members

CVC Inc.
FLIPCHIP Technologies
Intergrated System Engineering, Inc.
Microcosm Technologies, Inc.
Mission Research Corporation
Neo Linear, Inc.
Numerical Technologies, Inc.
PDP Solutions, Inc.
Physical Electronics Inc.
SILVACO International
Tessera, Inc
Testchip Technologies, Inc.

SRC US Government Participants

DARPA
National Inst. Of Standards and Tech.
National Science Foundation
U.S. Army Research Office

SRC Strategic Partners

SEMATECH
Semiconductor Industry Association

In TECHCON 1990, Gordon Moore insisted that global competitiveness of US semiconductor industries relied heavily on technology leadership and a technologically oriented higher education. During that year, SRC was also asking for a "technology strategy for government and industry." In 1993, the slogan moved towards "bright young people entering the workforce and the unity of industry." In 1994, the SRC seriously considered university directions and methods as important strategic items besides technology transfer, revenue base, and mission and operations. During the year of 1995, the SRC presented the semiconductor R&D catechism in a newsletter in April, highlighting 6 points:

1. Semiconductors are seminal
2. Industry leadership is important
3. Structure of US semiconductor R&D has changed
4. US Leadership is challenged
5. Roles/responsibilities of participants is key
6. Research infrastructure appears inadequate

To overcome these many historical concerns of SRC, a new organizational strategy in bringing government, industries, and students to work together is of urgent need. Environmental concerns among industries' players also have risen. Environmental manufacturing is a theme in itself, which deviates from conventional research and development. This disruptive technology is therefore an ideal idea to unite the semiconductor industries to satisfy EPA's concerns. To handle disruptive technology, a common strategy is to set up a subsidiary. To oversee the progress of this subsidiary, government participation is necessary. This idea has therefore enhances the birth of ERC in 1996, a new subsidiary of SRC sponsored by the National Science Foundation (NSF) and SRC. ERC focuses on having university students to solve industrial problems in the area of environmental benign manufacturing in semiconductor industry.

5.7.4 Historical background and organization of ERC

5.7.4.1 The initial vision and goal of ERC

ERC performs research and educates young people about ESH issues in IC industry. The ultimate goals are:

1.Internationally recognized for having the best interdisciplinary program for cross-disciplinary personel.
2. The largest group of high quality projects and investigators anywhere in the world
3. ERC being recognized as the first name coming to mind in the area of research and education [18].

5.7.4.2 The organization

The University of Arizona was chosen as the center of ERC. Three other universities, MIT, Stanford, and UC Berkeley are the seeding universities. These 4 universities formed the core of the Center. Research groups within the universities perform different types of ESH microelectronic research work.

Research work was categorized as "thrust area". Each thrust deals with particular environmental problems concerning a particular part of this semiconductor manufacturing chains within the manufacturing site [18].

Program is organized by thrust, and is sub-divided in task for specific area. Thrust A focuses on back-end processes, thrust B works on front-end processes, thrust C investigate factory integration, while thrust D works on patterning. Education is listed as another important topic.

5.7.4.3 Communication

The universities within each thrust have a weekly teleconference for an hour. The conversation includes student presentation of research accomplishments with the assistance of the Internet as a media for slide shows. There is also an effort towards educating high school students to get interested in microelectronic industries.

In addition, there are two annual conferences. One is a funding conference in February; this conference has researchers from SRC and industry representative to evaluate our research progress. In addition, constant feed back from students about how to improve mentors (the research staffs from industries) and learners (the students) relationships are addressed. There is another conference in Stanford in August. This conference is less formal than the funding conference, but students are also asked to present their research in poster format. Industries also participate in this conference, but with less enthusiasm. The summer conference is more or less a social conference between universities' members, students, and industry's representative.

The center also encourages students to communicate with each other. There are representatives within each university to improve relationship and research coordination among universities. The students' social groups start from there.

Our member list contains new companies, which are part of the food chain in this semiconductor industry such as the chemical and gas companies. Unlike SEMATECH, and SRC, ERC has attracted both big and smaller players at both the national as well as international level. In addition, other parts of the technological food chain such as chemical companies and tool suppliers are also member of ERC. This demonstrated that ERC facilitates the possibility to provide a complete solution for implementation of new technology.[2](See Table 5.4 for membership companies.)

Table 5.3 ERC Membership and Affiliation (*SRC member as well)

Advanced Micro Devices*
Air Products and Chemicals
Applied Materials
Cadence Design Systems*
Du Pont
Eastman Kodak*
Eaton*
Elf Atochem
ETEC Systems*
FST International
Harris*
Hewlett Packard*
IBM*
Industrial Technology Research Institute (ITRI)
Intel*
International SEMATECH
KANTO
LAM research
LSI Logic*
Lucent Technologies*
Meissner + Wurst

---

[2] An example will be given in the strategic analysis section.

Motorola*
National Institute of Standard and Technologies
National Semiconductor*
Northrop Grumman*
Norvellus System*
Pall
Praxair
Sandia National Laboratories
SCP Global Technologies
Shipley*
SpeedFam/IPEC
Texas Instrument*

5.7.4.4 ERC in achieving global effort

This year, the ERC Policy Board set the goal as "aim for an international scope and be open to global interactions; work with IAB on guidelines and action plans" This strategy matches well with what is advocated by SIA and SEMATECH. There is a joint project underway with Queen University, at North Ireland, funded through the Tie Project from NSF. There is also a joint project with Elf Atochem (France and US) [18].

5.8 Strategy analysis of ERC

As a new concept, ESH technology deviates from the microelectronics industry main theme of technology development. University students, fresh and young, are susceptible to new ideas, and with proper guidance of professionals such as research advisors and industrial mentors, will serve well for this purpose. For example, when an interdisciplinary topic was to be taught at MIT to raise the awareness of students in environmentally benign manufacturing, there were collaboration between myself and two toxicologists, Prof. Peter Dedon and Graduate Student, Can Ozbal at MIT. I provided the knowledge and concern from a materials scientist prospective, while they provided the toxicology information and shared their point of view. As a result, this topic was well received in the Environmental Research Center's retreat at Stanford University, 1998.

A typical high end Engineer will earn approximately 92000 dollars per year. Including other expense such as health insurance, it can run up to 120000 dollars per year. Yet, a graduate student at MIT, including overhead is approximately 45000 dollars per year. Oftentimes, the individual company does not have to bear this cost because the stipends for students come from SRC, which in turn, collects funding from many sponsor companies. A particular company will sponsor the research projects only when those projects will increase their competitive position.[3]

Through teleconference, conference, and summer retreat, representatives from the microelectronics industry get to know the students both work wise and personality wise. Therefore, the students at ERC allow industry recruitment.

Last but not least, the ERC conference and retreat also allows international new players to break into the US market. For example, Kanto, a Japanese chemical company kindly donates chemicals for my projects. This allows them to communicate with my mentor at IBM.

---

[3] See example in the technology transfer section.

5.8.1 Students facilitate information flow

Students are only given limited amounts of funding. To match with the funding needs, students will learn to focus on solving industrial problems. Through this close collaboration with industry, the time necessary for technology transfer is reduced.

ERC encourages students to communicate with their thrust mentors frequently. Mentors are invited to participate in the weekly teleconference. The industrial mentors very much enjoy this relationship because this gives them a chance to be educators. Moreover, interaction with students provides no threat to them. Therefore, they feel more comfortable to discuss the industrial trend to provide research direction. This information is more detailed and clear as compared to the general survey collected by SEMATECH as well as SRC.

5.8.2 How does ERC improve technology transfer problems?

Within 4 years of operations, ERC experienced easy technology transfer to industry. An interview with a ERC student at MIT revealed the transfer pathway. Novellus is interested in developing alternative chamber cleaning methods to replace CFC. Since CFC will be banned soon. new technology is needed urgently. Yet Novellus does not have the equipment, space, and the people to investigate in this technology, which deviates from their core research and development. Moreover, this is most likely a short-term project, therefore, this may imposed resources re-allocation problems after finishing the investigation. Most importantly, this company does not know what kind of research ideas they should look into.

Through ERC, Novellus System collaborated with another ERC student Laura Pruette at MIT to carry out a chamber clean replacement project in the Electronics and Electric Computer Science dept. A successfully new chamber clean was developed within 4 years. Throughout this development process, Laura was funded by ERC. In addition, the company invited Laura to be their summer intern to perform the same research project. She was eager to work with Novellus because this offered her exposure in industrial environment without jeopardizing her research progress. In addition, she was able to use the state-of the-art facility. In this way, low cost, efficient technology transfer is possible. In addition, students themselves are enthusiastic to push forward their own technology into the production line. This further accelerates technology transfer [52].

Laura Pruette filed a joint patent application and Novellus System to protect this new chamber clean technology. SRC also shares the patent as well. Upon graduation, Laura's thesis will be stored in the SRC achive. In this case, SRC will be informed that an alternative chamber cleaning process was developed. Thus, no funding will be wasted on doing the same research in this area. In addition, a change in particular technology will imply certain complimentary technology may be needed for R& D effort. Thus, this will allow both ERC and SRC allocate their research funding more effectively and efficiently.

My project contains novel surface preparation methods. I collaborate with my mentors at IBM, and am able to use their state of the art facility to achieve accelerated research results. My work has reflected the interests of alternative passivation.

Therefore, this can modify the funding strategy of SRC in support of other types of surface passivation technique. In this way, efficient utilization of funding is achieved.

5.8.3 Communication improvement

In addition, through presentation in the funding conferences, my research does raise awareness among many parts of the chain to help to refine my research direction. For example, people from the "end of pipe" abatement equipment suppliers talk to me about the issues of handling and disposal with the chemical that I am using.

ERC sponsor for social activities and supports a student group within the center. These interactions between students develop friendship and trust. This relationship leads to early cooperative effort even before graduation. For example, Dr. Tracy Burr, a formal ERC student in our group had collaborated with another ERC student, Renee from Stanford University, whom Tracy met in a social event in Stanford. In the long run, a lot of ERC students will work for the semiconductor industry. The friendship between us will facilitate future collaboration within the microelectronics industry.

5.8 Conclusion

First, environmental work itself enhances collaboration. This is because environmental enforcement agency, EPA, has imposed tough punishment for those who break its regulation. This is, therefore, a common concern to all participants in the semiconductor industry. Secondly, collaboration among American manufacturers are necessary because as international competitors, such as those in Japan, Korea, and

Europe, have been very collaborative in develop new technology to protect their international marketing position. Technology leadership in this semiconductor field means market leadership. Therefore, collaboration among American Semiconductors manufacturers are of urgent need. Therefore, new strategy is necessary to deal with this situation, and the strategy used, which is the creation of Engineering Research Center by NSF and SRC, has demonstrated success in providing environmentally benign manufacturing solutions to the semiconductor industry as well as enhancing collaboration along the chain of manufacturers in this industry.

In this chapter, I argue that university research groups are very much like the small start up companies in enthusiasm in performing innovative research solution to the market. The similarity are listed as follows: (1) The Professor runs this unit, providing funding and guidance. In addition, Professors have established industrial connections. These connections give guidance to the university research unit so that the innovation can be market-oriented. (2) Students are primary operators, who are enthusiastic and eager to get thing done. In addition to this small start up atmosphere, universities such as MIT processes large numbers of experts coming from different disciplines. Thus, interdisciplinary innovative solution can be achieved easily. Moreover, within the university, facilities are shared or charged at a lower cost. Thus, the cost of operation of university research group is lower than that of small entrepreneurial units. Therefore, the strategy of ERC in using university resources to provide innovative ESH solution to the industry is wise and cost effective.

5.9 Recommendation

As observed, the US position in the global economy is governed by two issues: 1.Technological leadership, 2: globalization. These two ideas do not go well with each other. This is because technology innovation comes from smaller units such as university environments, and its spin out (small hi-tech companies), while globalization requires money, which is always dominated by giant corporations! To merge these two is not easy. Yet, with proper development argument, and guidance, universities can turn into a low cost innovative sources for industries without losing the art or science. This Engineering Research Center has served well as an example for innovative technology transfer from university to industry through mentorship from industry to the students, where in our case the research agreement was drafted by the university and IBM.

Chapter 6

Achievement and implications

6.1 Achievement

In case study one, Chapter 2, by added two more steps, namely, increasing in methoxy coverage by an additional methanol bath, and subsequence removal of physisorb methanol with a water bath will form a hydrophobic and particle resistance surface for gate oxide production. Since this surface is very reproducible and even, high interfacial lifetime between this gate oxide and the substrate is recorded. This process optimization is possible only through in depth investigation in university level where science behinds what works will be explored.

In case study two, part 1, chapter 3, a toxicology understanding of chemical used in a process is illustrated to help engineers and scientists of manufacturing to cope with environmental safety needs in the future. In addition, this chapter also demonstrated that there is a need of new cost of ownership to incorporate environmental, safety and health cost and cost of accident to evaluate tool used.

In case study two, part 2, chapter 4, demonstrates that in-vitro studies allow rapid chemical evaluation for semiconductor industries because chemicals are isolated from operators. In addition, a new Environmental Safety and Health Cost of Ownership is developed, which includes 1) the risk of using a tool, 2) the cost of an accident, and 3) environmental responsibility of untreated waste.

In case study three, the key conclusion is that students themselves can facilitate collaboration among industrial players as a neutral outsider, and university research environment provides innovative and interdisciplinary solution for industry.

6.2 Implications

Global leadership in semiconductor industry requires interdisciplinary consideration. This thesis demonstrates that international policy , i.e., patents law change, " the new agreement on Trade-Related Aspects of Intellectual Property Rights (TRIPS)," and the new trend of trade protectionism such as tracing the toxicity of components of the imported goods by Germany and Sweden, should be carefully incorporated into research and manufacturing planning.

Chapter 2 demonstrates that university is a very good resource for industry to provide to deal with non-main theme research. In our case, environmentally benign manufacturing. While Chapter 3 and 4 demonstrate that university also provides a unique interdisciplinary environment to 1) raise awareness of future work force about the importance of environmentally benign engineering , and 2) to provide interdisciplinary innovative solution such as the Environmental Safety and Health Cost of Ownership to cope with policy change, and in this case, environmental responsibility and embargo.

Chapter 5 illustrates that by setting up a focus center, in our case, Engineering Research Center, will facilitate innovative research and technology transfer from university to industry, and collaboration along the chain of semiconductor industry.

Bibliographies

1. R Schaffer, B. Earle, and F. Agusti, International Business Law and Its Environment, 4th edition, An International Thomson Publishing Company, (1990)..
2. S. Verhaverbeke, M. Meuris, M. Schaekers, L. Haspeslagh, P. Mertens, M. M. Heynes, R. De Blank,, and A. Philipossian, A New Modified HF last Cleaning Process for High Performance Gate Dielectrics, 1992 Symposium on VLSI Technology, Washington, June 22, (1992).
3. M. Grundner, D. Graf, P.O. Hahn, and A.,Schnegg, Wet Chemical Treatments of Si Surface: Chemical Composition and Morphology, Sol. State Technol., 69 (1991).
4. M. Hirose, T.Yasaka, M. Takakura, S. Miyazaki, Initial Oxidation of Chemically Cleaned Silicon Surfaces, Sol. State Technol., 43 (1991)
5. M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada, Growth of Native Oxide on Silicon Surface, J. Appl. Phys. 68, 1272 (1990).
6. D. Tolliver, Handbook of Semiconductor Wafer Cleaning Technology—Science, Technology, and Applications, Noyes Publications, Ed. W. Kern., (1993).
7. H. O. Schmidt, Research Staff at IBM, Yorktown Height (2000).
8. H. H'saad, The Role of Surface and Bulk Perfection in the Processing and Performance of Crystalline Silicon., PhD thesis, MIT, (1994).
9. H.M'saad, J. Michel, J.J. Lappe and L.C. Kimerling, J. Electron. Mat., (1994).
10. A.J. Reddy, T.A. Burr, J.K. Chan, G.J. Norga, J. Michel, and L.C. Kimerling, Silicon Surface Defects: The roles of passivation and surface contamination, Proceeding of ICDS 19 (Aveira, Portugal, 1997).
11. T. A. Burr, Electrical Properties of Silicon Surfaces and Interfaces, PhD thesis, MIT, (1998).
12. C.H.P. Lupis, "Chemical Thermodynamics of Materials", North Holldand, New York (1983).
13. CRC Handbook of Chemistry and Physics. Edited by David R. Lide., 72 nd (1991-1992)
14. T. Swager, Professor in the Chemistry Department, M.I.T.(2000).
15. G.J.M. Norga, Chemistry and Physics of Metallic Impurities on Crytalline Silicon Surfaces, PhD thesis, M.I.T. (1992).
16. H.F. Okorn-Schmidt, Chris D'Emic, Henry Grabarz, IBM Researchers.
17. T.A. Miura, M., Niwano, D., Shoji, and N., Miyamoto, Kinetics of Oxidation on Hydrogen-Terminated Si(100) and (111) surfaces Stored in Air, J. Appl. Phys. 79 (8), 4373-4380 (1996).
18. C.Y. Chang and S.M. Sze, ULSI Technology, McGraw- Hill, (1996).
19. W., Harkions, and E.H. Loesser, J. Chem. Physics. 18, 556 (1950).
20. A. Streiwieser, A. Heathcock, E.M. Kosower, Introduction to Organic Chemistry, 4th edition., Von Hoffman Press, 204-244 (1992).
21. S.P. Griffing, Regional Sales Manager, EcoSys Corporation (2000).
22. White paper

23. ERC conference, NSF/SRC Engineering Research Center Environmentally Benign Semiconductor Manufacturing, (2000).
24. Novapure, telephone interview, (1998)
25. J. Washe, Eaton, telephone interview, (1998).
26. B. A. Flower, and J.B. Weissberg, Arsine poisoning, N Engl. J. Med. 291, 1171-1174 (1974).
27. H. L. Hong, B.A. Fowler, and G.A. Boorman, Hematopoietic Effects in Mice Exposed to Arsine Gas, Toxicology and Applied Pharmacology, 97, 173-182, (1989).
28. R.L. Brown, SDS Gas Source Feed Material Systems for Ion Implantation, IEEE (1997).
29. SEMATECH Web site, www.wemichips.org./stats/gsr/worldwide.pdf, July (2000).
30. W. Walter, SEMATECH, telephone interview, (1998).
31. OSHA, website,(2000).
32. NIOSH, website, (2000).
33. ACGIH, website, (2000).
34. Aulette,A, Regulatory Perspectives: TSCA in Genetic Toxicology, A Treatise. A.P. Li and R.H. Heflichs (Eds) (In Press)
35. P. Dedon, Microelectronic Processing Technology class, (3.155J/6.152 J/10.480J), Lecture, MIT, (Fall 1998).
36. J. M., Frazier, Chapter 1 "General Perpectives on In Vitro Toxicity Testing" of In Vitro Toxicity Testing: Applications to Safety Evaluation, J.M. Frazier (Eds), Marcel Dekker, inc. NY, (1992).
37. J.M. Frazier, Multiple endpoint measurements to evaluate the intrinsic cellular toxicity of chemicals, In Vitro Toxicol. 3: 349-357 (1990).
38. C.A. Tyson and N.H., Tracy, Chapter 2, "In Vitro Technology, Trends, and Issues" of In Vitro Toxicity Testing, Application to Safety Evaluation, J. M Frazier (Eds) Marcel Dekker, inc. NY, (1992)
39. Richard D. May and R.J. Fulton, Chapter 2, "In Vitro Tumor Toxicity with Antibody-Toxin Conjugates", of In Vitro Methods of Toxicology., R. R. Watson (Eds), CRC Press, inc. (1992).
40. Unfinished business, EPA pressed.
41. J.Jacoby, "Global Climate Change: Economics, Science, and Policy", Chapter 1 (2000).
42. Vogel, 1983.
43. E.J. Ringquist, Environmental Protection at the State Level: Polictics and Progress in Controlling Polution, M.E. Sharpe (Eds), Armonk, N.Y.
44. Organization for Economic Cooperation and Development (OECD), Managing the environment: the role of economic instruments, (1994).
45. R. Baggott, By voluntary agreement: The politics of instrument selection, Public Administration, 64, 51-67 (1986).
46. MNR Canada's Climate change: voluntary challenge and registry. (Minister of Natural Resources, Ottawa, (1995)
47. EPA, EPA's 33/50 program. Seventh progress report, Environmental Protection Agency, Washington, (1996).

48. Semiconductor Industry Association (SIA), Web site, "Cooperation: A Roadmap for Success," (1996).
49. EPA, Workshop on Pollution Prevention Research Needs for the Semiconductor and Electronics industries and Their Suppliers, EPA Cooperative Agreement No. CR 818419-01 (1995)
50. R. Schaffer, B. Earle, and F. Agusti, International Business Law and Its Environment, 4th edition, An International Thomson Publishing Company, (1999)
51. SRC web site, (2000)
52. R. Chatterjeer, an interview, Graduate Student at M.I.T, (2000)

THESIS PROCESSING SLIP

FIXED FIELD: ill. ____________ name ____________

index ____________ biblio ____________

▶ **COPIES:** [✓ Archives] Aero Dewey Eng Hum

Lindgren Music Rotch [✓ Science]

TITLE VARIES: ▶☐ ____________

NAME VARIES: ▶☐ ____________

IMPRINT: **(COPYRIGHT)** ____________

▶ **COLLATION:** ____________

▶ **ADD: DEGREE:** S.M. ▶ **DEPT.:** TPP

SUPERVISORS: ____________

NOTES:

cat'r date

page ▶ 531

▶ **DEPT:** MatSci & E

▶ **YEAR:** 2000 ▶ **DEGREE:** S.M.

▶ **NAME:** CHAN, Julia Ka[illegible]