A REPORT

ON

Oxidation Kinetics
and
Surface Properties
of
Silicon Dioxide

BY

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Prepared in partial fulfillment
of the requirements of the course

BITS C313 Lab Oriented Project

Under the guidance of

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ACKNOWLEDGEMENT

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ABSTRACT

Oxidation of Si to get Silicon Dioxide (SiO_2) is a highly studied topic subjecting to various property changes depending on the ambient conditions present during the oxidation process. This report aims at giving a brief overview on the various oxidation techniques, such as: dry, wet, and cyclic steps to grow different varieties of oxide surfaces. In this study we have characterized the oxide formation of silicon surfaces and the associated surface roughness by using Atomic Force Microscopy (AFM) as a tool.

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Acknowledgements

Abstract

INTRODUCTION

The oxidation process is one of the most important processes in VLSI fabrication. It is implemented in processes such as the gate dielectric growth, the quality of which is extremely important for the scaling and performance of today's integrated circuit technology. The process conditions such as oxidant condition, time, initial oxide thickness, temperature, pressure, crystal orientation decide a number of properties of the oxide formed.

Apart from elaborating the chemical reactions involved and kinetics parameters, this report focuses on the measurements techniques used to characterize the oxide. Silicon Dioxide is the first step of any VLSI fabrication process. Used for a wide range as mask against implant, for surface passivation, for dielectric isolation along with electrical Isolation and as a vital component in structures, oxidation is definitely the hyped topic with regards to scaling and present industry trends.

1. SILICON DIOXIDE:

Under exposure to oxygen, a silicon surface oxidizes to form silicon dioxide (SiO_2). Native silicon dioxide is a high-quality electrical insulator and can be used as a barrier material during impurity implants or diffusion, for electrical isolation of semiconductor devices, as a component in MOS transistors, or as an interlayer dielectric in multilevel metallization structures such as multi-chip modules. The ability to form a native oxide was one of the primary processing considerations which led to silicon becoming the dominant semiconductor material used in integrated circuits of today.

2.1 CHEMISTRY INVOLVED

Thermal oxidation of silicon is easily achieved by heating the substrate to temperatures typically in the range of 900-1200 °C. The atmosphere in the furnace where oxidation takes place can either contain pure oxygen or water vapor. Both of these molecules diffuse easily through the growing SiO_2 layer at these high temperatures. Oxygen arriving at the silicon surface can then combine with silicon to form silicon dioxide. The chemical reactions that take place are either

$$Si + O_2 \rightarrow SiO_2$$

for so-called "dry oxidation" or

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

for "wet oxidation". Due to the stoichiometric relationships in these reactions and the difference between the densities of Si and SiO_2, about 46% of the silicon surface is "consumed" during oxidation. That is, for every 1 um of SiO_2 grown, about 0.46 um of silicon is consumed (see Figure 1).

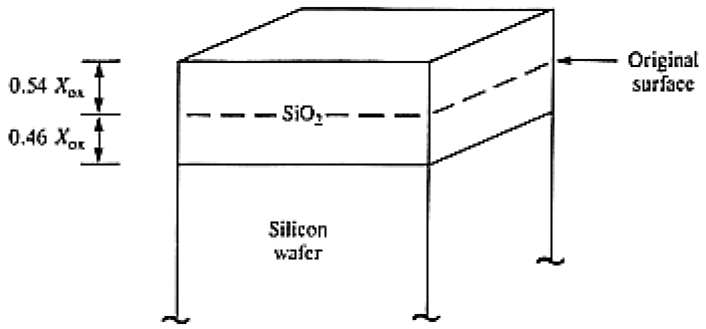


Figure 1

2.2 OXIDE GROWTH KINETICS:

Initially, the growth of silicon dioxide is a surface reaction only. However, after the SiO_2 thickness begins to build up, the arriving oxygen molecules must diffuse through the growing SiO_2 layer to get to the silicon surface in order to react.

A popular model for the oxide growth kinetics is the "Deal/Grove" model. This model is generally valid for temperatures between 700 and 1300 °C, partial pressures between 0.2 and 1.0 atmospheres, and oxide thicknesses between 0.03 and 2 microns for both wet and dry oxidation. To understand this model, consider Figure 2”

C_g = concentration of oxidant molecules in the bulk gas

C_s = concentration of oxidant molecules immediately adjacent to the oxide surface

C_o = equilibrium concentration of oxidant molecules at the oxide surface

C_i = concentration of oxidant molecules at the Si/SiO_2 interface

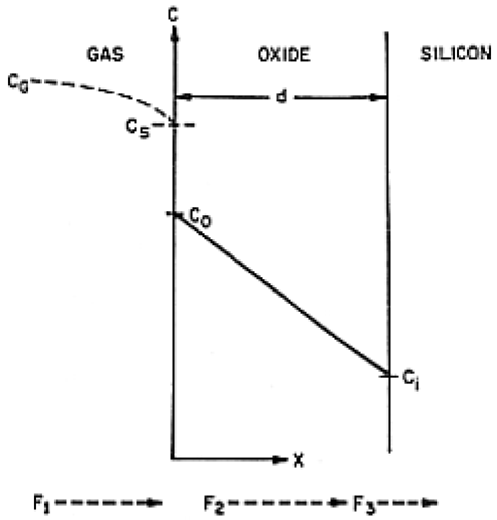


Figure 2

Note that: 1) $C_g > C_s$ (due to depletion of the oxidant at

the surface)

2) $C_s > C_o$ (due to the solubility limits of SiO_2)

The oxidizing species are transported from the bulk gas to the gas/oxide interface with flux F_1 (where flux is the number of molecules crossing a unit area per unit time). The species are transported across the growing oxide toward the silicon surface with flux F_2, and react at the Si/SiO_2 interface with flux F_3. Mathematically:

F_1 = flux of oxidant from gas -> surface

$$F_1 = Hg(Cg - Cs)$$

(where H_g = the gas phase mass transfer coefficient)

F_2 = flux through the oxide layer

$$F_2 = -D\frac{dC}{dx}$$

(where D is the diffusivity of the oxidant molecule in SiO_2)

If we assume a linear concentration gradient inside the oxide layer, then:

$$F_2 = D\frac{(Co - Ci)}{d}$$

(where d is the current value of the oxide thickness)

Finally:

$$F_3 = Ks \times Ci$$

(where K_s = the rate constant for the surface chemical reaction)

By Henry's Law:

$$Co = H \times Ps \quad \text{and}$$

$$C^* = H \times Pg$$

where H is Henry's Law constant, C* is the equilibrium concentration of oxidant molecules in the bulk SiO_2, and P_s and P_g are the partial pressures of the oxidant molecules adjacent to the SiO_2 surface and in the bulk gas, respectively. From the Ideal Gas Law, we have:

$$Cg = \frac{Pg}{kT} \quad \text{and}$$

$$Cs = \frac{Ps}{kT}$$

where k is Boltzman's constant and T is the temperature in degrees K. Therefore, F_1 can be re-written as:

$$F_1 = Hg(Cg - Cs) = Hg\left(\frac{Pg}{kT} - \frac{Ps}{kT}\right)$$

$$F_1 = \frac{Hg}{kT}(Pg - Ps) = \frac{Hg}{kT}\left(\frac{C^*}{H} - \frac{Co}{H}\right)$$

$$F_1 = h(C^* - Co)$$

where h = Hg/HkT. At steady-state, all three fluxes should be equal. In other words,

$$F1 = F2 = F3 \qquad \textit{Under these conditions:}$$

$$Ci = \frac{C^*}{\left(1 + \frac{Ks}{h} + \frac{Ks^*d}{D}\right)} \quad \text{and}$$

$$Co = \frac{\left(1 + \frac{Ks^*d}{D}\right)C^*}{\left(1 + \frac{Ks}{h} + \frac{Ks^*d}{D}\right)}$$

If the oxidation growth rate depends only on the supply of oxidant to the Si/SiO$_2$ interface, it is said to be "diffusion controlled”. Under this condition, D is close to zero. Therefore:

$$Ci \sim 0 \quad \text{and} \quad Co \sim C^*$$

If, on the other hand, there is plenty of oxidant at the interface, the growth rate depends only on the reaction rate. This situation is called "reaction-controlled". In this case, D approaches infinity, and:

$$Ci = Co = \frac{C^*}{(1 + \frac{Ks}{h})}$$

Now, we are finally ready to compute the growth rate itself. Let N1 be the number of oxidant molecules per cubic cm incorporated into the oxide layer. Then, we can write the following differential equation:

$$\frac{d}{dt} N1(d) = F3 = Ks \times Ci = \frac{Ks\ C^*}{(1 + \frac{Ks}{h} + \frac{Ks^*d}{D})}$$

Under the boundary condition that d = 0 when t = 0, we can solve the first order differential equation to obtain:

$$d^2 + Ad = B(t + T)$$

$$where:$$

$$A = 2D\left(\frac{1}{Ks} + \frac{1}{h}\right)$$

$$B = \frac{2DC^{*}}{N1}$$

$$T = \frac{(di^{2} + Adi)}{B}$$

di is the initial oxide thickness. For short times, the growth rate is reaction limited, and the oxide thickness is approximately:

$$d = \frac{B}{A}(t + T)$$

For longer times, growth is diffusion-limited, and the approximation used is:

$$d = \sqrt{Bt}$$

A and B are constants which correspond to the oxidation conditions (i.e. - temperature and wet or dry). They can typically be looked up in tables.

2.3 TYPES OF OXIDATION:

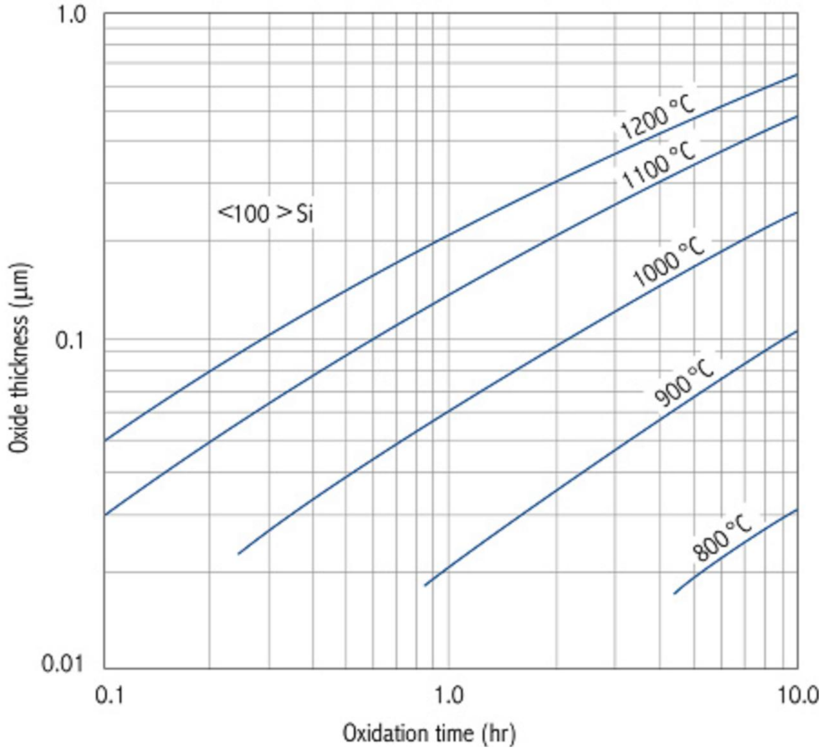
Following are the main types of oxidation:

- Dry oxidation
- Wet oxidation
- HCl Dry Oxidation
- Dry-wet-dry (cyclic) oxidation
- Steam oxidation
- High pressure oxidation
- Plasma oxidation

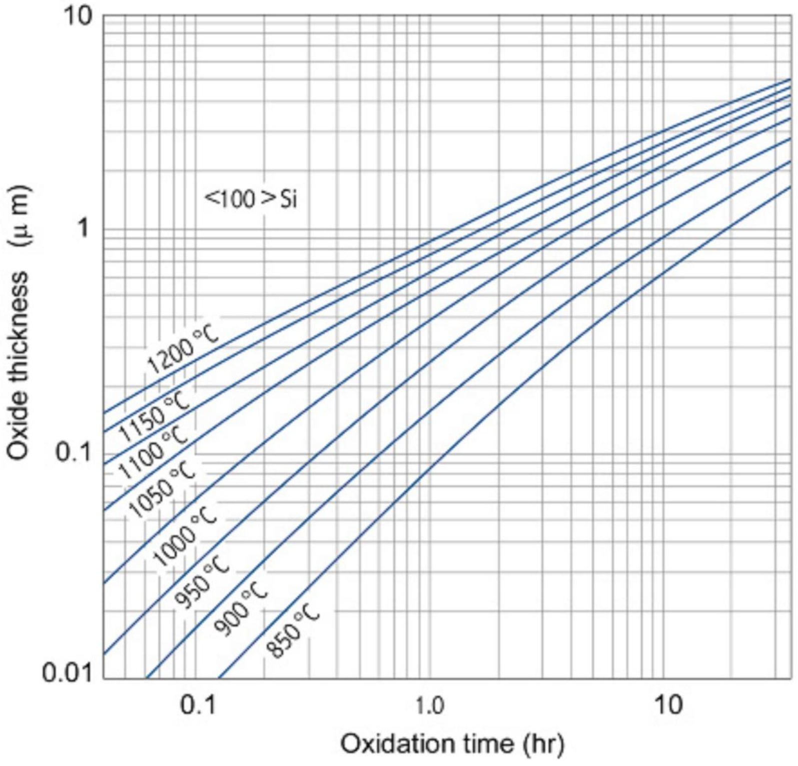
2.4 DRY vs WET OXIDATION:

Dry oxides are more dense and mainly used for gate oxides (<100 nm) while wet oxide used for thicker field oxides like the ones in masking. Comparing the speed, wet oxidation is much faster as OH ions act as catalyst in forming SiOH which later loses hydrogen to form oxide. Hence the reaction in the presence of water molecules is much faster. But, on the other hand wet oxidation decreases the quality of oxide formed. Hence, the actual process usually involves dry-wet-dry cyclic sequence.

Dry Silicon Oxidation



Wet Silicon Oxidation



The reason is that dry oxidation creates a higher quality oxide layer. The higher quality is due to a higher density, which has a higher breakdown voltage. High breakdown voltage is important when the oxide acts as an electrical insulator; therefore dry oxidation is used when the purpose of the oxide is to insulate. On the other hand, thickness is the only important factor when the oxide serves as a barrier to diffusion. The layer must be thick enough so that the dopant does not diffuse through the oxide into the silicon. Naturally, wet oxidation is used for this application.

2.5.1 Mixed Flows of O_2 with H_2O, HCl, and Cl_2:

The gas flow of O_2 can be mixed in the furnace with H_2O, HCl, and Cl_2 to get acceptable oxide quality at a higher growth rate. Besides a higher growth rate, Hydrochloric Acid (HCl) or Chlorine (Cl_2) is often used in oxidation in order to prevent metallic contamination and to help avoiding defects in the oxidation layer. HCl and Cl_2 have a cleaning effect of the furnace as well as an improvement of the oxide reliability. This means that HCl and Cl_2 additions provide benefits to the resulting device structures such as better ion passivation, higher and more uniform oxide dielectric strength, and improved junction properties due to lower current leakage.

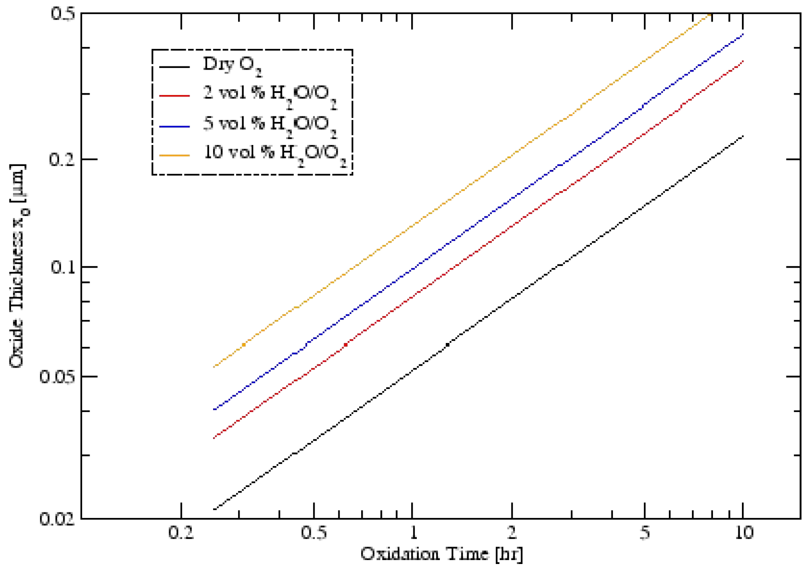


Figure 2.7: Oxide thickness versus oxidation time for (100) oriented silicon in

various H_2O/O_2 mixtures at 1000 °C.

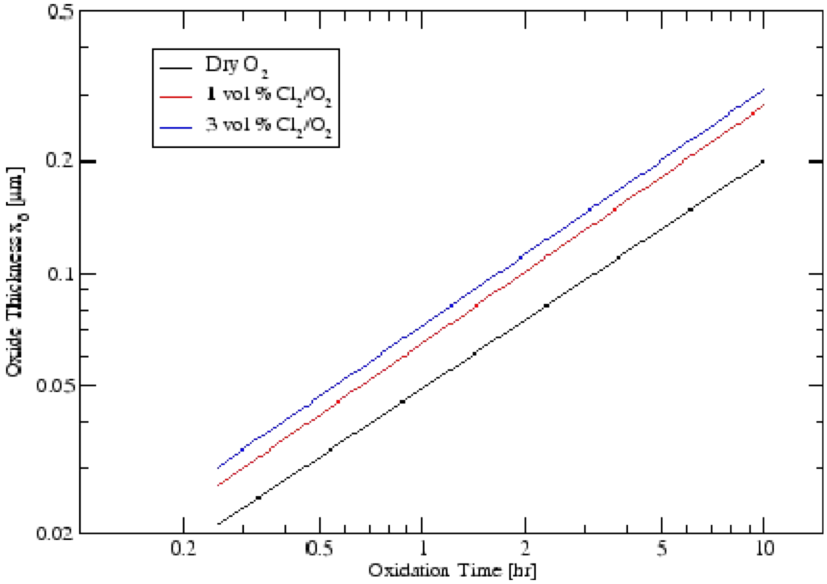


Figure 2.8: Oxide thickness versus oxidation time for (100) oriented silicon in various Cl_2/O_2 mixtures at 1000 °C.

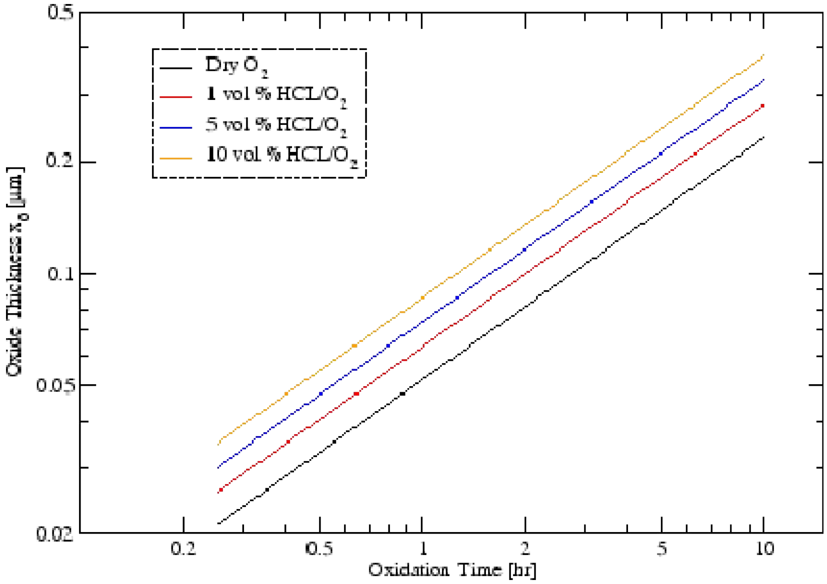


Figure 2.9: Oxide thickness versus oxidation time for (100) oriented silicon in various HCl/O_2 mixtures at 1000 °C.

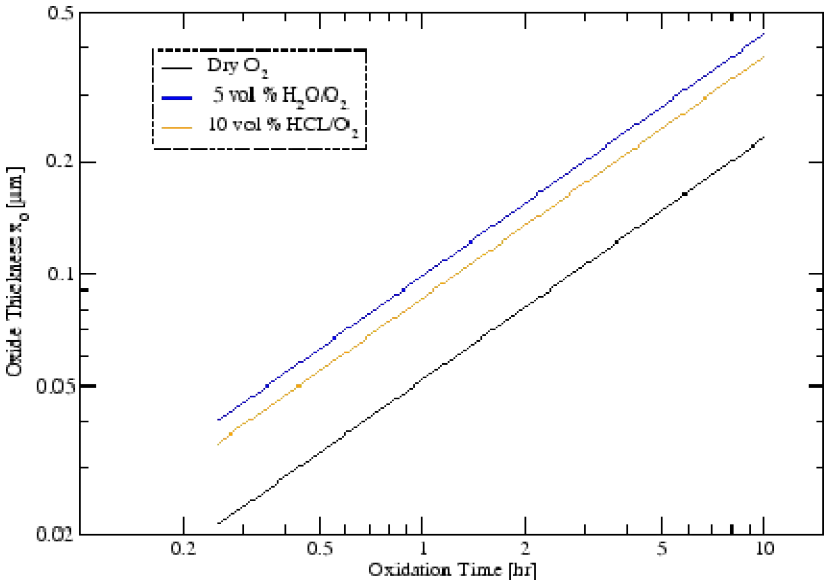


Figure 2.10: Oxidation rate of H_2O/O_2 mixture compared with HCl/O_2 mixture at 1000 °C.

The mixture of H_2O/O_2 has the highest increase of the growth rate, because it is in principle a combination of wet and dry oxidation. We can see in Fig. 2.7 that the same percentage of H_2O leads to a much thicker oxide at any time than HCl or Cl_2. Another interesting aspect is that the admixture of the same percentage of HCl and Cl_2 always leads to the same oxide thickness (compare Fig. 2.8 with Fig. 2.9).

The chemical reaction of HCl with oxygen is

$$4\,HCL + O_2 \rightarrow 2\,H_2O + 2\,Cl_2. \tag{2.3}$$

In wet oxidation the addition of HCl does not increase the oxidation rate, rather the oxidation rate is decreased for the same percentage as the amount of HCl is added. In H_2O-HCl ambients the thickness uniformity and appearance of these oxides were considerably better than in pure H_2O ambients. Also the defects in the oxide are considerably reduced.

2.5.2 Influence of Temperature

The oxidation rate increases significantly with the temperature in the furnace for dry as well as for wet oxidation. The temperature dependence of the oxidation rate is plotted in Fig. 2.11 for dry and

Fig. 2.12 for wet oxidation. For wet oxidation in Fig. 2.12 it can be seen that 100 °C more temperature leads to approximately double the oxidation rate, if the temperature is increased from 900 to 1000 °C. The important temperature effect can also be observed for dry oxidation in Fig. 2.11, where the same temperature increase from 900 to 1000 °C leads to much more than double the oxidation rate.

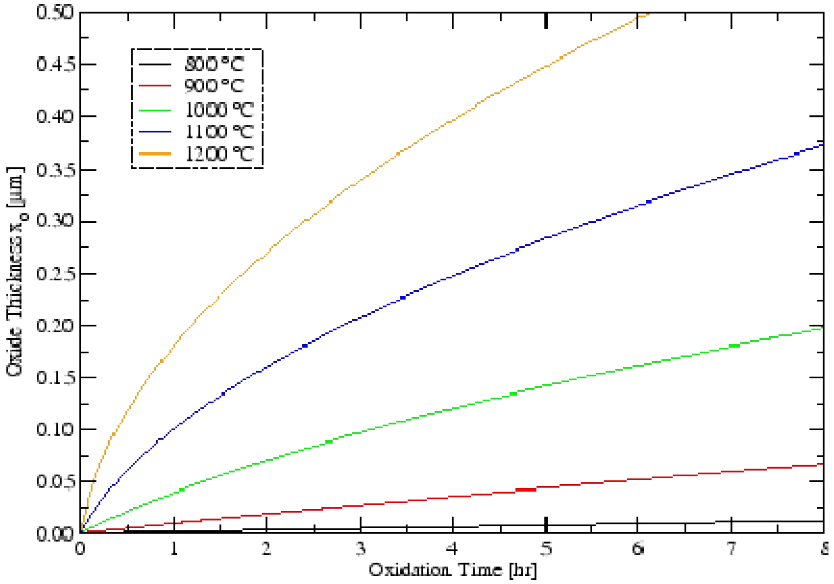


Figure 2.11: Oxide thickness versus oxidation time for (100) oriented silicon by dry oxidation (O_2) for various temperatures.

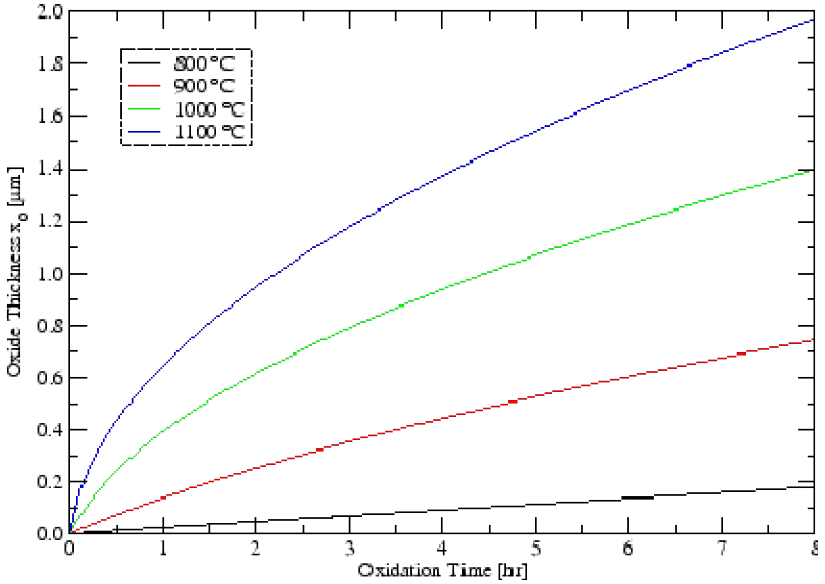


Figure 2.12: Oxide thickness versus oxidation time for (100) oriented silicon by wet oxidation (H_2O) for various temperatures.

The main reason of this striking temperature influence on the oxidation rate is the temperature dependence of the diffusivity of oxygen (O_2) and water (H_2O) in fused silica. The diffusivity of the oxidants depends on the temperature T in the way $\exp(-\frac{c}{T})$. The oxidant diffusivity is exponentially increased with higher temperature and exponentially decreased with lower temperature. Higher diffusivity means that more oxidants can reach the Si/SiO_2 interface and react there with silicon to form SiO_2.

2.5.3 Influence of Pressure

The oxidation rate increases with the hydrostatic pressure in the furnace for dry and wet oxidation in nearly the same way. The principal advantages of higher pressure oxidation over conventional atmospheric oxidation are the faster oxidation. The quality and integrity of higher pressure oxides have been found to be comparable to atmospheric oxides. Oxidation-induced stacking faults are significantly reduced with higher pressure oxidation, which leads to improved device performance.

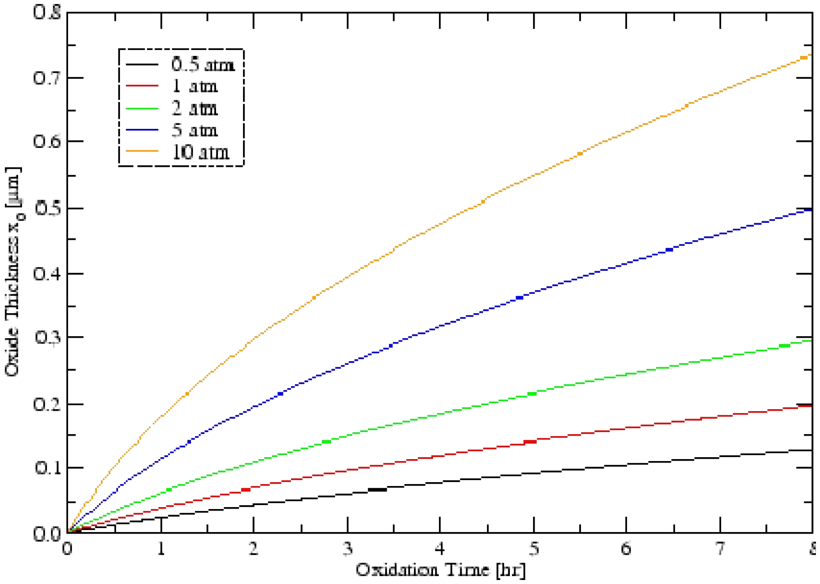


Figure 2.13: Oxide thickness versus oxidation time for (110) oriented silicon by dry oxidation at 1000 °C for various pressures.

2.5.4 Influence of Crystal Orientation

The studies of oxidation have shown that the oxidation rate also depends on the crystal orientation of the silicon substrate. Experiments have demonstrated many times that the oxide growth is faster on (111) oriented surfaces than on (100) oriented at any temperature for dry as well as wet oxidation.

It is important to understand orientation effects on oxidation more generally because many structures actually use etched trenches and other shaped silicon regions as part of their structure. The crystal orientation effect might be caused by differences in the surface density of silicon atoms on the various crystal faces. Since silicon atoms are required for the oxidation process, crystal planes that have higher densities of atoms should oxidize faster. Furthermore, not only the number of silicon atoms per cm^2 is important, but also the number of bonds matter, since it is necessary for Si-Si bonds to be broken for proceeding the oxidation. Calculated the ``available" bonds per cm^2 on the various silicon surfaces and concluded that oxidation rates in H_2O ambients should be in the order (111)>(100), which was also observed experimentally.

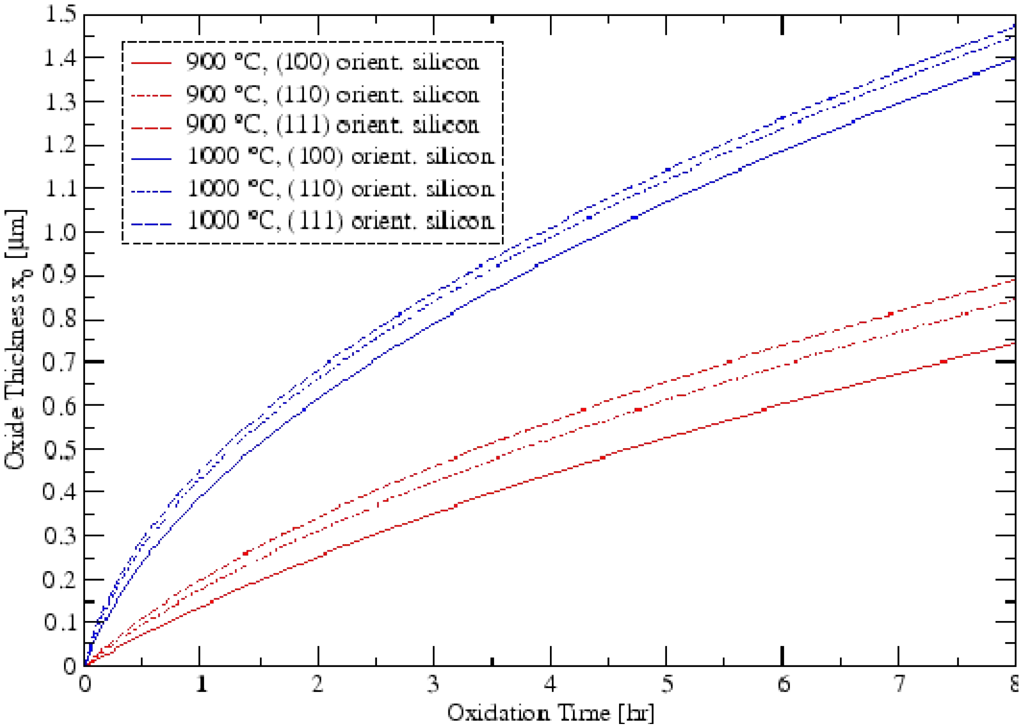


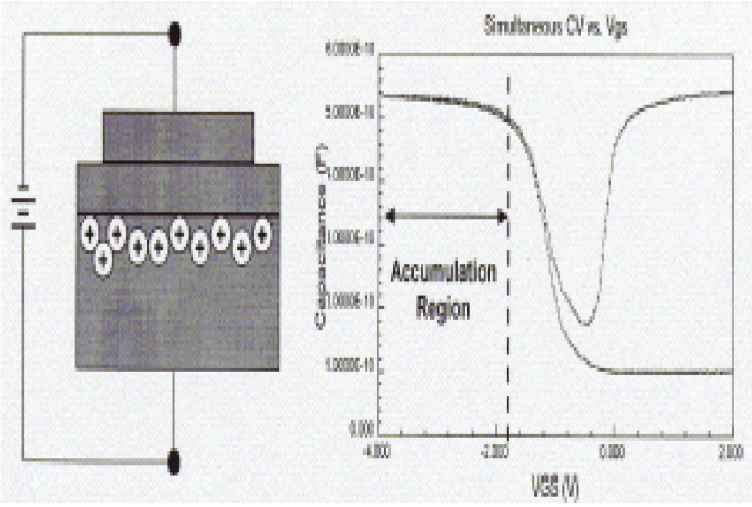
Figure 2.14: Oxide thickness versus oxidation time for (100), (110), and (111) oriented silicon by wet oxidation (H_2O).

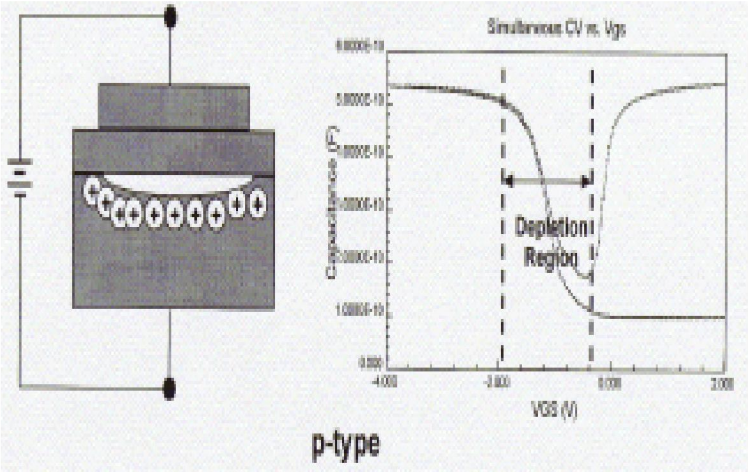
2.6 OXIDE TRAPPED CHARGES:

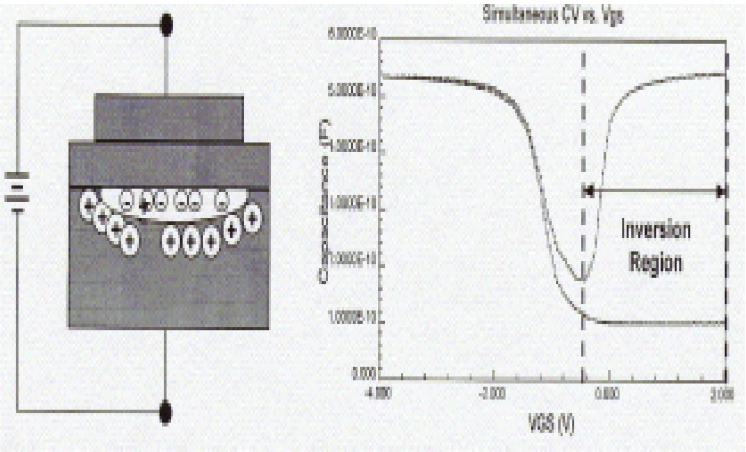
There are four main types of charges trapped in any SiO_2 layer namely:

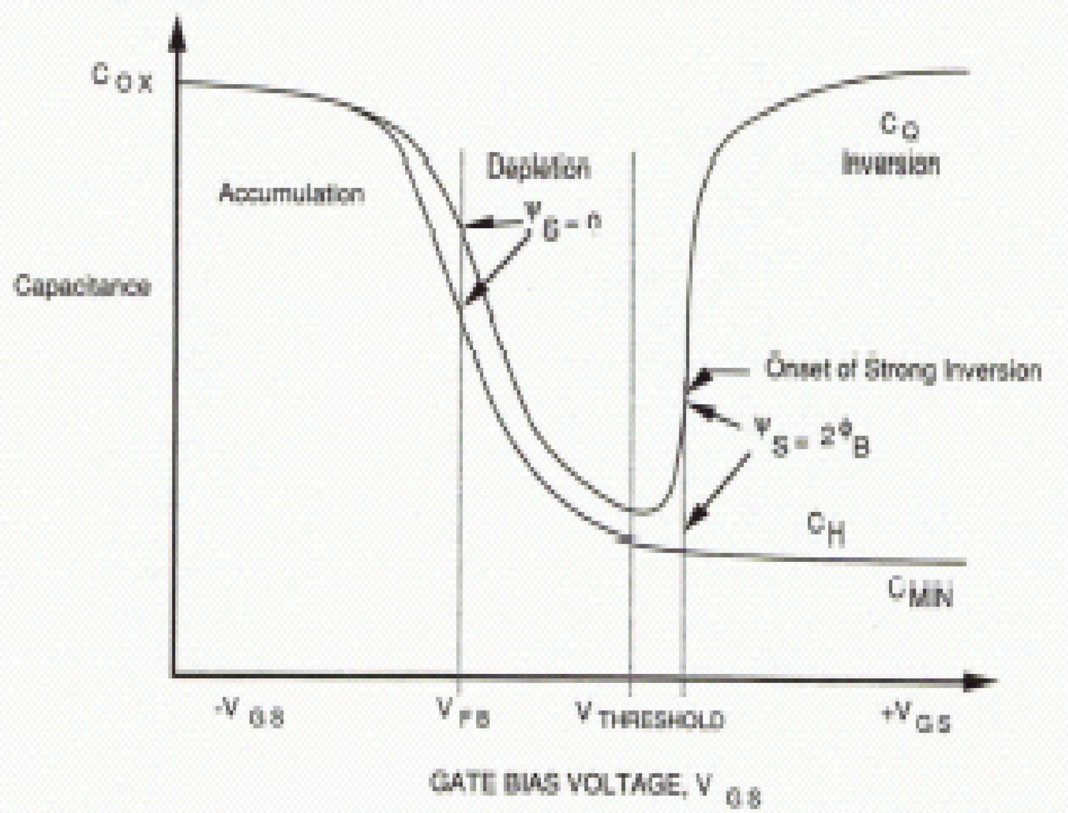
Q_f - fixed oxide charge
Q_{it} - interface trapped charge
Q_m - mobile oxide charge
Q_{ot} - oxide trapped charge

There are a number of measurement techniques used to characterize SiO_2 and the Si/SiO_2 interface. The most powerful of these is the C-V method









C-V Characteristics of p-type Material

3 CHARACTERIZATION:

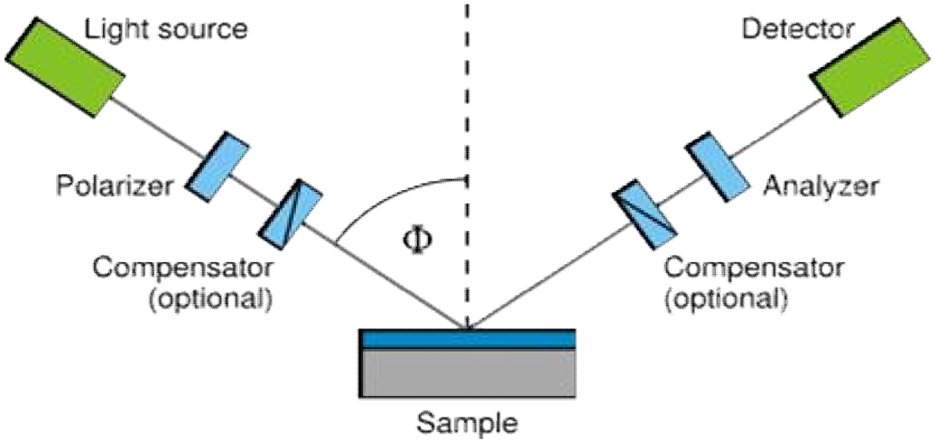
The oxide once formed has to be characterized by measuring its various parameters, namely:

- Thickness
- Composition
- Surface Property

3.1 Thickness:

Colour	Thickness (A)	Application
Grey	100	Tunneling Oxides
Tan	300	Gate oxides, capacitor dielectrics
Brown	500	Local Oxidation of Silicon Pad oxide
Blue	800	
Violet	1000 2800 4600 6500	
Blue	1500 3000 4600 6500	
Green	1800 3300 5200 7200	
Yellow	2100 3700 5600 7500	
Orange	2200 4000 6000	Masking Oxides, Surface passivation
Red	2500 4400 6200	Field oxides

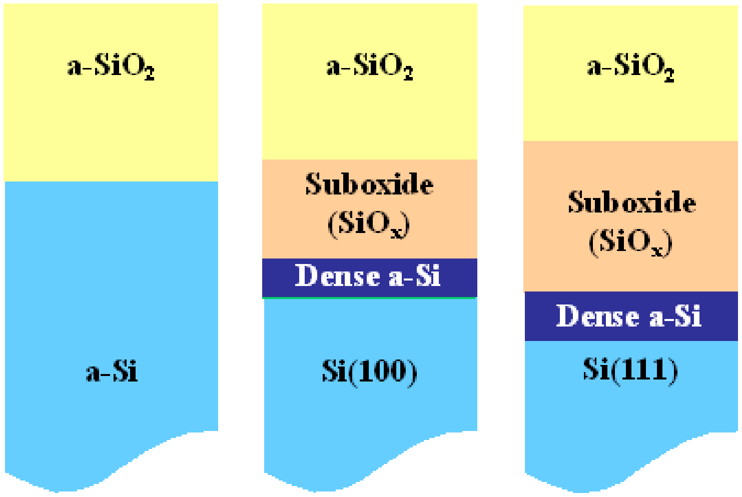
Polarized laser light is incident on the oxide covered wafer. The polarization of the reflected light, which depends on the thickness and index of refraction (known) of the oxide layer, is determined and used to calculate the oxide thickness. This method is known as ellipsometry.

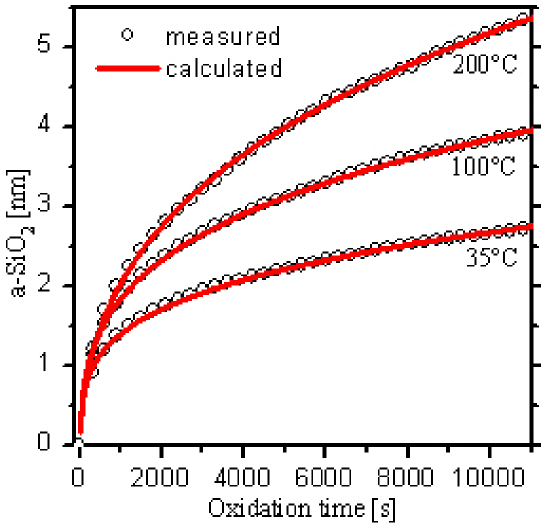


3.2 FTIR SPECTROSCOPY:

FTIR spectroscopy and ellipsometry (IR-UV) are employed to characterize (organic) surface terminations and ultrathin films and to monitor reaction processes in situ and in real time. The most important advantage of optical spectroscopy, compared to electron spectroscopy, is the applicability at higher pressures and in gas atmospheres, needed for chemical processing.

Of special interest in science and technology are ultrathin silicon-oxide layers with a thickness in the few nanometer region. Laser-induced oxidation of H-terminated silicon at defined oxygen or water vapor pressures was studied by using F_2-laser irradiation. This laser emits 7.9 eV photons (157 nm), which allow strongly enhanced self-limited growth of ultrathin silicon-oxide layers with nanometer thickness at 300 K. The different stages of the VUV-laser-induced oxidation process can be monitored spectroscopically by IR spectroscopy, namely the disappearing Si-H surface bonds and the appearing Si-O phonon bands. By spectroscopic ellipsometry the kinetics of the laser-induced growth of the silicon-oxide layer could be monitored in real time and simulated with a three-layer model, including an interface with a dense amorphous silicon (mono)layer, a 0.4-0.9 nm thick amorphous sub-oxide layer SiO_x, and the growing silicon-dioxide film, as shown in Fig. 4. With the assumption that reactive oxygen atoms are mainly responsible for the low-temperature oxide growth the kinetics of the self-limiting process can be descibed quantitatively (see Fig. 5)





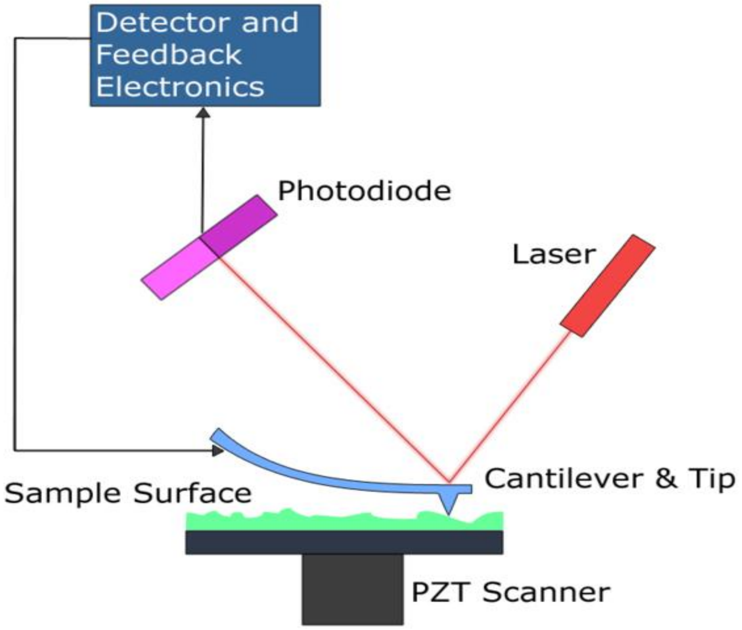
Fourier Transform Infrared spectroscopy is used to probe oxide structure and composition. Using infrared reflection properties of thin oxide and main concepts of angular and polarization dependence:

- Si – O stretching band at 1072 /cm
- Silicon oxynitride films: R = N_2/O_2 =gas flow ratio; *R=1.0* for SiO(1.9)N(0.04) to *R=6.7* for SiO(0.26)N(1.2)

One can analyse the composition of the oxide.

3.3 AFM MICROSCOPY:

The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge.



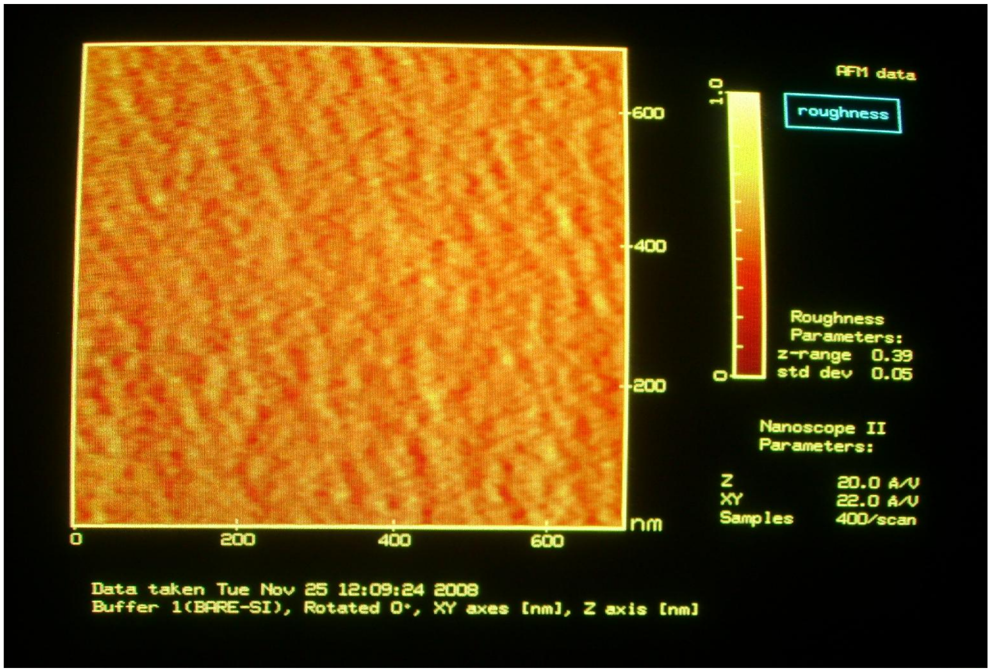
The practical results for 3 samples are illustrated below:

IMPLEMENT THE FOLLOWING:

1. Include the details of silicon wafer, oxidation steps carried out
2. Match the figure numbers at appropriate locations in running text
3. Make uniform format of the text and character fonts.

---G. Eranna

PLAIN SILICON:



Roughness
Parameters:
z-range 0.39
std dev 0.05

Nanoscope II
Parameters:
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XY 22.0 A/V
Samples 400/scan

Data taken Tue Nov 25 12:09:24 2008
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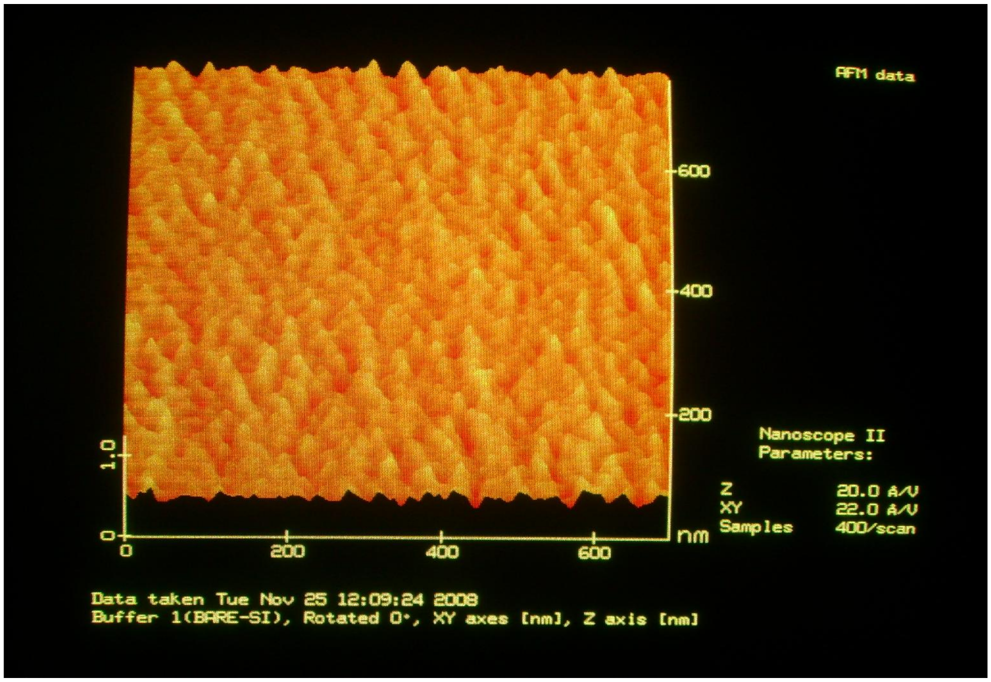

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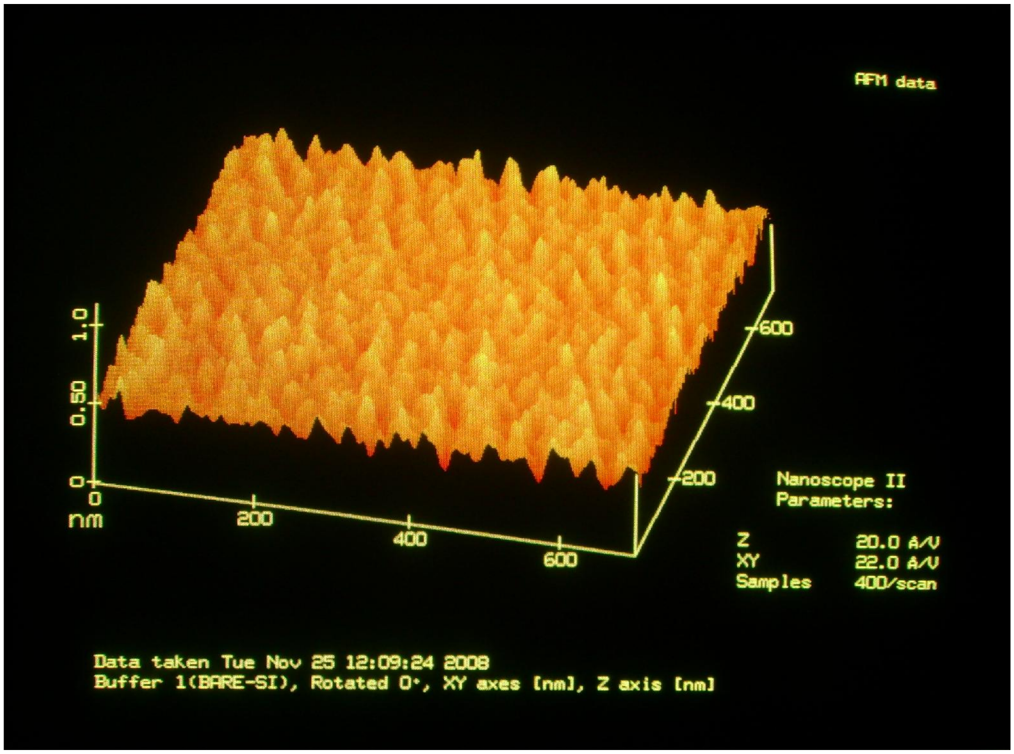
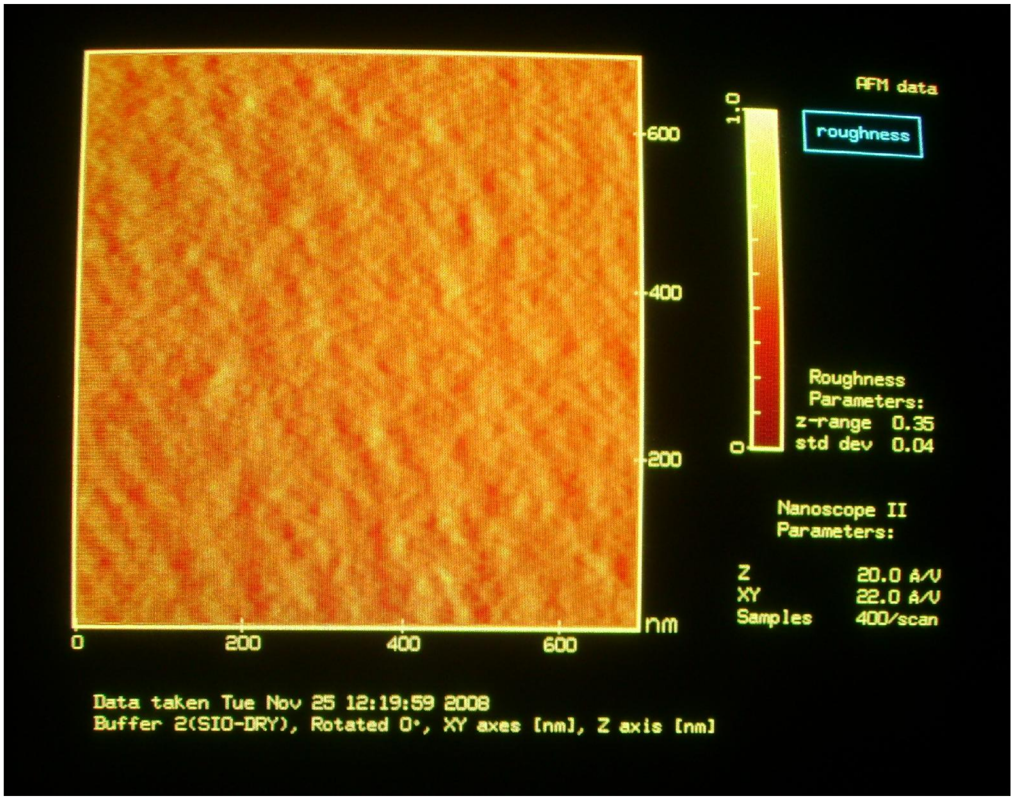
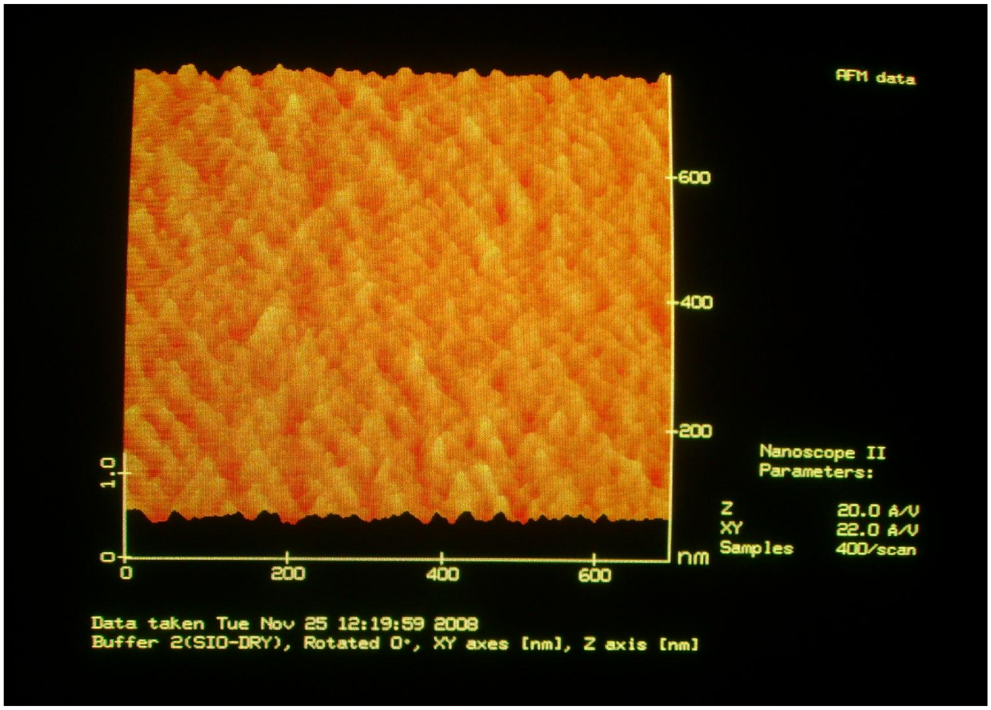


DRY OXIDATION:





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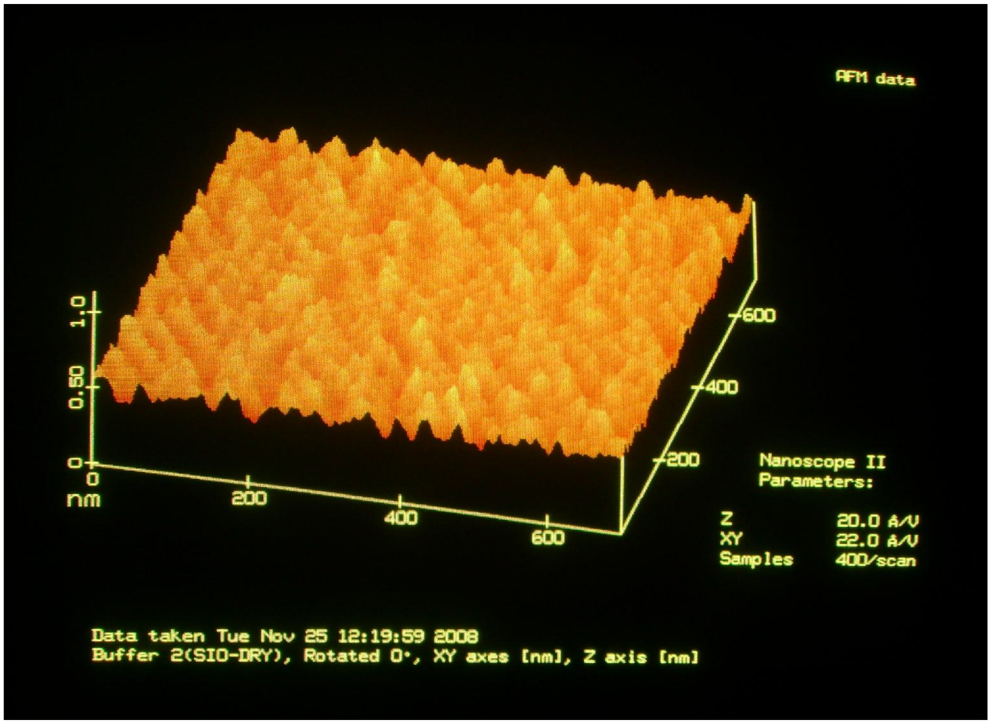

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Samples 400/scan

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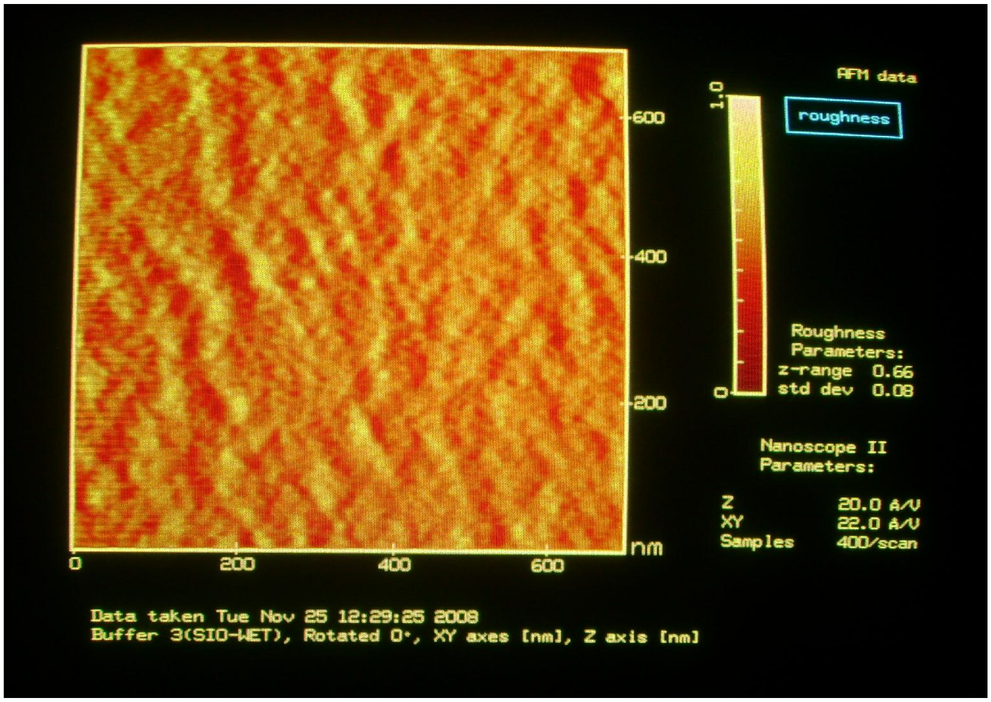
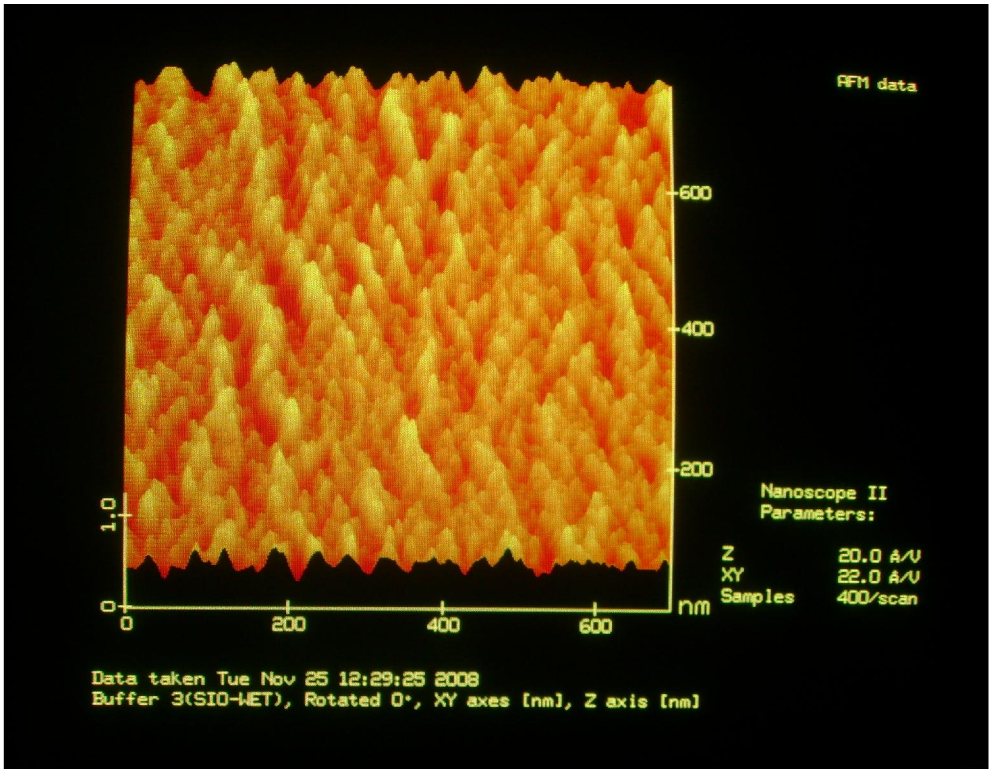
WET OXIDATION:



Roughness Parameters:
z-range 0.66
std dev 0.08

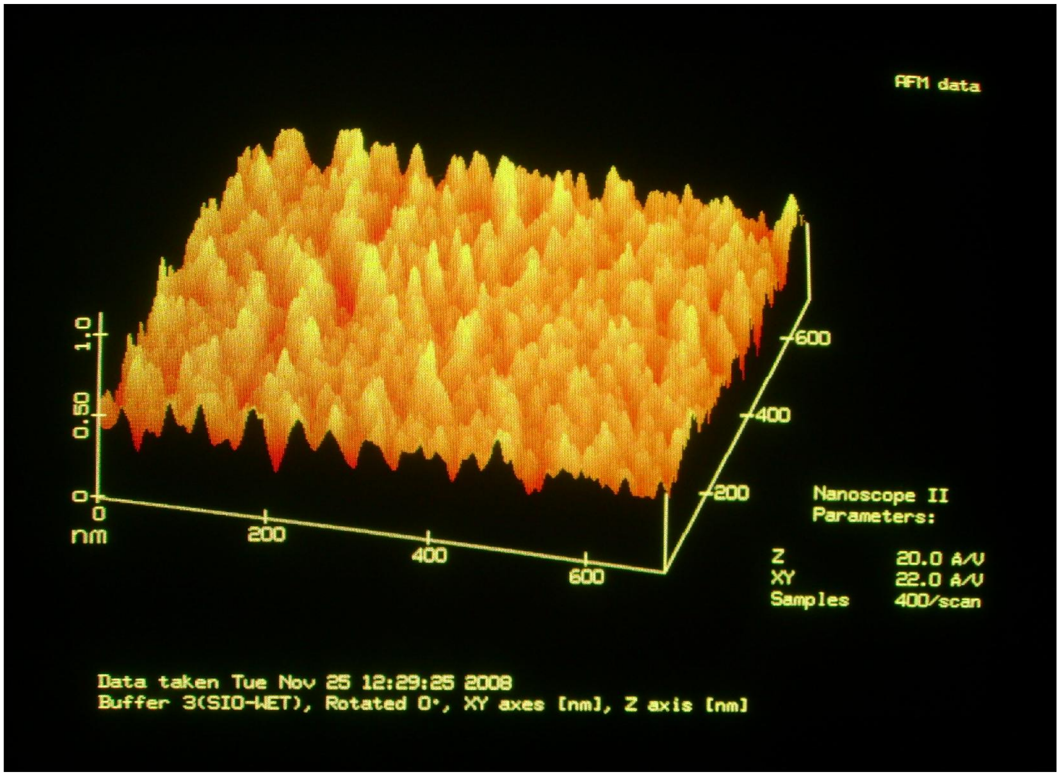
Nanoscope II Parameters:
Z 20.0 A/V
XY 22.0 A/V
Samples 400/scan

Data taken Tue Nov 25 12:29:25 2008
Buffer 3(SIO-WET), Rotated 0°, XY axes [nm], Z axis [nm]

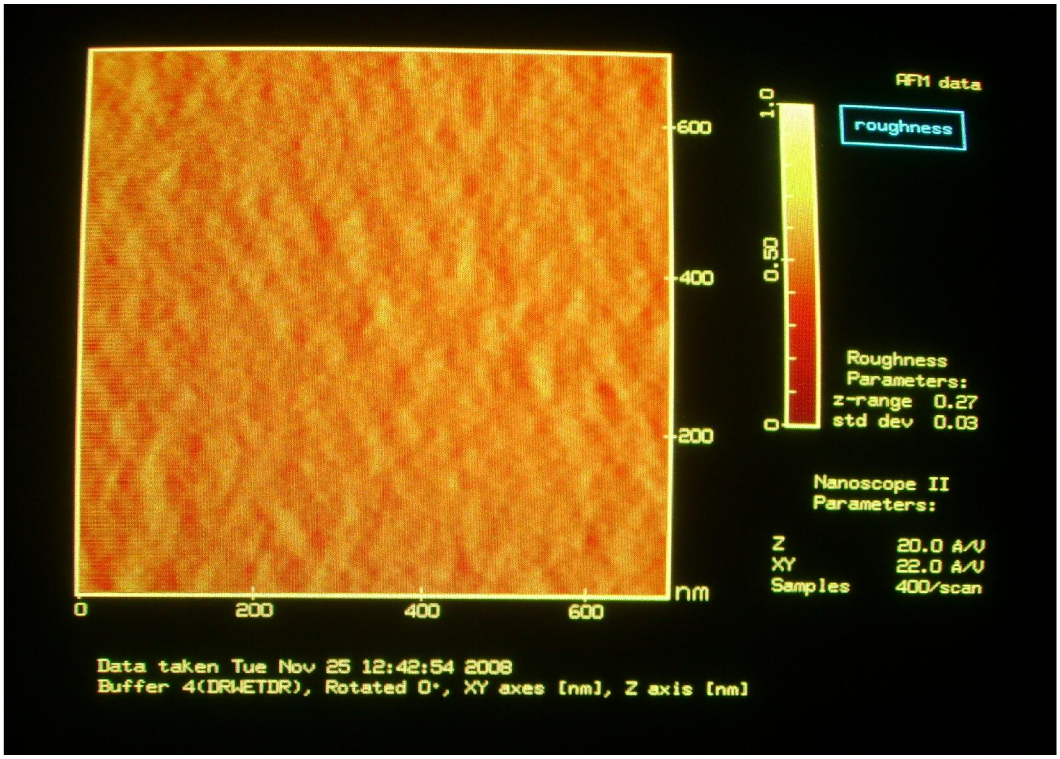


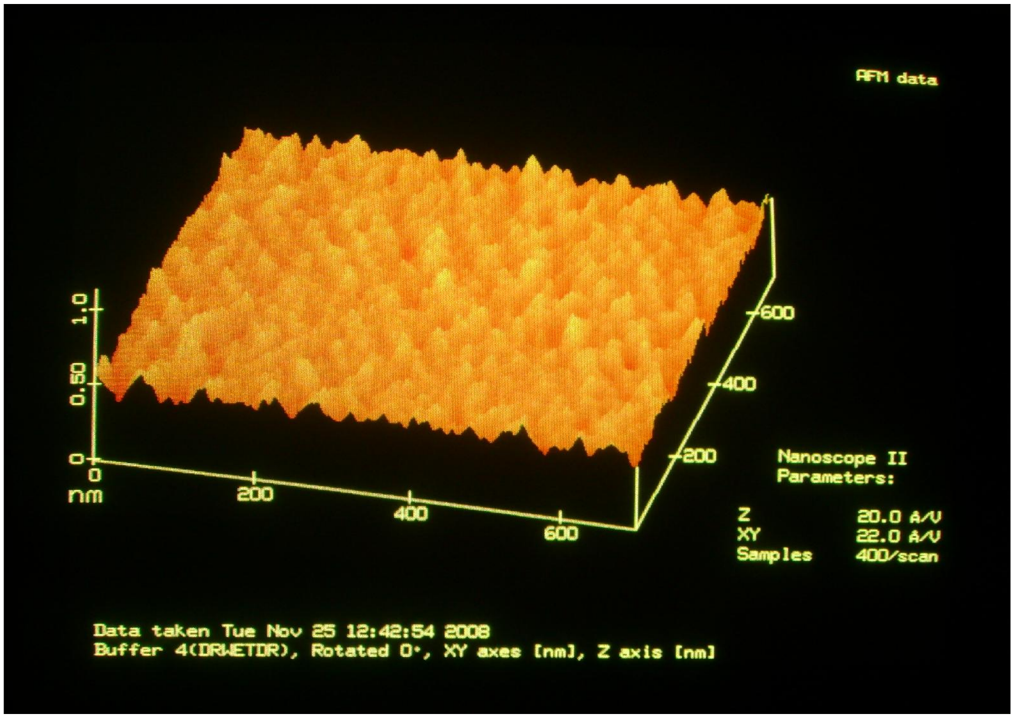
Nanoscope II Parameters:
Z 20.0 A/V
XY 22.0 A/V
Samples 400/scan

Data taken Tue Nov 25 12:29:25 2008
Buffer 3(SIO-WET), Rotated 0°, XY axes [nm], Z axis [nm]



DRY WET DRY OXIDATION:

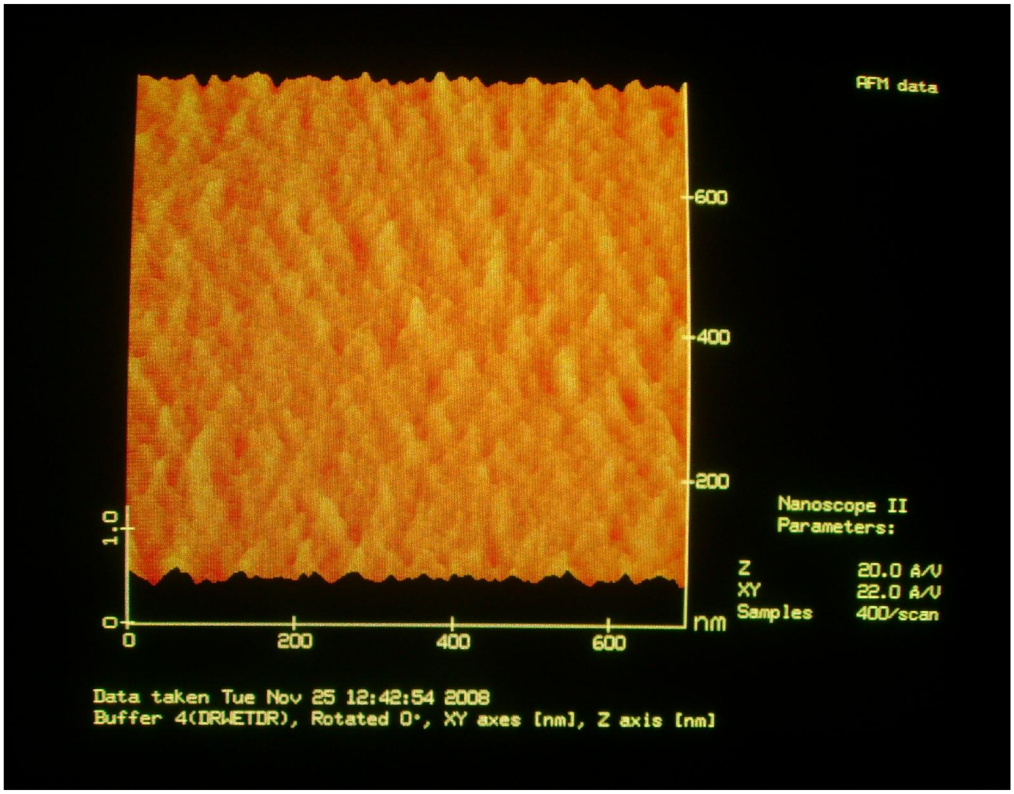




Nanoscope II
Parameters:

Z 20.0 A/V
XY 22.0 A/V
Samples 400/scan

Data taken Tue Nov 25 12:42:54 2008
Buffer 4(DRWETDR), Rotated 0°, XY axes [nm], Z axis [nm]



Nanoscope II
Parameters:

Z 20.0 A/V
XY 22.0 A/V
Samples 400/scan

Data taken Tue Nov 25 12:42:54 2008
Buffer 4(DRWETDR), Rotated 0°, XY axes [nm], Z axis [nm]

From all these photos and data about roughness, the following conclusions are very clear:

- Wet Oxidation causes maximum roughness of the surface, which in turn proves the poor quality of wet oxidation.
- Dry oxidation has lesser roughness (std. deviation) proving its higher quality in producing thinner oxides.
- Dry Wet dry compensates for the quality and speed and hence, is the most preferred case.

4. CONCLUSION

Oxidation is a very important step in the VLSI fabrication industry. The different types of oxidation and the atmosphere parameters play a vital role in the type of oxide formed. To calibrate and characterize this oxide has been an ever growing challenge owing to present trends of scaling down. Hence, techniques like ellipsometry, FTIR and AFM have a growing importance in the upcoming Silicon revolution.

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