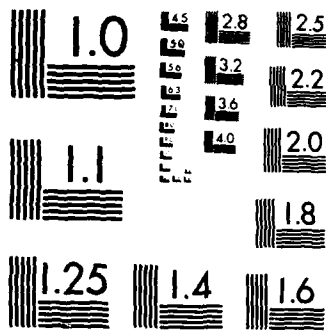


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The Influence of Silicon Surface Cleaning
Procedures on Silicon Oxidation

by

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ABSTRACT

This note reports the results of experiments which demonstrate the effect of pre-oxidation cleaning of silicon on the kinetics of oxidation for 5 different cleaning procedures. These cleaning treatments include simply rinsing samples as obtained from the manufacturer as well as combinations of $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$, $\text{HCl}-\text{H}_2\text{O}_2$ and HF solutions. The thickness vs. time data for 1 atmosphere oxidations at 980°C is analyzed to determine oxidation rates at thicknesses of 75.0, 275.0 and 405.0nm. Varying rates calculated at low thickness indicate an effect in the initial oxidation regime due to interfacial effects. Rate differences calculated at high thickness indicate a change in oxide structure due to cleaning treatment which is substantiated by ellipsometric measurements of refractive index which indicate a change in oxide density.

It has been previously demonstrated by Schwettman, Chiang and Brown¹ that the use of different pre-oxidation cleaning procedures can vary the rate of growth of SiO₂ via the thermal oxidation of silicon. Described here are the results of a similar study of oxidation kinetics following various silicon surface treatments including NH₄OH-H₂O₂, HCl-H₂O₂ and concentrated HF. These chemical treatments were chosen for study because they constitute those in the widely used RCA clean.² It is found that oxidation kinetics varied over the entire thickness range studied, that is 24-430nm.

Experimental

Oxidation data from five different pre-oxidation surface treatments, Groups 1-5, was evaluated in this experiment. The specifics of the treatments will be described below. The samples used were commercially available one inch p-type (100) wafers with 2 ohm-cm nominal resistivity in all cases. The oxidations were carried out in a 980°C furnace using a double walled fused silica furnace tube and dry oxygen at 1 atmosphere with less than 10ppm water as measured at the furnace exhaust. The thicknesses were measured with a research quality ellipsometer with an accuracy of 0.01° and two measurements were performed on each sample for greater precision.

Group 1 samples were exposed only to flowing deionized water produced at 18MΩ resistivity but with a measured resistivity of >7MΩ at the point of contact with the samples. This degradation in resistance is a result of

CO₂ uptake by the water. The wafers were used exactly as shipped with no other cleaning treatment. From a conversation with the manufacturer it was determined that the post polishing treatment of the wafers consisted of 6 steps to prepare the wafers for shipping. These steps were HF dip; rinse; 5 minutes in H₂SO₄-H₂O₂; rinse; spin rinse; and lastly deionized water plus alcohol to aid drying. The Group 1 samples will be referred to as "No Clean" throughout the paper. Wafers in Group 2 (called "No Clean+HF") were rinsed like the Group 1 samples but just prior to oxidation were dipped for 10 seconds in concentrated (49%) MOS grade HF and then rinsed for about 30 minutes in flowing deionized water.

The samples in Groups 3, 4 and 5 underwent various parts of the RCA clean² where all chemicals used were also MOS grade purity. The samples from Group 3 were put in an ultrasonic bath of 60-70°C 5:1:1 deionized H₂O:concentrated (29%) NH₄OH:30% H₂O₂ followed by about 10 minutes of rinsing in flowing deionized water. Group 4 samples were subjected to a 5 minute ultrasonic bath in 5:1:1 deionized H₂O:concentrated (37%) HCl:30% H₂O₂ at 60-70°C followed by rinsing in flowing deionized water for approximately 10 minutes. Group 3 samples will be called "Base Only" and Group 4 will be called "Acid Only" samples. The wafers of Group 5 were given first the basic treatment received by Group 3 with rinsing, then the acidic treatment received by Group 4 with rinsing and finally a 10 second dip in concentrated (49%) HF with at least 30 minutes of rinsing in flowing deionized water like the Group 2 samples. The treatment received by the Group 5 samples constitutes our standard pre-oxidation cleaning and this group will be referred to as "Base+Acid+HF" hereafter.

In each oxidation performed, two wafers were prepared identically for each of the groups and following the specific treatment and rinsing all wafers were blown dry in nitrogen. All wafers with different pre-oxidation treatments were oxidized together in a 980°C furnace. This is extremely important because slight variations in furnace temperature and water content of the oxygen gas can vary the kinetics of the oxidation from run to run. Since all the samples were oxidized together, any differences in oxide thickness can be attributed to the effect of the surface treatment used, not variations in the oxidation conditions.

Results

The thickness vs. time data for the 8 oxidations performed is shown in Figure 1. The thickness plotted is the average of at least 4 measurements, at least 2 measurements on each of 2 samples. The first four oxidations, where the oxidation time is less than 200 minutes, contained only "No Clean", "Base Only", "Acid Only" and "Base+Acid+HF" samples. The "No Clean+HF" group was added later to better understand the effect of HF pre-treatment on the oxidation.

First, it should be noted that the relative order of thickness in every oxidation is the same. The "Base+Acid+HF" always had the thickest oxide followed closely by "No Clean+HF" (where applicable) and "No Clean", in that order, while the "Acid Only" and "Base Only" groups had thinner oxides with the "Base Only" group always thinnest. The fact that all oxidations are in agreement regarding the relative thicknesses is strong evidence that the pre-oxidation treatments have a significant effect on

oxidation kinetics. This is concordant with the previous work of Schwettmann, Chiang and Brown¹ who also found oxidation rates to vary significantly with pre-oxidation clean. They found that a sample treated with $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$ yielded thinner oxides than a sample oxidized without treatment. This result is identical to the one obtained in this study with the "No Clean" samples having thicker oxides than the "Base Only" samples. Schwettmann et. al. also pre-treated a wafer with $\text{H}_2\text{SO}_4-\text{H}_2\text{O}_2$ and found that this led to thicker oxides than either of the other two treatments. The "Acid Only" samples used here were treated with a $\text{HCl}-\text{H}_2\text{O}_2$ solution and showed an intermediate oxide thickness, between the "No Clean" and "Base Only" treatments. This leads to the conclusion that the $\text{H}_2\text{SO}_4-\text{H}_2\text{O}_2$ treatment in the experiments of Schwettmann et. al. has some oxidation enhancing properties over a "no clean" procedure that are not simply due to the acidic nature of the treatment because in our experiments $\text{HCl}-\text{H}_2\text{O}_2$ yields thinner oxides than "No Clean".

The other major feature of the data of Figure 1 is the clustering of the points at shorter oxidation times with subsequent divergence at longer times. This is particularly evident when comparing the "Acid Only" and "Base Only" groups to the other three groups. In order to study this divergence further, the oxidation rates of the various groups were determined at several thicknesses. To avoid using any particular model for silicon oxidation to calculate the rates, they were determined numerically, simply by taking the derivative of analytic functions that were fit to the data. By plotting time (t) on the y-axis and thickness (L) on the x-axis, a second order polynomial function of the form $t=aL^2+bL+c$ can be quite precisely fit to any subset of the data points. Taking the inverse of the

derivative of the second order function ($[2aL+b]^{-1}$) and substituting in a specific thickness, the oxidation rate at that thickness can be found. Since only four points exist for the Group 2 samples, no rates were determined for the "No Clean+HF". In order to study the rates over the entire range of the oxidation, thicknesses of 75.0, 275.0 and 405.0nm were chosen for evaluation. The oxidation rates for each of the groups at these thicknesses are shown in Table 1. From this data it is seen that the relative oxidation rates for the 75.0 and 275.0nm thicknesses fall in exactly the same order as the thicknesses of the oxides throughout the oxidation. "Base+Acid+HF" has the highest rate followed by "No Clean", "Acid Only" and "Base Only" in that order.

If this experiment is analyzed in light of the linear-parabolic model of Deal and Grove³, the trends in the oxidation rates can be explained. The linear-parabolic model proposes that the initial stages of silicon oxidation are governed by the interface reaction of silicon with oxygen which yields a linear rate, while the later stages of oxidation are governed by diffusion of oxygen through the oxide to the silicon which yields a parabolic rate. It is reasonable to assume that any pre-oxidation treatment of the silicon would effect only the silicon surface and would therefore primarily influence the linear or early stages of the oxidation. For this reason, different chemical cleans would yield different oxidation rates for thinner oxide films as illustrated in Table 1 for the 75.0nm rates. As the oxide grows thicker, diffusion of the oxygen through the oxide becomes the limiting step in oxidation and so any effects due to the interface will diminish. The rates shown in Table 1 at 405.0nm support this

idea because they converge to nearly identical values at this large thickness.

Considering the fact that diffusion is thought to be important to the silicon oxidation rate after growth of about 1000\AA of oxide, it seems likely that the differences in rates at 275.0nm can be explained by assuming that the SiO_2 itself is somehow modified by the chemical treatments used. Ellipsometry enables accurate measurement of refractive indices for silicon dioxide in certain thickness ranges. These ranges are $n/2$ periods where n is an odd integer and the period for SiO_2 at the wavelength used (632.8nm) is about 140.0nm . Two of these ranges are 140.0 and 420.0nm which coincide with the 270 and 1910 minute oxidations. Refractive indices were measured for these samples as the average of at least 10 total measurements, that is at least 5 measurements performed on each of two samples for each group. At thicknesses near $n/2$ period (where n is an odd integer) errors of as much as 0.05° , which is 5 times greater than the accuracy of the instrument (0.01°), yield errors of less than 1 part per thousand in thickness and refractive index. The repetition of measurements insures precision of the refractive index of each sample and measurement in the proper thickness ranges insures accuracy of the indices. Using the Lorentz-Lorenz relationship

$$\rho = \frac{K(n^2 - 1)}{n^2 + 2}$$

where ρ is density, K is 8.0461 for SiO_2 grown at 1000°C in dry oxygen, and n is the refractive index from ellipsometry, densities of the SiO_2 are calculated⁴. Both the refractive index and density values from $1/2$ and $3/2$

period are shown in Table 2 and the trend evident is in agreement with the oxidation rate results at 275.0nm. Considering the standard deviations of the average refractive indices, it is not possible to distinguish a significant difference between the "Acid Only" and "Base Only" pair of groups or the "Base+Acid+HF" and "No Clean+HF" pair of groups in either period. However, a significant difference does exist between the "Acid Only" "Base Only" pair and the "Base+Acid+HF" "No Clean+HF" pair for both of the ellipsometric periods where refractive indices were measured. The "Base+Acid+HF" "No Clean+HF" pair has the highest oxidation rates and the lowest densities while the "Acid Only" "Base Only" pair has the slowest rates but the highest densities with the "No Clean" group falling between these two pairs with a corresponding intermediate rate and density. This correlation between rate and density is anticipated based on a published study⁵ which shows that lower density oxides enable faster diffusion of oxygen through the oxide and therefore a faster oxidation rate.

Summary and Conclusions

This study confirms the work of Schwettmann, Chiang and Brown¹, demonstrating that the use of different pre-oxidation cleaning procedures on silicon can have a significant effect on the kinetics of silicon oxidation. It was found that the five treatments studied exhibited the same relative order of oxide thickness for all the oxidations performed, with the "Base+Acid+HF", "No Clean+HF" and "No Clean" groups yielding thicker oxides and faster rates than the "Acid Only" and "Base Only" groups (except

at 405.0nm where the rates converge to about 0.136nm/min). The fact that significant oxidation rate differences were found at 275.0nm along with correlating SiO₂ density differences in the 140.0 and 420.0nm ranges indicates that the effect of the chemical treatments on silicon may extend beyond the initial oxidation region. As yet there is no good explanation as to why these chemical treatments would have such an effect at large thicknesses. In the study mentioned before⁵, where a similar correlation of high SiO₂ refractive index to slow oxidation kinetics was found, this behavior was linked to intrinsic film stress of the oxide which increases oxide density. An alternative explanation, supported by calculations by Irene⁶, is to suggest that the initial oxidation regime, where interface control dominates, extends to a greater thickness than anticipated. These are possible explanations for the results reported here, but continuing studies of the nature of these oxides and their electrical properties are in progress to better understand the effects of these chemical treatments.

Acknowledgements

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List of Tables

Table 1: Oxidation rates in nm/min for 4 pre-oxidation treatments at thicknesses of 75.0, 275.0 and 405.0nm.

Table 2: Refractive indices and densities calculated from 270 minute (1/2 period) and 1910 minute (3/2 period) oxidations.

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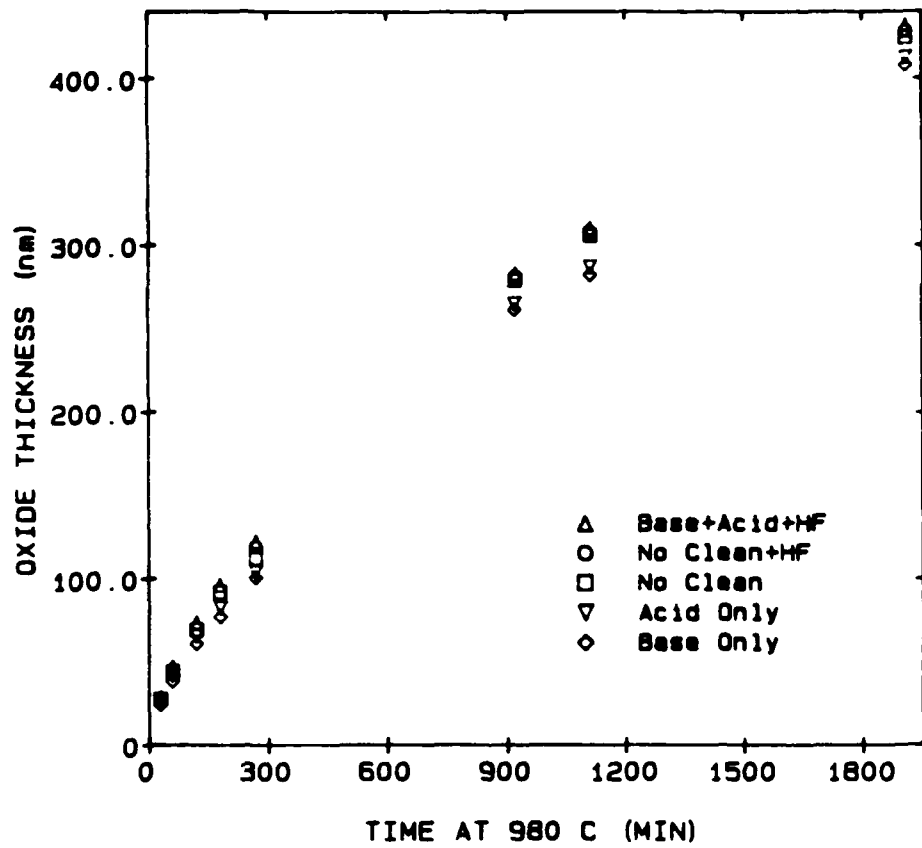
	Group 5 Base+Acid+HF Dip	Group 1 No Clean	Group 4 Acid Only	Group 3 Base Only
75.0nm	0.414	0.407	0.340	0.331
275.0nm	0.188	0.184	0.178	0.176
405.0nm	0.139	0.136	0.136	0.135

Table 2: Refractive indices and densities calculated from 270 minute (1/2 period) and 1910 minute (3/2 period) oxidations.

	Group 5 Base+Acid +HF Dip	Group 2 No Clean +HF Dip	Group 1 No Clean	Group 4 Acid Only	Group 3 Base Only
270 min. oxidation					
Ref. Index	1.464	1.465	1.466	1.468	1.469
Std. Dev.	0.0009	0.0005	0.0007	0.0017	0.0005
Density(g/cm ³)	2.220	2.224	2.228	2.237	2.241
1910 min. oxidation					
Ref. Index	1.460	1.460	1.462	1.463	1.464
Std. Dev.	0.0012	0.0009	0.0007	0.0009	0.0007
Density(g/cm ³)	2.204	2.204	2.212	2.216	2.220

List of Figures

Figure 1: Plot of oxide thickness vs. time for 5 pre-oxidation treatments.



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