An In-Situ Ellipsometric Study

of

Aqueous NH_4OH Treatment of Silicon

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ABSTRACT

In-situ ellipsometry is used to analyze silicon surfaces in an aqueous NH_4OH ambient. The ellipsometric data indicate that a surface which is optically quite similar to bare Si is obtained when the native SiO_2 film is etched from a Si substrate by aqueous NH_4OH. In contrast, the surface obtained by etching the native oxide in aqueous buffered HF leads to formation of a residual film on the Si substrate. Roughening of sample surfaces treated with either aqueous NH_4OH or BHF is observed by microscopy. The high degree of roughness obtained following NH_4OH treatment appears to influence ellipsometric measurements on samples, but this influence is not observed following BHF exposure where less roughness is noted.

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INTRODUCTION

The successful production of microelectronic devices from semiconductor materials requires surface preparation. The two most important elements of this preparation are cleaning and passivation. For the case of silicon, thermal oxidation is uniquely effective at surface passivation, reducing the number of surface states to well below acceptable levels for device operation. While successful pre-oxidation cleaning procedures for silicon exist(1), quantification of these procedures has been rather scarce(2-5). In previous work(6) both in-situ ellipsometric and contact angle measurements were shown to be useful for quantification of cleaning by aqueous HF. These techniques enable measurements of a sample surface to be performed while the sample is immersed in a liquid phase ambient, the standard cleaning environment for Si used for microelectronics processing.

In the previous work(6), it was shown that the silicon surface was covered by a residual film following HF treatment. While HF is an aggressive etchant of SiO_2, it is an extremely mild etchant of Si(7). When Si is placed in aqueous HF, any SiO_2 is rapidly etched away, but a denuded silicon surface is never exposed due to formation of a surface film rather than an etchable oxide film. Typical of most metals(8), the bare silicon surface has a high surface energy(9), thus this reactive surface will scavenge any species in order to lower its surface energy. Further indications of the effects of HF on Si surfaces are provided by Auger(4) and XPS(10) analyses of Si samples which indicate higher

surface carbon content as a result of HF exposure. Evidence of the effects of HF on Si is also provided by reports of enhanced oxidation rates observed on HF treated Si(2-5).

In this paper, the in-situ ellipsometric technique is used to study a silicon surface in an aqueous ammonium hydroxide ambient. Ammonium hydroxide is chosen because it is known to etch silicon at a much faster rate than HF, which should enable continuous creation of a fresh silicon surface. Through ellipsometric measurement the creation and preservation of this denuded silicon surface in NH_4OH can be monitored. Comparison of ellipsometric parameters obtained by in-situ measurement of Si surfaces in aqueous NH_4OH to those obtained in buffered HF (BHF) gives further evidence of growth of a residual film on Si following HF exposure.

EXPERIMENTAL

The features of the in-situ ellipsometric experiment have been presented elsewhere(6), so many of the details of this technique will not be repeated here. In any ellipsometric measurement, the two parameters Ψ (amplitude ratio) and Δ (phase difference) for the reflected light are always determined and can be used to calculate optical parameters of the sample. Assuming that all of the instrumental parameters, as well as the ambient refractive index are known, the thickness of a film on a substrate can be determined if the refractive indices of the substrate ($\tilde{n}_s$) and film ($\tilde{n}_F$) are known, or both the real (n) and imaginary (jk) parts of the complex substrate refractive index ($\tilde{n}_s$ with the form

n-jk) can be determined if the assumption is made that no film is present on the sample. An Abbe Refractometer with an accuracy of ±0.0001 units has been used to determine refractive indices for all ambients used in this experiment, the angle with which the light impinges on the sample is determined with an accuracy of 0.01° from a calibrated scale on the ellipsometer base and the refractive index used for SiO_2 is 1.465(11). An analysis of systematic error in these parameters was carried out previously(6) and it was shown that even gross errors led to variations of less than a few Angstroms in SiO_2 thicknesses.

As mentioned earlier NH_4OH is a far faster etchant of silicon than HF, but it etches SiO_2 at a much slower rate than HF does. Kern(12) reports an etch rate of 0.28nm/min for SiO_2 and an etch rate of over 25nm/min for both <100> and <111> orientations of single crystal silicon in 5:1 H_2O:NH_4OH at 85°C. To verify this result and test the feasibility of carrying out an in-situ experiment using ambient aqueous NH_4OH, the following trial was performed. Two Si substrates of <111> orientation, one with a gross thermal SiO_2 film of approximately 200nm, and one with a native oxide film of approximately 2nm were placed in a bath of 5:1 H_2O:NH_4OH at 85°C for 20 minutes. For the sample with the gross oxide film, an SiO_2 etch rate of 0.21nm/min was calculated in an ex-situ manner by taking ellipsometric measurements of thickness in an air ambient both before and after the 20 minute etch. It was evident from observation of vigorous bubbling on the sample with the native oxide film that there would be a problem

with gas evolution at the Si surface if a heated solution of NH_4OH was used. There was no gas evolution observed on the sample with the gross oxide film, so the bubbling was presumably hydrogen gas evolved as a product of the etch of Si. Since ellipsometry, as it is used here, is a reflection technique, the evolution of gas bubbles at the sample surface would make an in-situ measurement quite difficult because the incident light would be obscured from the surface by the bubbles. To minimize the problem of gas bubble formation at the Si surface, a room temperature solution of aqueous NH_4OH at varying concentrations is used because the reaction of the Si surface and NH_4OH is slowed at this reduced temperature. Decrease of this reaction rate reduces the evolution of gas at the sample surface and enables an in-situ measurement. The reduction of the solution temperature causes a decrease in the SiO_2 etch rate but the time needed to etch through the SiO_2 can be minimized by starting with Si samples covered only by a native oxide (typically 1-2nm in thickness). It is, however, imperative that the solution used for the experiment have a nonzero etch rate for SiO_2 in order to expose the Si substrate.

The samples employed for the in-situ ellipsometric measurements are two inch diameter p-type <100> oriented single crystal silicon wafers that are cleaved into quarters to fit in the in-situ cell. The quartz cell is first filled with the etch solution and then the sample is immersed and fixed in place. Null ellipsometric measurements are taken at periodic time intervals and after the ellipsometric measurables cease to change (that is,

after the calculated film thickness ceases to vary significantly in successive measurements), the solution is displaced by flushing the cell with pure deionized water. Both the initial etch of SiO_2 and the native SiO_2 film formation after flushing the cell are monitored ellipsometrically by calculation of the SiO_2 film thickness.

RESULTS

The oxide thickness vs. time data for ambient 5:1 $H_2O:NH_4OH$ is shown in Figure 1. As anticipated, the oxide thickness decreases slowly, at less than 0.02nm/min, as shown by the initial circles. A minimum thickness of 0.06nm is obtained 84 minutes into the experiment and the thickness apparently increases on subsequent measurements. Following exposure for just over three hours in 5:1 H_2O/NH_4OH, no further change is observed in the thickness vs. time data between successive measurements. At this time the ambient etch solution is displaced by pure water without exposing the sample surface to air. This event is indicated in Figure 1 by the vertical line at 190 minutes and ellipsometric measurements after this show oxide regrowth in H_2O.

Etch time vs. oxide thickness data was also collected for 2:1 H_2O/NH_4OH and concentrated NH_4OH etch solutions. The results are similar in that a minimum oxide thickness quite close to 0 is calculated, followed by an apparent increase in oxide thickness. The only significant difference is that the concentrated NH_4OH solution requires over three hours to etch the native SiO_2 film as

compared to just one hour for the 5:1 and 2:1 H_2O/NH_4OH. The concentrated NH_4OH contains less water, so the slower etch rate for SiO_2 in concentrated NH_4OH must be attributable to the decrease in the concentration of water in the etch solution. This points to the importance of water as a solvent for etch products in the reaction of SiO_2 and NH_4OH. This result will not be discussed further and since the different concentrations of NH_4OH behaved similarly with regard to all other experimental aspects, the forthcoming discussion will be limited to the 5:1 H_2O/NH_4OH experiment described first.

In order to better understand the data of Figure 1, it is helpful to analyze the raw ellipsometric data. Figure 2A is a graph of the ellipsometric parameters Ψ and Δ plotted against one another. The symbols in the plot correspond to the identical Ψ and Δ values used to calculate the thicknesses in Figure 1 and also shown are two theoretically calculated curves. The theoretical curve labelled "Ambient Aqueous NH_4OH" is composed of Ψ, Δ values for increasing SiO_2 film thickness on a Si substrate under the specific ambient refractive index, angle of incidence and wavelength of light conditions used for the measurement. The arrow pointing to the top of the "Ambient Aqueous NH_4OH" curve indicates the theoretically calculated Ψ, Δ point corresponding to a bare Si substrate or zero oxide thickness on a Si substrate. As the SiO_2 film thickness increases from zero, Ψ and Δ progress in such a manner to trace the solid line. In other words, as Ψ increases and Δ decreases from 1.1° and 171° respectively it is indicative of

increasing oxide thickness. Since ellipsometry is sensitive to the ambient refractive index and pure water has a different refractive index than 5:1 H_2O/NH_4OH, a second theoretical curve is derived to relate the raw data for ambient water. The curve labelled "Ambient Water" has zero oxide thickness values for Ψ and Δ similar to the ambient ammonium hydroxide curve and increasing oxide thickness occurs with increasing Ψ and decreasing Δ.

The circles in Figure 2A correspond to measurements taken while 5:1 H_2O/NH_4OH is present and the initial points progress from the center of the plot up toward the top (decreasing Ψ and increasing Δ). The progression in this direction corresponds to etching of the SiO_2. From Figure 1, the initial oxide thickness is about 1.9nm. The oxide thickness decreases to 0.06nm and then the apparent increase in oxide thickness is observed. The data that are obtained after the minimum thickness but before the etch solution is displaced (between 90 and 190 minutes in Figure 1) are shown as darkened circles in Figure 2A. When these Ψ, Δ values are used to calculate oxide thicknesses, it appears that an increase in SiO_2 film thickness takes place. It is believed that these points are indicative of something other than SiO_2 growth and further analysis of these particular points will be provided later in this paper. When the etch solution is displaced by water, the experimental points shift onto the "Ambient Water" curve as shown by the triangles. These experimental values progress down the curve, toward increasing oxide thickness as the native SiO_2 film reforms. The most important feature of Figure 2A is the proximity

of the calculated zero oxide thickness value to the point corresponding to the experimental minimum oxide thickness. This proximity evidence for the creation of a denuded Si surface in aqueous NH_4OH.

A comparison of the raw Ψ, Δ data obtained in an aqueous NH_4OH ambient to similar data (Figure 2B) obtained in an aqueous buffered HF ambient illustrates the fact that a bare Si surface is not produced in ambient HF. As in Figure 2A, this graph consists of experimental points and two theoretical curves. The theoretical curve labelled "Ambient BHF" is calculated for the buffered HF etch solution (1000:100:0.8 $H_2O/NH_4F/HF$) and the calculated Ψ, Δ point for a bare Si substrate for the specific conditions used for BHF etch is indicated by the arrow which points to the top of this curve. The theoretical curve labelled "Ambient Water" is calculated for pure water. The experimental points (circles) of Figure 2B begin at the bottom of the graph close to the BHF ambient line and progress with decreasing Ψ and increasing Δ, indicative of etching of the SiO_2 film. The conspicuous difference between Figures 2A and 2B is that the experimental points for the aqueous BHF ambient (Figure 2B) never closely approach the calculated zero oxide thickness point. For this experiment, no data points were ever obtained closer to the zero oxide thickness value than $\Psi \sim 0.8°$ and $\Delta \sim 145°$, and the sample was left in the BHF solution for almost 4 hours, at which time successive measurements did not vary. As in Figure 2A, there was an apparent increase in oxide thickness following the minimum SiO_2 thickness and the

measurements that were taken after the minimum are indicated by the darkened circles in Figure 2B. Comparison of this apparent increase with the same behavior in aqueous NH_4OH provides valuable information and this issue will be discussed later in the paper. After displacement of the etch solution by pure water, experimental points fall near the theoretical curve labelled "Ambient Water" and, over time, these points progress in the direction of increasing oxide thickness. Since the graphs in Figures 2A and 2B are plotted on identical Ψ and Δ scales it is apparent that the ambient aqueous NH_4OH yields a surface that is much closer to that of bare Si than the surface yielded by ambient BHF because Figure 2A shows a closer approach of experimental values to the expected bare Si values.

The Ψ-Δ plots of Figures 2A and 2B give a qualitative indication of the existence of a bare silicon surface in aqueous NH_4OH ambient as compared to the surface in BHF ambient. A quantitative comparison of these surfaces is provided when the complex substrate refractive index is calculated from the ellipsometric parameters by assuming that no film is present on the sample surface. These calculated values can be compared to an accepted value of $3.865-0.018i$(13) for the complex index of silicon. Complex substrate refractive indices are calculated for sample surfaces from the Ψ and Δ values that gave the minimum SiO_2 thickness because the best agreement with the accepted value is always obtained at minimum film thickness. For ambient aqueous NH_4OH a value of $3.868-0.019i$ is obtained and a value of 3.862-

0.031i results for ambient BHF. The agreement in the real part of the index is quite good in both cases, but the imaginary part of the index for the NH_4OH etched sample is only 6% different from the imaginary part of the accepted value as compared to 72% different for a BHF etched sample. It should be recognized that the results of these calculations inherently agree with the qualitative results seen in Figures 2A and 2B because the same Ψ and Δ data were used in both calculations, but the quantitative nature of the comparison adds more validity to the argument that bare silicon originates in NH_4OH.

To this point, the data collected has only been analyzed with respect to how closely the surface produced by etching in these ambients resembles bare silicon. More information about the effect of these etching ambients can be obtained by a closer inspection of the ellipsometric data collected while the etch solution was still present but after the minimum thickness was obtained. The region in Ψ, Δ space in which the darkened circles of Figures 2A and 2B fall can be indicative of film growth on the Si substrate. Though film growth after attainment of minimum oxide thickness has been observed for etch of SiO_2 films in HF(6), there are some important distinctions to be made between the use of HF containing ambients and NH_4OH ambients. It seems unlikely that any films could grow on the Si surface in aqueous NH_4OH because it is a rapid etchant of Si. The exposed Si surface is quite reactive, but silicon is constantly stripped from the surface in this basic medium, while in HF the Si is only mildly attacked, enabling

formation of a residual film. Further evidence of the different behavior in NH_4OH is given by the trajectory of the Ψ, Δ data. In the previous study, the film growth in ambient HF was evidenced by points that were found at smaller Ψ values than the Ψ value corresponding to the minimum thickness. In contrast, for ambient NH_4OH, the Ψ, Δ points in question (darkened circles of Figure 2A) are at larger Ψ than the Ψ value corresponding to minimum thickness.

A better explanation for the apparent increase in oxide thickness of NH_4OH etched samples is roughening of the Si surface. Upon removal of the samples etched in either aqueous BHF or aqueous NH_4OH from the sample cell, roughening is apparent on the sample surfaces. Analyses of the surfaces by SEM and optical microscopy with Normarski DIC conclusively identify roughening. Figures 3A and 3B are the optical micrographs, taken at 200X, for sample surfaces after exposure to NH_4OH and BHF respectively. The micrographs were obtained from the same samples from which ellipsometric data was collected and each sample was subjected to just under 4 hours in the etch solution followed by 3 hours in pure water. There is a greater degree of roughening evident on the sample etched in aqueous NH_4OH, than on the sample etched in buffered HF as expected due to the fast etch rate of Si in aqueous NH_4OH relative to the Si etch rate in BHF.

Roughening has been shown to have an effect on ellipsometric measurements(14), so the data in Figure 2A and 2B must be scrutinized for these effects. An approximation of the influence

of roughening of a sample surface on ellipsometric measurements can be made by assuming that the surface consists of two components with different refractive indices. One component is the actual substrate, in this case silicon with an index of 3.865-0.018i, and the other component consists of voids which are assigned the same refractive index as the ambient aqueous NH_4OH (1.3346-0.0i in this case). Using the Bruggeman effective medium approximation(15), the refractive index of a layer of a given void percentage can be obtained. This refractive index can then be used in a theoretical calculation of the resultant Ψ, Δ values corresponding to an increase in the thickness of this film assuming the film composition remains constant. Table 1 is a collection of such calculations performed for 5, 10, 20, 30, 40 and 50% voids at thicknesses of 0, 0.25, 0.50, 0.75 and 1.0nm for the exact conditions used in the experiment with ambient 5:1 H_2O/NH_4OH. The first column is the calculated film refractive index for a varying void percentage in a two component mixture. The remaining columns are the theoretical Ψ and Δ values that would be obtained for various thicknesses of a layer of roughness of the given refractive index. It should be noted that at 0 thickness the Ψ and Δ values are the same regardless of the refractive index of the layer because no film is present and that as the thickness increases, Ψ always increases and Δ always decreases.

The average values for Ψ and Δ of the darkened circles in Figure 2A are 1.067° and 168.188° respectively. By comparison of

these values with the Ψ, Δ values obtained in Table 1, it is apparent that roughness could indeed be responsible for the points illustrated by the darkened circles. From the table, it is also evident that a thin film of large void percentage and a thicker film of smaller void percentage influence Ψ and Δ in essentially the same manner. The exact void percentage or thickness of the roughness layer would be difficult to determine for the specific sample and this has not been attempted. It is quite reasonable to assume that both the void percentage and the layer thickness would be constantly changing as the sample surface is etched by the NH_4OH and this would account for the lack of closer agreement between the values in Table 1 and the experimental values. Coupling the microscopic evidence with ellipsometric evidence given by the Bruggeman analysis, it is believed that the apparent increase in thickness obtained between 90 and 190 minutes in Figure 1 is due entirely to roughening of the sample surface and not film growth.

Since roughness was also observed on the BHF etched sample, the data illustrated by the darkened circles of Figure 2B should be analyzed to determine if it is the result of roughness. From Table I it is evident that roughness can not give rise to Ψ values that are less than the Ψ value which corresponds to a bare Si substrate. The darkened circles of Figure 2B (BHF ambient) fall to the right of the theoretical curve which is at smaller Ψ than the Ψ for a bare substrate, so it is believed that these points are not the result of surface roughening. The analysis by Fenstermaker

and McCrackin(14) revealed that small amounts of roughening had almost no effect on ellipsometric calculations, so the conclusion is drawn that the roughening observed in BHF ambients does not effect the ellipsometric measurements and furthermore that the trajectory of the Ψ, Δ points obtained after the minimum thickness is indicative of film growth on the Si surface as determined in earlier work(6).

CONCLUSIONS

In-situ ellipsometry has been used to monitor the etch and regrowth of native SiO_2 from Si substrates in aqueous NH_4OH and compared with similar data obtained in ambient aqueous buffered HF solutions. It has been demonstrated that the use of ambient aqueous ammonium hydroxide for removal of SiO_2 films from silicon substrates allows creation of a denuded silicon surface. Comparison of raw Ψ, Δ data for ambient NH_4OH with raw data for ambient BHF, illustrates that the Ψ, Δ data collected using ambient NH_4OH approaches the expected Ψ, Δ values for bare Si significantly more closely than the raw data collected for ambient BHF. When the same Ψ, Δ data is used to calculate both components of the complex refractive index assuming that the sample is a bare substrate, the agreement with the accepted values for silicon is best for ambient aqueous NH_4OH.

In both BHF and NH_4OH ambients the raw ellipsometric data diverge from their closest approach to the expected Ψ, Δ values for a bare Si substrate before the etch ambient is displaced. The

trajectories of these divergences differ in the two ambients used. It was determined that surface roughening was responsible for this outcome in ambient NH_4OH and optical microscopy verifies the presence of severe surface roughness. Less roughness on the BHF etched sample was detected microscopically and the Ψ, Δ trajectory in this data could not be explained by roughness. It was concluded that the roughening was not significant enough to influence the ellipsometric data and that the diverging Ψ, Δ values were indicative of film growth on the Si surface. It is important to note that it is not the intention of this study to purport that aqueous NH_4OH constitutes a better cleaning treatment than BHF, since the roughening induced on the Si surface by the NH_4OH could render samples treated in this manner useless for device processing.

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Figure 1: Calculated SiO_2 thickness vs. time in 5:1 H_2O/NH_4OH. Minimum thickness of 0.06nm was obtained at 84 minutes and etch solution was displaced by pure deionized water at 190 minutes as shown by the vertical line.

Figure 2A: Raw ellipsometric data for aqueous NH_4OH etch experiment. Circles represent measurements performed while etch solution is present and triangles represent measurements performed while pure water is present. The filled circles are data collected after the minimum thickness value was obtained but before the etch solution was displaced. Note that in ambient NH_4OH these values are all at larger Ψ than the Ψ value corresponding to a zero oxide thickness.

Figure 2B: Raw ellipsometric data for aqueous BHF etch experiment. Circles represent measurements performed while etch solution is present and triangles represent measurements performed while pure water is present. The darkened circles represent data collected prior to etch solution displacement but after minimum oxide thickness has been obtained. It should be noted that in ambient BHF these values all lie at smaller Ψ than the value for Ψ that corresponds to a zero oxide thickness.

LIST OF FIGURES (cont)

Figure 3A: Optical micrograph of surface roughness observed on a sample etched for 236 minutes in 5:1 H_2O/NH_4OH. Magnification is 200X and Normarski DIC is used.

Figure 3B: Optical micrograph of surface roughness observed on a sample etched for 220 minutes in 1000:100:0.8 $H_2O/NH_4F/HF$. Magnification is 200X and Normarski DIC is used.

FIGURE 1

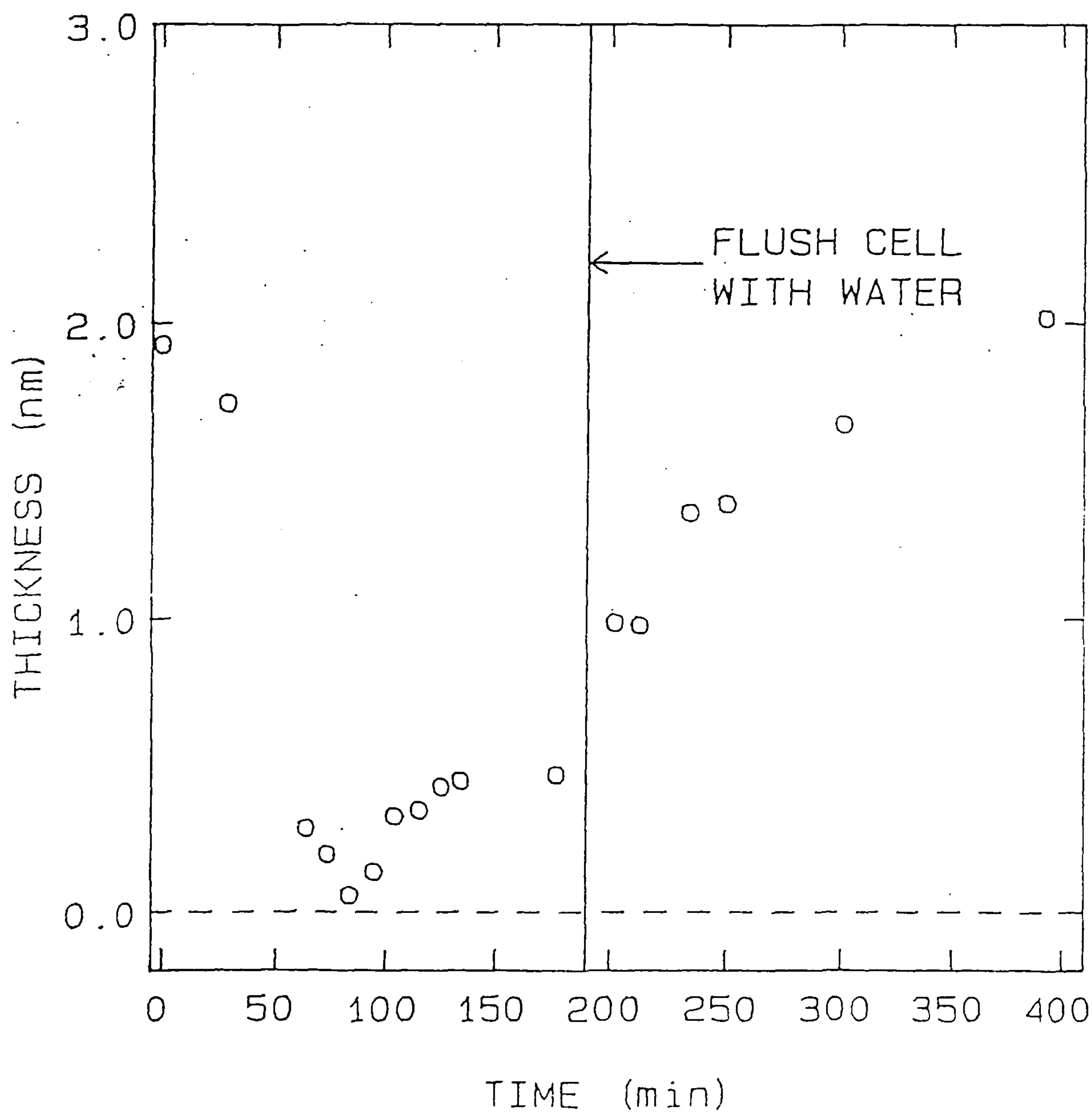

FIGURE 2A

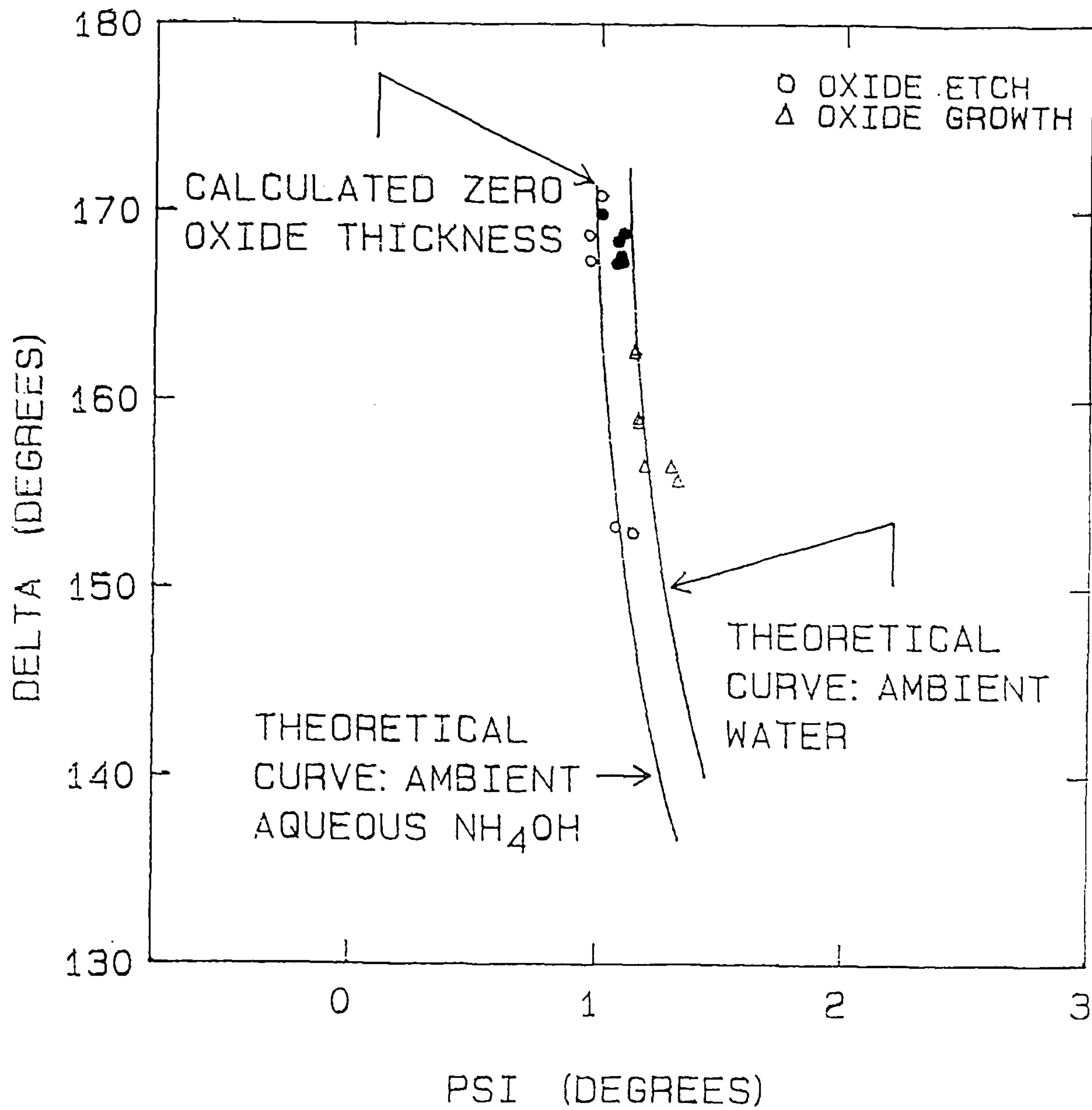

FIGURE 2B

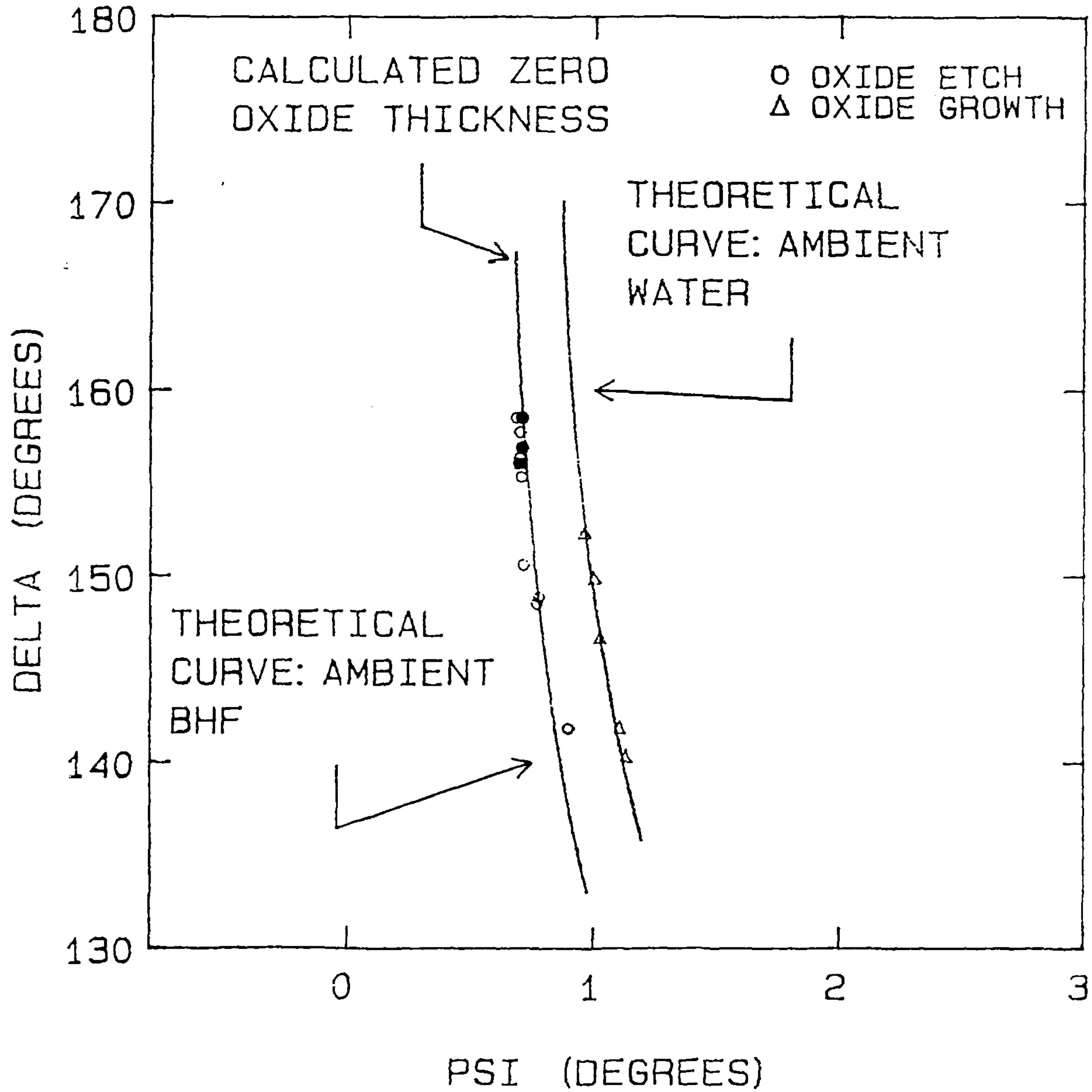

FIGURE 3A

[illegible]

FIGURE 3B

BHF Major Surface

LIST OF TABLES

Table 1: Effect of Surface Roughness on Ψ and Δ

TABLE 1

% VOID	$\tilde{n}_{eff}$	L = 0.0nm		L = .25nm		L = .50nm		L = .75nm		L = 1.0nm	
		Ψ	Δ	Ψ	Δ	Ψ	Δ	Ψ	Δ	Ψ	Δ
5	3.743-.017i	0.982	171.267	0.985	170.236	0.988	169.208	0.990	168.183	0.993	167.160
10	3.618-.016i	0.982	171.267	0.988	169.241	0.944	167.232	1.001	165.244	1.008	163.277
20	3.359-.015i	0.982	171.267	0.994	167.385	1.009	163.595	1.028	159.918	1.050	156.366
30	3.086-.013i	0.982	171.267	1.001	165.747	1.027	160.449	1.060	155.428	1.099	150.718
40	2.802-.011i	0.982	171.267	1.006	164.431	1.043	157.976	1.091	151.998	1.148	146.540
50	2.509-.008i	0.982	171.267	1.011	163.562	1.055	156.374	1.114	149.831	1.184	143.976