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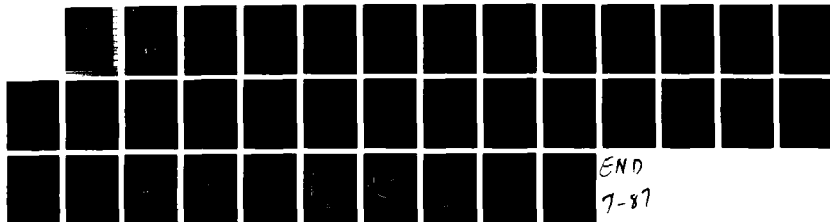
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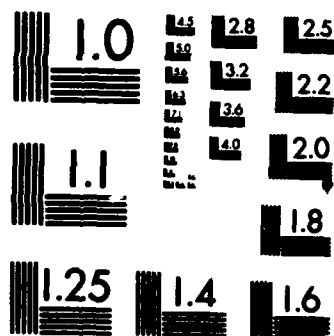
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An In-Situ Study of Aqueous HF Treatment of Silicon
by Contact Angle Measurement and Ellipsometry

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ABSTRACT

The use of two in-situ techniques for the study of semiconductor surfaces in solution ambients is reported. The techniques are in-situ ellipsometry and in-situ contact angle measurement and both should be applicable to any semiconductor surface in a solution medium. The specific experimental results discussed pertain to the Si surface in an aqueous HF medium and indicate the presence of a fluorocarbon film on the Si surface following etching away of an SiO_2 film.

INTRODUCTION

The operation of the MOSFET, one of the most common microelectronic devices, is dependent on application of an electric field across a thin insulating film (gate) of ~~SiO₂~~ ^{Silicon dioxide} to a Si substrate beneath. High quality performance of these devices requires cleaning and passivation of the ~~Si~~ ^{Silicon} surface. The use of hydrofluoric acid as a wet chemical etch for removal of SiO₂ from Si is common in the fabrication of MOSFET devices. Hydrofluoric acid is known to rapidly etch ~~SiO₂~~ ^{Silicon dioxide}, but to only mildly attack Si(1), which makes it a useful agent for removal of native SiO₂ from Si, before thermal oxidation to form the gate insulator, for delineation purposes and for opening contact holes through the SiO₂ to the Si substrate. Since the operation of MOSFET devices is dependent on the quality of the Si-SiO₂ interface, it is important to understand the effect of HF treatments on both SiO₂ and Si. In this paper we describe the results of experiments using ellipsometry and contact angle measurement applied in-situ, that is, in the solution ambient containing ~~HF~~ ^{Hydrogen fluoride}, to study the changes which HF solutions impart to Si and SiO₂ surfaces.

The effect of chemical treatments containing HF on Si and SiO₂ surfaces and the effect of such HF treatments on the kinetics of Si oxidation has been studied by a number of investigators. These investigators have employed XPS(2-5), AES(6-8), RBS(9), SIMS(10), multiple internal reflection (5), ellipsometry(2, 11-13) and radio tracers(14-16). Many of these studies indicate an effect of the HF treatment, but the only technique that can

routinely detect the presence of fluoride species on the Si or SiO₂ surface following HF treatment is the radio tracer analysis(14-16). The radio tracer analysis uses the radioactive species fluorine-18, ¹⁸F, to label the hydrofluoric acid used for etching, and subsequently count the ¹⁸F decay from the sample surface to determine the fluoride concentration present.

The previously noted analytical methods are all ex-situ analyses of Si or SiO₂ surfaces. Perhaps of even greater importance for the understanding of the interaction of Si and SiO₂ with HF is an in-situ approach, whereby the surface under analysis is immersed in the etch solution and analysis performed during this immersion, thus precluding extraneous ambient effects. We describe here the results of both in-situ ellipsometric and in-situ contact angle measurements which, when considered jointly, lead to a positive identification of fluoride at the Si surface following SiO₂ etch by dilute HF.

EXPERIMENTAL

The inability of vacuum analytical techniques such as XPS, AES, RBS and SIMS to routinely detect fluoride species on Si or SiO₂ surfaces leads to the requirement for in-situ analysis schemes. Ellipsometry and contact angle measurement are techniques with established high surface sensitivity, and both can be used in the presence of a liquid phase ambient allowing in-solution analysis for detection of low levels of surface contaminants. By

applying these techniques in-situ, we demonstrate that the process of etching of SiO_2 by dilute aqueous HF can be monitored.

A. Ellipsometry

For measurements of thin films on solid surfaces, ellipsometry has been widely used because of its convenience, accuracy, and extremely high sensitivity enabling detection of submonolayer coverage of surfaces by adsorbed species(17-19). In reflection ellipsometry, changes in polarization of light upon reflection from a solid sample are measured. These changes are the amplitude ratio, Ψ , and the phase change, Δ , which are related to the sample and ambient by the fundamental equation of ellipsometry:

$$\tan \Psi \exp(i\Delta) = f(n_a, n_f, \tilde{n}_s, \lambda, L_f, \varphi)$$

where n_a and n_f are the refractive indices of the ambient and film (or films) respectively, which could be complex but in this case, air or water in contact with a dielectric film, are real. The substrate refractive index, \tilde{n}_s , is complex with the form $\tilde{n}=n-ik$ (where n is the real part of the refractive index and k is the extinction coefficient), λ is the wavelength of light, L_f is the thickness of the film (or films) and φ is the angle of incidence with which the light impinges on the sample. The two quantities Ψ and Δ are measured, enabling calculation of any two of the variables related to the optical properties of the sample, assuming n_a , λ and φ are known for the measurement performed. This

means that ellipsometry enables determination of the thickness of a film on a substrate if the optical constants of the substrate (n_s) and film (n_f) are known, or determination of the complex substrate refractive index (\tilde{n}_s) if no film is present.

The sensitivity of ellipsometry makes it desirable for the study undertaken. As can be seen from the ellipsometric equation above, the calculation of sample optical properties requires knowledge of n_s and ψ . If the sample is to be immersed in solution then the ambient refractive index (n_a) will certainly change from the value for air. In order to position the sample in solution for measurement on our ellipsometer, the fused silica sample cell shown in Figure 1 was designed. The sample is held in the vertical plane such that the laser light passes through one window, reflects from the sample and passes out the other window. For typical ellipsometric measurements performed where air is the ambient, an angle of incidence of 70.00° is chosen because a high degree of sensitivity is obtained near this angle. The angle is set mechanically on the instrument prior to measurement, so ideally the sample cell would have windows allowing an angle of incidence of 70.00° , but construction of such a sample cell proves quite difficult. Unless the light passes through the windows at exactly normal incidence, the angle at which the light strikes the sample will be different from the angle set on the instrument due to refraction of light as it passes through the window into the solution medium. This refraction leads to a different angle ψ from that set on the instrument and, as stated earlier, ψ must be

accurately known in order to accurately calculate optical parameters of the sample.

Through an alignment procedure it was determined that an angle of incidence of 70.76° gave the best results for this particular sample cell. This procedure utilized the light reflected from the surface of the cell windows and consisted of adjusting the sample cell such that the beam incident from the laser, upon striking the first window of the sample cell, is reflected directly back into the incident beam, insuring normal incidence of the beam on the first window. The sample cell is fixed at this position and then the analyzer arm of the ellipsometer is rotated until the beam reflected from the sample, after passing through the second window, passes through a pinhole placed at the end of the analyzer arm. The angle between the arms is then read from a calibrated base with an accuracy of 0.01° . This alignment was verified by finding film thicknesses of SiO_2 on Si for samples measured both without the cell and in-situ in the cell with water as the ambient. All thicknesses recorded are the result of manual two-zone null ellipsometric measurements using an aligned and calibrated research quality ellipsometer with a 6328Å He-Ne laser light source. Using the ambient refractive index ($n_a = 1.333$) as that of water at 20°C (20) and the stated incident angle ($\phi = 70.76^\circ$), the two measurements of SiO_2 film thickness agreed within 10Å. This same accuracy is maintained for the Si- SiO_2 system in dilute aqueous HF. With the cell calibrated, a Si sample with an initial film of SiO_2 is immersed in the cell in

dilute aqueous HF. By taking periodic ellipsometric measurements and calculating the SiO_2 film thickness, the etch process is monitored.

The samples used were one inch diameter p-type single crystal silicon wafers of (100) orientation with $2\Omega\cdot\text{cm}$ nominal resistivity which were cleaned and thermally oxidized. The oxidation conditions were 700°C for 48 hours in dry oxygen ($<5\text{ppm H}_2\text{O}$ as measured at the furnace exhaust) which yields a SiO_2 film thickness of about 250Å. These samples are then placed in the sample cell at the focus of the ellipsometer and are immersed in 450:1 deionized water:concentrated (49%) MOS grade HF. Ellipsometric measurements are taken every 10 minutes initially and then every 5 minutes as the SiO_2 film thickness approaches zero.

B. Contact Angle Measurement

The contact angle measurement is a surface sensitive technique that has been previously shown to be able to detect changes on Si and SiO_2 surfaces(21, 22). The contact angle is defined by the equilibrium of the three surface tension vectors at a solid-liquid-vapor interface. The equilibrium is illustrated in Figure 2 for a liquid drop on a solid surface surrounded by vapor. The surface tensions are related to the contact angle by the Young Equation

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

where γ_{sv} is the solid-vapor surface tension, γ_{sl} is the solid-liquid surface tension, γ_{lv} is the liquid-vapor surface tension and θ is the contact angle. The solid-vapor and solid-liquid surface tensions generally are difficult to determine independently, though θ can be measured and γ_{lv} is known for many liquids. This makes it difficult to calculate either of the absolute solid surface tensions (γ_{sv} or γ_{sl}) using the Young Equation. However, the wetting behavior of solids is directly related to the contact angle. Large contact angles indicate hydrophobic or non-wetted surfaces while small contact angles indicate hydrophilic or wetted surfaces. In order to better understand the information available from the contact angle measurement in this study, further discussion of the relationship between solid and liquid surface tensions and their wetting interactions is needed.

In general, if a liquid has a lower surface tension than the solid which it contacts, the solid will be wet by the liquid, which is termed a hydrophilic situation, but if the solid has a lower surface tension than the liquid, the solid will not be wet by the liquid and the solid is said to be hydrophobic. This wetting behavior can be understood based on the thermodynamic tendency to minimize the energy of a system, namely the surface and the liquid. Solid surfaces can be divided into two classes, high energy and low energy solids. High energy solids include all

metals and metal oxides with surface tensions ranging from 500 to 5000 dynes/cm. Low energy solids include waxes and polymers with surface tensions of less than 100 dynes/cm. With the exception of the liquid metals, all liquids have surface tensions in the same range as the low energy solids, that is, less than 100 dynes/cm. The thermodynamic argument above leads to the conclusion that all liquids (excepting liquid metals) will wet all high energy solids. For the case of low energy solids, however, some liquids will wet a solid while others will not, depending on the specific solid and liquids used. Experimentally, it is expected that liquids with surface tensions lower than that of the solid will yield low contact angles which indicate hydrophilic interactions, while liquids of higher surface tension than the solid will yield high contact angles which indicate hydrophobic interactions.

Zisman has shown(23) that plots of the cosine of the contact angle vs. liquid-vapor surface tension ($\cos \theta$ vs. γ_{lv}) for low energy solids, wet by liquids with a variety of surface tensions, are generally linear with a negative slope. The surface tension (γ_{lv}) at the point where this line intersects a $\cos \theta = 1$ line is termed the critical surface tension (γ_c) of the low energy solid. By rearranging the Young Equation it is seen that $\gamma_{lv} = \gamma_{sv} - \gamma_{sl}$ when $\cos \theta = 1$ so, $\gamma_c = \gamma_{lv} = \gamma_{sv} - \gamma_{sl}$ at the point of intersection of the two lines. Physically, the intersection of the $\cos \theta = 1$ line with an experimentally derived line of $\cos \theta$ vs. γ_{lv} for a specific low energy solid gives the maximum liquid-vapor surface tension for a liquid to entirely wet the solid. That is if

$\cos \theta = 1$ then the contact angle is 0° so a perfectly hydrophilic situation results. A liquid with a liquid-vapor surface tension greater than γ_c will give an energy increase if it wets the solid, so the solid will be hydrophobic with respect to such a liquid. Conversely, all liquids with γ_{lv} less than γ_c will entirely wet the solid since it will lead to an energy decrease if the solid is covered by such a liquid. Thus, the lower the value of γ_c , the lower the surface tension of a liquid must be to wet such a solid. Zisman has shown that γ_c is closely related to the surface structure and composition of a low energy solid and determined that adsorbed layers of fluorocarbon species yielded the lowest critical surface tensions found(23).

In order to perform the contact angle measurement in solution, the inverted bubble technique of contact angle measurement(24) was used. The sample cell is shown in Figure 3 and is constructed entirely of fused silica. In this cell, the Si sample is completely immersed and held such that the surface to be investigated is inverted. A single nitrogen gas bubble can be released from the capillary and will float to the sample surface and establish the three-phase equilibrium shown in the inset box of Figure 3. This three-phase equilibrium is slightly different from that shown in Figure 2 in that a vapor bubble sits on a solid surface surrounded by liquid, but the important similarity is that the contact angle, θ , is the same. The key feature of this sample cell is that maximum exposure of the sample to the desired

solution is maintained and thus the sample is not exposed to the laboratory ambient during measurement.

In order to measure the contact angle, the associated instrumentation which is shown in Figure 4 is needed. The sample cell is placed on a leveling platform which is fixed on X-Z translation stages in the focus of a horizontally mounted stereo microscope that is continuously variable from 1.0X to 2.5X. The microscope is fitted with a 2X supplementary lens and interchangeable 10X or 20X widefield eyepieces yielding a total magnification ranging from 20X to 100X. The leveling platform (LP) is used to adjust the sample such that bubbles will remain stationary on the inverted sample and not float to a more elevated position. The X and Z translation stages (TS₁ and TS₂) enable positioning of the gas bubble in the objective of the microscope. The front face of the sample cell is polished fused silica to enable viewing, while all other faces are constructed of ground fused silica. Light from the illuminator lamp (L) reflected from the mirror (M) is diffused by the rear ground silica face of the cell providing suitable lighting of the sample and gas bubble. A polaroid camera is clamped to one of the eyepieces for photography of the three phase equilibrium and the contact angle is measured from the photograph.

The samples used for the in-situ contact angle measurement are identical to those used in the ellipsometric analysis. These samples are first immersed in deionized water and then a 500:1 solution of H₂O:concentrated (49%) HF is introduced. Photographs

are taken before the etch solution is introduced and throughout the etch process and from these photographs, the contact angle is measured with an accuracy of $\pm 3^\circ$. Once again, this in-situ type of analysis allows monitoring of the etching of SiO_2 by dilute aqueous HF as the etching takes place.

RESULTS AND DISCUSSION

The film thickness vs. etch time data for the in-situ ellipsometric monitoring of etching of SiO_2 by dilute HF is shown in Figure 5. It is evident from the linearity of the plot that the etch rate is constant at 3.1Å/min. to a thickness of just less than 50Å (70 minutes). Beyond 70 minutes (below 40Å SiO_2 film thickness), the etch rate decreases significantly and at 90 minutes the SiO_2 film thickness reaches a minimum of 20Å. After 90 minutes, the film thickness remains virtually constant, though a slight increase is observed. The constant etch rate in the initial stages of immersion in etchant is expected because hydrofluoric acid is known to etch SiO_2 (1). The unexpected result is that the film thickness never reaches a zero value, and the nonzero value is well outside the experimental error of $\pm 10\text{\AA}$.

One explanation for the apparent 20Å residual film, could be depletion of the HF in the etch solution. Calculation shows that over 30,000Å of SiO_2 could be etched from the sample cell walls and the Si sample before the HF would be entirely depleted. Since HF etches SiO_2 , and calculation shows that there is a large enough quantity of HF to entirely remove the SiO_2 , there should be no

SiO₂ film on the Si substrate. The Δ , Ψ data has been analyzed under the assumption that an SiO₂ film is present. It is also possible to analyze the Δ , Ψ data to obtain the substrate optical constants, assuming no film is present on the substrate. A calculation of this type for the data beyond 90 minutes in Figure 5, yields a value of 3.866 - 10.074 for the complex index of the sample surface. This is an average value of all measurements taken after 90 minutes with a deviation of ± 0.002 in the real part and ± 0.005 in the extinction coefficient. This value can be compared to accepted values for the optical constants determined for a Si substrate(25,26) which are 3.865 - 10.018. There is quite close agreement in the real part but less than satisfactory agreement in the imaginary part.

The existence of the 20A residual in the etch experiment indicates that a bare Si substrate does not result from etch by HF, so the calculation of the substrate optical constants is not expected to agree with the accepted values, but it is useful to compare the calculated and accepted values. The best evidence that a residual film exists on the HF etched Si surface is seen in a plot of the raw Δ , Ψ data, Figure 6, for similar etch experiments. The open circles representing the experimental SiO₂ etch data fall close to the theoretical solid line for an SiO₂ film on Si, but once the minimum thickness has been reached (near $\Delta=155^\circ$), the points fall on a different curve as illustrated by the filled circles. The fact that the Δ , Ψ points fall on a different curve leads to the conclusion that a film or layer other than SiO₂ is

formed on the Si surface in HF solution following etching. However, since the new film composition is unknown, the optical constants of the film are unknown and so no actual film thickness can be obtained. The only positive conclusions from the in-situ ellipsometric analysis are that etching of SiO_2 in dilute aqueous HF proceeds from 230Å down to 20Å film thickness and that beyond this point a film that is resistant to and/or forms in HF remains on the Si substrate, but the film identity and thickness are unknown. It is the in-situ contact angle measurement that is able to provide information regarding the identity of the film.

Starting with about 230Å of SiO_2 film on Si, a contact angle of 39° is measured in deionized water before any etch solution is introduced. When the etch solution is introduced, the contact angle changes quickly from the initial value of 39° to 8° and stays at this value throughout the etch process. After sufficient time passes for removal of all the SiO_2 , the contact angle changes very rapidly to a value of 78° and this value persists for as long as the etch solution is present. The initial change from 39° to 8° is, at this time, not yet fully explained but obviously must be attributed to the etch solution. From the Young Equation it is known that θ is dependent on γ_{lv} , and γ_{lv} for dilute HF would be different than γ_{lv} for pure water. However, the etch solution is so dilute that a significant change in the liquid-vapor surface tension (γ_{lv}) would not be expected and therefore the initial contact angle change must be attributed to some other effect of the HF solution. Since the two obvious characteristics of the etch

solution are acidity and the presence of fluoride ions, the change in contact angle can most likely be attributed to one or the other or both of these elements. When a sample of 100Å of SiO_2 on Si is placed in 500:1 $\text{H}_2\text{O}:\text{HCl}$ a contact angle of 37° is measured, and it remains unchanged for the one hour duration of the experiment. When a similar sample is placed in 400:1 $\text{H}_2\text{O}:\text{NH}_4\text{F}$ the contact angle changes to 8° after about 30 minutes. Ellipsometric measurement of SiO_2 thickness for an SiO_2 film on an Si substrate before and after immersion for 16 hours in 250:1 $\text{H}_2\text{O}:\text{NH}_4\text{F}$ indicates that NH_4F does not etch SiO_2 . We therefore ascribe the initial contact angle change to some effect of fluoride ion on the oxide surface.

The final contact angle change, from 8° to 78° , is of more importance as far as analysis of the ellipsometric results. From the earlier discussion, it is evident that the 8° contact angle is indicative of a hydrophilic oxide surface as anticipated for an oxide, while the 79° angle is indicative of a hydrophobic surface. The fact that the wetting behavior changes so drastically, means that the sample surface changes significantly as the SiO_2 is etched completely away. The wetting behavior during the etch process is hydrophilic as soon as dilute HF is introduced and remains hydrophilic throughout the etch of SiO_2 , but becomes hydrophobic simultaneous with the appearance of a new surface film on the Si as seen using ellipsometry.

Since this new film is hydrophobic, this surface must be low energy. It could be argued that silicon, as a semiconductor, would

not be considered a metal and so should not be considered a high energy solid. However, independent measurements of the surface tension of the (100) plane of Si by measurement of the minimum energy required to propagate a crack yield values of over 2000 dynes/cm(27) which certainly categorizes Si as a high energy solid. Another explanation for the low surface energy of the etched Si could be due to adsorption, which is known to drastically alter the wetting behavior (and therefore the surface energy) of a solid. According to this explanation, the wetting behavior of the Si surface indicates coverage of a layer of material impervious to the etch solution that is of lower surface tension than the ambient etch solution.

Since the residual film on the etched Si is apparently a low energy solid, a plot of $\cos \theta$ vs. γ_{lv} can be derived through measurement of the contact angle of liquids with various surface tensions on the Si substrate. By increasing the proportion of methanol in a methanol/water solution the surface tension of the solution can be varied continuously from 72 dynes/cm (pure water) to 23 dynes/cm (pure methanol)(20). Five different methanol/water solutions were prepared and, in each of the solutions, 1% HF was maintained to insure that a native SiO_2 layer did not form on the Si surface. Samples of Si substrates that had been etched in concentrated (49%) HF were immersed in each of the methanol/water solutions and the contact angle was measured. The $\cos \theta$ vs. γ_{lv} plot which results is shown in Figure 7. First, it is noted that the plot is not perfectly linear which has been shown to be due to

hydrogen bonding between the liquid and solid(23). The point of intersection between the line and the $\cos \theta = 1$ line gives a γ_c value of 27 dynes/cm. Table 1 shows possible surface structures and corresponding values of critical surface tension for films adsorbed on metal surfaces(23). Only hydrocarbon and fluorocarbon structures are found to have critical surface tensions close to 27 dynes/cm. The purely hydrocarbon structure can be ruled out due to the evidence of hydrogen bonding between the solid and liquid because carbon-hydrogen bonds are not polar enough to hydrogen bond. However, fluorine-carbon bonds are polar enough to allow hydrogen bonding between the solid and liquid. This is not to say that a specific fluorocarbon structure can be identified with the silicon surface, but simply to say that the presence of a fluorocarbon species at the Si surface is the most probable explanation of a significant lowering of the solid surface tension by a species that can hydrogen bond with the liquid.

CONCLUSIONS

The process of etching of SiO_2 films on Si substrates by dilute aqueous HF was studied by using two novel in-situ techniques - ellipsometry and contact angle measurement. The in-situ ellipsometric analysis indicates that SiO_2 is etched by HF, but the etch rate drops from 3.1Å/min. to 0 before a SiO_2 film thickness of 0 is reached and while a significant H^+ concentration remains. Calculation of substrate optical constants, assuming no film is present on the etched sample surface, show an expected

less than satisfactory agreement with the actual optical constants for a bare Si surface. A plot of the ellipsometric parameters Ψ vs. Δ shows that a film that is not SiO_2 forms on the sample surface following HF exposure. The optical constants of this film are unknown so no calculation of thickness can be made. The in-situ contact angle measurement shows that a Si substrate with a thermally grown SiO_2 film on it is somewhat hydrophobic following oxidation, hydrophilic in the presence of dilute aqueous HF throughout etching and, following removal of the SiO_2 by dilute HF etch, the substrate surface is hydrophobic. Following HF etch the substrate is more hydrophobic than the initial thermally oxidized SiO_2 film as evidenced by the larger contact angle on that surface. In both cases the hydrophobic behavior of the surfaces is only possible if the surface is that of a low energy solid. Silicon dioxide and silicon surfaces are high energy and so the hydrophobic behavior of the surfaces in these experiments indicates the existence of an adsorbed low energy film. Further study is underway to understand the behavior of the initial thermal SiO_2 film. Identification of the film present on a Si substrate following aqueous HF etch is provided by analysis of the critical surface tension of a Si substrate from which the SiO_2 film has been etched by HF. A film containing some type of fluorocarbon species appears to be the only possibility to satisfy all the experimental evidence.

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LIST OF FIGURES

Figure 1: Fused silica sample cell used for in-situ ellipsometric measurements.

Figure 2: Schematic representation of the equilibrium of a liquid drop on a solid surface surrounded by vapor. The surface tension vectors are parallel to the surfaces that they represent and the contact angle is the angle θ between the solid and a line tangent to the liquid.

Figure 3: Fused silica cell for in-situ contact angle measurement. The three-phase equilibrium and the resulting contact angle for the inverted bubble are shown in the inset box.

Figure 4: Instrumentation for contact angle measurement. The leveling platform (LP) is used to adjust the sample cell so the bubble will remain stationary. The X and Z translation stages (TS_x and TS_z) are used to position the bubble in the field of view of the microscope and the lamp (L) is used to illuminate the sample by reflection from mirror (M). The camera is not shown here.

Figure 5: Plot of Etch Time vs. SiO₂ Film Thickness for an SiO₂ film on a Si substrate immersed in 450:1 H₂O:HF solution.

Figure 6: Plot of ellipsometric parameters Ψ vs. Δ for several in-situ etch studies. Open circles are before minimum thickness reached and filled circles are after the minimum thickness. The solid line represents the theoretical Ψ , Δ relationship for SiO₂ on Si in water ambient.

LIST OF FIGURES (cont.)

Figure 7: Plot of $\cos \theta$ vs. γ_{LV} for methanol:water solutions in contact with Si substrate from which the SiO_2 has been etched by HF. The intersection of the plotted points with the $\cos \theta = 1$ line gives a γ_c of 27 dynes/cm.

FIGURE 1

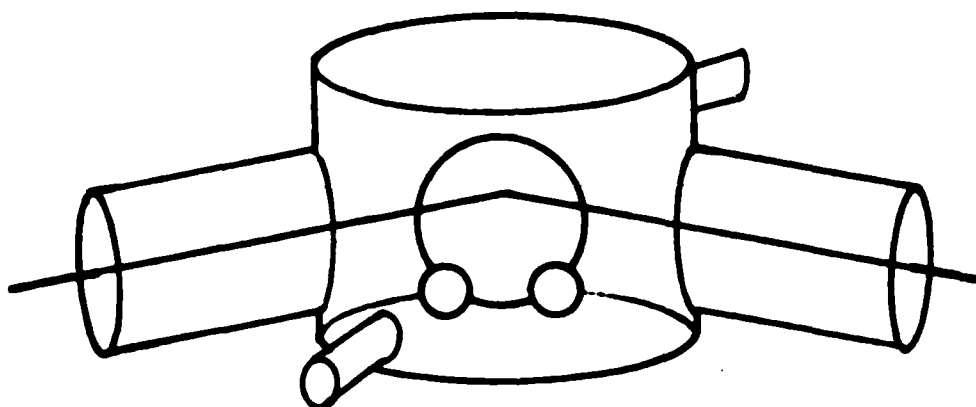


FIGURE 2

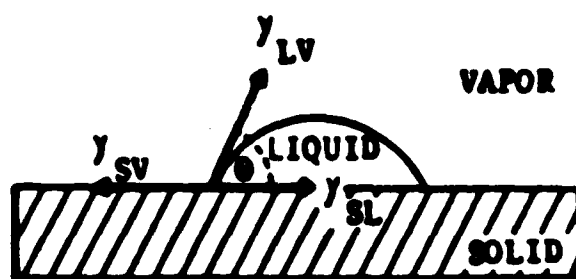


FIGURE 3

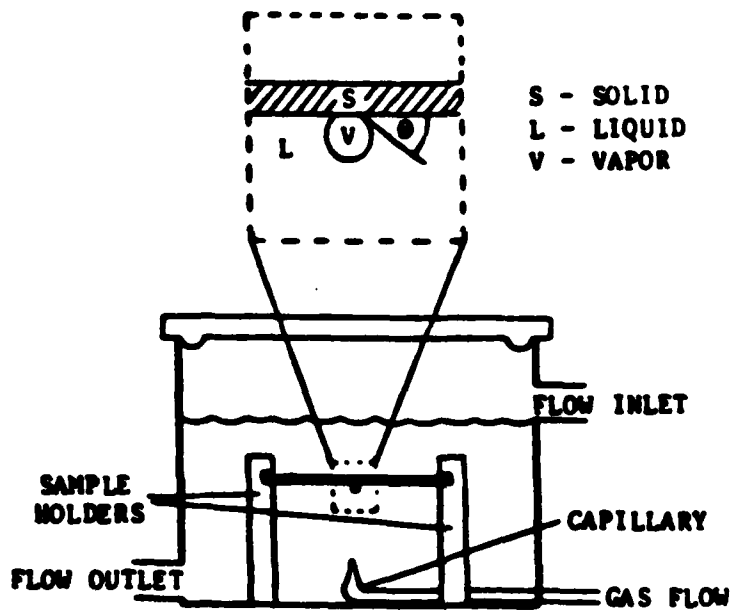


FIGURE 4

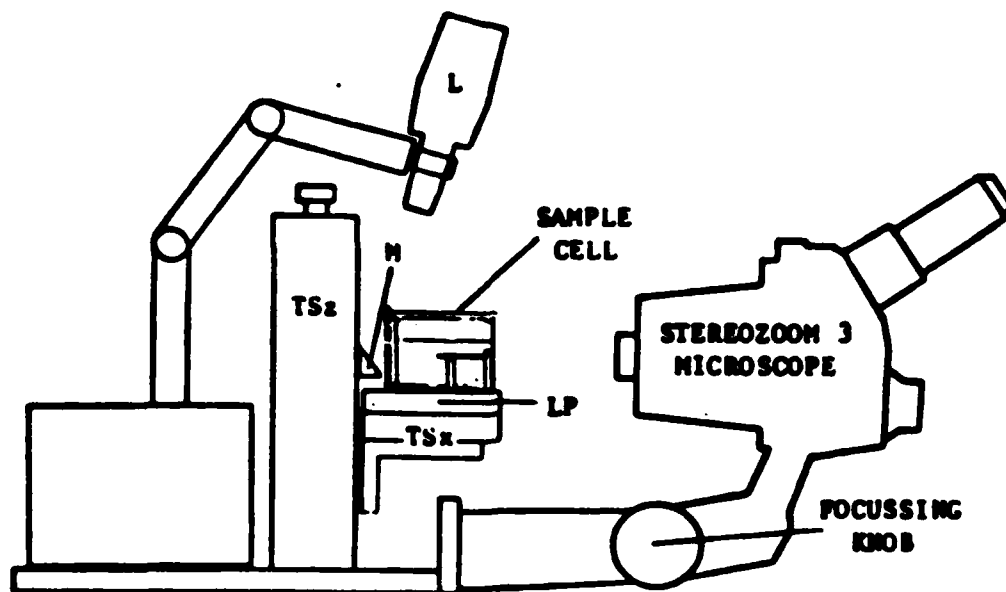


FIGURE 5

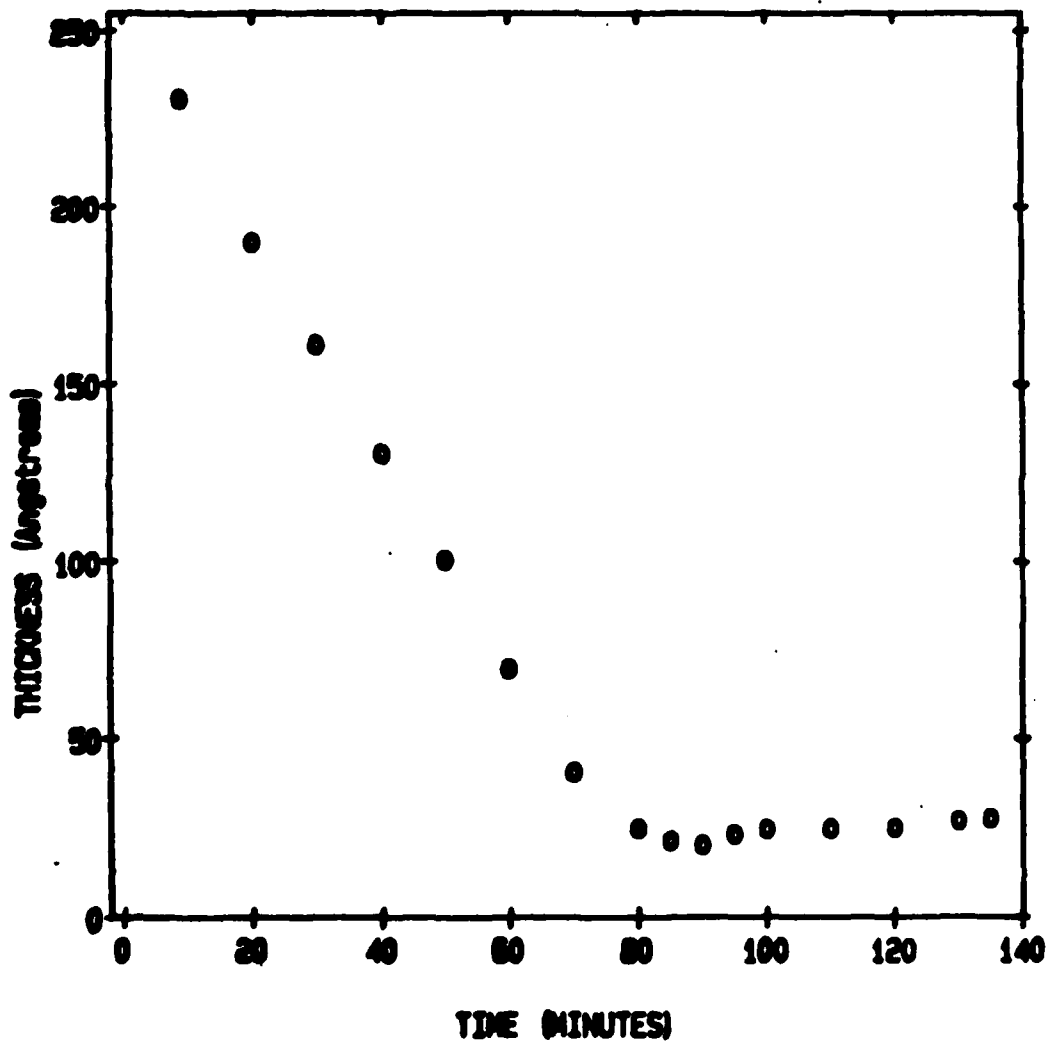


FIGURE 6

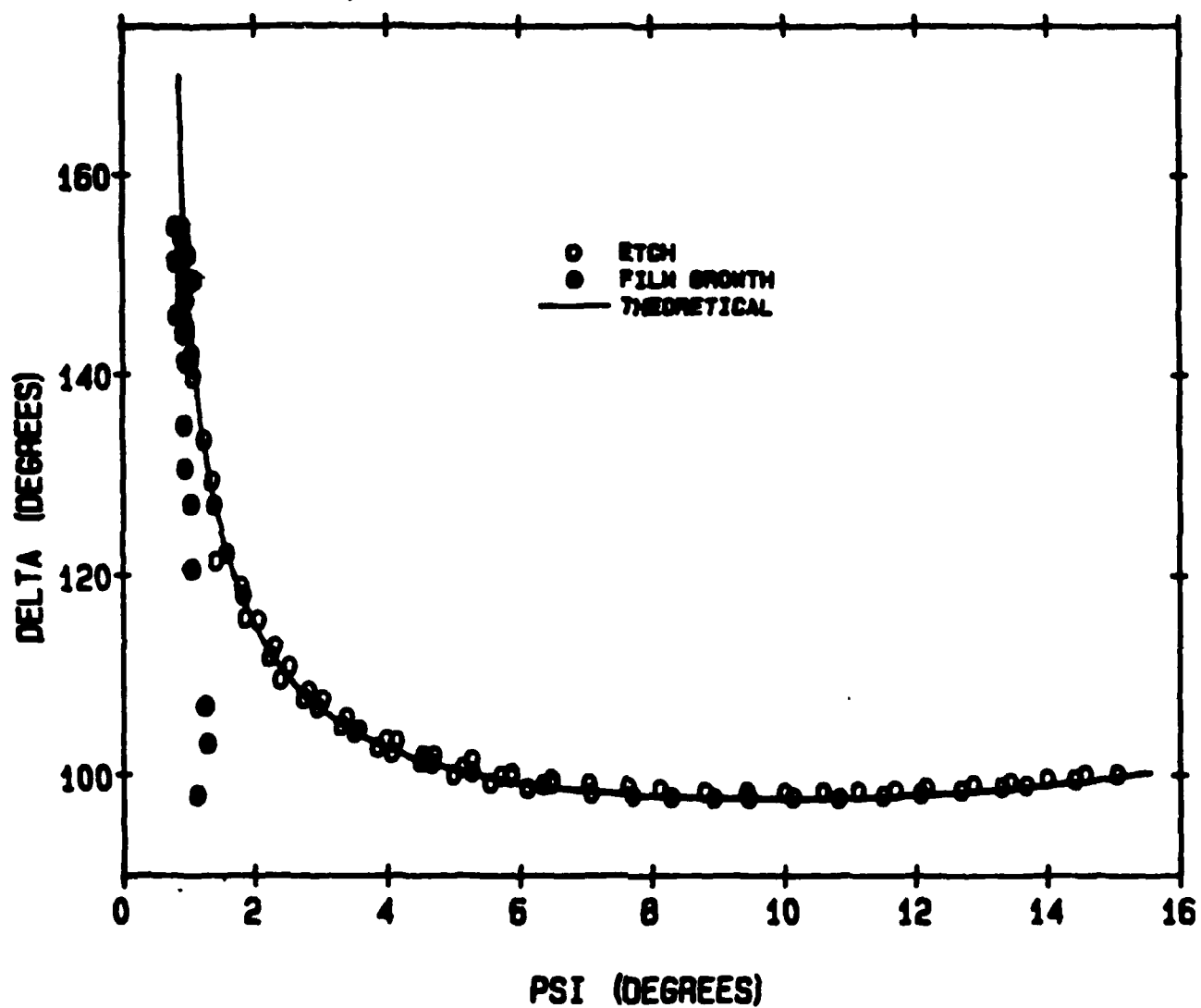
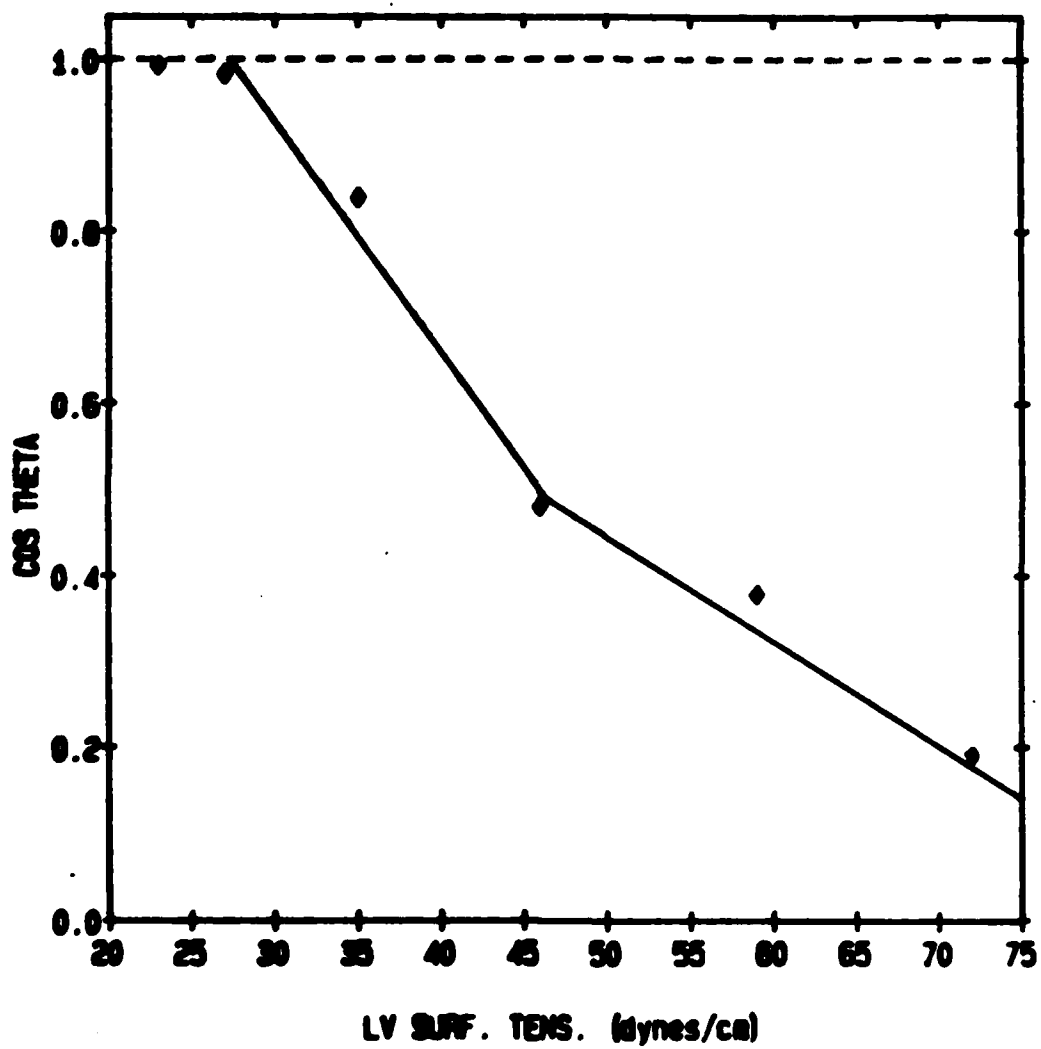


FIGURE 7



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TABLE 1: Surface constitution of various low energy films adsorbed on metal surfaces and the measured critical surface tension of the film (after reference 23).

TABLE 1

Surface Constitution	γ_c dynes/cm at 20°C
Fluorocarbon Surfaces	
-CF ₃	6
-CF ₂ H	15
-CF ₃ and -CF ₂ -	17
-CF ₂ -	18
-CH ₂ -CF ₃	20
-CF ₂ -CFH-	22
-CF ₂ -CH ₂ -	25
-CFH-CH ₂ -	28
Hydrocarbon Surfaces	
-CH ₃ (crystal)	22
-CH ₃ (monolayer)	24
-CH ₂ -	31
-CH ₂ - and -CH-	33
-CH- (phenyl ring edge)	35

