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Structural Changes of Oxide Films during Anodization of P Doped Silicon in Aqueous Ammonium Fluoride

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DISCLAIMER

STRUCTURAL CHANGES OF OXIDE FILMS DURING ANODIZATION OF P DOPED SILICON IN AQUEOUS AMMONIUM FLUORIDE

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ABSTRACT

The growth and structural changes of the silicon dioxide film on boron doped silicon have been investigated during electrochemical oxidation in acidic ammonium fluoride solution. A high-speed spectroscopic ellipsometer was employed to obtain in-situ measurements while the silicon was subjected to anodic potential steps. These observations indicate that silicon dioxide does not dissolve in 0.10 M ammonium fluoride solution as acidic as pH 3.5. An alternative model to dissolution-limited film growth is proposed.

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INTRODUCTION

An oxide surface layer forms on silicon during electrochemical anodization in acidic fluoride electrolyte. The silicon dioxide film grows via electric field driven ion transport between the bulk silicon and the film/solution interface. Mackintosh and Plattner[2] have demonstrated that the anodic film growth occurs by oxygen anion vacancy flux by tracking noble gas marker atoms with Rutherford backscattering spectroscopy. One commonly held film growth mechanism is that of solution phase mass transfer control. In the model, the film grows up to the thickness at which the SiO_2 formation rate at the silicon/oxide interface is balanced by the dissolution rate of the oxide film into the electrolyte at the oxide/solution interface. In fluoride solution, the dissolving species is most likely fluorosilicate anions.

$$SiO_2 + 6\ HF \rightarrow SiF_6^{2-} + 2H^+ + 2H_2O \qquad [1]$$

The pH is buffered by the hydrofluoric acid equilibrium, pKa =3.45 in excess fluoride. Under these conditions, the steady-state current is determined by the dissolution mass transfer rate assuming the SiO_2 to fluorosilicate reaction is very fast. Silicon dioxide film dissolution mechanisms have been studied by numerous researchers.[6, 10, 11]

There is evidence, however, that dissolution of the oxide film may not be the thickness limiting parameter. In rotating disk studies of the SiO_2 dissolution mechanism by Memming and Schandt[6], the dissolution rate does not follow the Levich relation, an indication that the dissolution is not controlled by solution-phase mass transfer. Mass transfer control also implies a linear dependence between the steady-state film thickness and the applied overpotential, given constant surface overpotentials at the oxide/electrolyte interface. In silicon dioxide, a dielectric, the electric field strength is uniform and equal to the applied potential divided by the film thickness. Therefore in the film dissolution model, for a given applied potential, the film thickness increases or decreases to reach the electric field strength which provides the oxygen anion vacancy flux to balance the silicon dioxide dissolution rate.

At higher anodic overpotentials, potentiostatic steps are met by large periodic current oscillations. The period of these oscillations depends on the electrolyte mass transfer parameters: the bulk fluoride and hydrogen ion concentrations, and the rate of convection. A typical period of these oscillations is approximately ten seconds in these experiments and those conducted by Gerischer and Lübke[1].

Similar oscillatory behavior has been noted by Russell and Newman[3] working with passive films on iron in sulfate electrolyte. This behaviour was attributed to pH gradients within a porous precipitated layer of iron sulfate covering a compact layer of iron hydroxide. In the present system, the transients may be caused by an analogous structure where HF is periodically depleted in a porous layer of ammonium fluorosilicate covering the film of SiO_2.

EXPERIMENTAL

Polished wafers of heavily boron doped (111) silicon (0.01 Ohm-cm) were cleaved into 2 x 6 cm. strips. The samples were masked with a hard-baked phenolic photoresist (Shipley S-1400-31) leaving a 2 x 2 cm. active area and a 1 x 2 cm. area for electrical contact. Four-zone spectroscopic ellipsometer measurements were made on the active area in air. This initial surface was typically covered with 18 - 25 Angstroms of native SiO_2 having a refractive index $1.460 \pm .005$ over the visible spectrum (5000-7200 Angstroms).

The sample cell was sparged with nitrogen prior to sample addition to remove dissolved oxygen. The nitrogen sparging also provided forced convection in the solution during the experiment. The samples were then immersed in 0.10 M ammonium fluoride solution adjusted to pH 3.5 with hydrochloric acid. Spectroscopic ellipsometer measurements were taken immediately and after one hour using a high speed self-nulling spectroscopic ellipsometer.[5] Electrode potentials and current were measured with an EG&G model 273 potentiostat. Potentials were measured relative to a Hg/HgO reference electrode connected to the cell through a capillary placed 2 cm. from the working electrode surface.

The experiments consisted of applying anodic potential steps, allowing the current transient to decay, then stepping to open circuit. The next anodic step was made after the open circuit potential reached a steady value. Spectroscopic ellipsometer measurements were taken at each steady-state.

The selection of masking materials was greatly complicated by the discovery of surface contamination from organic residue. After allowing the samples to stand for periods ranging from 1 hour to 48 hours in the fluoride electrolyte, comparisons between ellipsometer measurements of masked and unmasked substrates showed radical differences. An organic residue leached from the mask coatings was visually detectable and could be removed with acetone. Kynar resin baked for 1 hour at 250 ° C, stop-off lacquer, and beeswax all contaminated the exposed surface and showed loss of adhesion, even though each of the films had been cured at 50 ° C under vacuum for 24 hours prior to the experiments to remove volatiles. Shipley S-1400-31 photoresist was found not to contaminate the surface, however lack of adhesion did occur after several hours in the ammonium fluoride solution. Figure 1 illustrates the drastic optical changes caused by a stray organic contaminate film.

RESULTS

Silicon samples having 18 Angstroms of native oxide, measured with the ellipsometer in air, were placed in 0.10 M ammonium fluoride solution of pH 3.5 and measured immediately, after 1 hour, and after 2.5 hours. These samples failed to show dissolution of the native oxide layer as determined by in-situ four-zone ellipsometer measurements applied to a simple homogeneous SiO_2 film model. Spectral refractive index data for the silicon substrate and the SiO_2 film are taken from the handbook by Palik[4]. Figure 2 shows the modeled vs. measured ellipsometer parameters, delta and psi.

A series of anodic potential steps demonstrates the silicon dioxide film growth characteristics. The film thicknesses are shown in figure 3 with the applied potential function. The film grows to a steady value during the potential step. The ultimate thickness increases with

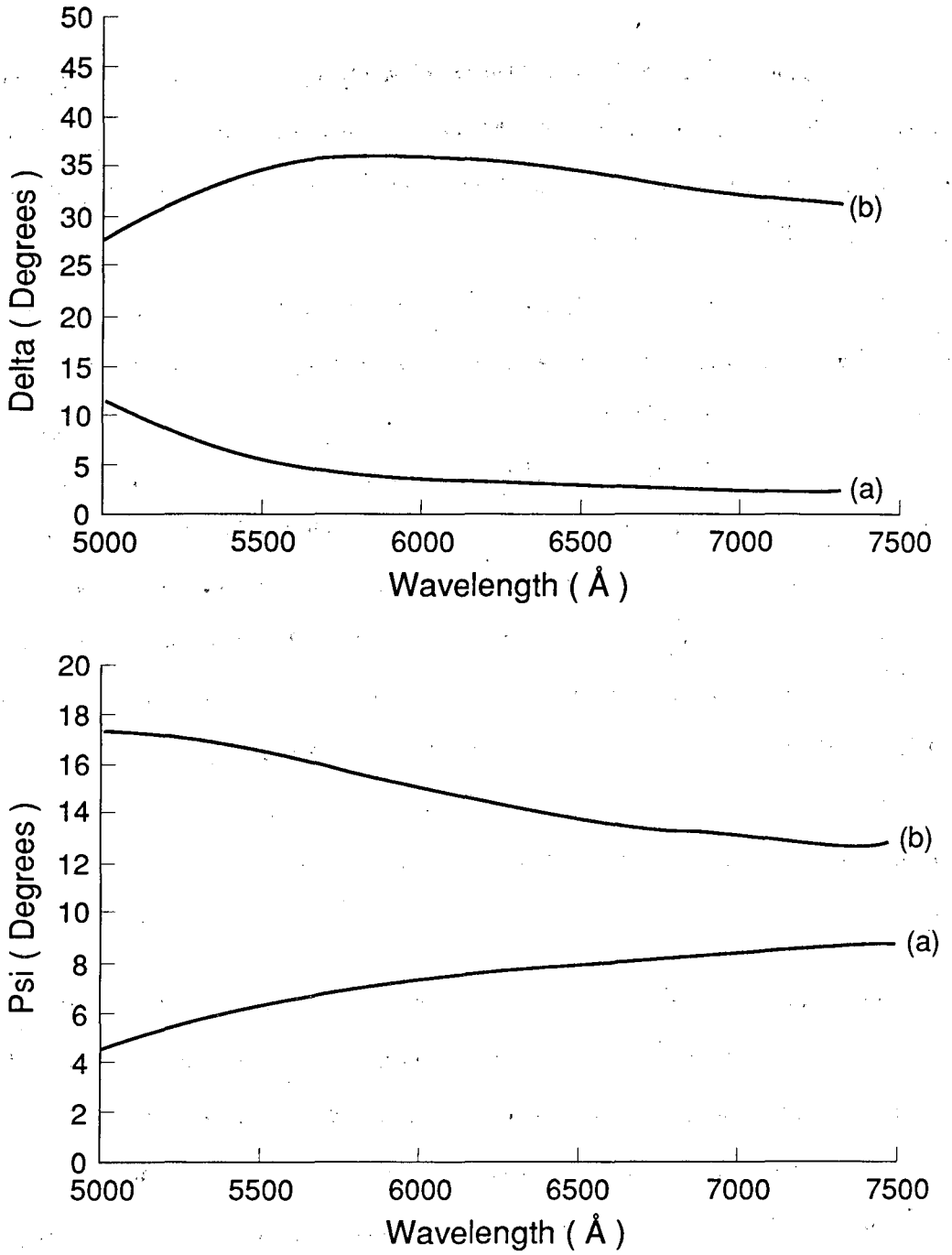

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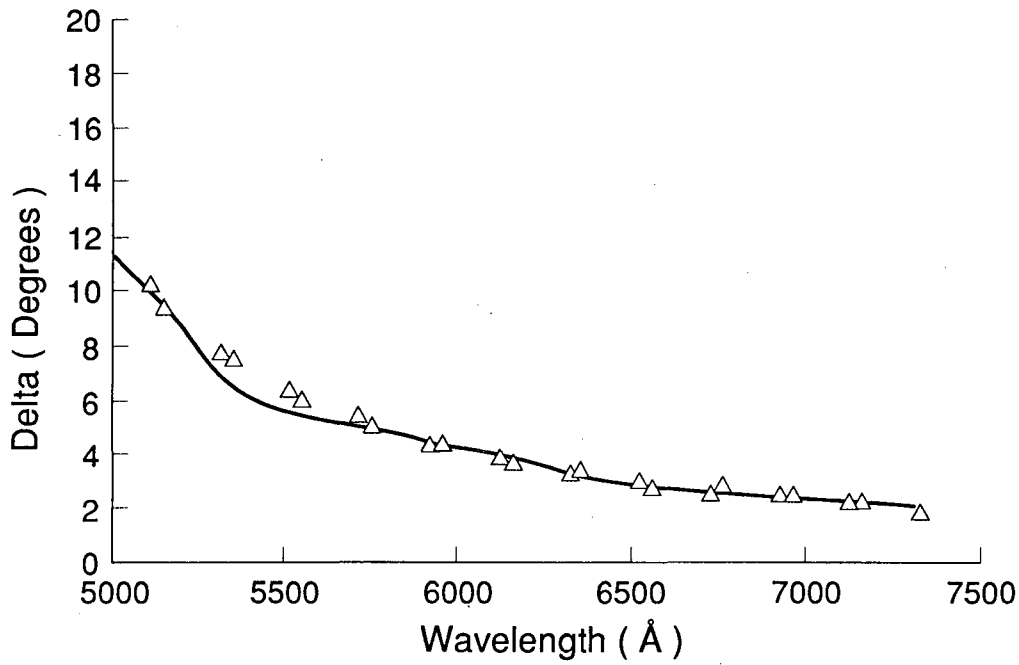
Figure 1.--Measured ellipsometric parameters, delta and psi.
Two scans shown, symbols represent every tenth measurement.
(a.) Silicon with 15 Angstroms of native oxide in 0.10 M NH_4F, pH 4.0.
(b.) Same sample 4 hrs. later with contaminate film from Kynar masking material.



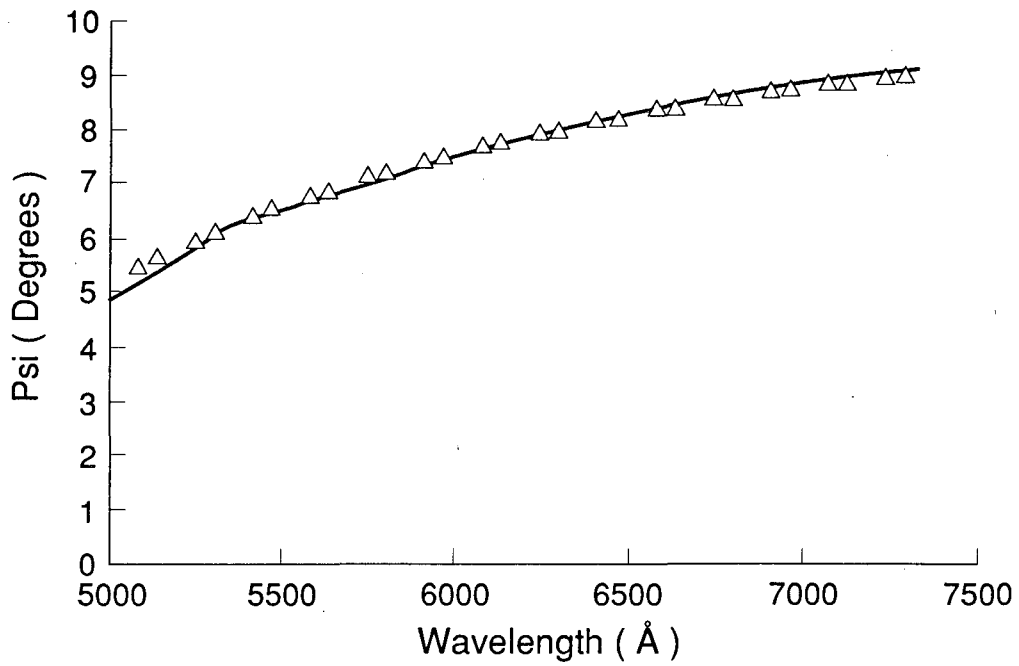


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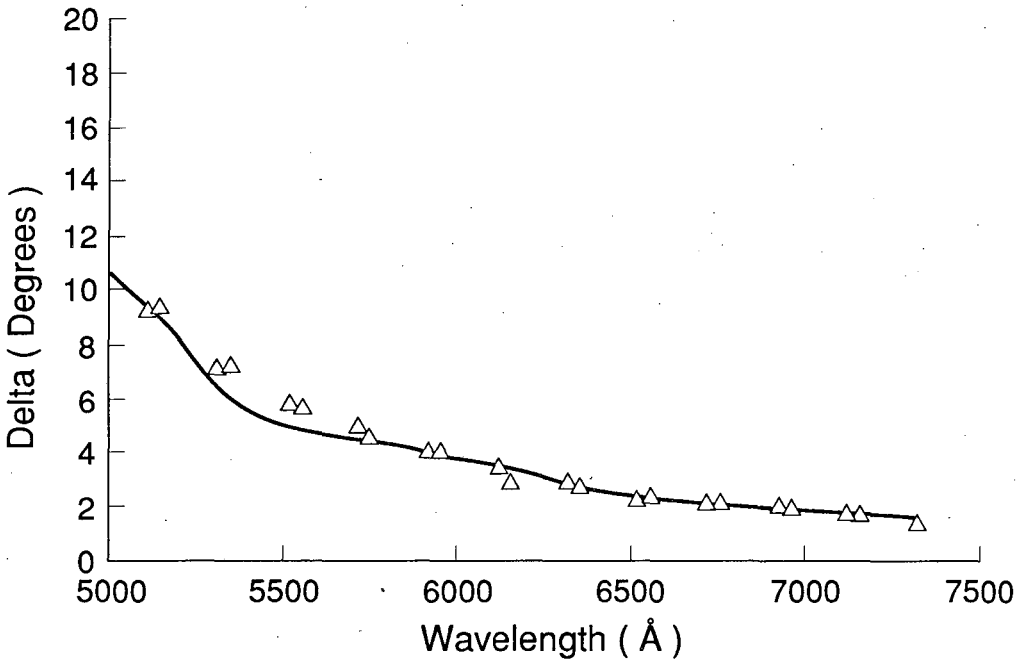
Figure 2a.--Ellipsometric parameters, optical model(solid curve) for film thicknesses given and measured values(Δ), of silicon sample immersed in NH_4F, pH 3.5 at open circuit over time. Measured upon immersion, and computed for 18 Angstroms of SiO_2.



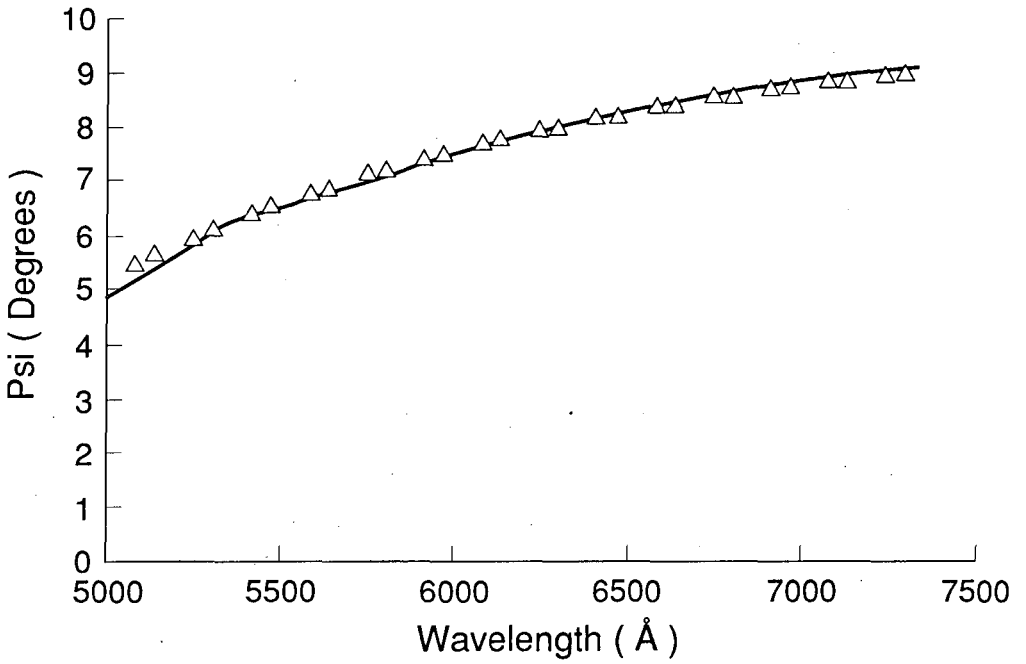


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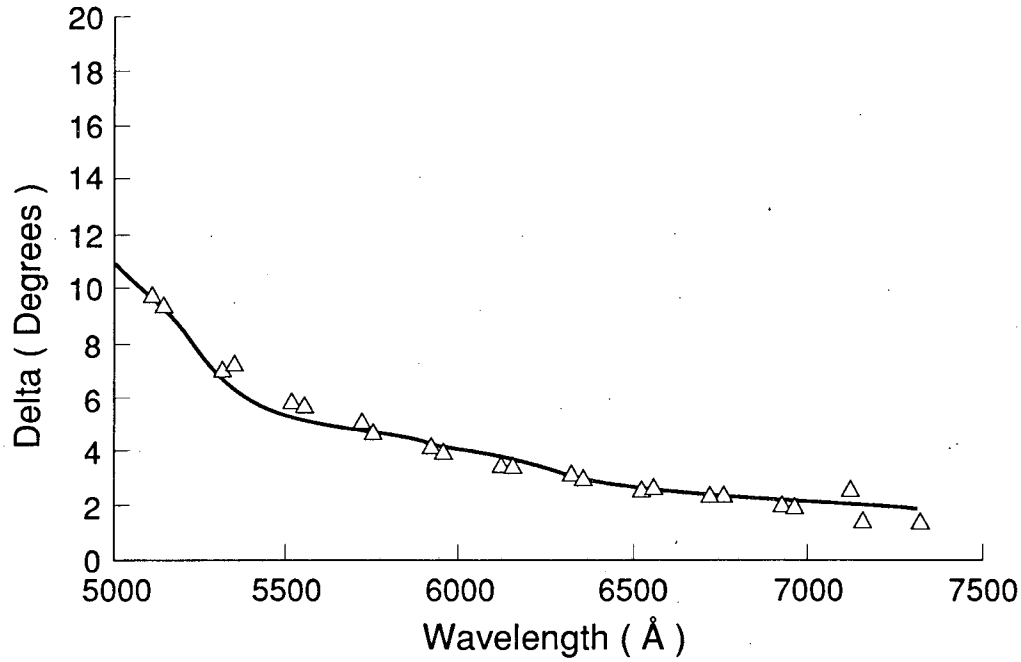
Figure 2b.--Ellipsometric parameters, optical model(solid curve) for film thicknesses given and measured values(Δ), of silicon sample immersed in NH_4F, pH 3.5 at open circuit over time. Measured 1 hr. after immersion, and computed for 16 Angstroms of SiO_2.



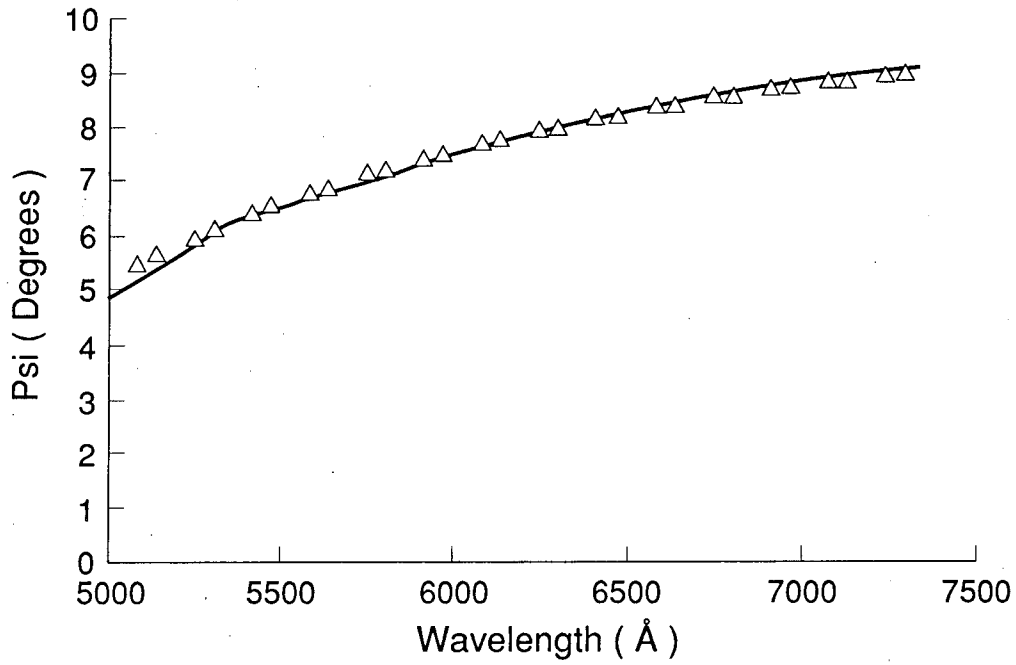


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Figure 2c.--Ellipsometric parameters, optical model(solid curve) for film thicknesses given and measured values(Δ), of silicon sample immersed in NH_4F, pH 3.5 at open circuit over time. Measured 2.5 hrs. after immersion, and computed for 16 Angstroms of SiO_2.

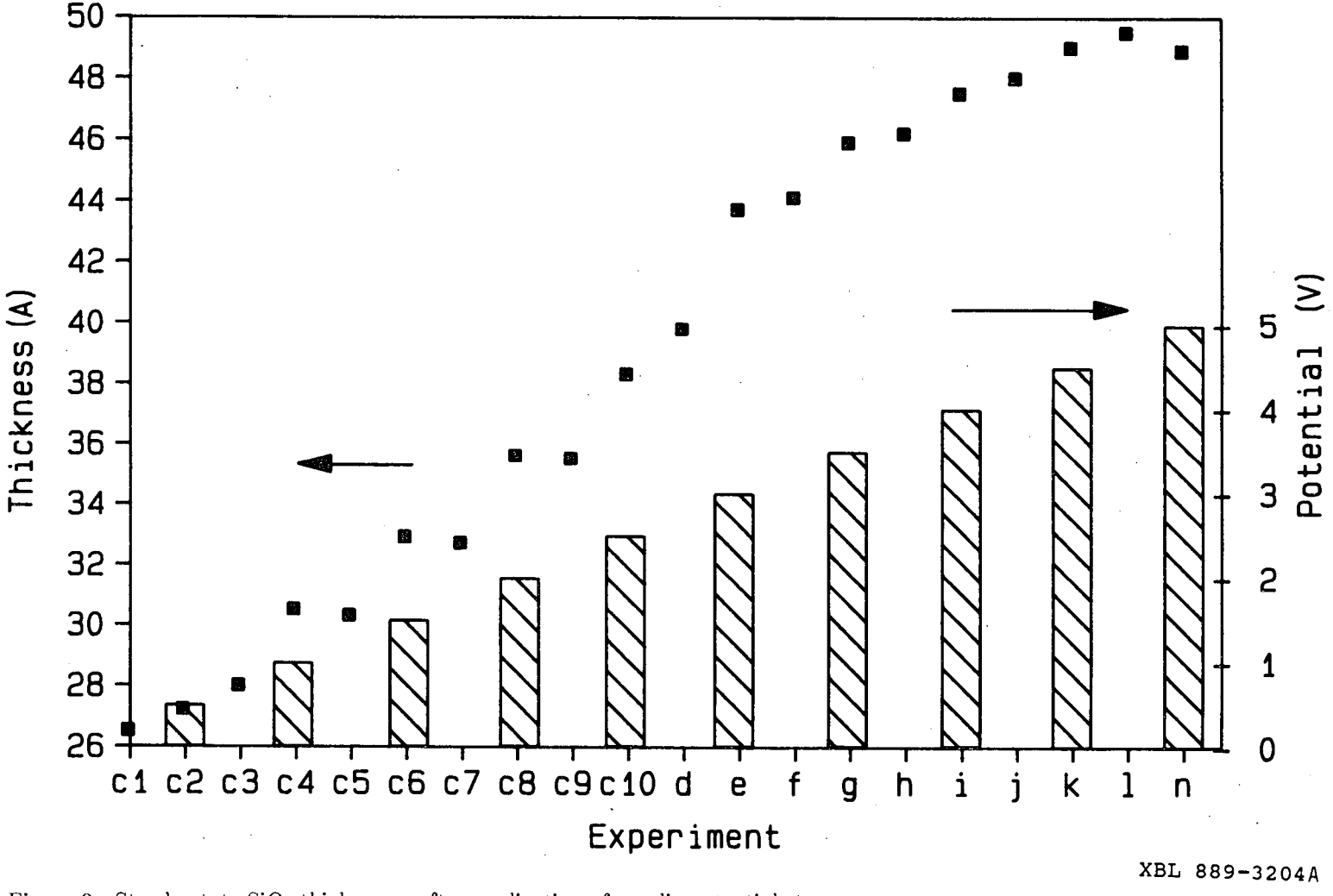

Figure 3.--Steady-state SiO_2 thicknesses after application of anodic potential steps.
Each potential step (approx. 5 min.) is followed by an open circuit period (approx. 10 min.)

magnitude of the potential. However, the film does not significantly dissolve during the open circuit period when the overpotential is removed. The sample remained at open circuit while the potential relaxed to a steady value, this typically took 5-10 minutes. During the experiment, electrolyte convection over the sample was driven by nitrogen sparging. Figures 4 and 5 show modeled and experimental values for the ellipsometric parameters. Since the scale of the differences is much smaller than the range of the parameters over the spectrum, the results are presented as the difference of the ellipsometric parameters from the state of the sample before the anodic potential steps were applied.

The steady-state dissolution current in figure 6 shows a dependence on the applied potential. This dependence indicates that the steady-state current is not controlled by the solution-phase mass transfer, particularly in region below 3.0 Volts. This suggests that the current is controlled by the cation transport across the film or by some field-enhanced dissolution mechanism.

Interestingly, the transition at 3.0 Volts, occurs at the same potential where current oscillations were seen under identical experimental conditions. These sustained oscillations in response to potential steps, illustrated in figure 7, are similar to those previously reported by Gerischer and Lübke[1]. The oscillations are dependent on both the solution-phase mass transport and the applied bias. As shown in figure 7, the amplitude of the oscillations increases with applied anodic potential. The period of the oscillations decreases with enhanced mass transfer by either increasing the convection or lowering the pH of the solution. Since the SiO_2 films do not dissolve and the oscillations do depend on mass transfer, some other soluble species must be responsible for the periodic behaviour. One candidate is ammonium fluorosilicate, $(NH_4)_2SiF_6$, in an analogous mechanism to that proposed by Russell and Newman.[3] In the present system, the transients may be caused by periodic depletion of HF in a porous layer of ammonium fluorosilicate covering the film of SiO_2 .

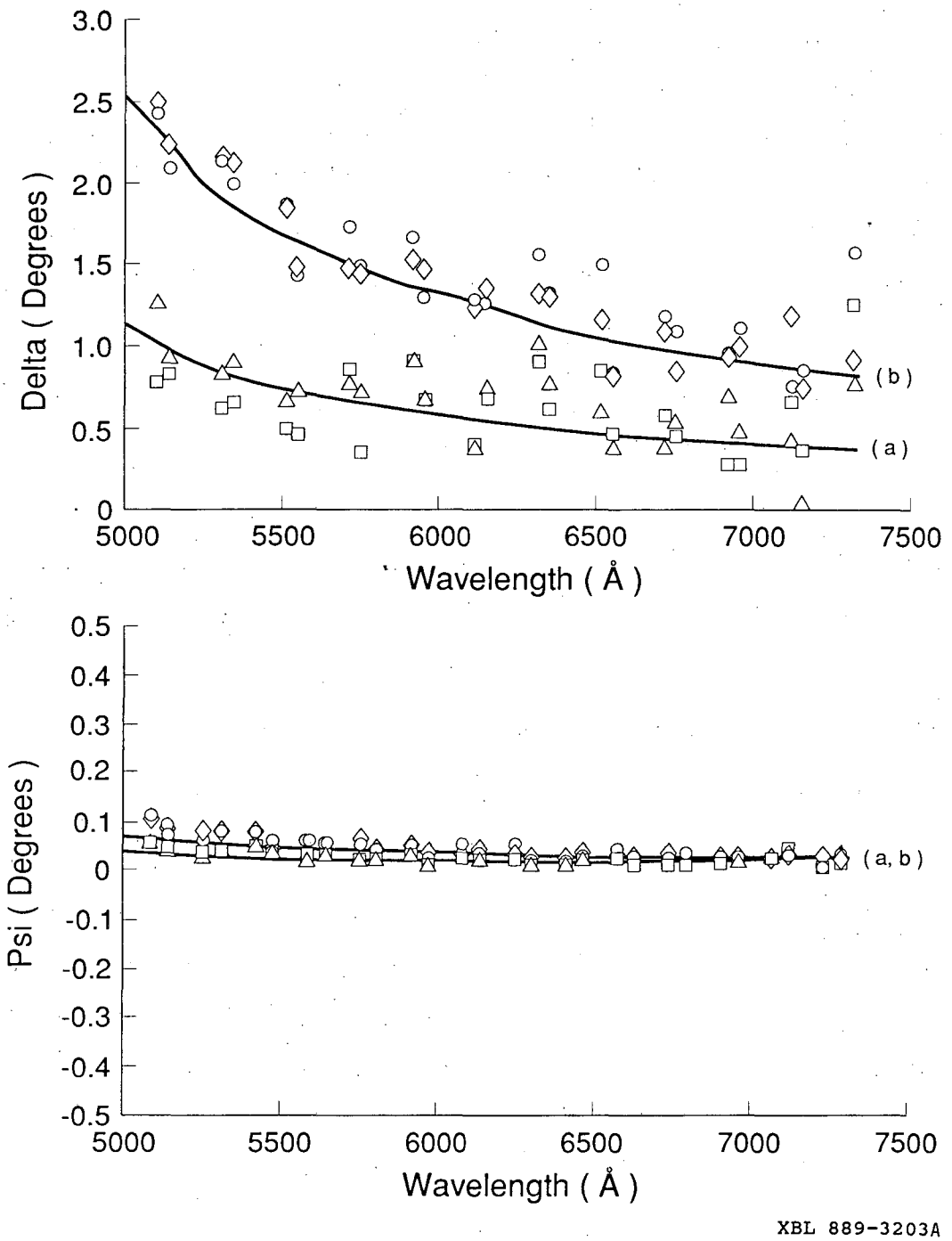

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Figure 4.--Incremental changes of ellipsometric parameters as result of the application of different anodic potential steps. Optical model(solid curve) and data pts. reported as differences from initial state prior to anodic biasing.
(a.) 30 A film model, △: 1.0 V., □ : Open circuit at steady-state potential.
(b.) 35 A model, ◇: 2.0 V, ○: subsequent open circuit data.

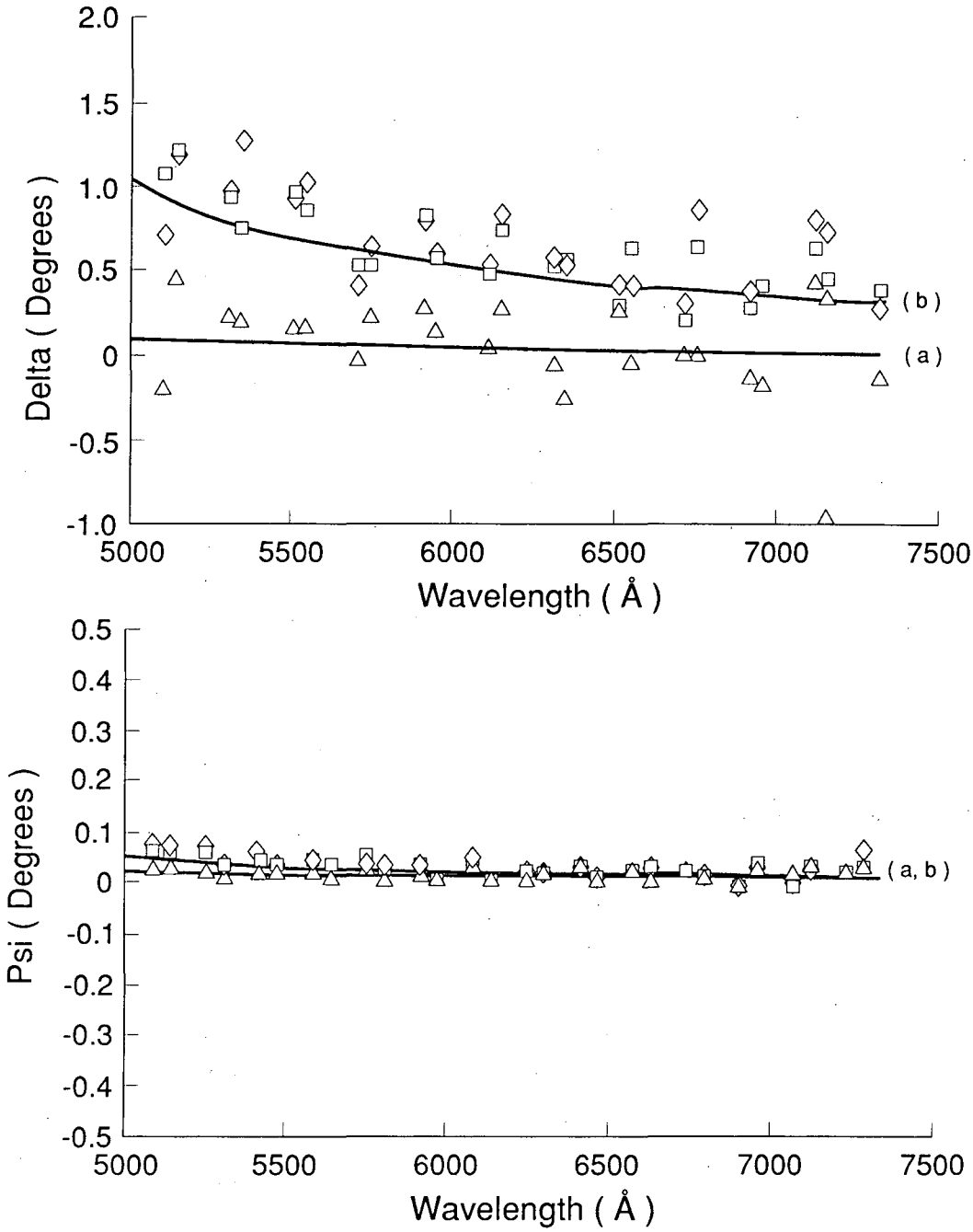

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Figure 5.--Incremental ellipsometric data, optical model(solid curve) and measured pts., relative to 3.0 V data set (a.) Δ: Open circuit measured values.
(b.) 45 A model, □ : 4.0 V data, ◇ : subsequent open circuit measurements.

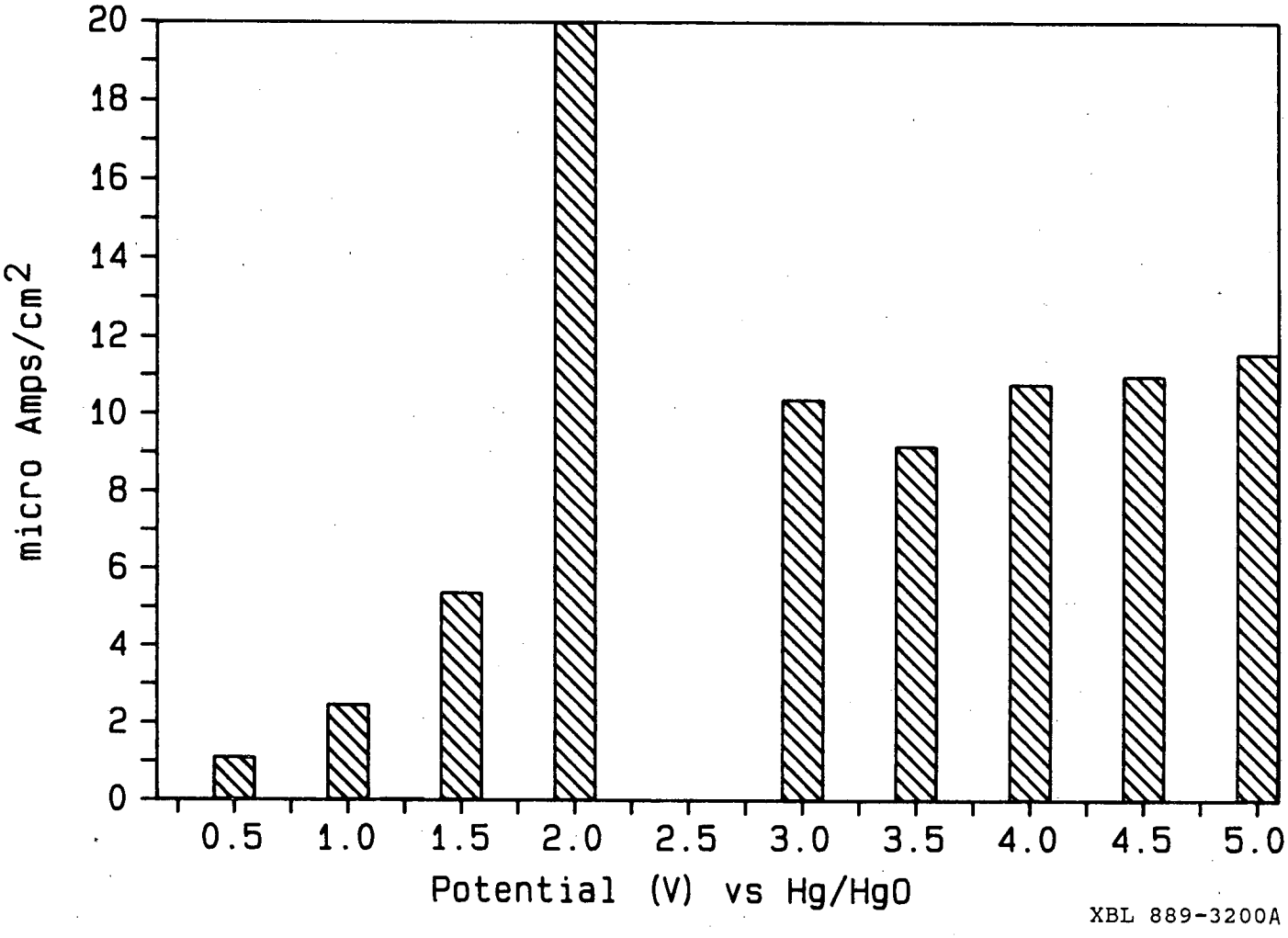

Figure 6.--Steady-state current density versus anodic bias. p-Silicon in 0.10 M NH_4F, pH 3.5

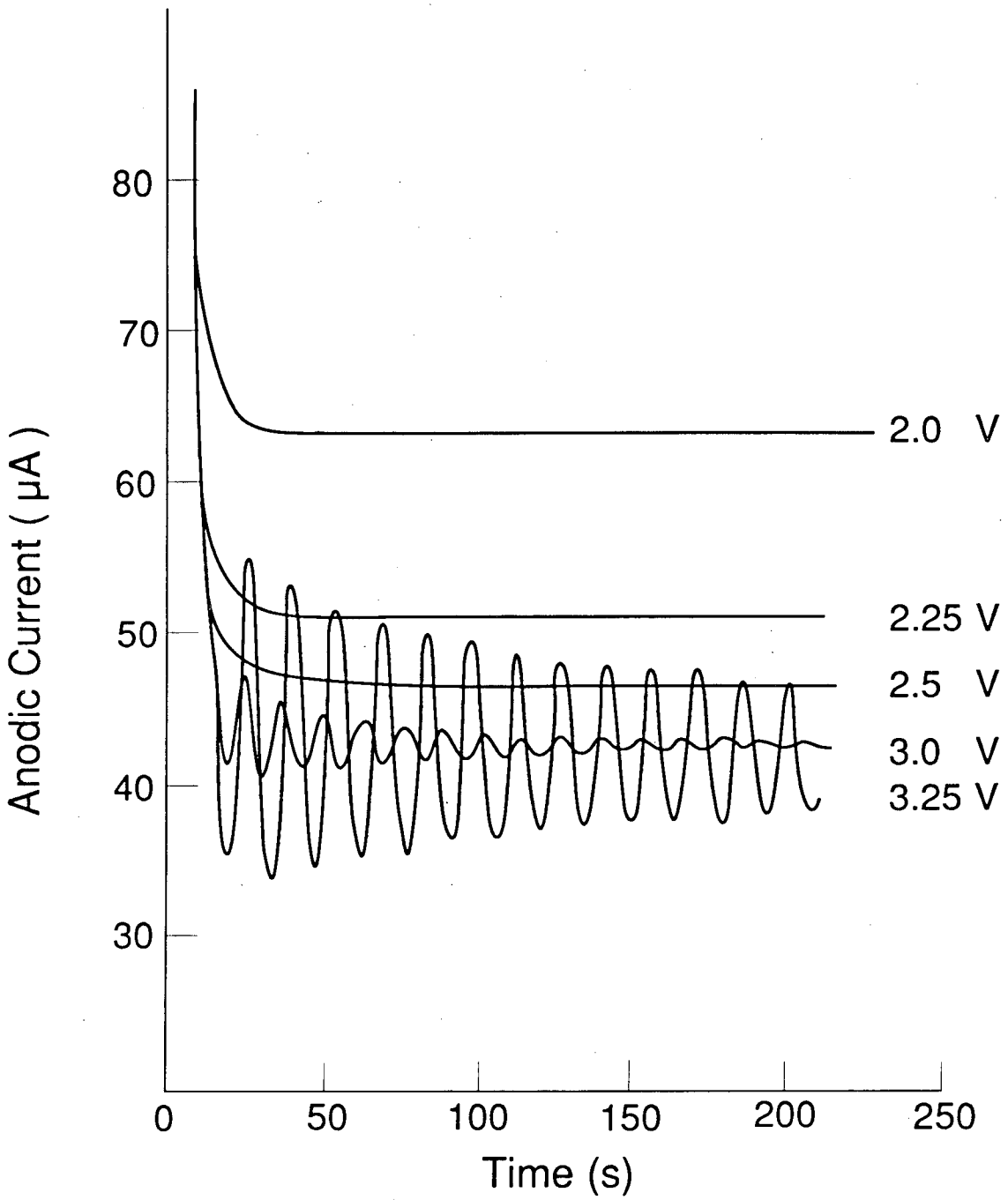

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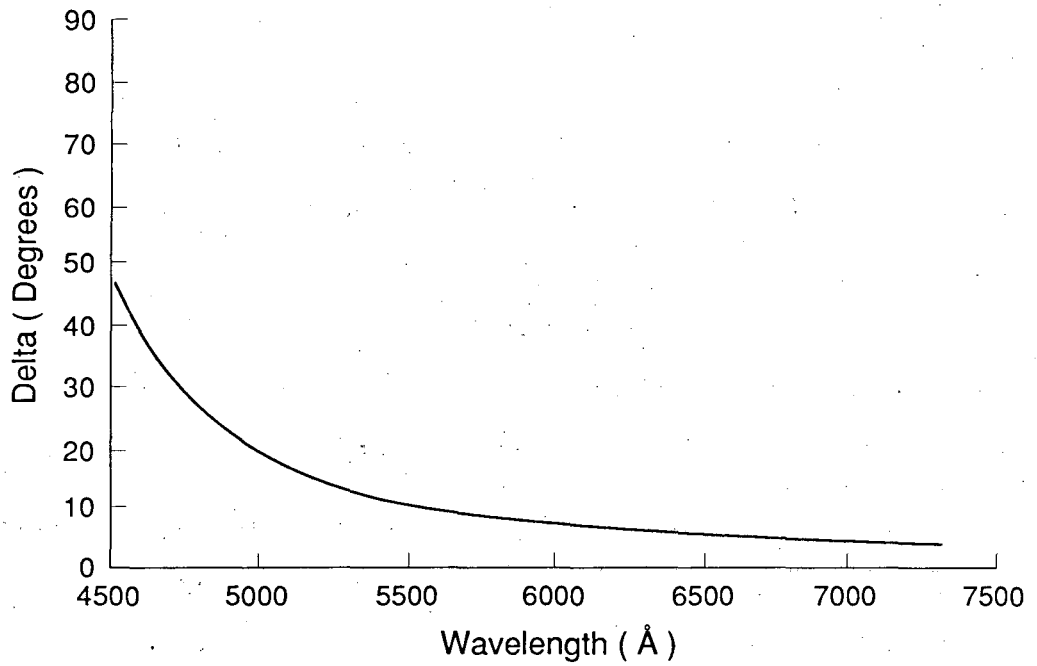
Figure 7.--Transient current response to potential steps from open circuit to potentials between 2.0 and 3.25 Volts. Transition from an exponential decay to oscillatory response occurs between 2.75 and 3.0 Volts.

DISCUSSION

The results of these experiments contradict the premise that the SiO_2 film is etched in 0.10 M ammonium fluoride at pH greater than 3.5. The ellipsometer measurements indicate that the film thickness increases with applied potential but is not significantly decreased by dissolution at open circuit, even in the presence of forced convection. Thus, the steady-state current cannot be SiO_2 film dissolution and film repair, but is more likely silicon cation vacancy migration through the film and dissolution, leaving the oxide structure unchanged.

Memming and Schandt[6], in their work on SiO_2 dissolution mechanisms, noted that the dissolution current did not follow the Levich relation for the rotating disk electrode. This is an indication that the flux of the dissolving species is not controlled by solution-phase mass transfer. If the cations were the dissolving species, one would expect the rate controlling step to be migration across the film. Gould and Irene[8] also concluded from in-situ ellipsometer measurements of thermally grown SiO_2 films in 0.05 mM HF, that the films did not dissolve down to bare silicon. The minimum thickness they found was 20 Angstroms. In the same study, they concluded that the oxide film was not etched at all in 0.1 mM NH_4F over a period of 16 hours. Aspnes and Theeten[9] have studied the Si/SiO_2 interface using spectral ellipsometry and proposed that the interfacial region is non-stoichiometric $SiO_{.4\pm.2}$ spanning 7 Angstroms. The optical properties of residual films in the experiments by Irene and Gould[8] correspond to the properties of the interfacial layer proposed by Aspnes and Theeten[9].

The ellipsometer data in the present study were modelled with two different film structures in an effort to resolve changes at the interfacial region during anodization. An optical model consisting of a silicon monoxide film sandwiched between the silicon substrate and the SiO_2 film was compared to the simplest film model of SiO_2 on Si. In the visible spectral range between 5000 and 7500 Angstroms, outside the absorption region of SiO, the two models predict identical ellipsometric parameter values and are indistinguishable as demonstrated in figure 8.



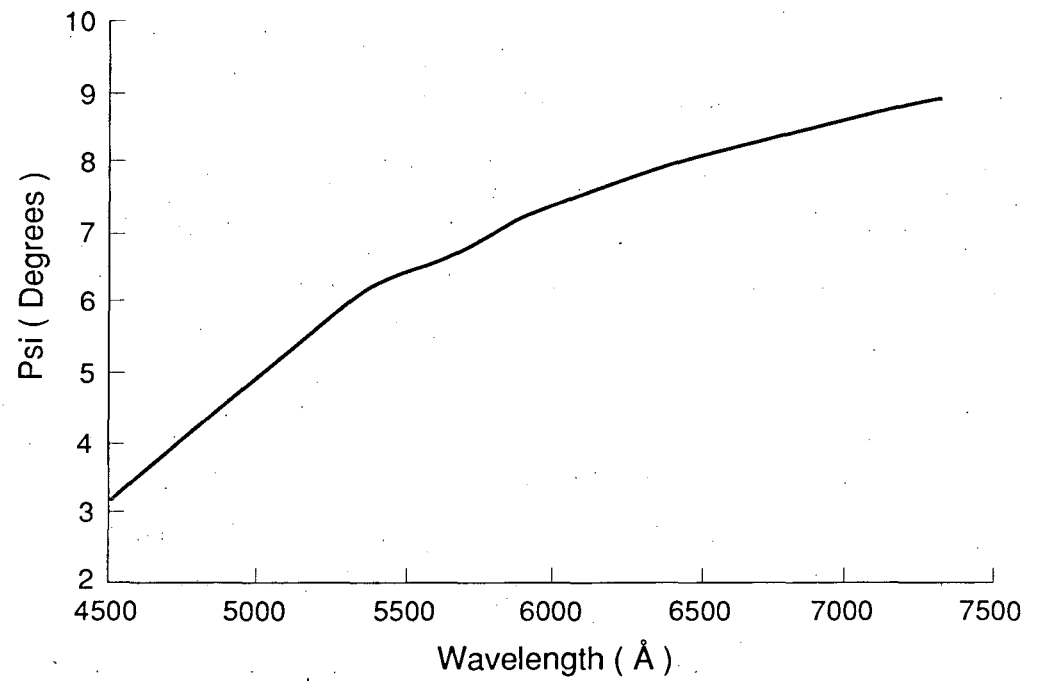


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Figure 8.--Degenerate optical models. Coincident computed curves correspond to both Δ : 42.5 Angstroms of SiO_2 on Si and □ : 29.6 A of SiO_2 on top of 4.6 A of SiO on top of Si. Spectral values of optical constants were taken from the literature.

Since the film fails to dissolve under the mild fluoride conditions of our experiments, an alternative to the oxide dissolution model is needed. One alternative film growth model is similar to the point defect model proposed by Chao, Lin, and MacDonald[7]. In this model, one splits the total current into the corresponding ionic fluxes:

At the oxide/solution interface, there is rapid adsorption and desorption of oxide/hydroxide species and oxide anions filling oxygen vacancies emerging from the film. Using Kroger-Vink notation,

$$H_2O + V_{O}^{\cdot\cdot} \rightarrow O_O + 2H^{+}_{(aq)} \qquad [2]$$

where O_O indicates an oxygen atom occupying an oxygen position in the film lattice and $V_{O}^{\cdot\cdot}$ indicates an oxygen vacancy which is positively charged with respect to the anion which is missing.

At the silicon/oxide interface, silicon oxidation occurs by hole injection and oxygen vacancies are generated.

$$Si_m + 4h^+ \rightarrow Si_{Si} + 2V_{O}^{\cdot\cdot} \qquad [3]$$

This treatment assumes stoichiometric film formation and tetra-valent silicon cations based on the net reaction, though the interface itself may be non-stoichiometric.

Generation of cation vacancies occurs at the film/solution interface with silicon cations being dissolved into the solution phase.

$$Si_{Si} + 6F^- \rightarrow SiF^{2-}_{6(aq)} + V_{Si}^{4x} \qquad [4]$$

At the Si/SiO_2 interface, silicon oxidation consumes the cation vacancies migrating to the silicon/film interface.

$$Si_m + 4h^+ + V_{Si}^{4x} \rightarrow Si_{Si} \qquad [5]$$

If one assumes that both cation and anion vacancies are mobile in the film under the substantial electric field from the applied bias (on the order of 4 million Volts/cm.), the sum of eqs. [2] and [3] shows film formation as the net reaction. The sum of eqs. [4] and [5] shows only dissolution of the silicon cations.

Recognizing that the oxide film does not dissolve, the steady-state current under anodic bias must be predominately a result of the cation flux, since anion flux would increase the film thickness and cause the current to continue to decrease. With no film dissolution and high field ionic transport, the anion flux should result in an inverse logarithmic film growth law. If one assumes that the electric field is uniform across the film and equal to the applied potential divided by the film thickness, then the flux relations should be:

$$N_i = A_i \exp(\frac{\beta_i \Delta\Phi}{l}), \quad i = V_{Si^{4+}}, V_O{}'' \qquad [6]$$

where A and β are temperature dependent material constants including a lattice vibration frequency factor and the activation energy for vacancy hopping.

The film growth rate can then be written in terms of the oxygen vacancy flux in the manner of Cabrera and Mott [12]:

$$\frac{dl}{dt} = \frac{s_i A_i}{\rho_{ox}} \exp(\frac{\beta_i \Delta\Phi}{l}), \quad i = V_O{}'' \qquad [7]$$

where s is the stoichiometric number of oxygen anions in SiO_2, and ρ_{ox} is the molar density of the film.

An approximate solution for the film thickness is the usual inverse logarithmic form:

$$\frac{1}{l(t)} = \frac{1}{l_0} + \frac{\ln(1+t\ \Lambda(l))}{\beta_i\ \Delta\Phi} \qquad [8]$$

$$\Lambda(l) = \frac{A_i\, s_i\, \beta_i\ \Delta\Phi}{\rho_{ox}\ l^2}, \quad i = V_O{}'' \qquad [9]$$

where l_0 is the initial film thickness.

The current density through the film is then obtained from the flux equations [6]:

$$j = \sum_i z_i N_i, \quad i = V_O{}'', V_{Si^{4+}} \qquad [10]$$

If the mobility of the cations is somewhat greater than that of the anions, this expression will give a rapid current decay to non-zero pseudo-steady state. This is expected since the current decreases as the film thickens, but only the anions contribute to the film growth. The silicon cations should be more mobile than the oxygen anions since the cations have half the ionic

radius of the oxygen anions and twice the charge.

CONCLUSIONS

The results of these preliminary experiments point to several specific conclusions:

1. Thin silicon dioxide films do not dissolve at an appreciable rate in dilute NH_4F in the pH range 3.5 to 5.

2. Silicon dioxide film dissolution is not the film thickness limiting factor during anodic silicon oxidation.

3. Steady-state currents during anodic bias must be due to silicon cation dissolution.

4. Ellipsometry cannot unambiguously resolve SiO interfacial sublayers in the spectral region between 5000 and 7500 Angstroms.

Table 1.--Values of optical constants used in optical models given at selected wavelengths for silicon, silicon monoxide, and silicon dioxide.
Values were taken from the handbook by Palik.[4]

Selected Refractive Index Data[4]						
	Silicon		Silicon Monoxide		Silicon Dioxide	
Wavelength(A)	n	k	n	k	n	
4999	4.298	.073				
5085					1.4619	
5166	4.215	.060	2.021	.0355		
5461					1.4601	
5486	4.089	.044				
5636	4.042	.032	1.994	.0215		
5770					1.4588	
6019	3.943	.025				
6199	3.906	.022	1.969	.0118		
6438					1.4567	
6526	3.847	.016				
6888	3.796	.013	1.948	.0052		
6965	3.787	.013				
7065					1.4552	
7469	3.736	.009				
7749	3.714	.008	1.929	.0015		
8521					1.4525	

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