ELLIPSOMETRIC INVESTIGATION OF THE SILICON / ANODIC-OXIDE INTERFACE

E. Palik, V. Bermudez

▶ **To cite this version:**

E. Palik, V. Bermudez. ELLIPSOMETRIC INVESTIGATION OF THE SILICON / ANODIC-OXIDE INTERFACE. Journal de Physique Colloques, 1983, 44 (C10), pp.C10-179-C10-182. 10.1051/jphyscol:19831036 . jpa-00223493

HAL Id: jpa-00223493

https://hal.science/jpa-00223493

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

JOURNAL DE PHYSIQUE
Colloque C10, supplément au n°12, Tome 44, décembre 1983

ELLIPSOMETRIC INVESTIGATION OF THE SILICON / ANODIC-OXIDE INTERFACE

E.D. Palik and V.M. Bermudez

Naval Research Laboratory, Washington, D.C. 20735, U.S.A.

Résumé - On présente les résultats de mesures d'ellipsométrie effectuées pendant la croissance et le décapage de couches d'oxyde anodique sur le silicium dans 2M KOH. Il se produit des variations importantes de ψ et de Δ au moment où le décapage chimique atteint l'interface SiO_2/Si, et aussi dans la première phase de l'anodisation. Les résultats sont interprétés par un changement dans la stoechiométrie et l'épaisseur d'une couche de transition SiO_x ($0\leqslant x\leqslant 2$).

Abstract - Ellipsometric measurements have been carried out during growth and etch back of anodic oxides on Si in 2M KOH. Pronounced variations in ψ and Δ occur as etching proceeds through the SiO_2/Si interface and also during the initial stages of re-anodization. The results are interpreted in terms of changes in the stoichiometry and thickness of an SiO_x ($0<x<2$) connective layer.

The technological importance of orientation-dependent chemical etching of Si /1,2/ has indicated a need to understand the Si/anodic-oxide interface which, unlike Si/thermal-oxide, has received little attention. To date, work has focused on I-V and/or C-V data /1-3/ which have provided information on the kinetics of anodization and open-circuit etch back and on the existence of electronic states at the interface. For Si/thermal SiO_2, spectroscopic ellipsometry /4/ has been used to characterize the interface as a 7 ± 2 Å-thick layer of average composition SiO_x ($x = 0.4 \pm 0.2$). However, obtaining the required sensitivity necessitates a thick oxide ($>10^3$ Å). We have taken an alternative approach of using real-time, in-situ ellipsometry at fixed wavelength to follow anodization and etching, with the goal of characterizing the interface and determining the etching mechanism(s).

I. EXPERIMENTAL

Ellipsometric measurements were made using a spectroscopic polarization-modulation system /5/ ($\Theta = 60.6°$ angle of incidence) at λ = 3190, 4358 and 8000 Å. The Si samples were mounted in a hollow 60° prism (BK-7 glass) containing 2M KOH electrolyte, a standard calomel reference electrode and a Pt counter electrode, all connected to a potentiostat /2/. N_2 was bubbled through the solution for mixing and O_2 purging. A microcomputer read the cell current (I) and voltage (V) and the ellipsometric angles ψ and Δ as functions of time. Standard n- and p-type Si {100} and {111} wafers were studied. Anodic oxides were grown after etching off the native oxide and a few thousand Ångstroms of Si. Dry thermal oxides were grown at 900°C after initial growth and stripping of 5000 Å of thermal oxide.

II. ANALYSIS

The basis for data analysis is a model consisting of a semi-infinite crystalline Si (c-Si) substrate, an SiO_x ($0< x <2$) connective layer, an amorphous SiO_2 (a-SiO_2) oxide film and an aqueous KOH ambient. Different anodization and etching scenarios can be evaluated by variation of the parameters (complex indices of refraction, $\tilde{n} = n-ik$, and/or layer thicknesses) and comparison of the observed and calculated /6/ ψ and Δ. For c-Si and a-SiO_2, $\tilde{n}$ was obtained from the literature /7,8/. For SiO_x, $\tilde{n}$

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:19831036

vs. x was calculated /9/ in terms of $\tilde{n}$ of amorphous Si (a-Si) /10/ and of a-SiO_2 /8/. The index of the electrolyte (n_e) was obtained from the n vs. λ data for pure H_2O /11/ and the n vs. molarity results (λ = 5893 Å) for $NaOH/H_2O$ /12/. The SiO_x connective layer is approximated as a homogeneous layer of average composition x, which is adequate /13/ for the wavelengths used here. The model used /9/ to compute $\tilde{n}$ vs. x for SiO_x is based on a physical mixture /4/ of Si and SiO_2. This is justified for two reasons: (1) the calculated x-dependence of the SiO_x absorption edge /9/ agrees with experiment and (2) fixed-λ measurements cannot distinguish a physical from a chemical mixture on the basis of $\tilde{n}$. Measurements at λ = 3190 and 4358Å offer high sensitivity to the SiO_x layer since $\tilde{n}$ is very different for a-Si and c-Si; whereas, $\tilde{n}$ is similar for both forms at 8000Å /10/. Other than at 3190Å, there is no prominent electroreflectance structure /14/ which might influence optical data under changing dc bias.

III. RESULTS

I, V, ψ and Δ vs. time of etch back and growth of the anodic oxide are shown in Fig. 1. For λ = 4358 Å at t = 0 (Fig. 1b, point a) the previously grown anodic oxide (-0.4V) is etching back at open-circuit conditions. Abrupt decreases and increases in ψ and Δ begin to occur at point b just as a characteristic broad dip occurs in the open-circuit potential (OCP) near point c. The full width at half maximum (FWHM) of Δ is ~3-4 min. ψ and Δ level off near point d and etching of Si begins. The OCP remains constant while etching of Si occurs until an external bias is applied at point e' and current begins to flow. At point f formation of a surface film begins with a drop in I near -0.75V. Further increase in V produces a second peak and a final drop in I. Then, Δ levels out near g before further thickening of the oxide film occurs at h. The double peak in I obscures the definition of the passivation potential (PP), but we assign the PP to the smaller current peak. Note that the changes in ψ and Δ from f to g are comparable to but larger than the corresponding changes from points b to d. We suggest that the connective layer is established first in the region f-g before the SiO_2 begins to stabilize and/or grow from point g to h. Figs. 1(a,c) show similar results for ψ and Δ at λ = 3190Å and 8000Å. Since the {111} surface is a slow etching surface (~30 Å/min at 22°C), it did not roughen quickly and several cycles of anodization and etch back could be performed before the values of ψ and Δ near point d began to shift systematically (ψ increasing and Δ decreasing) indicating roughening. Although not obvious in Fig. 1, the peak in ψ occurred after the peak in Δ by ~30 s. Results for n{111} Si were similar to those for p{111}, except that the peak in ψ was not as prominent.

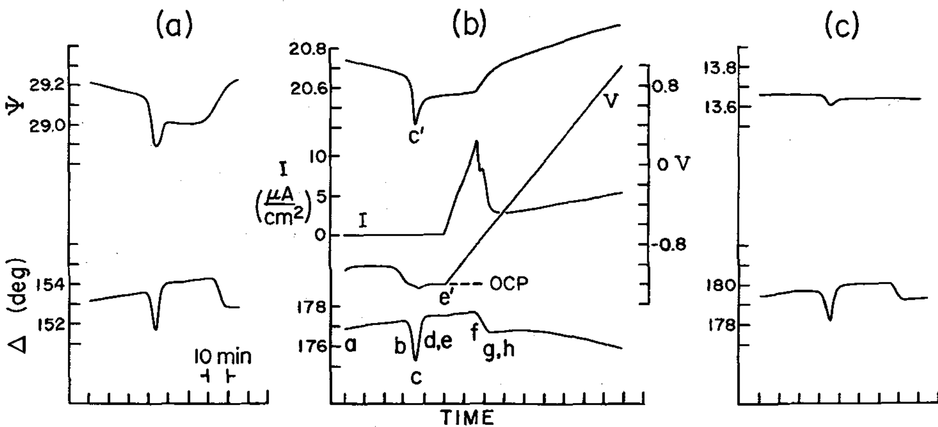

Fig. 1 - Observed changes in ψ and Δ during anodic-oxide etch back, and subsequent re-anodization, for p-type Si(111) with resistivity ≈9.7 Ωcm (N_A≈1.4 x 10^{15} cm^{-3}) (a) = 3190 Å, (b) λ = 4358 Å with open-circuit and applied potential and current density during the same time period (c) = 8000 Å.

Previous work /1/ indicated that the anodic-oxide growth rate at low bias is ~6.8 Å/V, while above 5 V it changes rather abruptly to ~41.7 Å/V. We have labeled these soft and hard anodic oxides, respectively. The etch-back rates of soft, hard and thermal oxides are 0.6, 0.16 and 0.1 Å/min, respectively. We have measured etch-back properties of a number of hard anodic oxides grown to ~7 V with respect to the PP at 4358 Å and some thermal oxides grown to 60-100 Å on n and p {111} Si. The changes in ψ and Δ from b to c, $\delta\psi$ and $\delta\Delta$, were larger ($\delta\psi$<10°, $\delta\Delta$<50°); the FWHM varied from 10-20 min; the peak in Δ occurred after the peak in ψ by ~2 min. The magnitude of $\delta\psi$ was 2-4 times smaller than that of $\delta\Delta$. Because of the much larger values of $\delta\psi$ and $\delta\Delta$, the present model is applied only to the soft anodic oxide as discussed below. Interestingly, we are able to observe visually the thermal and hard anodic oxides in the 10-20 min period when ψ and Δ changed significantly and noticed the gradual appearance and disappearance of a gray-tan "film" on the surface. Similar etch-back experiments for soft anodic oxides on the {100} surface have been less detailed. The decreases in ψ and Δ as the connective layer is reached are much larger than those shown in Fig. 1 often by several factors of two, with the FWHM still 3-4 min. Immediately after this large change, the ψ and Δ continue to increase and decrease, respectively, due to roughening of the surface making repetitive runs more complicated. The {100} Si etch rate is ~350 Å/min.

Fig. 2 shows the results of model calculations that reproduce the essential features of the anodic-oxide data in Fig. 1. The (arbitrary) starting point represents 20 Å of SiO_2 with a 7 Å SiO_x (x = 0, 0.2 and 0.4) connective layer /4/. Segment a-b is the thinning of the SiO_2 to zero thickness (point b). Segment b-c-d represents the "oxidation" of SiO_x, with x starting at the initial value (point b) and gradually increasing through x = 0.8 (point c) to x = 2.0 (point d). For $\delta\psi$, the peak occurs at x = 0.9 (point c'). Part d-e is the dissolution of the remaining 7 Å film (modeled here as SiO_2). From e to f represents etching of c-Si. Part f-h represents the re-anodization of the sample with application of a linear voltage ramp where step f-g is the regrowth of the connective layer, crudely modeled by assuming an SiO_x layer of constant x (= 0.4) and increasing thickness (d = 0 at point f and d = 7 Å at point g). Segment g-h is the regrowth of SiO_2 to 20 Å; hence, points a and h are the same, as are points b and g. The λ dependence of the results reflects those of the constituent $\tilde{n}$. For an alternative mechanism, in which the SiO_x dissolves without first being "oxidized", the b-c-d-e segment is eliminated, and no peak is observed in $\delta\Delta$ vs. time, in clear disagreement with the data in Fig. 1. Inclusion of a Helmholtz layer, a mass-transport boundary layer or any other type of dielectric layer (n > 1, k = 0) affects only Δ, not ψ, if the layer is optically thin ($4\pi n_e d\cos\Theta/\lambda \ll 1$). A thicker layer causes opposite changes in ψ and Δ, in disagreement with the data.

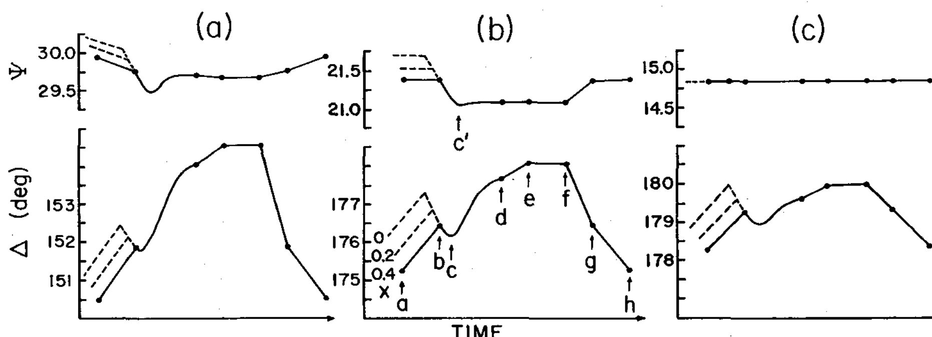

Fig. 2 - Calculated changes in ψ and Δ (a) 3190 Å (b) 4358 Å and (c) 8000 Å during an etch-back/re-anodization cycle as described in the text. The points indicated (a, b, c, etc.) label specific steps in the process.

The qualitative agreement between the anodic-oxide data and the calculations is reasonable and could be improved by varying the connective-layer thickness. Note that the time scale used in Fig. 2 is arbitrary, since the rate of the b-c-d-e step is unknown. The calculated region d-e in Fig. 2, where the SiO_2 dissolves away to the Si substrate, may not actually exist, since we expect some sort of transition layer to occur between Si and liquid during etching. Furthermore, we have made the simplifying assumption that the b-c-d segment (x increasing) and the d-e step (thickness decreasing) occur consecutively, whereas, they probably take place concurrently. In contrast to the soft anodic-oxide case, the much larger (but qualitatively similar) ψ,Δ effects observed for the thermal and hard anodic oxides are difficult to explain quantitatively under the present assumptions, without invoking a fairly thick connective layer. It may be that the thermal-oxide connective layer changes drastically (e.g., the thickness temporarily increases) as the last layer of oxide is removed and the previously buried connective layer and c-Si are exposed to the etchant.

IV. DISCUSSION

The essential results are as follows. ψ and Δ have been measured during open-circuit etch back of anodically-formed $Si/SiO_x/SiO_2$. The ellipsometer is able to "see" the connective layer since $\tilde{n}$ of the a-Si constituent of SiO_x is very different from that of c-Si. The data indicate that, once the SiO_2 layer has dissolved, the exposed SiO_x is first oxidized or hydrolyzed to form a layer with a "dielectric-like" optical index. The second step is dissolution of the "hydrolyzed" or "oxidized" connective layer. Comparison of the observed and calculated ψ and Δ rules out a process in which the exposed SiO_x simply dissolves without a significant change in stoichiometry. Assuming that the mechanism for etching the SiO_x (which is initially Si-rich) is the same as that for the c-Si substrate, these results imply that the rate-limiting process is attack by H_2O and/or OH^- to form a surface phase which is then rapidly dissolved. In this context, recent surface vibrational studies /15/ on atomically-clean Si{100} and {111} surfaces are interesting. It is found that H_2O reacts dissociatively with dangling bonds on both surfaces (to form Si-H and Si-OH) but at a rate which is a factor of at least 100 greater for the {100} than for the {111} plane. Although a similar etching mechanism (slow attack by H_2O followed by rapid dissolution in the alkaline medium) has been suggested previously /16,17/, we believe that this is the first direct observation of a part of this process.

REFERENCES

1. FAUST, JR. J.W. and PALIK E.D., J. Electrochem. Soc., 130 (1983) 1413.
2. PALIK E.D., FAUST, JR. J.W., GRAY H.F., and GREENE R.F., J. Electrochem. Soc. 129 (1982) 2051, and references therein.
3. MADOU M.J., LOO B.H., FRESE K.W. and MORRISON S.R., Surf. Sci. 108 (1981) 135
4. ASPNES D.E. and THEETEN J.B., J. Electrochem. Soc. 127 (1980) 1359.
5. BERMUDEZ V.M. and RITZ V.H., Appl. Optics 17 (1978) 542; BERMUDEZ V.M., Surf. Sci. 74 (1978) 568.
6. AZZAM R.M.A. and BASHARA N.M., "Ellipsometry and Polarized Light" (North-Holland, Amsterdam), 1977, Chap. 4.
7. JELLISON, JR. G.E., and MODINE F.A., J. Appl. Phys. 53 (1982) 3745.
8. MALITSON I.H., J. Opt. Soc. Am. 55 (1965) 1205.
9. ZUTHER G., Phys. Status Solidi A59 (1980) K109.
10. ASPNES D.E., THEETEN J.B. and HOTTIER R., Phys. Rev. B 20 (1979) 3292.
11. IRVINE W.M. and POLLOCK J.B., Icarus 8 (1968) 324.
12. OLSEN A.L. and WASHBURN E.R., Trans. Kansas Acad. Sci. 40 (1937) 117.
13. JELLISON, JR. G.E. and MODINE F.A., J. Opt. Soc. Am. 72 (1982) 1253.
14. DAUNOIS A. and ASPNES D.E., Phys. Rev. B 18 (1978) 1824.
15. CIRACI S. and WAGNER H., Phys. Rev. B 27 (1983) 5180.
16. REPINSKII S.M. and PERSHKOVA S.V., Russ. J. Phys. Chem. 46 (1972) 519.
17. IZIDINOV S.O., J. Appl. Chem. USSR 44 (1971) 1660.