Title

HIGH RESOLUTION ELECTRON MICROSCOPY STUDIES OF NATIVE OXIDE ON SILICON

Permalink

Authors

Mazur, J.H.
Gronsky, R.
Washburn, J.

Publication Date

1983-06-01

LBL-16272 c.2
UC-25

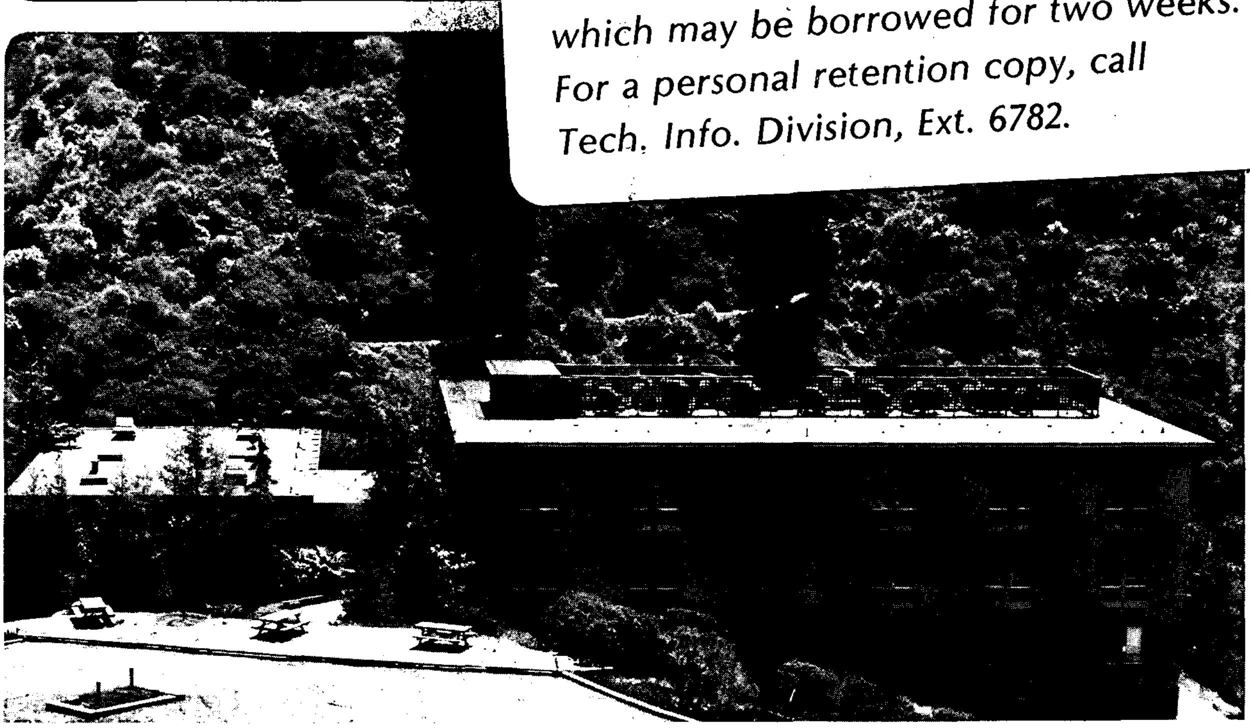
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

HIGH RESOLUTION ELECTRON MICROSCOPY STUDIES OF NATIVE OXIDE ON SILICON

J.H. Mazur, R. Gronsky, and J. Washburn

June 1983



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

HIGH RESOLUTION ELECTRON MICROSCOPY STUDIES OF NATIVE OXIDE ON SILICON

J.H. Mazur, R. Gronsky and J. Washburn

Materials Science and Molecular Research Division,
Lawrence Berkeley Laboratory
Berkeley, CA 94720

ABSTRACT

High resolution electron microscopy (HREM) of cross-sectional specimens has shown that the thickness of the native oxide on silicon is 20 ± 3Å, independent of surface orientation. This result has confirmed the value 21 ± 4Å determined by ellipsometry assuming a stoichiometric SiO_2 native oxide. Previous reports of a nonstoichiometric transition layer between Si and SiO_2 containing an excess of 10^{15} cm^{-2} Si atoms have also been alternatively explained by the observed morphological features of the Si-SiO_2 interface.

1. INTRODUCTION

Knowledge of the structure and chemistry of very thin (<100Å) silicon oxide films on silicon is important both for an understanding of the initial stages of the oxidation process and for the optimization of processing steps used in VLSI MOS device and solar cell technology[1,2]. In this paper attention is directed toward the native oxides grown in air at room temperature. Earlier ellipsometry studies of native oxide growth kinetics[3,4,5] indicated that within a few hours after removal of the oxide from the Si surface about 10Å of a new native oxide was formed. It is therefore expected that in many technological processes involving deposition of materials on silicon a thin layer of native oxide will always be present at the interface[6]. These oxides can obscure understanding of interfacial phenomena as for example the initial stages of high temperature oxidation. In the present study high resolution electron microscopy was used for direct measurements of the native oxide thickness. These measurements were compared to thickness measurement by ellipsometry. In addition the morphology of the Si-SiO_2 interfaces of the native oxide was compared to that of the interfaces developed during high temperature oxidation.

2. EXPERIMENTAL PROCEDURES

The native oxide was grown in air for 29 days on HF etched, p-type, B doped 1.5-17Ωcm resistivity Si wafers having three different orientations: exact (100), 2° off (100) and 3° off (111). In addition observations were made on a 200Å-thick oxide grown on a (100) Si surface at 900°C in dry oxygen.

Cross-sections of the specimens were prepared by gluing two pieces of wafers face to face with epoxy, then cutting the sandwich with a diamond saw perpendicular to a {110} trace. After mechanical grinding and double sided polishing to less then 100 μm, the section was glued to a support grid and ion milled to perforation. In this method of specimen preparation the edge containing the native oxide film was protected against milling by a layer of glue which was finally evaporated in the microscope column under a highly-focused electron beam. This method of preparation avoided the high temperature associated with deposition of a more conventional surface protective coating. The highest temperature to which the specimens were exposed was that due to ion beam heating, and was less than 150°C[7].

All high resolution electron microscopy observations were made in a JEOL JEM 200CX electron microscope with ultrahigh resolution pole piece.

The ellipsometry measurements were carried out on a Geartner ellipsometer having the He-Ne laser light source (λ = 6328Å).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Thickness measurement by HREM: The thickness of the oxide films on silicon was measured directly from the high resolution micrographs of the cross-sections imaged along a $<110>$ crystallographic direction. The $\{111\}$ lattice fringes having a spacing of 3.14Å served as an internal standard of distance.

Observed cross-sections of native oxides on (100), 2° off (100) and 3 off (111) Si surfaces are shown in figures 1, 2 and 3 respectively.

The thickness of oxides as measured between the Si-SiO_2 and SiO_2-vacuum interfaces (fragments of the epoxy glue were still present on some surface areas) is the same for all Si surfaces and is within 20 ± 3Å. The oxide is uniform over the entire length of the observed interfaces; its observed mottled contrast is typical of that for amorphous materials.

3.2 Measurement of native oxide thickness by ellipsometry: In the ellipsometry experiments, the relative phase change (Δ) and relative attenuation ($\tan\psi$) are measured for light reflected from the semiconductor surface which is covered by the oxide film. These measurements allow determination of film thickness and the refractive indices of the substrate and film. However for films of very small thicknesses, the refractive index values for both the substrate and the thin film must be assumed as these two parameters cannot be determined directly from the experiment. In addition, it is sufficient to measure the relative phase change to determine the thickness of a very thin film[8].

The measured values of Δ for oxides on (100), 2° off (100), and 3° off (111) Si surfaces, average over four zones, were 172.8°, 172.7° and 172.8° respectively. The corresponding thickness d of the oxides was calculated as a function of refractive index (figure 4) from equation (1) derived by Twu[8].

$$d = \lambda(\Delta - \Delta_o) \{n_s^2(n_s^2-1)\ (n^2-1) \cos\theta \sin^2\theta / n^2\ (n_s^2-1)\ n_s^2 \cos^2\theta - \sin^2\theta))\}/720 \qquad (1)$$

where $\lambda = 6328Å$ is wavelength of light, $\theta = 70°$ is incidence angle of light, $n_s = 3.89$ is the refractive index of silicon substrate at 6328Å, $\Delta_o = 178.87°$ is the relative phase change for bare silicon, n is the thin film refractive index, and Δ is the measured relative phase change for substrate with film. The curve "a" in figure 4 was obtained for the average value of $\Delta = 172.8°$.

The curves b and c represent the error of the calculated thickness d corresponding to a variance of $\theta = 1°$ of the values measured in four zones. Assuming that the native oxide is stoichiometric SiO_2, (n = 1.46), the calculated oxide thickness, (21 ± 4Å) is in good agreement with the HREM thickness measurements 20 ± 3Å. However, as can be seen from figure 4 the calculated thickness for a whole series of compositions with corresponding refractive index ranging from 1.46 (SiO_2) to 2.5

(SiO_{2-x}) would still give agreement within the experimental error of the HREM measurements.

Interest in the chemical composition of the interfacial region has stimulated ESCA studies of the $Si-SiO_2$ interface[5,9,10]. These investigators suggested a model of a nonstoichiometric region of the interface less than 15Å wide containing about 10^{15} cm^{-2} nonoxidized Si-Si bonds/cm^2. The transition region was narrower and less steeply graded in very thin oxides formed on (100) Si then on (111) Si substrates, but remained independent of oxidation conditions, oxidant or substrate doping.

These Si rich transition layers were assumed to account for discrepancies between ellipsometry and ESCA measurements of ultrathin oxide thickness. Further ellipsometry studies of thermally grown oxides on Si[11,12] were also interpreted using a three layer model with an intermediate layer containing nonstoichiometric, Si-rich oxide. The present work suggests however that there is no need to make such assumptions. Even with a fully stoichiometric oxide[13], the apparent nonstoichiometric transition layer can be explained by the observed morphology of the $Si-SiO_2$ interface.

3.3 Morphology of the $Si-SiO_2$ interface:

The morphology of the $Si-SiO_2$ interface depends critically on the silicon surface orientation. For an exact (100) Si surface with native oxide as shown in figure 1 the interface can be characterized by a hill-and-valley structure with an asperity of 2-4Å and correlation length of about 20Å. These values are similar to those observed for the 200Å thick oxide grown at 900°C in dry O_2 shown in figure 5, as well as those reported earlier for oxides grown under different oxidation conditions.

The native oxide interface on the 2° off (100) Si substrate, figure 6, appears to be rougher although qualitatively similar to the (100) interface. By comparison the structure of the 3° off (111) interface is best described as a terrace-ledge configuration, with atomically smooth terraces about 60Å wide and connecting ledges of 3.14Å height. A similar structure has also recently been observed for oxides grown at 1000° C in dry oxygen[16].

Significantly, these morphologies produce an average excess of about 10^{15} cm^{-2} Si atoms in the layers of oxide immediately adjacent to the silicon. An example of the morphology of the (100) $Si-SiO_2$ interface is shown schematically in figure 7, where the atomic positions on the Si side of the interface are identified. Note that the small irregularities marked "a", "b" and "c" can result in the observed interface with a degree of roughness that corresponds to that estimated from mobility measurements in MOS inversion layers at high gate fields[17]. Computer simulations are in progress to determine whether the model is consistent with the observed details of phase contrast changes at the $Si-SiO_2$ interface.

4. CONCULSIONS

High resolution electron microscopy studies of cross-sectional specimens of native oxides on silicon have demonstrated that:

a) the native oxide on silicon is 20 + 3Å thick, and this thickness is independent of Si orientation.

b) ellipsometry estimates of the native oxide thickness, 21 + 4Å are in good agreement with the HREM measurements.

c) The Si-SiO_2 interface for native oxides and high temperature oxides grown on (100) silicon can be characterized by hill-and-valley structure with asperity of 2-3Å and correlation length of about 20Å.

d) The Si-SiO_2 interface for 3° off (111) consists of atomically smooth (111) terraces connected by ledges of 3.14Å in height.

e) A morphological model of the Si-SiO_2 interfaces offers an alternative explanation for the nonstoichiometry region suggested by other techniques.

5. ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. J. D. Plummer, ed., Computer-Aided Design of Integrated Circuit Fabrication Process for VLSI Devices, Stanford Electronics Laboratories, Research Report TR DXG501-82.
2. R. B. Godfrey and M. A. Green, Appl. Phys. Lett. 34, 790 (1979).
3. R. J. Archer, J. Electrochem. Soc. 104, 619 (1957).
4. F. Lucas, Surface Sci. 30, 91 (1972).
5. S. I. Raider, R. Flitsch and M. J. Palmer, J. Electrochem. Soc. 122, 413 (1975).
6. C. D'Anterroches, Proceeedings of 3rd Oxford Conference on Microscopy of Semiconducting Materials, to be published (1983).
7. C. Ahn, private communication (1979).
8. B. I. Twu, J. Electrochem. Soc. 126, 1589 (1979).
9. R. Flitsch and S. I. Raider, J. Vac. Sci. Technol. 12, 305 (1975).
10. S. I. Raider and R. Flitsch, J. Vac. Sci. Tech. 13, 58 (1976).
11. E. Taft and L. Cordes, J. Electrochem. Soc. 126, 131 (1979).
12. D. E. Aspnes and B. Theeten, J. Electrochem Soc. 127, 1980 (1980).
13. A. Ishizaka and S. Iwata, Appl. Phys. Lett. 37, 392 (1980).
14. O. L. Krivanek and J. H. Mazur, Appl. Phys. Lett. 37, 392 (1980).
15. O. L. Krivanek, D. C. Tsui, T. T. Sheng and A. Kagmar, in The Physics of SiO_2 and its Interfaces ed., S. T. Pantelides (Pergamon, New York) 356 (1978).
16. J. H. Mazur, Proc. 41th. Annual EMSA Meeting, Phoenix, to be published (1983).
17. Y. C. Chang and E. A. Sullivan, Surface Sci. 34, 717 (1973).

FIGURE CAPTIONS

Fig. 1. Native oxide on (100) Si surface; thickness 20 ± 3Å.

Fig. 2. Native oxide on 2° off (100) Si surface: thickness 17 ± 3Å.

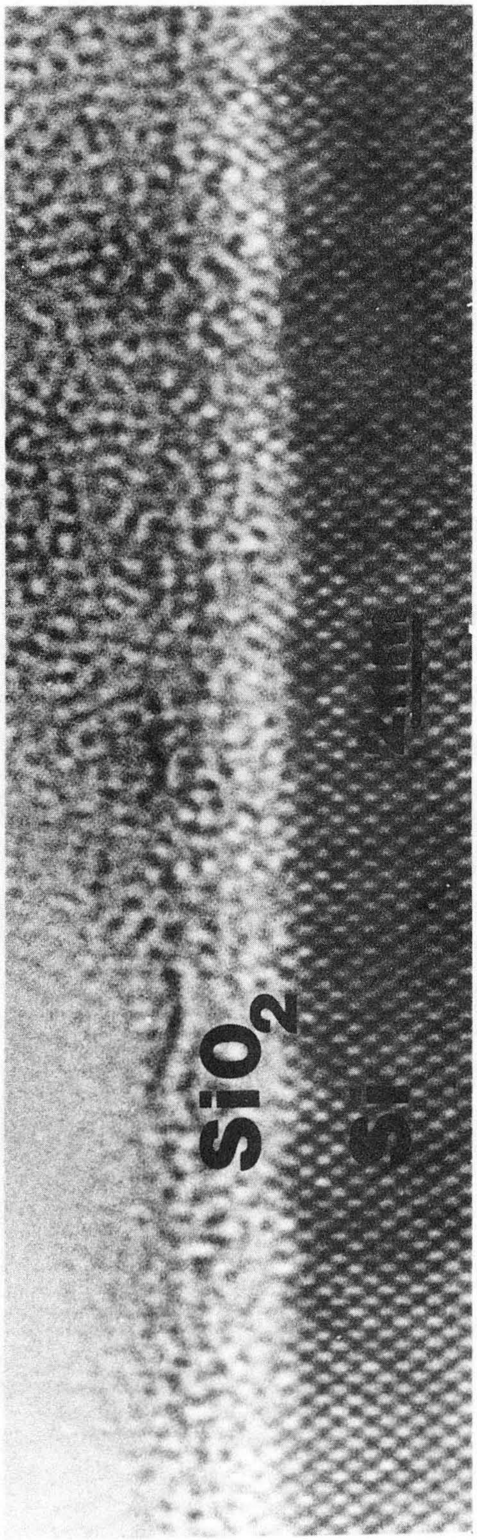
Fig. 3. Native oxide on 3° off (111) Si surface; thickness 20 ± 3Å.

Fig. 4. Variation of the oxide thickness d with the refractive index n of the oxide film calculated for a) Δ = 172.8°, b) Δ = 173.8°, c) Δ = 171.8°.

Fig. 5. High resolution image of the Si-SiO_2 interface of a 200Å thick oxide grown on (100) Si at 900°C in dry O_2.

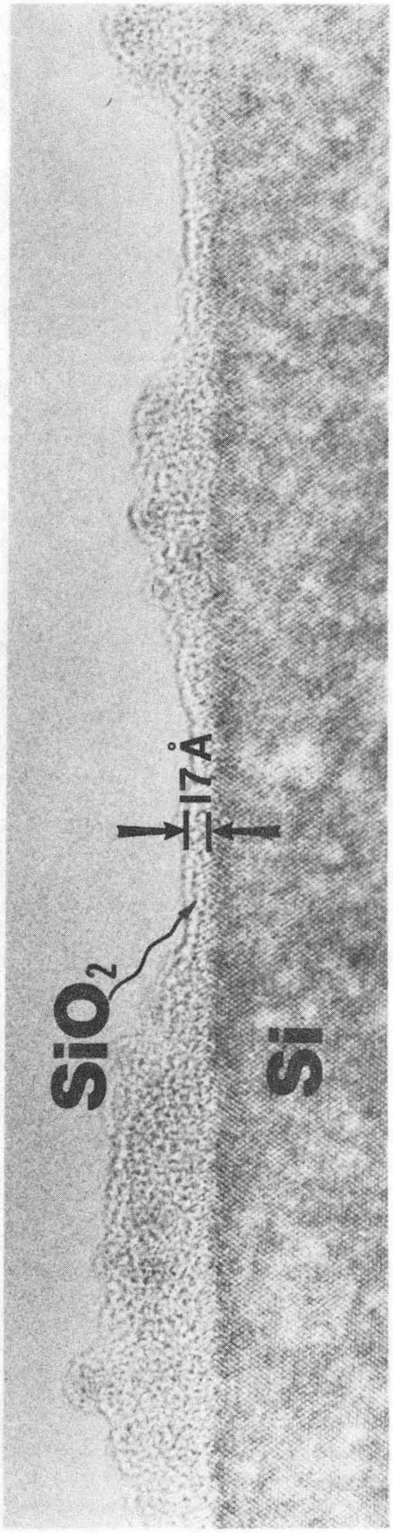
Fig. 6. High resolution image of 20Å thick native oxide on 2° of (100) Si surface.

Fig. 7. Possible arrangement of the Si atoms in crystalline silicon at the (100) Si-SiO_2 interface resulting in correlation length about 20Å and asperity 2-3Å.



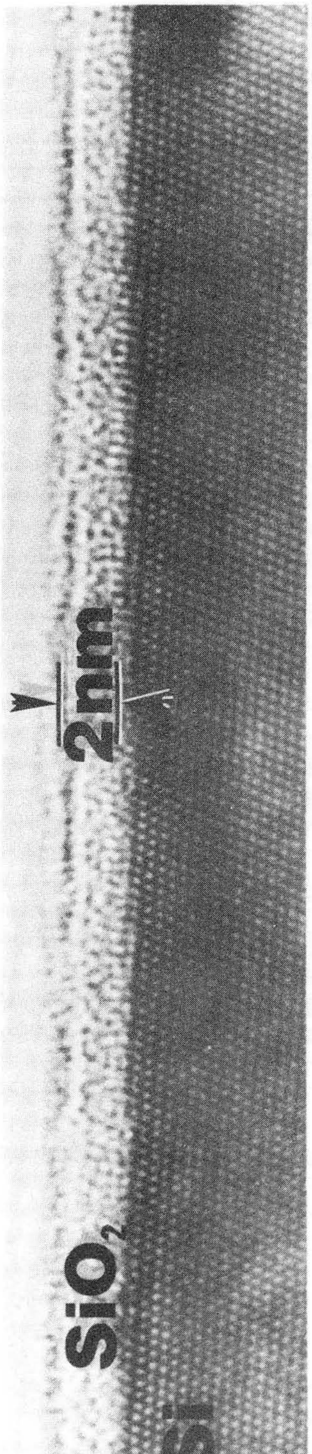
XBB 833-2309

Fig. 1



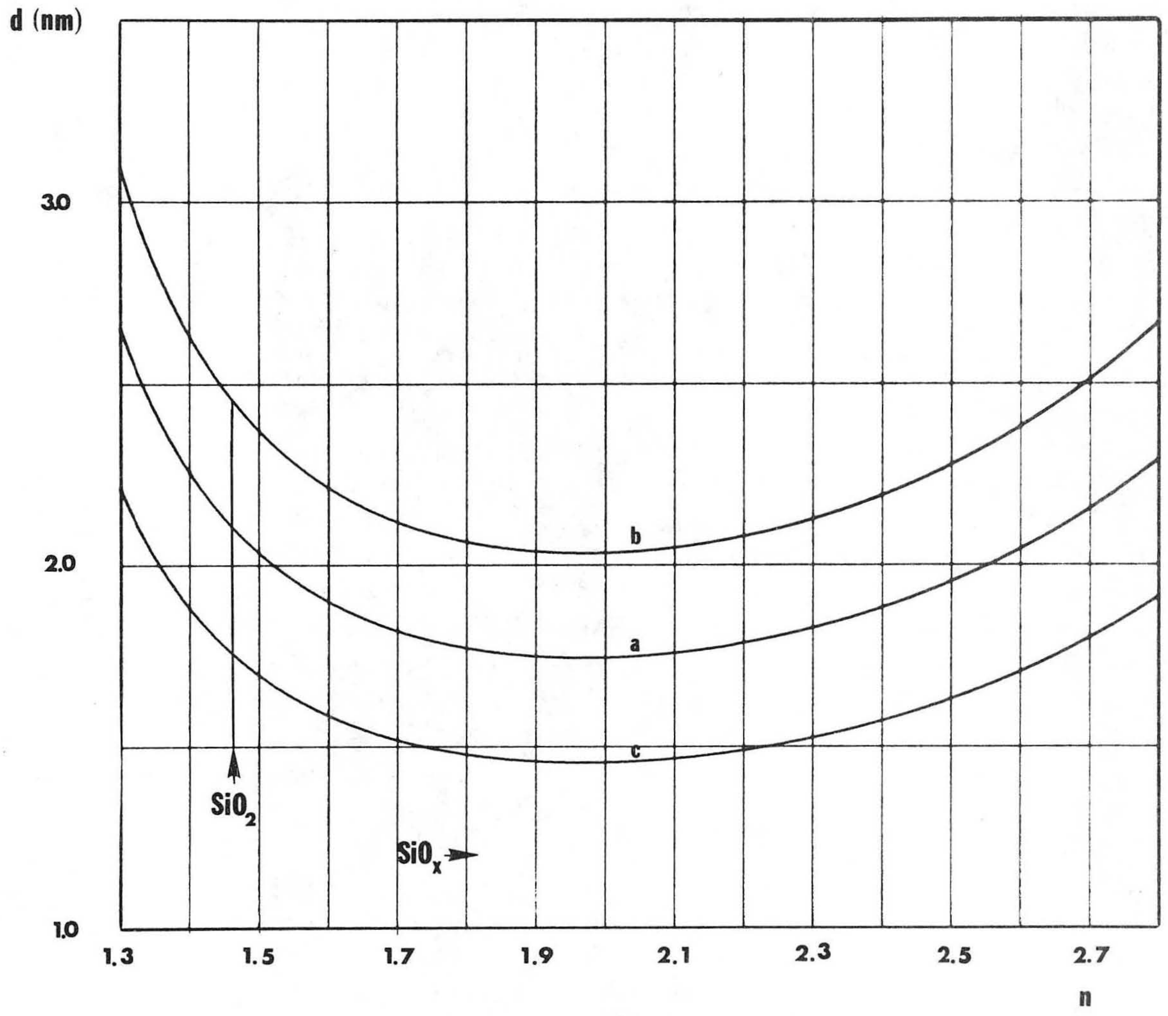
XBB 834-2499A

Fig. 2



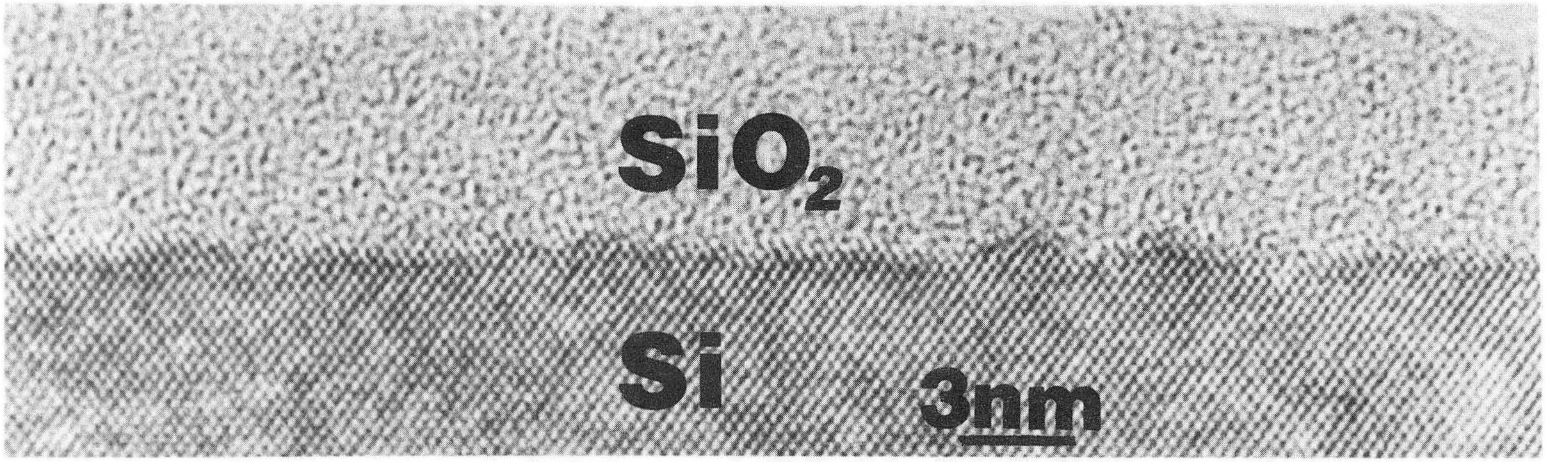
XBB 834-3022

Fig. 3



XBL 834-9192

Fig. 4



XBB 834-3055

Fig. 5

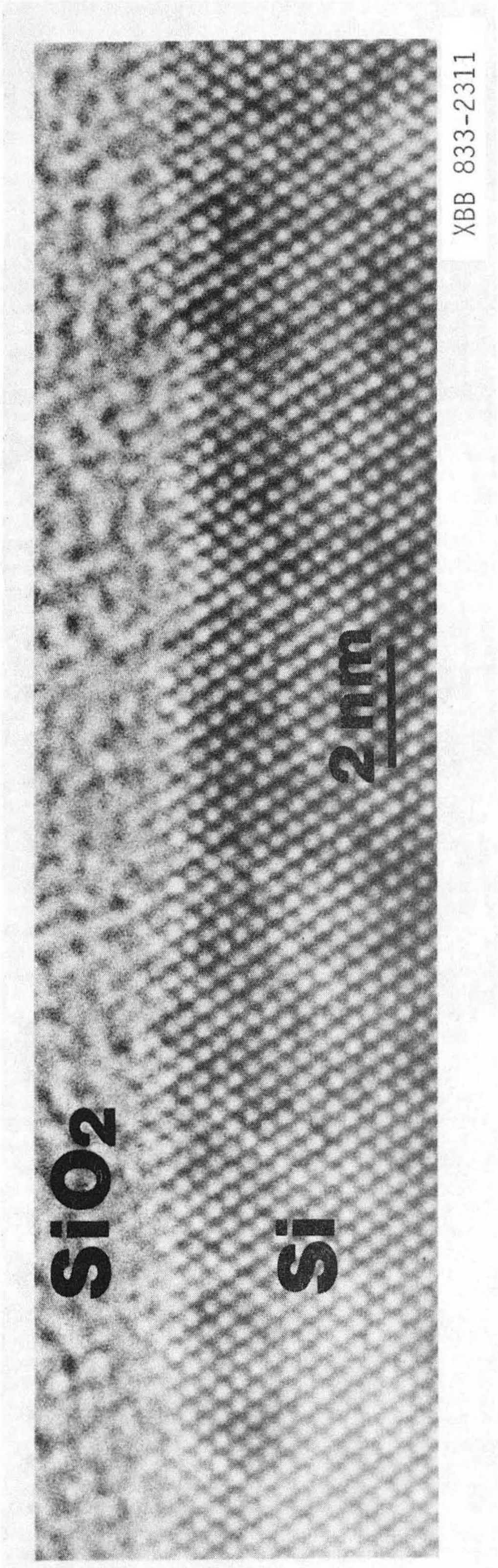
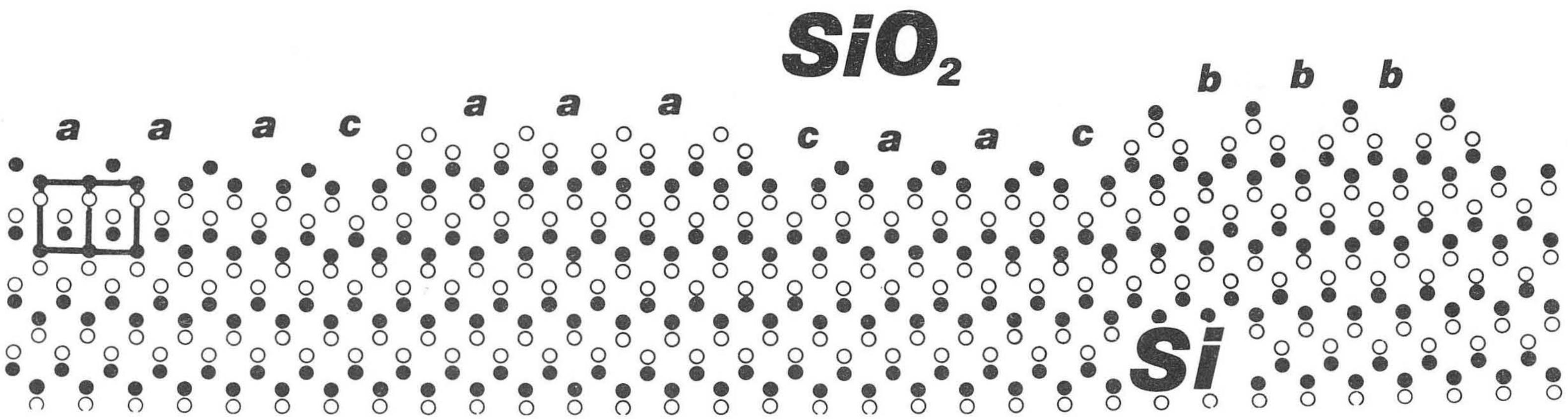


Fig. 6



XBL 834-9193

Fig. 7

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720