Title

OXIDATION OF SINGULAR AND VICINAL SURFACES OF SILICON: THE STRUCTURE OF Si-SiO2 INTERFACE

Authors

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

Publication Date

1984

LBL-17458

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

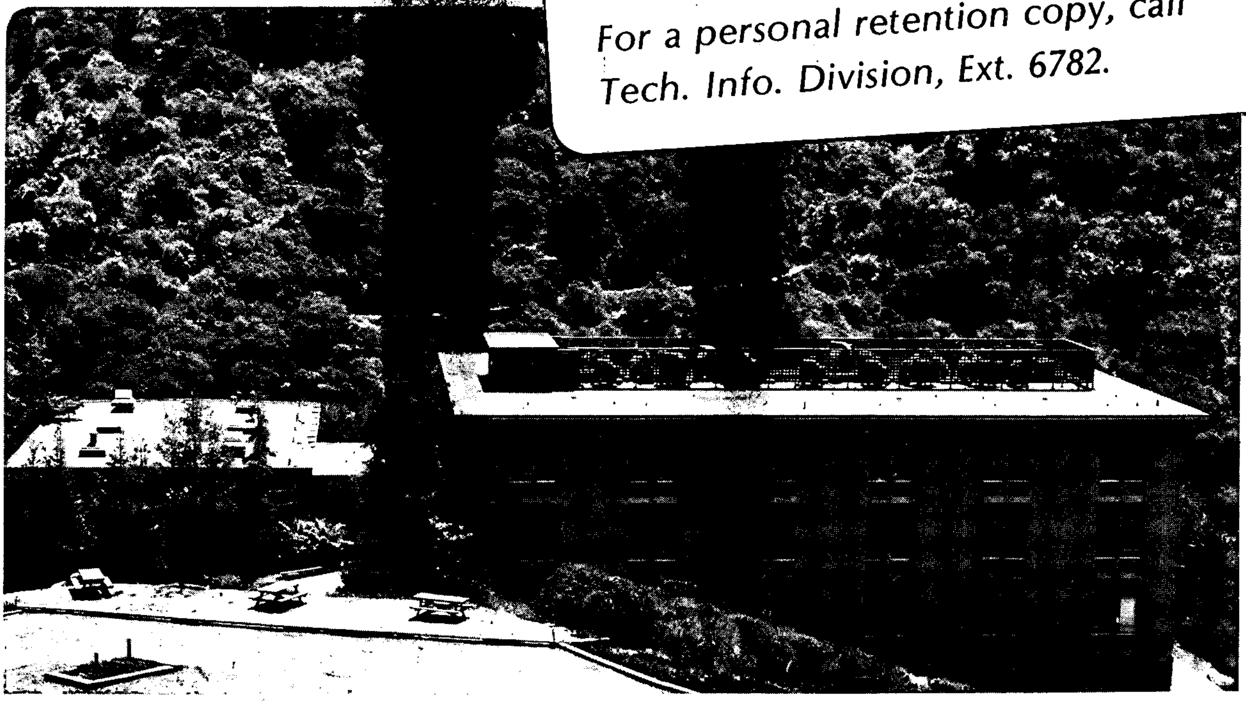
Materials & Molecular Research Division

Presented at the Los Angeles Technical Symposium of
SPIE, Conference 463, Los Angeles, CA,
January 24-25, 1984

OXIDATION OF SINGULAR AND VICINAL SURFACES OF SILICON: THE STRUCTURE OF Si-SiO_2 INTERFACE

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

January 1984



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

DISCLAIMER

Oxidation of Singular and Vicinal Surfaces of Silicon: The Structure of $Si-SiO_2$ Interface

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

Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
University of California,
Berkeley, CA 94720

Abstract

The structure of interfaces between silicon oxides grown in dry oxygen on singular and vicinal (111) surfaces of silicon has been studied using cross-sectional high resolution transmission electron microscopy. Crystalline silicon was found to terminate abruptly on (111) planes, where it transforms to amorphous SiO_2. One interplanar distance high ledges, separated by (111) terraces were found to be present on all surfaces studied. The width of the terraces was surface orientation dependent. It is suggested that such a structure of the interface can be explained by a terrace-ledge-kink model and that high temperature oxidation proceeds by a ledge mechanism similar to that for evaporation from the surface.

Introduction

The $Si-SiO_2$ interface has been extensively studied during the last few decades due to the application of thermally grown SiO_2 dielectric films in processing of bipolar and especially metal-oxide-silicon (MOS) electronic devices. This research has as its goal a better understanding of the correlation between $Si-SiO_2$ interface structure and electronic properties, and of the chemistry and mechanism of oxidation. This knowledge will be useful to the development of computer-aided design of integrated circuit fabrication processes.[1,2,3] In this paper high resolution electron microscopy (HREM) studies are reported of the structure of $Si-SiO_2$ interfaces resulting from oxidation of singular (minimum surface energy) surface of exact (111) orientation and those of vicinal orientations (within 3° of exact (111)). A few HREM studies of $Si-SiO_2$ interface structures have been published.[4,5,6,7,8] However no systematic structural studies of singular and vicinal (111) oxidized surfaces exist.

Experimental Procedures

The oxide films were grown in dry O_2 on p-type B doped (7-17 Ωcm) silicon singular surfaces having (111) orientation and two vicinal orientations, i.e., 2° off (111) towards $[11\bar{2}]$ and 3° off (111) towards $[1\bar{1}0]$. The orientation of the crystal surfaces were checked by the x-ray back reflection Laue technique.

The wafers were cleaned prior to oxidation in a series of six rinses (1) 5:1:1 H_2O: NH_4OH: H_2O (2) deionized water (D.I.), (3) 5:1:1 H_2O: HCl: H_2O_2, (4) D.I., (5) 50:1 H_2O: HF, (6) D.I. After drying in N_2 the wafers were transferred into the furnace with an oxygen atmosphere. Oxidation continued for a time sufficient to grow about 100 nm of oxide, and wafers were removed from the furnace within five minutes.

Cross-sectional transmission electron microscopy (TEM) specimens were prepared using the standard technique.[6] High resolution TEM images were obtained using a JEM 200 CX electron microscope operating at 200 kV and equipped with a high resolution pole piece (C =1.2 mm). The interface was imaged along the [1$\bar{1}$0] orientation of the exact (111) wafer and the wafer having 2° vicinal orientation. For the 3° vicinal wafer, the interface was imaged along a [10$\bar{1}$] direction.

These orientations allowed direct imaging of two sets of $\{111\}$ crystal planes and one set of $\{200\}$ Si crystal planes from the Si matrix by phase contrast procedures.[9]

Experimental Results

Structure of the Oxidized Singular (111) Si Surface

Oxidation at 1100°C in dry O_2 resulted in the structure of the interface shown in Fig. 1. The oxide is amorphous as it can be deduced from the characteristic mottled contrast and the interface between silica and silicon is very abrupt and flat over the entire area observed. Careful observation furthermore reveals the existence of steps only one 111 interplanar distance (.314 nm) high. This can be seen more clearly on the higher magnification micrograph shown in Fig. 2. The width of the terraces between positive and negative steps varies and is dependent upon defocus which indicates that these steps may not extend through the whole TEM specimen thickness. A possible interpretation is shown schematically on Fig. 3. Another interesting feature that was observed is shown in Fig. 2. The last row of crystal image spots is displaced as would be expected if there was a stacking fault parallel to the surface. Computer modeling of the image is in progress to see if alternative explanations exist.[10]

Structure of an Oxidized 2° Vicinal Si Surface

Vicinal surfaces in contact with vacuum (vapor) are expected to have steps which connect terraces of minimum surface energy, and the intesection of such steps with the terraces are themselves low energy <110> directions.[11] Figure 4 shows the 2° vicinal Si-SiO_2 interface which conforms to this model. The interface consists of approximately equally spaced ledges with the width of the terraces 7.0 - 11.0 nm and their height equal to .314 nm. The width of the ledges calculated for the inclination of the surface based on purely geometrical considerations would correspond to 9.0 nm. The terraces are atomically flat, however some positive-negative step pairs are also found to be present on some terraces as is shown in Fig. 5.

Structure Of An Oxidized 3° Vicinal Si Surface

Dry oxidation at 1000°C of a surface 3° off (111) towards [$1\bar{1}0$] resulted in the structure shown in Fig. 6.[7] The HREM image shows that (111) planes are inclined 3° off the interface plane. The Si substrate terminates abruptly at (111) terraces about 6.0 nm wide with the ledges one interplanar distance (.314 nm) high. The structure of this interface was found to be independent of the oxidation temperature and time.

In contrast to the less inclined vicinal surface no extra steps on the terraces were found.

Discussion and Conclusions

The results of this investigation demonstrate that oxidation occurs layer by layer very uniformly over large areas of the Si surface. The roughness of the surface corresponds to the height of the individual steps (.314 nm). The oxide growth corresponds to removal of the Si atoms from the substrate surface. The observed structure of the interface suggests that this process occurs at the ledges. In the case of singular (111) surfaces formation of the ledges might be envisioned as occurring by two dimensional nucleation corresponding to the formation of an oxide island in the next layer of silicon atoms. In the case of vicinal surfaces, structural ledges are already present at the interface providing sites for oxidation. However for too low a density of such ledges two dimensional nucleation still takes place resulting in terraces with additional positive and negative ledges. A similar process is observed for evaporation or dissolution of atoms from a surface into vapor or solution.[12,13] Although the Si surface in this case is in contact with solid silica the interface structure appears to behave very much as it would in contact with a liquid. This is perhaps not surprising because viscous flow of silica occurs above 960°C[14] and oxidations in these experiments were performed at 1100 and 1000°C.

In conclusion, high resolution electron microscopy studies of cross-sectional specimens of oxidized singular and vicinal (111) surfaces have demonstrated that:

(a) The SiO_2 is amorphous right up to the interface.

(b) The Si substrate terminates abruptly on atomically flat (111) terraces at the Si-SiO_2 interface.

(c) Steps one interplanar distance ($d_{\{111\}}$ = .314 nm) high are observed on both singular and vicinal oxidized surfaces.

(d) The observed structure suggests a terrace-ledge-kink model for the interface and that high temperature oxidation proceeds by a ledge mechanism similar to evaporation from the surface.

Acknowledgement

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. Stanford Electronic Laboratories Research Report TR DXG 501-82, J.D. Plummer, Ed., Stanford University, (1982).
2. Stanford Electronic Laboratories Research Report TR DXG 501-81, J.D. Plummer, Ed., Stanford University, (1981).
3. Stanford Electronic Laboratories Research Report TR DXG 501-80, J.D. Meindl, Ed., Stanford University, (1980).
4. O.L. Krivanek et.al., in The Physics of SiO_2 and its Interfaces, S.T. Pantelides, Ed., Pergamon Press, N.Y. (1978), p.356.
5. O.L. Krivanek, J.H. Mazur, Appl. Phys. Lett. Vol. 37, (1980), p. 392.
6. J.H. Mazur, R. Gronsky, J. Washburn, Inst. Phys. Conf. Ser. Vol. 67 (1983), p.77.
7. J.H. Mazur in Proc. 41st Annual EMSA Meeting, G.W. Bailey Ed., San Francisco Press Inc., (1983), p.106.
8. S.M. Goodnick et. al., J. Vac. Sci. Technol, B 1, (1983), p. 803.
9. R. Gronsky, in Treatise on Materials Science and Technology, Vol. 19B, H. Herman, Ed., Academic Press, N.Y. (1983), p. 325.
10. J.H. Mazur, J. Washburn to be published.
11. B.Z. Olshanetsky, in Studies in Surface Science and Catalysis, Vol. 9, M. Láznička, Ed., Elsevir Scientific Publishing Company, Amsterdam (1982), p. 214.
12. D.K. Burton, et.al., Phil. Trans. Roy. Soc. Vol.243A, (1950), p. 299.
13. J.P. Hirth in Energetics in Metallurgical Phenomena, Vol. 2, W.M. Mueller, Ed., Gordon and Breach, N.Y. (1965), p.1.
14. E.P. EerNisse Appl. Phys. Lett., Vol. 35 (1979), p.8.

Figure Captions

Figure 1. Low magnification HREM image of cross-section of oxide film grown on exact (111) Si wafer (dry O_2, 1100°C).

Figure 2. Higher magnification HREM image of a cross-section of the oxide film grown on exact (111) Si surface with clearly resolved steps one interplanar distance high.

Figure 3. Schematic of possible <110> ledge arrangement in the $Si-SiO_2$ interface (exact (111) Si wafer). Broken lines in the top figure are possible ledge contours in the interface plane.

Figure 4. Low magnification HREM image of a cross-section of the oxide film grown on Si surface 2° off (111) towards $[11\bar{2}]$.

Figure 5. Higher magnification image of Fig 4. Structural (one sign) and additional positive and negative ledges on atomically smooth terraces are clearly resolved.

Figure 6. High magnification image of a cross-section of the oxide film grown on Si surface 3° off (111) towards $[1\bar{1}0]$ (dry O_2, 1000°C). Structural steps are clearly resolved. (Courtesy of San Francisco Press, Inc., from reference [7]).

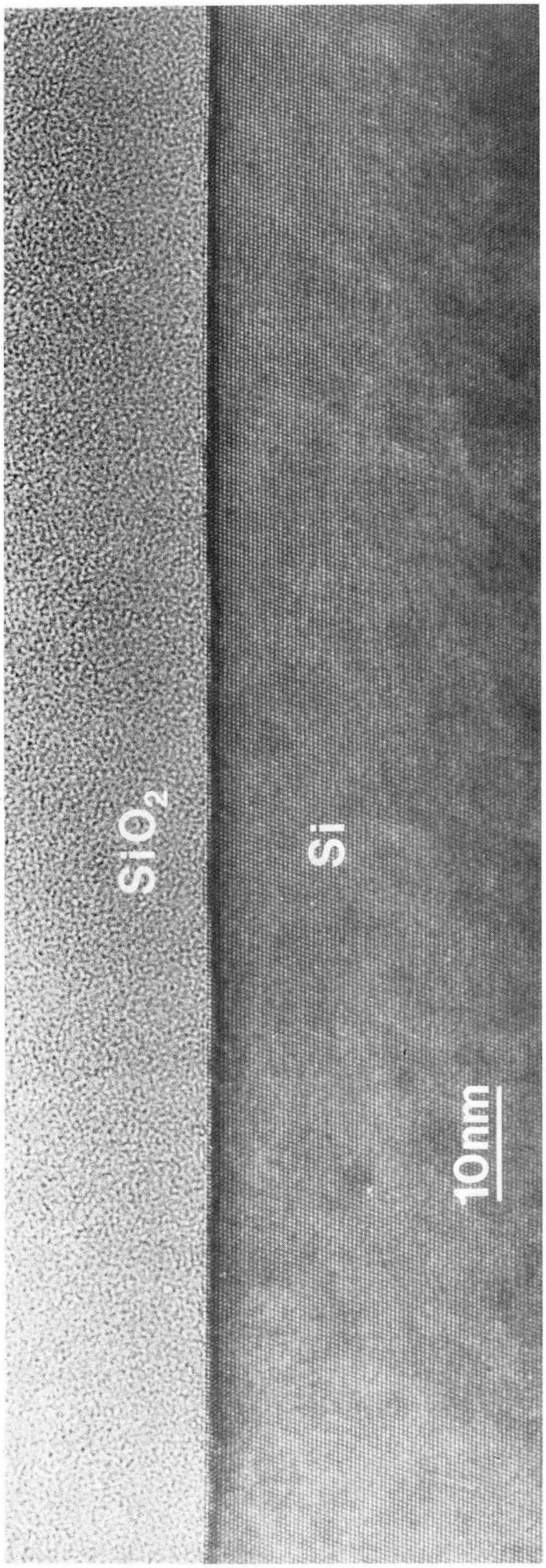
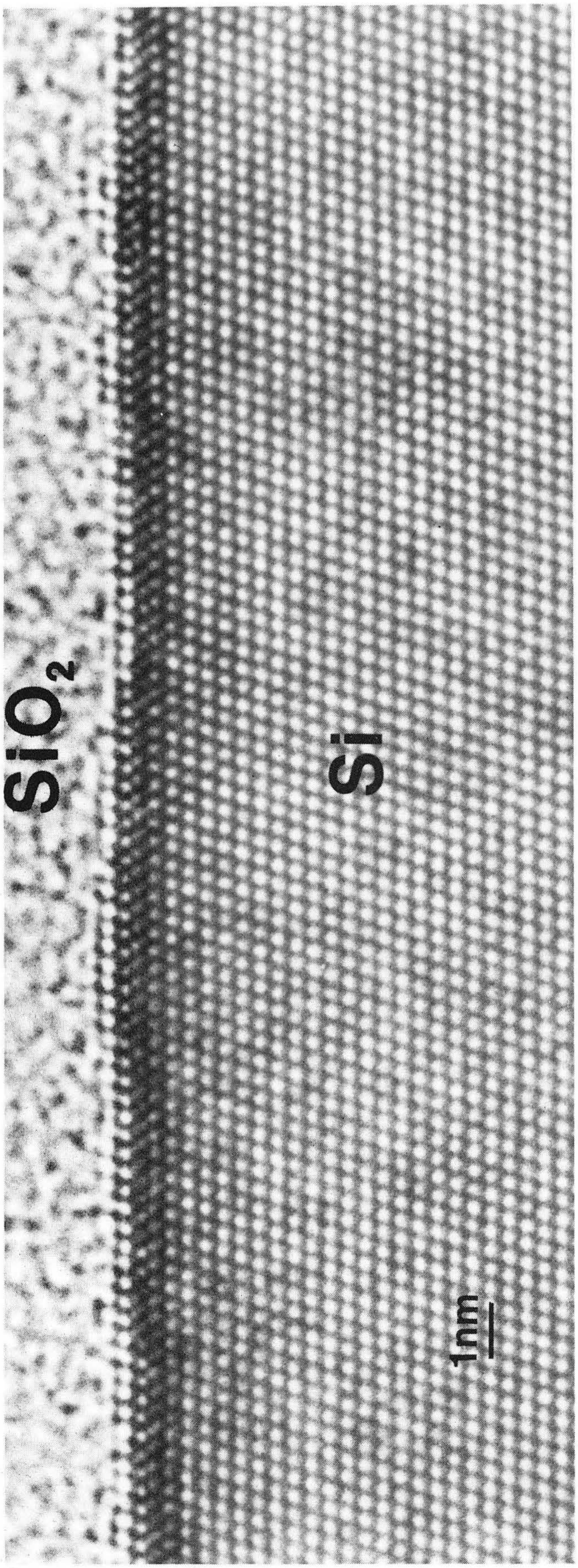


Figure 1.


SiO2
Si
1nm

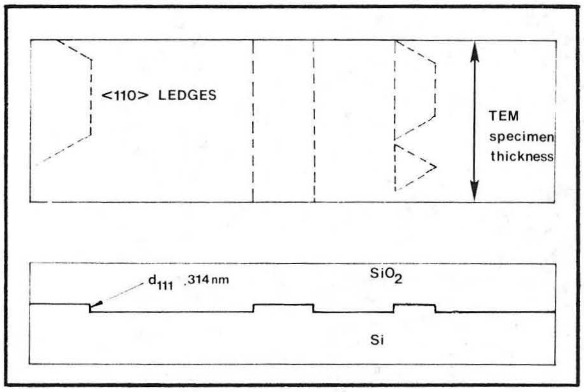


Figure 3

XBL - 842-654

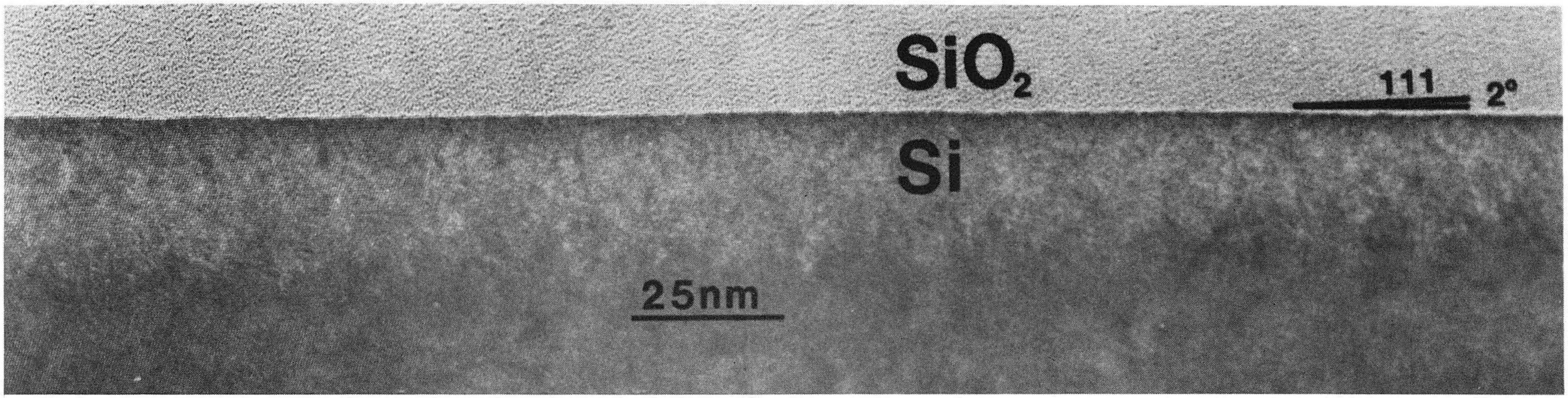


Figure 4.

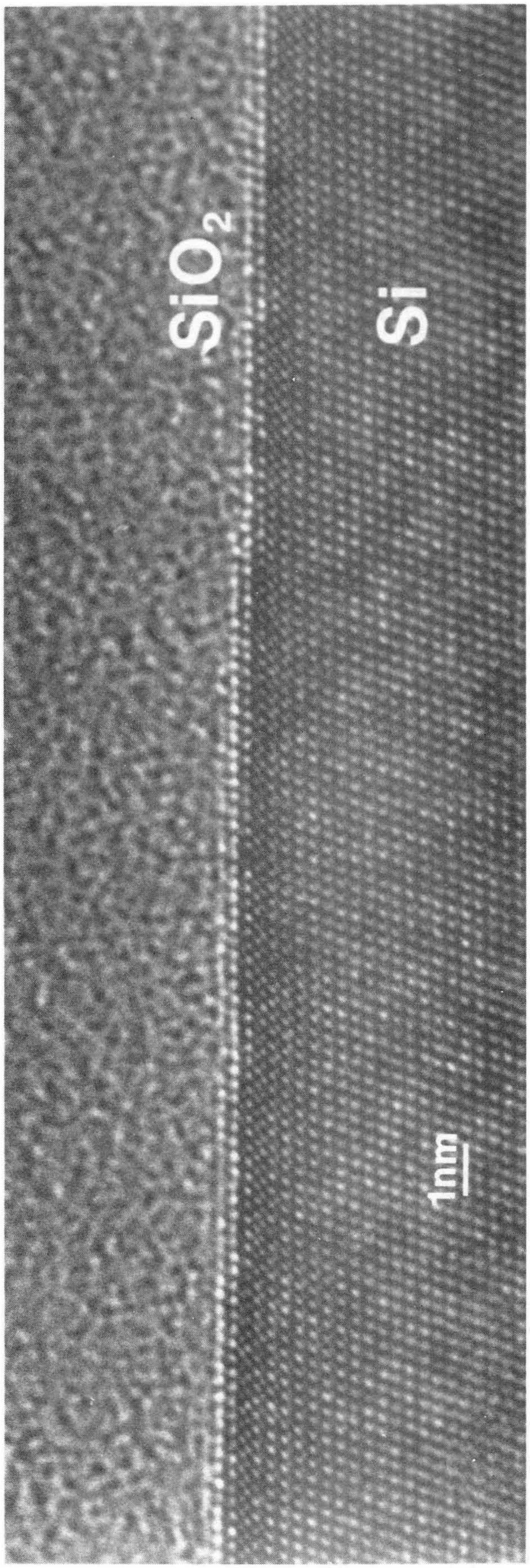


Figure 5.

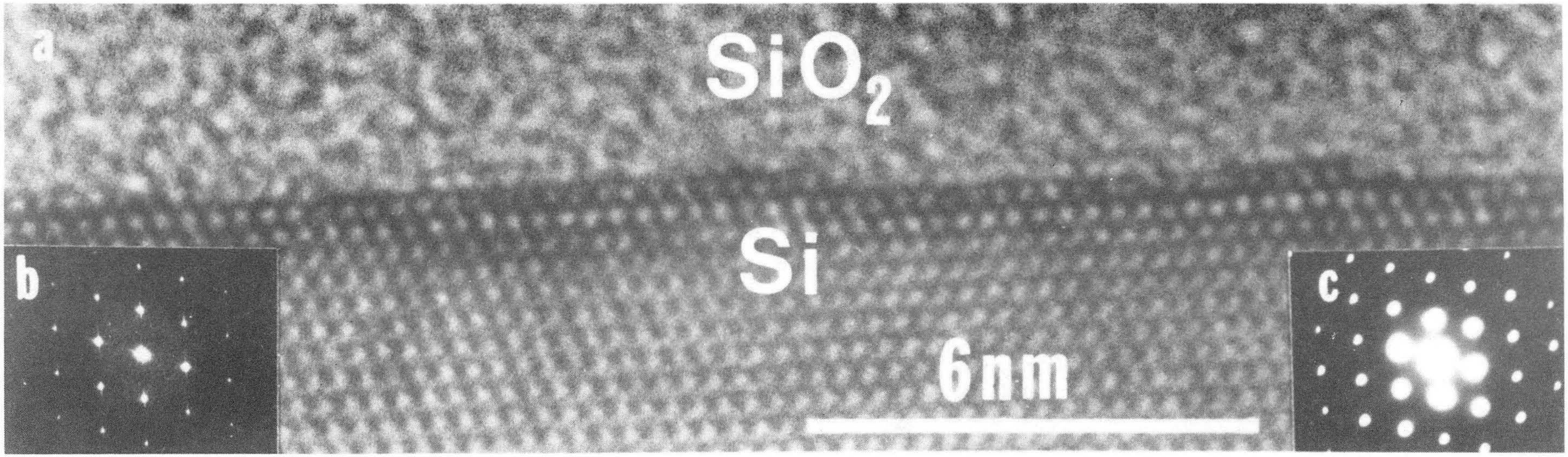


Figure 6.

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