Title

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Publication Date

1984-07-01

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Materials & Molecular
Research Division

To be presented at the International Conference
on Physics of VLSI, Palo Alto, CA, August 1-8, 1984

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July 1984

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

DISCLAIMER

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ABSTRACT

The atomic structure of Si-SiO_2 interfaces resulting from oxidation of singular $\{111\}$ and vicinal $(111)3°[1\bar{1}0]$ and $(111)2°[11\bar{2}]$ has been studied by high resolution electron microscopy. The transition from crystalline Si to amorphous SiO_2 was found to be very abrupt. The structure of the interface can be described by a terrace-ledge-kink-model. This structure is consistent with a ledge mechanism of silicon oxidation.

INTRODUCTION

The Si-SiO_2 system has been the subject of extensive investigations due to the application of thermally grown SiO_2 dielectric films in both bipolar and MOS technologies including large and recently very large scale integration.[1] Electronic processes at the Si-SiO_2 interfaces[2] which are important for MOS devices are known to be determined, in general, by interface structure which in turn is a function of the oxidation mechanism. This research attempts to establish an atomistic model of the Si-SiO_2 interface structure for different oxidizing conditions using high resolution electron microscopy (HREM) and from the interface structure deduce the oxidation mechanism.

EXPERIMENTAL PROCEDURES

Singular (111) and vicinal $(111)2°[11\bar{2}]$ and $(111)3°[1\bar{1}0]$ surfaces of CZ grown p-type, B-doped, 7-17 Ωcm silicon were oxidized at temperatures above 960°C in dry O_2. The wafers were cleaned before oxidation using procedures described elsewhere.[3] Before oxidation the native oxide was removed using 50:1 H_2O:HF solution followed by a rinse in deionized H_2O, and blow drying in N_2.

The wafers were immediately loaded in the oxidation furnace with argon or nitrogen flowing. After five minutes the ambient was changed to dry O_2 for the time necessary to grow about 100 nm of oxide. The wafers were then removed from the furnace again in the argon or nitrogen ambient within 2 minutes.

Cross-sectional transmission electron microscopy specimens were prepared by gluing two pieces of a wafer face to face with epoxy, and cutting such a sandwitch with a diamond saw normal to $\{110\}$. After grinding and double sided polishing to less than 100 μm, the section was glued to a support grid and ion milled to perforation at 5 kV and 15° incident angle. All observations were performed in a JEM 200 CX electron microscope equipped with a high resolution pole piece (C_s = 1.2 mm) operating at 200 kV. The specimens were imaged with the $<110>$ Si substrate zone axis parallel to the electron beam. This configuration of the specimen allowed imaging of two sets of $\{111\}$ planes and one set of $\{200\}$ planes edge on.

EXPERIMENTAL RESULTS AND DISCUSSION

Oxidation of singular (the lowest surface energy) {111} Si surfaces at 1100°C in dry O_2 resulted in the Si-SiO_2 interface structure shown in Fig. 1. The oxide is amorphous as is revealed by a characteristic mottled contrast. The interface between silica and silicon is very abrupt and flat over the entire area observed except for the existence of ledges only one {111} interplanar distance (.314 nm) high. The ledges can be seen more clearly on the higher magnification micrograph shown in Fig. 2. The width of the terraces between positive and negative ledges varies and is dependent upon defocus which indicates that these ledges do not always extend through the entire TEM specimen thickness. Another interesting contrast 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 in order to see if alternative explanations exist.

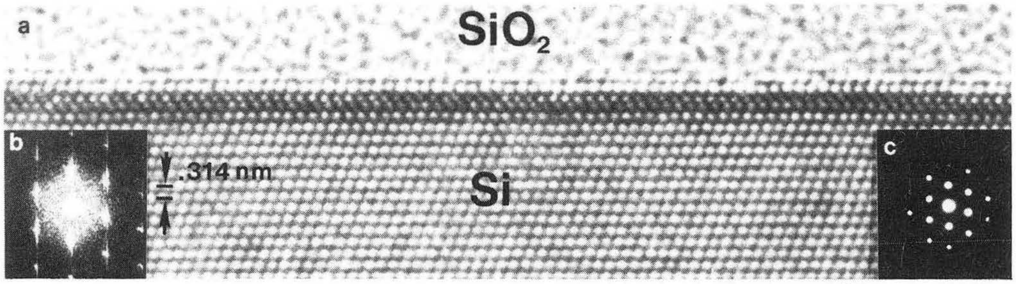

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Fig. 1. (a) High resolution electron micrograph of a 100 nm thick oxide film grown on a singular (111) Si surface at 1100°C in dry O_2, (b) and (c) optical and selected area diffraction patterns respectively demonstrating imaging conditions.

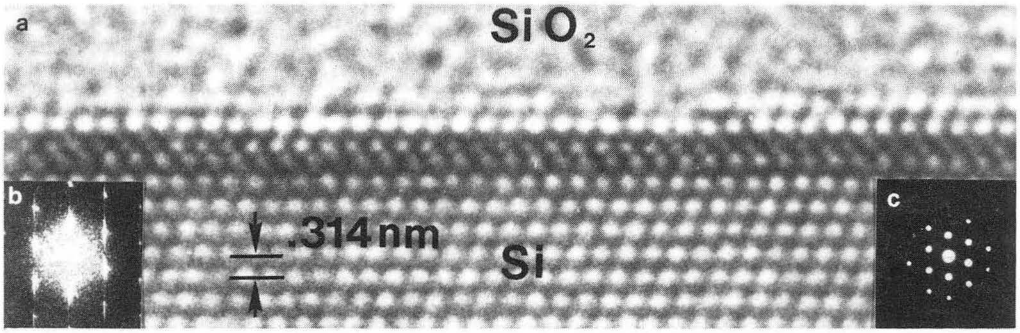

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Fig. 2. Higher magnification image of the cross-section in Fig. 1 showing details of the ledge structrue at the interface and change of stacking order near Si-SiO_2 boundary, (b) optical diffraction pattern of the image (c) selected area electron diffraction pattern.

Figure 3 shows the Si-SiO_2 interface structure resulting from the oxidation at 1000°C of a vicinal (111)3°$[1\bar{1}0]$ Si surface.[3] (Vicinal surfaces in contact with vacuum are expected to have ledges which connect terraces of minimum surface energy and the ledges would be expected to lie along low energy <110> directions). The transition from crystalline Si to amorphous SiO_2 in these specimens also takes place at flat (111) terraces about 6.0 nm wide, which are now separated by ledges all of the same sign, one interplanar distance

(.314 nm) high. This agrees very well with the calculated terrace width assuming ledges of one {111} interplanar spacing in height for a 3° inclination of the interface away from (111). A similar morphology at the Si-SiO_2 boundary has been observed for 2.0 nm thick native oxide formed on vicinal $(111)3°[1\bar{1}0]$ Si surfaces at room temperature (Fig. 4).

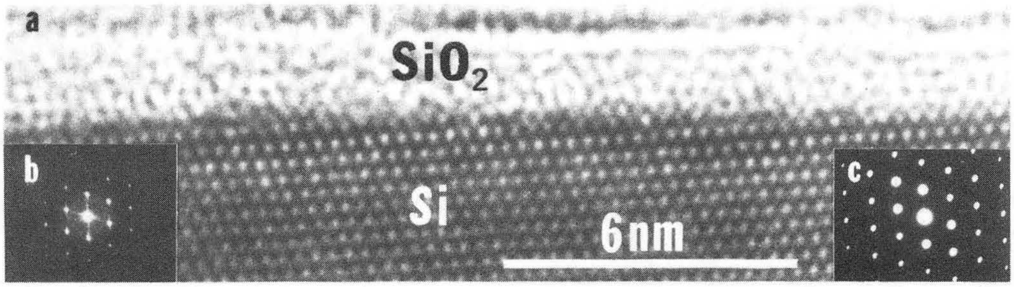

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Fig. 3. High resolution image of a cross-section of a 100 nm thick oxide film grown on vicinal $(111)3°[1\bar{1}0]$ Si surface in dry O_2, (b) optical diffraction pattern of the image (c) selected area electron diffraction pattern.

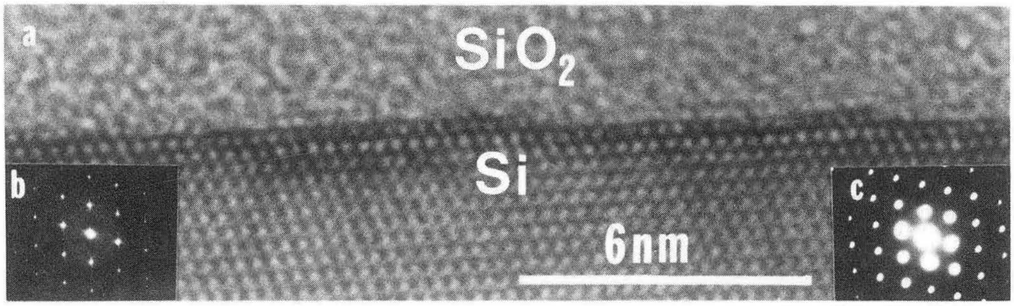

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Fig. 4. (a) High resolution image of 2 nm thick native oxide on silicon, (b) optical diffraction pattern of the image, (c) selected area electron diffraction pattern.

The structure of the Si-SiO_2 interfaces resulting from oxidation at 1100°C of vicinal $(111)2°[11\bar{2}]$ Si surfaces is shown in Fig. 5. In contrast to the more inclined Si surfaces some positive-negative ledge pairs on the terraces were observed. These step pairs are similar to those observed on singular {111} Si-SiO_2 interfaces.

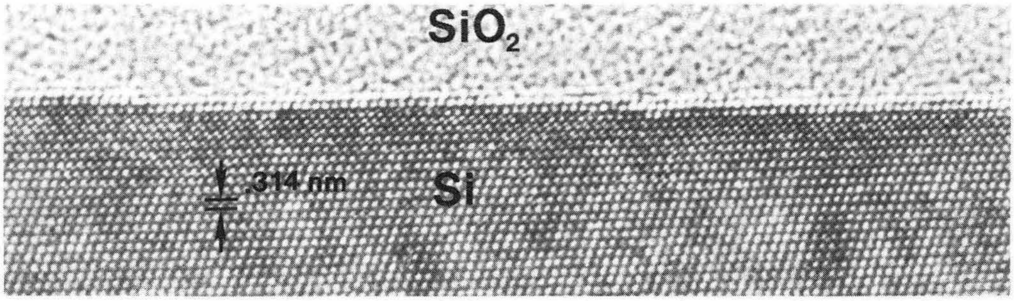

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Fig. 5. High resolution image of a 100 nm thick oxide film grown on a vicinal $(111)2°[11\bar{2}]$ Si surface.

The results of this investigation suggest that oxidation on {111} surfaces occurs layer by layer uniformly over large areas. Oxide growth apparently involves removal of Si atoms from the surface only at the ledges, probably at kinks. In the case of singular {111} surfaces, formation of the ledges must require repeated two dimensional nucleation corresponding to the formation of an oxide island in the next {111} layer of silicon. For 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 was observed to take 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.[4,5] Although the Si surface in this case is in contact with solid silica, the interface structure appears to behave as it would in contact with a liquid. This is perhaps not surprising because viscous flow of silica occurs above 960°C[6] while oxidations in this work were performed at 1100 and 1000°C.

Thus a ledge mechanism for high temperature oxidation of silicon appears to be likely and is consistent with the observed interface structure.

CONCLUSIONS

These high resolution electron microscopy studies of the Si-SiO_2 interface structure resulting from oxidation of singular and vicinal (111) surfaces have demonstrated that:

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

(b) The SiO_2 appears to be amorphous right up to the interface.

(c) Ledges one {111} interplanar distance (.314 nm) high are observed on both singular and vicinal oxidized surfaces.

(d) The observed structure suggest a terrace ledge-kink model for the interface and a ledge mechanism for high temperature oxidation similar to the mechanism of evaporation.

ACKNOWLEDGEMENTS

The authors acknowledge Dr. J. Plummer of Stanford University for providing the facilities for oxide growth and Ms. R. King for performing some of the oxidations. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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