$Si \rightarrow SiO_2$ Transformation: Interfacial Structure and Mechanism

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We show that the c-$Si \rightarrow a$-SiO_2 transformation takes place via an ordered crystalline oxide layer $\simeq 5$ Å thick. Modeling of high-resolution transmission electron-microscope lattice images in two projections suggests the crystalline oxide to be tridymite, a stable, bulk form of SiO_2.

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It has been said of silicon that were it not for the high quality of its oxide, its inferior electronic properties would have prevented its use as the dominant electronic material of semiconductor technology. More fundamentally, the oxidation of a material is an important chemical and physical process, the understanding of which is basic to our knowledge of solid-state reactions. Intense and sustained scientific activity by a variety of means for over three decades has shown the oxide in the Si-SiO_2 system to be amorphous and stoichiometric down to $\simeq 1$ nm from the interface. However, two questions of fundamental importance still remain. The first concerns the possible presence and nature of a transition layer *within* 1 nm of the interface, through which the structural change from perfect order in c-Si to disorder in a-SiO_2, and the concomitant chemical change, are affected. Thus the extent, structure, and chemical composition of such a layer remain to be established. The second, whose answer may follow from a resolution of the first, regards the microscopic mechanism by which the oxidation of Si proceeds.

Attempts to model the Si-SiO_2 interface can be broadly divided into three categories. In the first, the $Si \rightarrow SiO_2$ transition is thought to proceed via an ordered, stable, bulk phase of SiO_2, which bears an epitaxial relationship to the Si substrate. Since cristobalite is obtained by the simple insertion of oxygen atoms between the Si—Si bonds of c-Si, it has been widely suggested as the most likely candidate for an epitaxial oxide. However, although cristobalite is structurally similar to Si, its lattice parameter is 40% larger. An epitaxial relationship between Si and cristobalite is therefore difficult to achieve, and results in unrealistically severe bond distortions. The second approach proposes that the $Si \rightarrow SiO_2$ transition is affected through a "substoichiometric" oxide layer, which, although absent from the bulk phase diagram, is nevertheless stabilized by the special conditions pertaining at the Si-SiO_2 interface. Finally, it has been pointed out that it is structurally feasible to achieve an abrupt transition from c-Si to a-SiO_2, with no intervening layer.[1] None of these proposals has found convincing experimental support.

In this Letter we establish for the first time that the c-$Si \rightarrow a$-SiO_2 transition takes place via an ordered, crystalline oxide, whose structure (and hence stoichiometry) appear to be those of a stable, bulk phase of SiO_2, namely tridymite.[2] On this basis a microscopic mechanism for the $Si \rightarrow SiO_2$ transformation can be inferred. Our results may have important implications for the fabrication of Si-SiO_2 interfaces of potentially exceptional perfection.

Our samples were produced by growing 2000 Å of Si on a high-resistivity (p-type, 2000–3000 Ω cm) [001] Si substrate by molecular-beam epitaxy. This procedure produces atomically flat surfaces, which, as will become apparent below, is the key to the success of our experiments. The samples were then removed from the ultrahigh-vacuum chamber, and allowed to form a native oxide ($\simeq 15$ Å thick), or annealed in dry oxygen at 800 °C for 30 min to form an 80-Å oxide layer. Plan-view samples were prepared by chemical etching from the back and examined in a transmission electron microscope (TEM) operating at 120 kV with the electron beam parallel to the [001] direction, while cross-sectional samples were ion milled to perforation and examined in a high-resolution TEM operating at 400 kV, with the beam parallel to the [110] or $[1\bar{1}0]$ direction. The same features were observed at the Si-native oxide and Si-thermal oxide interfaces.

The samples were observed to be unusual in transmission electron diffraction (TED) with the beam parallel to the [001] direction, because they displayed intense and sharp (110) and $(1\bar{1}0)$ reflections. These reflections, forbidden in the bulk, are expected from an ideal Si surface, but have never been previously observed in samples exposed to air.[3] A 20-s sputtering of the surface with 3-keV Ar ions at glancing incidence (calibrated to damage/remove $\simeq 20$ Å) totally destroys the (110)-type reflections, thus confirming them to arise from the surface or its close vicinity. The origin of these reflections is

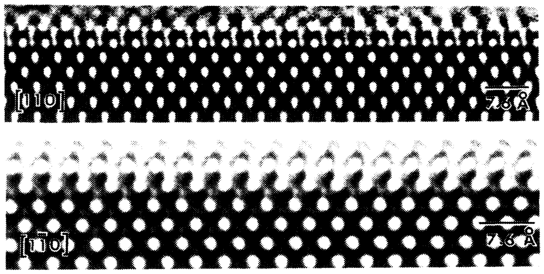

FIG. 1. Lattice images of the [001]Si-SiO$_2$ interface in two orthogonal ⟨110⟩ projections. Note the flatness and sharpness of the interface and the presence of a new interfacial structure.

at once apparent from lattice images obtained in cross section, with the electron beam parallel to the [110] or [1$\bar{1}$0] direction (Fig. 1). The *c*-Si–*a*-SiO$_2$ interface is atomically flat[4] and displays a remarkable phase at the interface about 5 Å thick, with strong (110) periodicity. This periodicity is observed under essentially all defocus conditions, but the interface appears most strikingly different from normal Si at defocus values away from the Scherzer value. This is characteristic of crystalline oxide phases of Si.[5] Although the interface displays the same periodicity in both [110] and [1$\bar{1}$0] projections, the lattice images are remarkably different in detail. This indicates the interfacial phase to have twofold symmetry. The observation of this interfacial structure constitutes the major point of this Letter and, for the first time, directly elucidates the nature of the Si→SiO$_2$ transition on the subnanometer scale.

Because of the difference in the atomic numbers of Si and oxygen, oxides display complex lattice images, whose features do not in general bear a simple relationship to the atomic positions. The determination of the structure of an interfacial oxide must therefore proceed with the matching of experimental images with simulated images of trial structures. Assessment of the reliability of the resultant structural model is complicated by the absence of quantitative means for judging the success of a fit and the problem of uniqueness. In the following we describe the procedure we have used to determine the structure of the Si-SiO$_2$ interface. We cannot be certain that the resultant model is unique.

To determine the structure of the phase observed at the interface, we have conducted a systematic search of all known phases of Si (including possible but undiscovered high-pressure analogues of Ge), as well as all known phases of SiO$_2$, as follows. To establish the candidacy of a particular phase, we required that it exhibit two planar spacings within 20% of Si(110) with the angle between these planes lying within 15° of a right angle. In this way we were seeking phases which could, with or without distortion, reproduce the observed TED. When such a candidate was found, we attempted to obtain a match between its simulated images and our experimental lattice images. It is noteworthy that while every known phase of SiO$_2$ satisfied the candidacy requirements on the basis of the diffraction information alone, only one phase, tridymite, gave rise to simulated images[6] which even resembled our experimental images. Tridymite is a stable form of SiO$_2$ with a hexagonal structure ($a=5.046, c=8.23$ Å).[7,8] The orientational relationship between the Si substrate and the tridymite satisfying the TED and imaging requirements is Si(1$\bar{1}$0)‖tridymite (100), mismatch 13.2%; Si(110)‖tridymite (002), mismatch 6.7%; Si[001]‖tridymite [010].

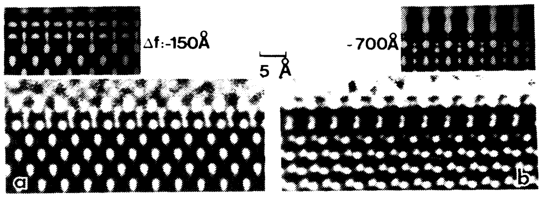

FIG. 2. Lattice images of the [001]Si-SiO$_2$ interface in the [110] projection at two defocus values. Insets: Corresponding simulated images. Sample thickness 150 Å.

Starting with the atom positions of perfect, high tridymite,[8] we have refined the interfacial structure by comparing experimental and simulated images over the thickness range 50–250 Å and the defocus range −(100–800) Å, seeking fits in the two orthogonal [110] and [1$\bar{1}$0] projections. The fitting of experimental images at defocus values far from the Scherzer value (−460 Å) is a sensitive means of structure determination and, at the same time, represents a severe test of the correctness of the model.[9] By using the *Pendellösung* oscillations and optical diffractometry to determine the sample thickness and image defocus, respectively, and fitting images over a wide range of experimental parameters in two orthogonal projections (see, e.g., Figs. 2 and 3), we have deduced the three-dimensional map of atom positions at and near the interface shown in Fig. 4.[10] As an example of our sensitivity to structural detail, the removal of the first oxygen layer bonding to Si, with no other changes, shifts the simulated image of the tridymite shown in Fig. 1(a) by $\frac{1}{4}$(Si[1$\bar{1}$0]) = 1.9 Å with

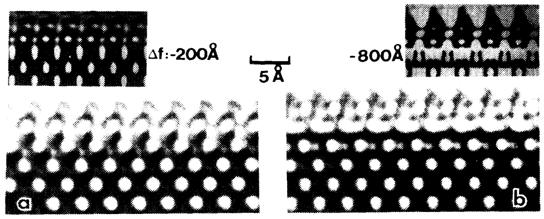

FIG. 3. Lattice images of the [001]Si-SiO$_2$ interface in the [1$\bar{1}$0] projection at two defocus values. Insets: Corresponding simulated images. Sample thickness 150 Å.

respect to the substrate, destroying the match with experiment. The character of the simulated images is not a sensitive function of the particular values assumed for the fitting parameters, but changes gradually and smoothly as the latter are varied. In particular, changes of $\simeq \pm 30$ Å in defocus or thickness do not significantly change in quality of the fits.

If we assume the oxide indeed to have the tridymite structure, the following observations can be made. The crystalline oxide is 5 monolayers (ML) thick, where each ML denotes a layer of atoms at a particular height above the interface plane. The in-plane lattice spacings of tridymite are compressed to match those of the Si substrate and provide perfect epitaxy. Detailed matching of experimental and simulated images suggests that the tridymite lattice sites in the third layer have an occupancy of $\simeq \frac{3}{4}$, while the fourth- and fifth-layer lattice sites are only half occupied and are sheared with respect to the interface. These features indicate loss of perfect epitaxy and order, most probably due to stress relief. The Si surface lattice vector $\frac{1}{2}[110]$ is 3.8 Å long, while the parallel (compressed) tridymite lattice vector [001] is 7.6 Å in length. Thus tridymite can grow epitaxially on the Si substrate in two configurations, which are identical but shifted with respect to each other by $\frac{1}{2}(\mathrm{Si}[110])$. Our lattice images in the $[1\bar{1}0]$ projection show that over the thickness of our sample ($\simeq 100$ Å), we observe both configurations in superpositions. Thus the tridymite overlayer contains planar defects, which have been extensively observed in oxides in general and tridymite in particular.[5,7,8] We further note that the Si-SiO$_2$ interface can be simply reconstructed to leave no dangling bonds by the dimerization of the remaining Si bonds. Thus the Si-tridymite interface represents the best epitaxial arrangement between Si and one of its oxides proposed to date.

On the basis of the tridymite model, the oxidation of Si is accompanied by a diamond cubic$\rightarrow$ wurzite hexagonal transition. As the deformation of Si, for example by indentation,[11,12] produces wurzite hexagonal Si, the oxidation could proceed either via a local deformation of the Si substrate, the creation of a hexagonal Si precursor phase, and its subsequent oxidation, or directly from Si to tridymite. In either case, the oxidation leads to the formation of a crystalline, epitaxial oxide phase which is in compression, and the process can be simply regarded as a particular example of strained-layer epitaxy. Since the overriding constraint is that of epitaxy with the substrate as the oxidation proceeds, and as the crystalline oxide can grow only to a certain critical thickness before stress relaxation, its extent perpendicular to the interface is limited by simple strain considerations. In this way one can understand the small thickness of the crystalline oxide and the formation of a-SiO$_2$ as simple consequences of stress relaxation. Indeed our results provide strong indication that the relaxation begins after 2 ML and is complete after 5 ML.

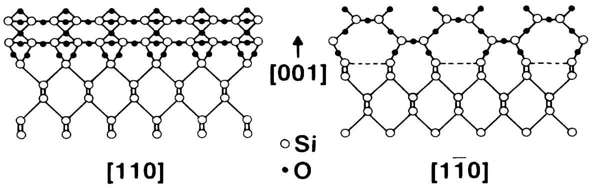

FIG. 4. Schematic representation of the interfacial atomic configuration deduced from lattice imaging. Only one of the two possible arrangements in the $[1\bar{1}0]$ projection is shown. The other is shifted by $\frac{1}{2}(\mathrm{Si}[110]) = 3.8$ Å, but is otherwise identical. Both are observed in superposition in Fig. 2. The dashed lines indicate possible dimerization of unsaturated bonds. (The small shifts of oxygen atoms from the "ideal" high tridymite sites are not shown for clarity, but used in the image simulations.)

High-resolution transmission electron microscopy has been extensively employed to study the Si-SiO$_2$ interface, but has hitherto failed to reveal the presence of an interfacial ordered oxide.[13] Our work elucidates the reasons for the previous lack of success. The essential point lies in the realization that, while the Si surface is structurally fourfold symmetric, the overlying oxide has twofold symmetry, and that the orientation of its in-plane axes (a and c for tridymite) is uniquely determined by the bond directions of the Si substrate. A step of monolayer height on the Si surface rotates the dangling bonds through 90° and thus causes a similar rotation and hence an interchange of the (tridymite) a and c axes. In other words, the overlying oxide has a grain size, which is determined by the spacing between the steps on the Si surface prior to oxidation. This argument is based on symmetry and bonding considerations alone, without reference to any particular oxide structure, and it was this realization which motivated our investigation of the oxidation of molecular-beam-epitaxy-grown samples. When the initial Si surface contains steps whose average spacing is much smaller than the thickness of a TEM sample ($\simeq 100$ Å),[13] many rotated grains of the oxide are superimposed in a cross-sectional view and the ordered structure cannot be resolved. This at once clarifies the requirement for the fabrication of an atomically perfect interface, namely the atomic smoothness (or the freedom from the presence of monolayer steps) of the initial surface. This has enabled us to produce interfaces with oxide overlayers which, on the basis of "spot checks," appear monocrystalline over macroscopic distances. The investigation of the electronic properties of such interfaces is an exciting adventure awaiting us.

In conclusion, we have firmly established that the transformation c-Si$\rightarrow$ a-SiO$_2$ proceeds via a crystalline transition layer $\simeq 5$ Å thick. The fitting of lattice images indicates its structure to be that of tridymite, a well-known, crystalline, bulk phase of SiO_2. On this basis, the oxidation process is a particular instance of strained-layer epitaxy. Our results elucidate the possible microscopic mechanism for the oxidation of Si, provide a procedure for the fabrication of interfaces of exceptional perfection, and may stimulate realistic calculations of the electronic properties of the Si-SiO_2 interface.

We acknowledge valuable discussions with A. Bourret, L. C. Feldman, P. H. Fuoss, R. E. Howard, J. C. Phillips, P. Pirouz, and W. J. Skocpol.

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[1] S. T. Pantelides and M. Long, in *Physics of SiO_2 and its Interfaces,* edited by S. T. Pantelides (Pergamon, New York, 1978), p. 339.

[2] We have previously shown that when a surface reconstruction is so strong that it survives oxidation, it is buried under an ordered oxide 2 ML thick [A. Ourmazd *et al.*, Phys. Rev. Lett. **57**, 1332 (1986)]. This is a special case where the oxygen can *only* saturate those bonds left unoccupied by the reconstruction and *necessarily* results in an ordered oxide, whose structure reflects the symmetry of the underlying reconstructed surface.

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[4] When the sample normal is inclined by $\simeq 0.5°$ to the [001] direction, we clearly resolve the resulting surface steps. In our samples, we detect no steps over our field of view of several thousand *angstroms*.

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[6] Standard simulation of high-resolution lattice images, multislice, 128 square array, supercell size $7.68^2 \times 27.2$ Å^3, half empty, 1500 beams, slice thickness 3.8 Å, objective aperture 0.6 Å^{-1}, C_s 1 mm, Δ 100 Å, 400 kV. Care was taken to ensure that Fresnel fringes did not extend over the entire empty half of the unit cell.

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[8] W. A. Dollase, Acta Crystallogr. **23**, 617 (1967).

[9] A. Bourret, J. Thibault-Dessaux, C. d'Anterroches, J. M. Penison, and A. deCrecy, J. Micros. **129**, 337 (1982).

[10] Experience in several laboratories including ours has shown tilt misalignment to be the limiting factor in modern lattice imaging. We generally find that we obtain the best fit for the first member of a through-focal series of images [cf. Figs. 2(b) and 3(a)]. We believe that this is due to tilt drift and foil buckling in the course of obtaining a through-focal series.

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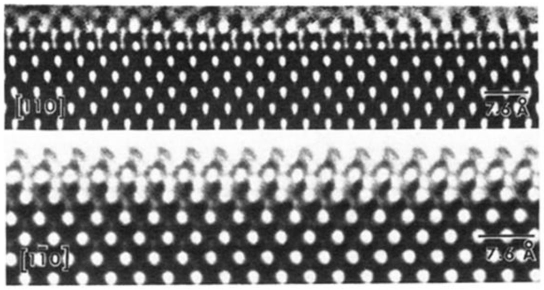
[13] See, e.g., S. M. Goodnick, D. K. Ferry, C. W. Wilmsen, Z. Liliental, D. Fathy, and O. L. Krivanek, Phys. Rev. B **32**, 8171 (1985).



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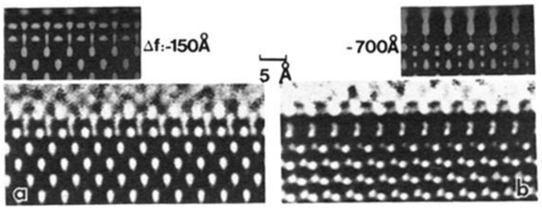

FIG. 2. Lattice images of the [001]Si-SiO$_2$ interface in the [110] projection at two defocus values. Insets: Corresponding simulated images. Sample thickness 150 Å.

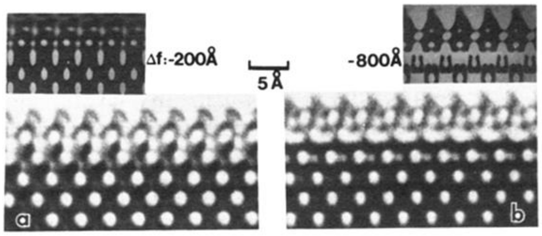

FIG. 3. Lattice images of the [001]Si-SiO_2 interface in the [1$\bar{1}$0] projection at two defocus values. Insets: Corresponding simulated images. Sample thickness 150 Å.