Dynamic Observations of Interface Propagation during Silicon Oxidation

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We have observed in real time the nature and motion of the silicon(111)/oxide interface during oxidation *in situ* in a transmission electron microscope. Oxidation occurs by the reaction of discrete monolayers with no flow of surface steps. This is in dramatic contrast to oxygen etching of silicon at high temperatures, which is initially also a terrace reaction but is followed by an evaporative process from steps.

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The behavior of surface steps and terraces is a sensitive diagnostic component in understanding the mechanism of surface reactions. We describe in this Letter how observations of terraces and steps during oxidation of the Si(111) surface lead to revisions in our understanding of the oxidation reaction. Our observations were made *in situ* in a transmission electron microscope (TEM) and show for the first time dynamic propagation of the silicon/oxide interface during oxidation. By observing the reaction of individual atomic planes in real time we show that surface steps, two monolayers in height, *do not move* noticeably during oxidation of several atomic layers of the silicon specimen. This, together with analysis of the changes in appearance of the terraces, demonstrates that oxidation is a terrace-attacking process and suggests that it occurs one monolayer at a time, with each monolayer reacting completely before the next is attacked. We discuss the implications of these results for currently held beliefs concerning the oxidation reaction, in particular on the diffusion of silicon interstitials through a reactive layer at the silicon/oxide interface. In contrast, for the "etching" of silicon by oxygen at higher temperatures, in which the volatile oxide SiO is formed, we *do* observe bilayer step movement. We deduce a mechanism which again involves oxygen reaction on the terraces, but with subsequent preferential evaporation from steps. Although not in the pressure and temperature range commonly used in commercial oxide growth, we believe that these results form a useful and interesting extension of our knowledge about the oxidation reaction, relying on our ability, unique to this experimental technique, to resolve step and terrace configurations even when buried under an oxide film.

Our experiments were done in a JEOL 200CX TEM, modified by the addition of a UHV system of 10^{-9}-Torr base pressure, a specimen heating holder, and a gas inlet valve [1]. Chemically prethinned specimens of (111)-oriented p-doped 10-Ω cm silicon were used. Surface sensitive information was obtained by analysis of *transmitted* electrons. Suitably thin clean areas were formed by resistively heating the specimen to 1200 °C so that the surface oxide desorbs and the surface flows to create locally thin regions. Upon cooling, diffraction patterns show the presence of both $\frac{1}{3}\langle 422\rangle$ reflections and the 7×7 surface reconstruction [2]. Scattering to the $\frac{1}{3}\langle 422\rangle$ position is normally disallowed in the diamond structure, but can occur if there is a nonintegral number of unit cells in the thickness of the specimen [3,4]. Since the scattered intensity is thus a sensitive function of the number of atomic layers in the specimen, images formed using electrons scattered into these reflections show steps (on either surface of the specimen), an abrupt change in intensity marking step positions (Fig. 1). We refer to these images as forbidden reflection (FB) images. The contrast re-

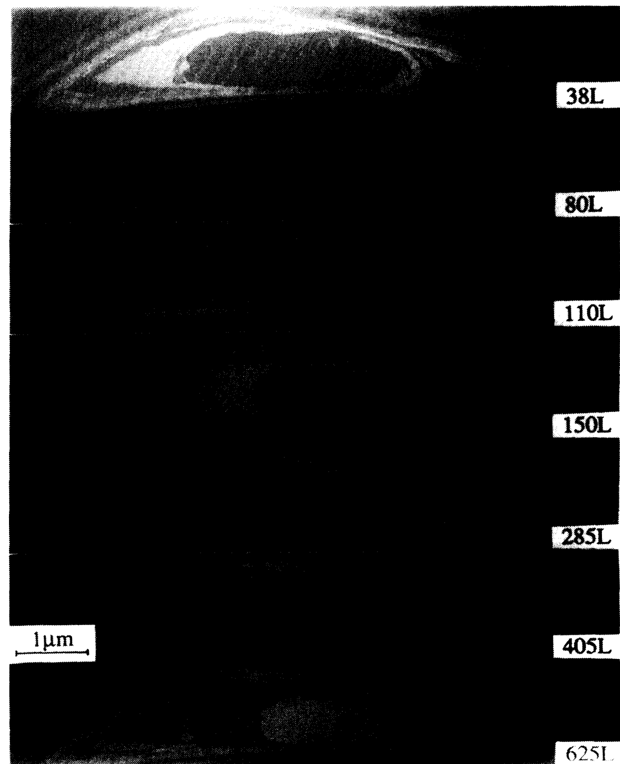

FIG. 1. Part of a series of FB images showing terrace contrast changes upon exposure at RT to 2.5×10^{-7}-Torr H_2O. Doses are given in langmuirs (1 L$=10^{-6}$ Torr sec). The image resolution is limited by the objective aperture to about 2 nm.

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mains even when the Si surface is buried, so we can follow interface step behavior during oxidation as well as etching.

Further information is obtained from FB images by comparing terrace intensity levels with calculated values. We use the multislice algorithm [5] which is widely applied for quantitative analysis of TEM results to approximate the interaction of electrons with a crystal and includes the effects of dynamical diffraction. Calculated intensities are sensitive to both the type of termination [4] and the presence of a surface reconstruction. We can thus determine how the surface configuration changes during oxidation.

We have observed oxidation from RT to 900 °C by both O_2 and H_2O under pressures ranging from 10^{-8} to 10^{-3} Torr (the electron beam remaining on during the reaction) as well as 1-atm O_2 (with the beam off), recording both diffraction patterns and FB images photographically or on videotape. The first change upon exposure of a clean surface at RT to low pressures of O_2 or H_2O is the disappearance of the 7×7 diffraction spots and a reduction in terrace contrast. This can happen very fast (within seconds at 10^{-5} Torr) under electron irradiation, but is beam induced, proceeding several thousand times slower on unirradiated areas [6]. In the case of O_2 this initial disruption of the 7×7 structure proceeds by attack of the adatom backbonds [6].

By recording FB images we can now observe the progressive reaction of deeper atomic layers at higher doses. Figure 1 shows a series of images taken during water vapor oxidation. The most striking feature is that although the terraces cycle through different shades of grey [Fig. 2(a)], corresponding, as we shall demonstrate, to the oxidation of several atomic layers, their boundaries do not move within the resolution of the images. In other words, interface steps do not move during oxidation. The same is true for native oxidation (as suggested by preliminary experiments [7]), and preliminary *ex situ* results at 800 °C and 1-atm O_2 suggest that the same also occurs during the growth of much thicker films. Thus the result is not peculiar to low-pressure oxidation. Oxidation under these conditions is clearly a terrace reaction and does not occur preferentially at the surface steps, as has previously been assumed (e.g., [8]). Oxidation at steps would randomize step positions after the reaction of only one atomic layer. This is in interesting contrast to the etching of silicon by O_2 [9]. We find that this reaction to form SiO [10,11] does proceed by step movement (Fig. 3). Furthermore we find a linear relationship between step nucleation rate and oxygen pressure, suggesting that again oxygen initially attacks the terraces, but subsequent evaporation of SiO occurs from step edges once the terraces have reacted.

Silicon surface steps are bilayers of height 0.31 nm, i.e., $\frac{1}{3}$c for the hexagonal unit cell (Fig. 4). Evidence for this comes from our observations of the newly formed surface at high temperature, and also of the contrast

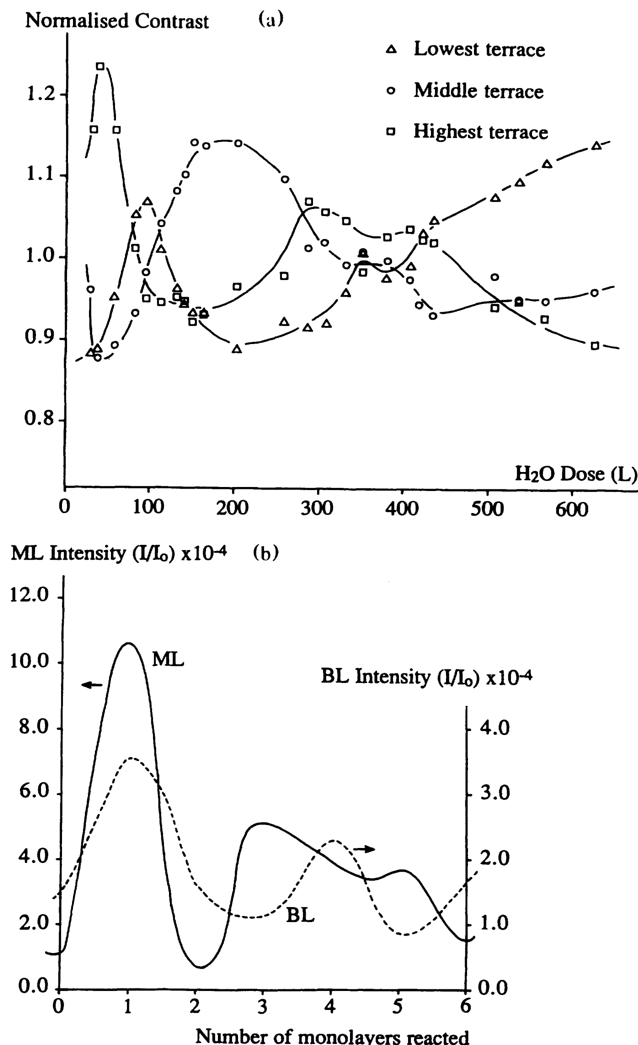

FIG. 2. (a) Conversion of the results of Fig. 1 to numerical values by digitizing the negatives and measuring the average photographic density on the terraces. Intensities are normalized to take into account the different overall brightness of the images. The central terrace in Fig. 1 is assumed to be the lowest. (b) Calculated intensities for the BL and ML models at an estimated specimen thickness of 40 nm. High values correspond to a bright shade of grey at the terrace. Only one of the three terrace levels is shown for clarity; the others are obtained approximately by translating sideways by two monolayers. All three terraces change color in a way similar to that seen experimentally. At intermediate points we assume random attack of unit cells and average the intensities.

changes upon cooling through the 1×1→7×7 transition at 860 °C. Interestingly, our measurements of the intensity levels of successive terraces during etching demonstrate directly that the termination above 860 °C is the (expected) "shuffle" [4].

Contrast changes during both etching and oxidation reflect a substantial movement of Si atoms (by more than about 0.5 Å) off crystal sites as they either evaporate or

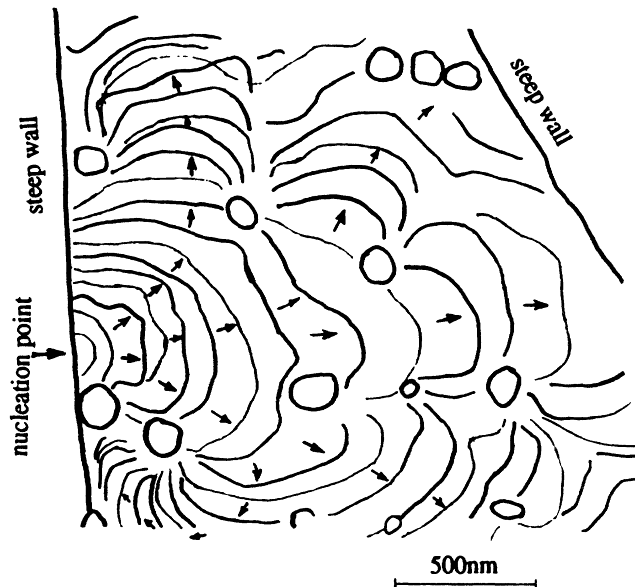

FIG. 3. The position of an individual step traced from successive video frames ($\frac{1}{30}$ sec apart) recorded during etching of the Si(111) surface at $875 \pm 50\,°C$ by 2.8×10^{-6}-Torr O_2. Note the flow around surface obstacles (SiC particles).

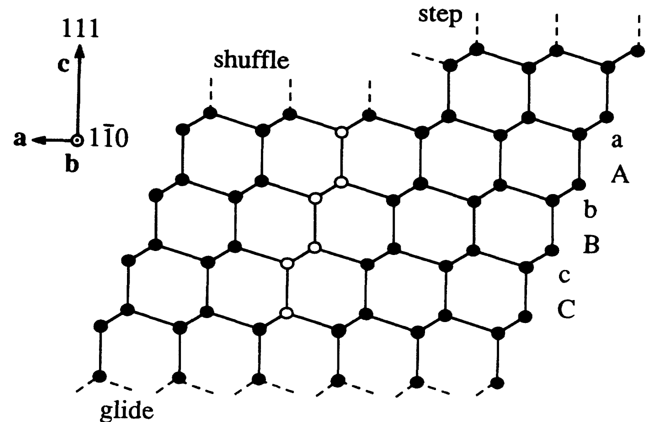

FIG. 4. Silicon projected in the $(1\bar{1}0)$ direction. The hexagonal unit cell is shown ($c = 9.4$ nm) with its six layers a–C. Two surface terminations, shuffle and glide, are possible, differing in the number of dangling bonds per atom (one or three). Bilayer steps preserve the termination.

are incorporated into an amorphous oxide. We now discuss in more detail the contrast changes observed during oxidation. An important feature of all our data [e.g., Fig. 2(a)] is that intensity levels return to high values at certain times. At such points we assume that an integral number of atomic layers have oxidized, returning the terrace to a flat configuration. (Simulated contrast levels are highest for flat surfaces.) Random attack of Si bonds would roughen the silicon/oxide interface, giving it a width proportional to the square root of the oxide thickness, whereas it has been known for some time that the interface is sharp even after thick thermal oxidation [12]. Thus it appears that oxidation occurs one layer at a time, with a lower layer not reacting until the upper layer is completely (or almost completely) reacted.

We have thus considered two possible terrace attack modes for the oxidation: first that "bilayer units" (e.g., $A+b$ in Fig. 4) are reacted at once (or in quick succession) as oxygen arrives at the surface (BL model), and second that the surface reacts one *monolayer* (a or A) at a time, the second monolayer not reacting until the first is completely oxidized (ML model). The essential difference between these is that the surface returns to atomic level flatness after every monolayer in the ML model but only every bilayer in the BL model. Computer simulations for the models are different at most specimen thicknesses and favor the second scenario for the three data sets we have analyzed [Fig. 2(b)]. (The specimen thickness is not accurately known in these experiments, which may lead to ambiguity in the results if only a single data set is analyzed. We are at present considering thickness measurements to improve the matching process.) Several important points support this suggestion of a monolayer reaction.

(a) First, it provides a natural explanation of the immobility of bilayer steps. At the intermediate stages of oxidation in the BL model there is nothing special about the site of the original surface step. Step positions will thus drift during oxidation, although perhaps not become randomized as quickly as in a step reaction mechanism. Preliminary results suggest that step positions do not drift even after the growth of thick thermal oxides.

(b) As a mechanism to encourage layer-by-layer oxidation by preventing attack below the surface, we suggest that Si-Si bonds may react preferentially if one of the Si atoms already has an Si-O bond or a dangling bond. This appears to happen in the reaction of O_2 with the *backbonds* of the 7×7 adatoms [6]. It will lead to regular growth by monolayers. Asymmetrically bonded Si atoms are polarized due to differences in electronegativity and this may be particularly important in enhancing their reaction with H_2O (or OH fragments) as happens during water vapor oxidation.

(c) As silicon reacts, the shuffle and glide terminations alternate. This is in contrast to the removal of bilayer units during etching. In the latter case the large energy difference between the two terminations may dominate the kinetics; when the surface is covered by oxide, however, the dangling bonds are saturated and this energy difference is probably much reduced.

Finally, note that a strong correlation of atomic positions in the oxide with the underlying lattice could modify the overall intensity levels we calculate, although not the way the levels change as silicon is removed. (The possibility that the reaction rate is not uniform, particularly concerning the rates for layers A and a, can also affect

the match of simulations with data.) More detailed modeling would be required to detect crystalline structure in the oxide. However, any crystalline phase must be present in low coverage ($<10\%$) or have one of a restricted range of structures in order to leave no detectable trace in the diffraction patterns. We thus envisage an abrupt crystalline-amorphous change at the interface. Furthermore, the layer-by-layer growth we propose leads naturally to a stoichiometry of SiO_2 within a monolayer of the interface, in agreement with some compositionally sensitive results [13,14].

We finally consider the relation of these results to oxidation models. In the progress of the reaction, stress, caused by the volume change, will certainly play a role. We suggest that stress is likely to be more important than is presently supposed, partly because we can discount the suggestion [15] that oxidation at step edges (or at jogs) will not introduce strain at the interface. Several oxidation models consider the effects of stress but a few, notably the reactive layer model of Stoneham, Grovenor, and Cerezo [16], also address the atomic level structure of the interface. Our results are consistent with this model with one important reservation. Modeling stress levels around steps [17] suggests that it is overwhelmingly likely that Si interstitials would be emitted at steps rather than from terraces. Any oxidation mechanism which relies on the diffusion of Si interstitials is thus also very likely to involve step movement. Thus we do not feel that Si interstitials can be the species which diffuse through the reactive layer, as proposed in [16]. Instead we suggest the diffusion of another species such as an oxygen vacancy, as in the model of Robertson [18], to account for the isotope results addressed by the reactive layer model in the initial stages of oxidation.

Although we cannot observe terrace intensities in real time during atmospheric pressure oxidation, we do know that this is also a terrace process and thus that our discussion of low-pressure oxidation has more general application. We are presently extending our technique into the pressure and temperature range addressed by most oxidation models, and we also plan to examine the (100) surface, on which steps can be imaged using (110) forbidden reflections.

In summary, we have observed the behavior of terraces and steps dynamically during etching, native oxidation, and also during low-pressure, electron-beam-induced oxidation by H_2O and O_2. We propose that oxidation occurs monolayer by monolayer at terraces with one layer fully reacted before the next begins, a mechanism which does not favor the movement of Si interstitials and which suggests an abrupt crystalline-amorphous transition. A fascinating contrast is provided by oxygen etching; it is also a terrace reaction but is followed by an evaporative process from steps. Our novel technique clearly has many other applications in the study of the atomic scale chemistry of crystal growth, adsorbates, and surface defects.

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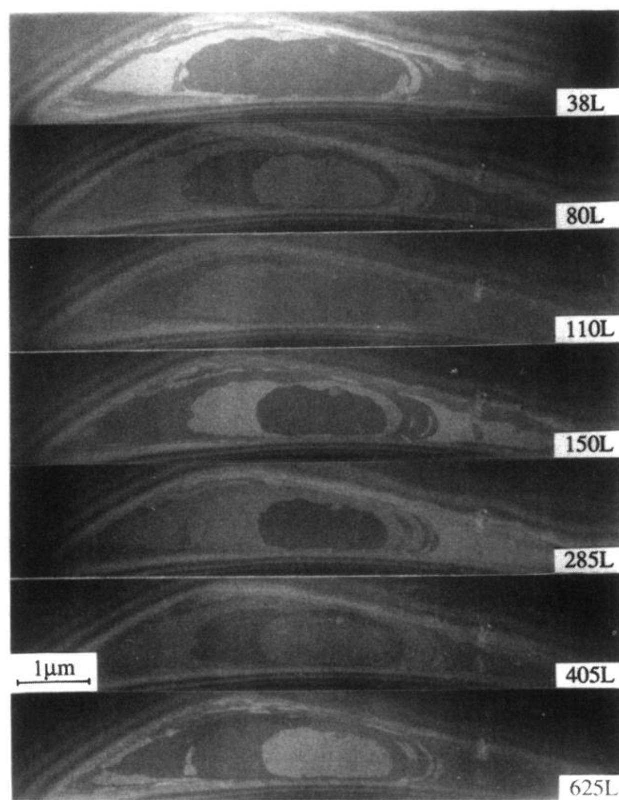

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