# Metastable oxygen-induced ordered structure on the Si(001) surface

F. K. Men and J. L. Erskine
*Department of Physics, University of Texas at Austin, Austin, Texas 78712*
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We report an oxygen-induced metastable ordered structure on a Si(001) surface. The $c(4\times4)$ structure is obtained after extensive annealing of a clean Si(001)-$2\times1$ surface dosed with oxygen at room temperature. This $c(4\times4)$ structure appears only after the completion of the $2\times1$ structure, which disappears in the early annealing stage. The $c(4\times4)$ structure reverts back irreversibly to the $2\times1$ structure after the surface is heated to above 720 °C. Possible structural models for the $c(4\times4)$ reconstruction are discussed.

The oxidation of silicon is one of the most technologically important surface reactions. Requirements for better insulating gates in metal-oxide semiconductors have stimulated intense and sustained scientific work[1] over three decades aimed at a more precise understanding of the physical properties of the Si-$SiO_2$ system, as well as the chemical processes which lead to the oxide layer and govern the interface structure.

It is now well established that the oxide resulting from oxidizing silicon is amorphous and stoichiometric to within approximately 1 nm of the interface. Ordered (bulk) oxide phases of Si exist, and several experiments[2–5] have indicated the presence of an ordered oxide layer within 1 nm of an Si interface through which the transformation from the ordered (*c*-Si) lattice to the disordered (*a*-$SiO_2$) occurs. While extensive surface studies[6–12] of the initial stages of oxidation of Si have been carried out, there appear to be no reports of stable ultrathin ordered oxide phases or ordered chemisorbed oxygen phases at silicon surfaces. The existence of such phases would have important implications in understanding the chemical processes leading to Si/$SiO_2$ interfaces, and for the fabrication of Si-$SiO_2$ interfaces of exception perfection.

We report an ordered metastable surface structure which is obtained by extensive annealing after the initial oxidation of clean Si(001) at room temperature. Figure 1(a) displays a photograph of the low-energy electron diffraction (LEED) pattern produced by the surface structure which exhibits a $c(4\times4)$ symmetry[13] superimposed on the clean Si(001)-$2\times1$ reconstruction. The diffracted beams are designated in Fig. 1(b), a schematic drawing of Fig. 1(a). In Fig. 1(b), large filled circles are integral-order beams, small filled circles are half-order beams coming from a clean, nominally flat Si(001)-$2\times1$ surface, and small open circles are from the $c(4\times4)$ structure. We emphasize that this $c(4\times4)$ structure is different from the $c(2\times4)$ buckled dimer structure[14] which has been observed on the clean Si(001) surface at low temperature. We first describe the experimental procedures used in preparing the ordered structure, and then discuss the nature and behavior of the structure.

Our experiments were performed in two separate UHV chambers equipped with LEED and other surface characterization capabilities. One chamber incorporates commercial Varian four-grid LEED optics with a double-pass cylindrical mirror analyzer Auger spectrometer and a high-resolution electron energy loss spectrometer (HREELS); the second chamber contains a high-resolution LEED system[15] which uses microchannel plates and a resistive anode position-sensitive detector to digitize LEED images. The $c(4\times4)$ pattern was obtained using both the conventional Varian LEED system (beam currents $\sim1\ \mu$A) and with the channelplate LEED system (beam currents $\leq1$ nA). We observed no apparent degradation of the pattern resulting from the electron beam. However, CO from the Auger electron gun and the conventional LEED system electron gun resulted in a fairly rapid deterioration of the $c(4\times4)$ pattern. The structure is apparently very sensitive to carbon contamination as indicated in the Auger study which will be discussed later.

Two types of Si(001) surfaces were used in our study: nominally flat surfaces with the surface normal direction within 0.1° of the (001) axis, and 4° vicinal surfaces with the surface normal direction 4° off the [001] direction toward the [110] direction. The 4° vicinal surface produces predominantly single $2\times1$ domain structures whereas the nominally flat surface yields approximately equal sizes of two orthogonal $2\times1$ domains. All samples were cleaned by standard procedures, including cleaning at 1250 °C and annealing at 900 °C, which yield sharp $2\times1$ LEED patterns associated with clean, well-ordered Si(001) surfaces.

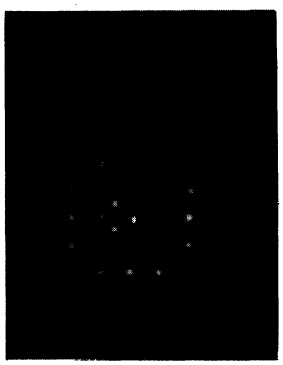
The $c(4\times4)$ structure was obtained by dosing the clean Si(001)-$2\times1$ surface at room temperature with between ten to a few tens Langmuirs of oxygen (1 $L=1\times10^{-6}$ torr sec) at an oxygen partial pressure in the $10^{-8}$-torr range, followed by extensive annealing. The pressure was measured by a Varian UHV ion gauge. Annealing at temperatures between 600 and 650 °C produced the $c(4\times4)$ structure after several hours. The surface temperature was measured using an infrared pyrometer which had been calibrated against a commercial blackbody source, and taking into account the sample emissivity and effects of the viewport. Emergence of the $c(4\times4)$ structure did not depend on whether the ion gauge was

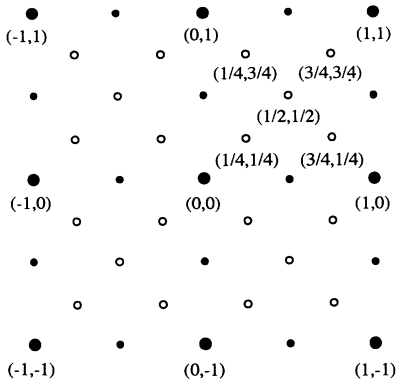
on or off during oxygen dosing.

Figure 2 illustrates the evolution of LEED images (after the oxygen dose) as a function of annealing time along with a clean surface image for comparison. The images were obtained by using a 1-in. channel plates/resistive anode detector at an incident beam energy and angle of 162 eV and 45°, respectively. The high spatial resolution of the 1 in. detector (400 line pairs) permitted analysis of the digitized spot profiles, but the limited size only allowed the (0,0), $(-\frac{1}{2},0)$, and $(-\frac{1}{4},-\frac{1}{4})$ diffracted beams to be simultaneously monitored.

The sequence of images are described in detail in the Fig. 2 caption. Immediately after the oxygen dose the $(-\frac{1}{2},0)$ beam is weak but still visible as shown in Fig. 2(b), in agreement with early LEED studies.[6] It is possible to observe the beams during annealing without disturbing the annealing process. However, the images displayed in Fig. 2 were obtained after temporarily allowing the sample to cool to room temperature thus avoiding thermal effects in the diffraction pattern.

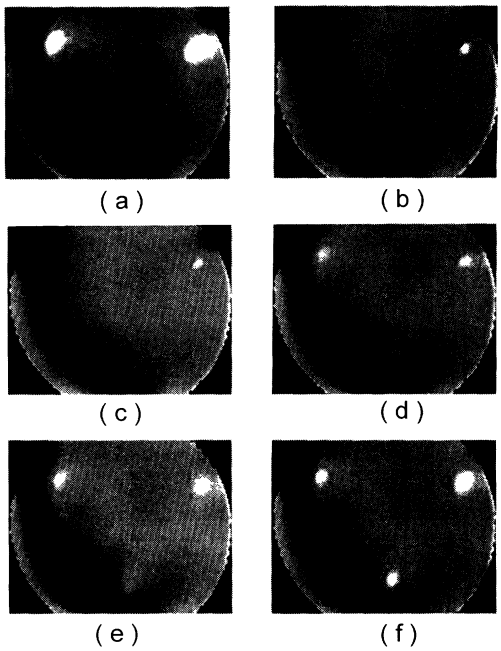


(a)




(b)

FIG. 1. The LEED pattern of the $c(4\times4)$ reconstruction. In (a), a picture of the $c(4\times4)$ LEED pattern is shown with an incident electron beam energy of 49 eV at normal incidence. The image of the sample holder can be seen in the center-upper-right region. In (b), a schematic drawing of (a) is shown. Large filled circles are integral-order beams. Small filled circles are from two domains of $2\times1$ surface structure, which are expected for a nominally flat, clean Si(001)-$2\times1$ surface. The open circles are the reflections from the new surface structure after the annealing of an oxidized surface.



(a) (b) (c) (d) (e) (f)

FIG. 2. LEED images of Si(001) surface before and after oxygen adsorption. In (a), a clean surface $2\times1$ pattern, shown are (0,0) and $(-\frac{1}{2},0)$ beams at upper-right- and upper-left-hand side corners, respectively; (b) immediately after room-temperature oxygen adsorption; (c) after 30-min annealing; (d) 307-min annealing, a beam, $(-\frac{1}{4},-\frac{1}{4})$, begins to emerge at bottom; (e) 370-min annealing; (f) 698-min annealing. Annealing temperature was at 635 °C. The beam separations in the vertical direction were expanded due to a 45° incident angle.

From the digitized images shown in Fig. 2, we have plotted in Fig. 3 the integrated spot intensities as a function of annealing time for the three beams. During the first 100 min of annealing, the (0,0) beam intensity diminishes substantially, and the $(-\frac{1}{2},0)$ beam disappears indicating that the $2\times1$ dimer structure is destroyed. After 300 min of annealing, the $(-\frac{1}{2},0)$ beam returns suggesting a reformation of a dimerlike reconstruction. As the intensity of the $(-\frac{1}{2},0)$ beam approaches its new steady state value, a new surface ordering emerges as indicated by the appearance of the $(-\frac{1}{4},-\frac{1}{4})$ beam. We believe that the reappearance of the $2\times1$ structure is a prerequisite for the formation of the $c(4\times4)$ structure. Both (0,0) and $(-\frac{1}{4},-\frac{1}{4})$ beam intensities approach their respective steady-state values after further annealing.

The structure associated with the quarter-order beams is stable at room temperature under ultrahigh vacuum conditions. Only minor deterioration of the pattern occurs after 12 h. The $c(4\times4)$ structure reverts back irreversibly to the $2\times1$ structure (on both flat and vicinal surfaces) after the sample is briefly heated to temperature above 720 °C. Repeated attempts to obtain the $c(4\times4)$ structure without oxygen doses have failed, and we must conclude that surface oxygen is required for its formation. These attempts to obtain the $c(4\times4)$ structure also rule out a mechanism associated with bulk impurities precipitating to the surface during annealing. The

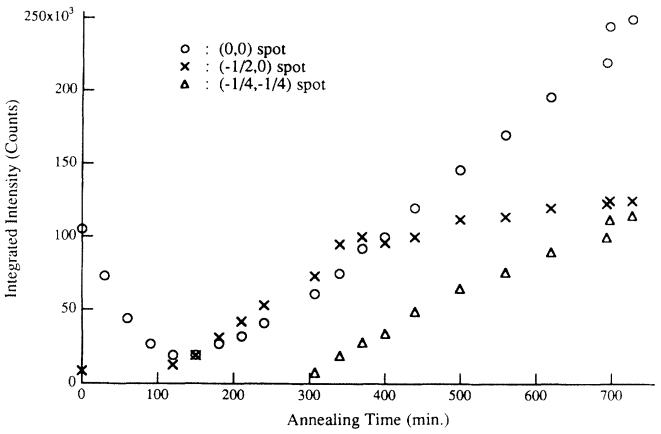



FIG. 3. Integrated intensity vs annealing time for the (0,0), $(-\frac{1}{2},0)$, and $(-\frac{1}{4},-\frac{1}{4})$ beams. $T=0$ is the time immediately after oxygen adsorption but before annealing starts. The $(-\frac{1}{4},-\frac{1}{4})$ beam appears as the $(-\frac{1}{2},0)$ beam intensity approaches its steady-state value. Both (0,0) and $(-\frac{1}{4},-\frac{1}{4})$ beam intensities approach their respective steady-state values after further annealing (not shown in the figure).

$c(4\times4)$ structure has been produced on a variety of samples cut from several different wafers, and does not depend on the particular wafer. To obtain the $c(4\times4)$ structure, it is important to dose oxygen on a clean surface. Surface impurities inhibit the development of the structure.

We have carried out an Auger analysis of our clean surfaces (which exhibit the $2\times1$ dimer structure), of the surfaces immediately after dosing with oxygen, and of the surfaces which exhibit the $c(4\times4)$ structure. These studies revealed only Si and O Auger peaks after the oxygen dose, and after annealing revealed significantly reduced O concentration. Our Auger studies rule out the possibility of C or other impurities accounting for the $c(4\times4)$ structure, and have permitted us to also deduce that CO contamination from the Auger electron gun will destroy the $c(4\times4)$ structure as the C Auger peak becomes observable. The oxygen Auger signal obtained from a surface which exhibits the $c(4\times4)$ structure is small and right around the detection threshold. We were unable to detect a well-defined (narrow) oxygen vibrational level for the $c(4\times4)$ surface using HREELS but did successfully reproduce published vibrational spectra for higher oxygen concentrations which existed prior to annealing.[16]

We have analyzed the diffracted-beam spot profiles taken from nominally flat surfaces at various stages of annealing. This analysis shows that both the $(-\frac{1}{2},0)$ and $(-\frac{1}{4},-\frac{1}{4})$ beams are initially broad, but narrow considerably as a function of annealing time. This behavior suggests that the surface ordering may nucleate from small patches which increase in size with annealing. All beam widths are instrument limited after the quarter-order beams reach their final steady-state values. From the transfer width of our system, we can place a lower bound on the average size of ordered patches on the surface of several hundred angstroms.

As discussed earlier, the onset of the $c(4\times4)$ structure occurs only after the completion of the $2\times1$ reordering and the half-order beam intensities remain unchanged as the quarter-order beam intensities approach the steady-state values. This puts a severe limitation on how surface atoms can rearrange themselves to achieve the structure. Tabata, Aruga, and Murata[14] have shown in their LEED study that the half-order beam intensity stays unchanged throughout the buckled dimer $c(2\times4)$ to the symmetric dimer $(2\times1)$ transition apart from the Debye-Waller effect. This may suggest that the $c(4\times4)$ reconstruction results from some type of long-range buckling among surface dimers.

The $c(4\times4)$ LEED pattern has been observed by a number of groups with different preparation methods.[17–19] Wang, Lin, and Wang[17] observed the $c(4\times4)$ structure by annealing clean Si(001) surfaces between 580–630 °C. By dosing a Si(001) surface with hydrogen atoms followed by annealing between 570 and 690 °C, Kato, Ide, Nishimori, and Ichinokawa[18] also detected the $c(4\times4)$ reconstruction. A reduction of diffuse scattering and sharpening of diffracted beams of the LEED pattern at a temperature $>690$ °C where the $c(4\times4)$ transfers to a $2\times1$ pattern were also reported by Kato *et al.* Based on the observation that the $c(4\times4)$ structure survives the exposure of atomic hydrogen, both groups suggest an ordered missing-dimer model as the $c(4\times4)$ structure. Wang, Shi, and Rabalais[19] also observed the $c(4\times4)$ structure by either the H adsorption on the clean Si(001) surface followed by annealing or annealing a surface recently exposed to H atoms. However, they reported the conversion of the $c(4\times4)$ to a $1\times1$ dihydride structure by exposing the $c(4\times4)$ surface to H atoms, which is contradictory to the observations made by the other two groups. Wang, Shi, and Rabalais[19] also suggested a missing-dimer structure (crosswise linked dimer) for the $c(4\times4)$ surface.

It is difficult to speculate if the oxygen-induced $c(4\times4)$ structure is the same $c(4\times4)$ structure as observed by other groups. It appears, however, that our observation cannot be the result of the H adsorption because subsurface hydrogen atoms diffuse toward the surface only through heating samples to $>1000$ °C, as observed by Wang, Shi, and Rabalais.[19] Our annealing process was performed at temperatures $\leq650$ °C.

Can the long-range ordering of missing dimers be the structural model for the $c(4\times4)$ reconstruction? The transition from $c(4\times4)$ to $2\times1$ occurs at a temperature too low to allow any appreciable sublimation of surface Si atoms to occur which would reduce the missing-dimer concentration. Neither is the step migration rate high enough to permit absorbing missing-dimer sites.[20]

In summary, we have discovered a $c(4\times4)$ metastable oxygen-induced structure on the Si(001) surface. The $2\times1$ structure is a prerequisite for the formation of the $c(4\times4)$ structure. We speculate that a combination of bulk diffusion which reduces the surface oxygen concentration, and surface diffusion subject to repulsive oxygen interactions are required to establish the $c(4\times4)$ structure. While a structure based on an ordered surface oxygen phase is considered, we cannot rule out the possibility of a clean surface reconstruction stabilized by oxygen atoms. Further investigations to establish the correct

$c(4\times4)$ atomic model and examine the link between oxygen-induced and H-adsorbed $c(4\times4)$ structures are clearly needed.

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[1]For example, see *The Physics and Chemistry of $SiO_2$ and the Si-$SiO_2$ Interface 2,* edited by C. R. Helms and B. E. Deal (Plenum, New York, 1993), and references cited therein.

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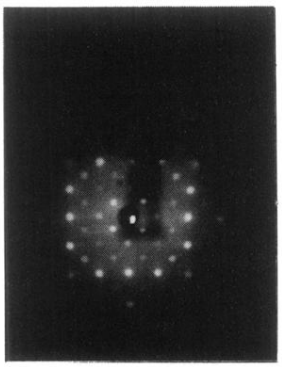
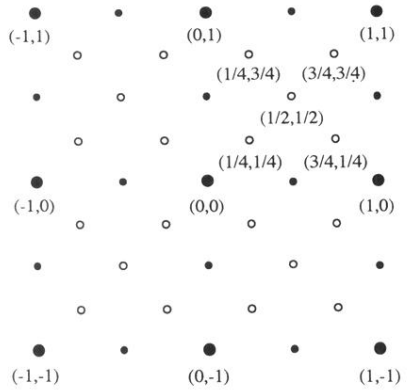


( a )




( b )

FIG. 1. The LEED pattern of the $c(4\times4)$ reconstruction. In (a), a picture of the $c(4\times4)$ LEED pattern is shown with an incident electron beam energy of 49 eV at normal incidence. The image of the sample holder can be seen in the center-upper-right region. In (b), a schematic drawing of (a) is shown. Large filled circles are integral-order beams. Small filled circles are from two domains of $2\times1$ surface structure, which are expected for a nominally flat, clean Si(001)-$2\times1$ surface. The open circles are the reflections from the new surface structure after the annealing of an oxidized surface.

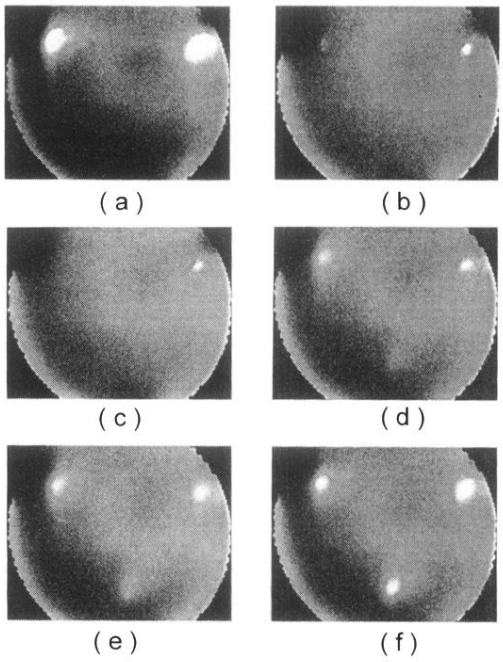



FIG. 2. LEED images of Si(001) surface before and after oxygen adsorption. In (a), a clean surface $2\times1$ pattern, shown are (0,0) and $(-\frac{1}{2},0)$ beams at upper-right- and upper-left-hand side corners, respectively; (b) immediately after room-temperature oxygen adsorption; (c) after 30-min annealing; (d) 307-min annealing, a beam, $(-\frac{1}{4},-\frac{1}{4})$, begins to emerge at bottom; (e) 370-min annealing; (f) 698-min annealing. Annealing temperature was at 635 °C. The beam separations in the vertical direction were expanded due to a 45° incident angle.