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X-ray reflectivity studies of SiO$_2$/Si(001)

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X-ray reflectivity has been utilized in a study of the SiO$_2$/Si interfacial structure for dry oxides grown at room temperature on highly ordered Si(001) surfaces. Scattering near ($\pm$ 110) demonstrates the Si lattice termination of the wafers studied is characterized by a highly ordered array of terraces separated by monoatomic steps. Specular reflectivity data indicate the "native" dry oxide thickness is approximately 5 Å with a 1-Å vacuum interface width.

Residual laminar order in the oxide electron density along the oxide/Si interfacial normal decays exponentially from the oxide/Si interface with a $\sim$ 2.7-Å decay length.

The wafers employed in this study were aligned to within 0.05° of the [001] crystallographic axis. Following evaporative removal of a protective Shiraki oxide, residual disorder in the Si lattice termination was healed through a combination of Si MBE deposition and thermal annealing. Oxides were formed in the vacuum chamber by exposing room-temperature wafers to dry oxygen at 1-atm pressure for 12 h (wafer 1) or similar dry oxidation for two weeks (wafer 2). X-ray scattering measurements were conducted at the National Synchrotron Light Source (NSLS) on beam lines X20A and X22B in a vertical scattering geometry using doubly focused radiation of 1.54-1.57-Å wavelength. To prevent uncontrolled wet oxidation, the wafers were maintained continuously in a dynamic vacuum ($2 \times 10^{-9}$ Torr) throughout transport and during the x-ray measurements.

The x-ray scattering observed in transverse scans at ($\pm$ 110) for wafer 1 is presented in Fig. 1. Scattering at ($\pm$ 110) is forbidden for an infinite Si crystal; however, truncation of the Si lattice results in diffuse rods of scattering extending in reciprocal space along the interfacial normal away from the bulk diffraction peaks.

Since the crystal is slightly miscut from the [001] crystallographic axis, rods emanating from the ($\pm 1 \pm 1$) Bragg peaks do not coincide at ($\pm$ 110), resulting in the two principal maxima observed in each of the transverse scans of Fig. 1. The secondary maxima apparent in Fig. 1 are an indication that the lattice termination is characterized by an ordered terrace structure which is the microscopic manifestation of the crystallographic miscut.

Electron scattering from stepped surfaces has been discussed by several authors. The formalism developed for electron scattering is applicable to the x-ray scattering case provided the scattering factor for the truncated column of scatterers is explicitly included. Since [001] is a fourfold screw axis for Si there are two types of lattice terminations (denoted A and B) which are related by a 90° rotation about the [001] axis. At (110) the scattering factor for a column of scatterers with a B termination vanishes while that of the A termination is nonvanishing. At (1 - 10) the situation is reversed. Using the formalism of Pukite et al., the scattering cross section for a terraced structure with monoatomic steps can be written...
FIG. 1. Scattering at (±110) for wafer 1 (●). The different peak separations at (110) relative to those at (-110) result from spectrometer resolution and scan trajectory effects. The lines represent the results of the fit to the terrace ordering model.

\[
\frac{d\sigma}{d\Omega}(110) = \frac{|F_A|^2}{\delta q_A} \Re \left[ \frac{(1 - P_A)(1 + P_B \delta^3_s)}{1 + P_A P_B \delta^2_s} \right],
\]

(1)

where this form is derived by approximating the actual terrace structure as a series of terraces with straight edges and the size of any individual terrace is assumed statistically independent of the size of all other terraces. 

\( F_A \) is the scattering factor for a column of scatterers ending in an A-type termination, \( \delta q_A \) is the in-plane momentum transfer along \( \hat{n} \) measured relative to (110) [i.e., \( \delta q_A = (q - G_{[10]} - \hat{n}) \) where \( \hat{n} \) is the in-plane unit vector normal to the terrace edges, \( l_A \) is the average type A terrace size, \( P_A \) and \( P_B \) are the Fourier transforms with respect to \( \delta q_A \) of the A and B terrace size distributions, \( S_+ = S_+ - S_- \), and \( S_- (S_+) \) is the probability of a step up (down). At (-110) the scattering cross section is identical to Eq. (1) with A and B interchanged and \( \delta q_A = (q - G_{[-110]} - \hat{n}) \).

The solid lines shown in Fig. 1 depict the results of a simultaneous fit to both transverse scans to the form of Eq. (1) after convolution with the spectrometer resolution function and using Gaussians to represent the terrace size distributions (i.e., \( P_A = e^{\delta q_A^2 / 2} - e^{\delta q_A^2 / 2} \)). The Gaussian terrace size distribution parameters determined from the fit are \( l_A = 1480 \pm 30 \text{ Å}, \ l_B = 1760 \pm 35 \text{ Å}, \ \sigma_A = 300 \pm 30 \text{ Å}, \ \sigma_B = 470 \pm 50 \text{ Å}, \) and \( S_+ = 0.994 \pm 0.006 \). The projection of the miscut into the [100] × [010] crystallographic plane (i.e., \( \hat{n} \)) is 1.6° ± 1.0° towards [100] from [010]. Comparable quality fits were obtained using exponential terrace size distributions with similar values for \( l_A, l_B \) and the miscut projection and \( \sigma_A = 240 \pm 25 \text{ Å}, \ \sigma_B = 370 \pm 40 \text{ Å}, \) and \( S_+ = 1.00 \pm 0.006 \). Regardless which functional form is utilized to represent the terrace size distribution, it is apparent the Si lattice termination is accurately described as an ordered array of large terraces separated by monoatomic steps with the average terrace size determined by the wafer miscut. We believe the perfection of the order in this terrace structure reflects the MBE preparation of the Si surface prior to oxidation rather than an intrinsic property of SiO_2/Si interfaces.

X-ray specular reflectivity data collected from wafer 1 are depicted in Fig. 2. The absolute reflectivity approaches 1.0 at small momentum transfer (not shown) as expected for a semi-infinite medium. The reflectivity data were collected with the wafer [100] axis in the scattering plane such that the staircase of terraces resulting from the miscut ascends in the direction perpendicular to the scattering plane. Since the spectrometer resolution is very coarse in this direction (100 Å typical coherence length) the observed specular scattering does not result from the coherent interference of scattered fields from adjacent terraces. Thus any interfacial normal order invoked to explain the specular reflectivity data represents the average order along the interfacial normal of any one average terrace and not an effect associated with the steps in the lattice termination level.

The specular reflectivity data were fit by comparing the measured scattering with that calculated for a model system. The model system consists of an abruptly truncated Si lattice with the oxide electron density represented by two components: ordered along the interfacial normal (i.e., laminar order) and amorphous. The laminar component decays exponentially away from the SiO_2/Si interface. This component is embedded in a smoothly varying amorphous component such that the average total electron density in any oxide layer is constant until the oxide terminates at the vacuum interface. In the Born approximation the reflectivity is given by the expression:

\[
R_q = \frac{1}{1 + \frac{1}{\delta q_A^2} \frac{P_A}{P_B} \frac{\delta^3_s}{\delta q_B^2}}
\]

FIG. 2. Absolute scattering intensity along the specular rod (●) for wafer 1. The solid (broken) line represents the results of the fit to the model with (without) a laminar oxide component. The inset depicts the average electron density along the crystal normal as determined from the fit represented by the solid line. The Si lattice extends for \( z < 0 \).


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TABLE I. Parameters from the best fits to the specular reflectivity data of wafers 1 and 2. ρ0 is scaled by the electron density of crystalline Si, d_{oxide} is the oxide thickness, and σ_{vacuum} is the oxide/vacuum interface width. The χ²'s were determined using counting statistics to represent the reflectivity data uncertainty.

<table>
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<tr>
<th>Parameter</th>
<th>Wafer 1</th>
<th>Wafer 2</th>
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<tbody>
<tr>
<td>ρ0/ρ_s</td>
<td>0.86</td>
<td>0.89</td>
</tr>
<tr>
<td>d_{oxide}</td>
<td>4.93 Å</td>
<td>4.57 Å</td>
</tr>
<tr>
<td>σ_{vacuum}</td>
<td>0.95 Å</td>
<td>1.08 Å</td>
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<tr>
<td>D</td>
<td>2.85 Å</td>
<td>2.46 Å</td>
</tr>
<tr>
<td>d_1</td>
<td>1.37 Å</td>
<td>1.35 Å</td>
</tr>
<tr>
<td>d_2</td>
<td>1.36 Å</td>
<td>1.31 Å</td>
</tr>
<tr>
<td>d_3</td>
<td>1.16 Å</td>
<td>1.19 Å</td>
</tr>
<tr>
<td>χ²</td>
<td>5.0</td>
<td>3.2</td>
</tr>
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\[
\frac{I(q)}{1} = \frac{16\pi^2 r_s^2 P(q)}{a^2 q^4} \left[ \frac{2f_s e^{-q^2/4}}{1 - e^{-\eta q^2/4}} + \sum_{n=1}^{\infty} \frac{\eta^2}{n} \right] \left[ e^{-q^2/4} + a^2 \int \rho_\text{a}(z) e^{iqz} dz \right]^2
\]

where \( r_s \) denotes the incident flux, \( r_s \) is the Thompson radius, \( P(q) \) represents a polarization correction, \( a \) is the Si lattice constant (5.431 Å), \( q \) is the momentum transfer along the surface normal, \( f_s \) is the Si atomic form factor, and \( e^{-q^2/4} \) is the crystalline Si Debye-Waller factor. The term proportional to \( 1/(1 - e^{-\eta q^2/4}) \) results from the exponentially decaying ordered oxide with characteristic decay length \( D \). The scaled Si atomic form factor \( f_s \) represents the effective atomic form factor of the ordered oxide and the Debye-Waller term \( e^{-q^2/4} \) approximates the effect of static disorder on the reflectivity. The final term denotes the scattering from the amorphous component of the oxide where the amorphous electron density \( \rho_\text{a}(z) \) has the following properties. The interface between the amorphous oxide and vacuum is described by an error function profile. Away from the vacuum interface, the total average electron density in any oxide layer \( n \) is constant (\( \rho_0 \)) with the average amorphous electron density in the layer given by

\[
\rho_\text{a}(z) = 0 = e^{-(x_0^2/2)} \int \rho_\text{a}(z) e^{iqz} dz
\]

Within a given layer \( \rho_\text{a}(z) \) varies linearly (subject to the constraint on the layer average amorphous density) such that \( \rho_\text{a}(z) \) is continuous.

The results of the best fit to the reflectivity data of wafer 1 are depicted as the solid line in Fig. 2. The parameters determined from this fit and a fit to the specular reflectivity data of a second wafer dry oxidized for two weeks are listed in Table I. The number of ordered oxide layers was restricted to three owing to the thickness of the oxide; however, inclusion of a fourth layer does not substantially alter the results. The Debye-Waller factor \( \sigma = \frac{1}{2} \) was fixed at 0.2 Å and the scale factor \( b \) was fixed at 2 which roughly the expected value for a perfectly ordered oxide. The uncertainties in the tabulated fitting parameters are typically less than the interval.

The final term denotes the scattering from the amorphous component of the oxide where the amorphous electron density \( \rho_\text{a}(z) \) has the following properties. The interface between the amorphous oxide and vacuum is described by an error function profile. Away from the vacuum interface, the total average electron density in any oxide layer \( n \) is constant (\( \rho_0 \)) with the average amorphous electron density in the layer given by

\[
\rho_\text{a}(z) = 0 = e^{-(x_0^2/2)} \int \rho_\text{a}(z) e^{iqz} dz
\]

Within a given layer \( \rho_\text{a}(z) \) varies linearly (subject to the constraint on the layer average amorphous density) such that \( \rho_\text{a}(z) \) is continuous.

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9. Momentum transfers are reported in bulk Si reciprocal lattice units (1 cm = 1.157 Å⁻¹) unless noted.
16. X-ray grazing incidence diffraction data from wafer 1 indicate the presence of weak 2×1 order at the SiO₂/Si interface. Measurements of the absolute scattering cross section of the 2×1 order demonstrate the interface coverage is only ~10% and the structure is rather disordered. (See Ref. 3 for details). Consequently, the contribution of this structure to the total scattering factor at (±110) is small and, for simplicity, we disregarded it.
17. Biatomic steps were not included since room-temperature oxidized Si(001) wafers miscut 0.05° towards [010] do not exhibit biatomic steps. G. Renaud and P. Fuoss (private communication). See also O. L. Alerhand, A. N. Berker, J. D. Joannopoulos, D. Vanderbilt, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. 64, 2406 (1990); T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, ibid. 65, 2161 (1990).