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X-ray scattering has been utilized in a study of the SiO₂/Si(001) interfacial structure. Scattering data provide evidence for a low coverage 2×1 epitaxial structure at the SiO₂/Si interface for dry oxides grown on highly ordered Si surfaces at room temperature. The observed scattering is consistent with distorted dimer models of the interfacial structure. Thermal annealing substantially reduces the order of the 2×1 structure while prolonged exposure to humid air almost eliminates the 2×1 symmetry scattering. These findings suggest that the observed 2×1 order is associated with a metastable, intermediate state of the dry oxidation process.

The oxidation of crystalline semiconductors, one of the most physically fundamental and technologically ubiquitous of solid-state processes, is poorly understood at the atomic level. For example, oxides grown on Si(001) are structurally amorphous, stoichiometric SiO₂ to within ~7 Å of the SiOₓ/Si interface; however definitive characterization of the structural and chemical evolution from crystalline Si to amorphous SiO₂ and the associated oxidation mechanism remains elusive. A broad range of experimental techniques provide conflicting evidence for (1) an atomically abrupt crystalline Si to amorphous SiO₂ transition,[1] (2) the existence of a substoichiometric SiOₓ interfacial layer up to 7 Å thick,[2] and (3) the presence of an epitaxial SiO₂ interfacial layer.[3-7] Particularly noteworthy is the evidence for an epitaxial oxide. X-ray grazing incidence diffraction (GID) data suggest that microcrystallites with a structure similar to the bulk SiO₂ phase cristobalite are present in thin thermal and native oxides.[3] More recently, a reflection high-energy electron diffraction (RHEED) and high-resolution transmission electron microscopy (HRTEM) study has demonstrated that microcrystallites, which are a structural variant of cristobalite, are formed at step edges of vicinal Si(001).[4] Conversely, HRTEM lattice images of thin oxides grown on highly ordered Si(001) surfaces prepared by molecular beam epitaxy (MBE) deposition reveal a twofold symmetric epitaxial interfacial structure which is not localized to step edges.[5] These lattice images are consistent with a model of the epitaxial order consisting of five monolayers of tridymite, another bulk SiO₂ phase, rotated and strained into registry with the Si lattice. As asserted by the authors,[5] however, uniqueness problems preclude a definitive structural determination based exclusively on lattice images. Recent GID data indicate the presence of weak 2×1 order in oxides formed by dry oxidation followed by several hours air exposure.[7]

In this letter the results of an x-ray GID and fractional order rod scattering study of the SiO₂/Si interfacial order for oxides grown at room temperature on well oriented, MBE prepared Si(001) surfaces are discussed. The scattering data support recent observations of a 2×1 interfacial structure[7] and, more important, address several crucial unresolved issues such as the extent, thermal/chemical stability, and atomic structure of the 2×1 interfacial order.

The wafers employed in this study were well aligned to the (001) crystallographic axis (<0.05° miscut). 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. Dry oxides were formed by room temperature, dry oxidation for 12 h (wafer 1) or similar dry oxidation followed by a 1 h vacuum anneal at 550 °C (wafer 2a). X-ray specular reflectivity data indicate these oxides are 5 Å thick with 1 Å typical vacuum interface roughness.[8] Wafers prepared as wafer 1 but dry oxidized for up to 14 days yield similar oxides.[8] Wet oxides were formed by exposing wafer 2a to room temperature, ~70% humidity air for 2.5 or more hours (wafers 2b and 2c).

X-ray scattering measurements were conducted at the National Synchrotron Light Source on beam lines X20A and X20C. Fractional order rod data were collected with the incident beam restricted to prevent the beam from overstepping the wafer. With a properly configured resolution function,[9] this permits absolute scattering cross-section measurements. GID data were collected with the incident beam overstepping the wafer. The wafers were maintained continuously in a dynamic vacuum (2×10^{-9} Torr) throughout transport and during the x-ray measurements.

Initial discussion is restricted to the oxide formed at room temperature in dry oxygen (wafer 1). GID measurements over two quadrants of in-plane reciprocal space resulted in observable scattering at 21 fractional order momentum transfers of the form $[m/2, n/2, 0]$ with m, n odd integers.[10] Reciprocal space symmetries reduce this set to the eight fourier components listed in Table I. The absence of scattering above background levels at $[m, 0, 0]$ indicates the observed scattering pattern results from 2×1 (coexisting with 1×2) interfacial order rather than 2×2 order. Systematic variations in the rocking curve widths indicate the correlation function is anisotropic. Correlation lengths (reciprocal of the GID peak half widths at half maximum corrected for instrument resolution) range from 5700 Å in the direction parallel to Si lattice termination terrace edges to 600 Å in the direction perpendicular to the terrace

TABLE I. GID integrated intensity data after correction for viewed area and lorentz factors and fit results. The GID data include an arbitrary scale factor; however, an approximate scale is provided in the row denoted scale where the relative rod scattering intensities at $(1/2, 1/2, \sim 1/2)$ are listed.

$(h\ k)$	Wafer 1	Model 1	Model 2	Wafer 2a	Model 3	Wafer 2b	Wafer 2c
$(-1/2, 1/2)$	1000 ± 127	977	971	1000 ± 120	1115	1000 ± 230	1000 ± 270
$(-3/2, 3/2)$	1220 ± 155	819	1379	194 ± 32	230	141 ± 44	~ 0
$(-1/2, 5/2)$	63 ± 8	62	68	~ 0	4	~ 0	~ 0
$(1/2, 3/2)$	351 ± 32	347	313	154 ± 12	136	248 ± 41	183 ± 49
$(3/2, 5/2)$	140 ± 15	164	127	~ 0	3	~ 0	~ 0
$(1/2, 7/2)$	156 ± 28	126	168	~ 0	~ 0	~ 0	~ 0
$(5/2, 7/2)$	32 ± 8	38	42	~ 0	~ 0	~ 0	~ 0
$(3/2, 9/2)$	75 ± 24	58	63	~ 0	~ 0	~ 0	~ 0
scale	1.0	--	--	0.37	--	0.12	0.005

edges. Rod data were collected for three in-plane momentum transfers. The pronounced decrease of the scattering intensity with increasing momentum transfer along the interface normal (l) in the rod data of Fig. 1 is due in part to a $1/l^2$ dependence of the resolution function. The absence of intensity modulations along the rods implies the 2×1 interfacial structure does not exceed ~ 2–3 Å in thickness.

On the basis of the symmetry of the observed GID scattering pattern, two notable models for the SiO_2/Si interface structure are excluded since the proposed epitaxial variants of bulk cristobalite[11] and tridymite[5] have 2×2 symmetry rather than the observed 2×1 symmetry. Although a wide range of model structures were examined, this discussion is restricted to several of the more promising or obvious models. Two-dimensional Patterson function analysis of the measured structure factors reveals an electron density autocorrelation map qualitatively similar to those of models of the 2×1 dimer reconstruction of the bare Si(001) surface.[12-14] Consequently, least-squares fits to several models[12-14] of the bare surface dimer reconstruction were attempted. Simultaneous variation of an overall scale factor, surface coverage and a Debye–Waller-like factor representing the static disorder of the unit cell resulted in unacceptably poor fits to the GID data ($17 < \chi^2 < 34$).

Using the first two layers of the symmetric dimer model[12] as a starting point, various distortions of the dimer were examined.[15] GID data were utilized to refine the in-plane structure while absolute scattering intensity data collected along the fractional order rods were employed to
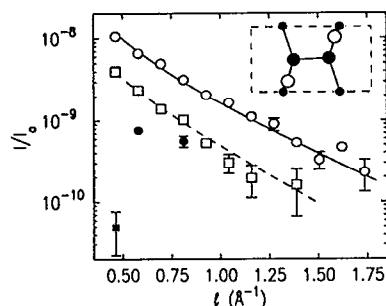

FIG. 1. Absolute scattering along the $(-1/2, 1/2, l)$ rod: wafer 1 ($\bigcirc$), wafer 2a ($\square$), wafer 2b ($\bullet$), wafer 2c ($\blacksquare$). The solid (broken) line represents the oxidized dimer fit to wafer 1 (wafer 2a) data. The inset is a plan view of the oxidized dimer model. The closed (open) circles represent Si (O) atoms.

determine the interface coverage. In principle, intensity variations along the rods provide a characterization of the interface normal structure; however, the absence of significant observable structure in the rods limits the resolution of the atomic structure along the interface normal. Reasonable agreement ($\chi^2 = 2.3$, three parameter fit) with the GID data was obtained for a 21° rotation of the dimer axis about the surface normal with a slight contraction of the dimer bond length (model 1 in Tables I and II). The fractional coverage of the interface by the 2×1 structure was determined to be $\sim 11\%$ from fits to the rod data ($\chi^2 = 3.3$, one parameter fit). In fitting the rod data, the spacing along the interface normal between the dimer and the underlying plane of Si atoms was fixed at the symmetric dimer model value of 1.15 Å.[12] Static disorder in the unit cell was included as a Debye–Waller term (u was fixed at 0.3 Å in-plane and 0.5 Å out of plane).

Models based on the ordered incorporation of oxygen and silicon atoms into modified dimer structures were also investigated. A structure based on saturation of the dimer dangling bonds with atomic oxygen while preserving the dimer bond provided the best fit to the data (model 2). Four parameters representing a scale factor, the oxygen atom in-plane coordinates and the angle of rotation of the dimer bond relative to the unit cell axis were varied to yield a $\chi^2 = 1.4$ fit to the GID data. The spacing between the dimer plane and the second layer Si plane was fixed at 1.15 Å while fitting the rod data. These fits indicate the oxygen atoms are roughly localized to the plane of the dimer ($+0.5$ Å$/-1$ Å). After fixing the oxygen atoms in the plane of the dimer, fits to the rod data indicate the fractional coverage is $\sim 8\%$ ($\chi^2 = 2.3$, one parameter fit). Static disorder in the unit cell was included in the model with u fixed at 0.25 Å in-plane and 0.5 Å out of plane. All bond lengths are within 15% of their bulk values.

The quality of the foregoing fits suggests that a structure based on a distorted dimer is responsible for the ob-

TABLE II. Atomic coordinates (Å) of the atoms in the interfacial layer of models 1–3. Each of these models includes an additional pair of Si atoms at $(\pm 1.80, \pm 1.92, -1.15)$.

Model	Dimer Si	Oxygen
1	$(\pm 1.04, \pm 0.40, 0)$	--
2-3	$(\pm 1.13, \pm 0.05, 0)$	$(\pm 1.50, \pm 1.29, 0)$

served 2×1 interfacial order. The oxidized dimer model, in particular, finds support in the literature. Photoelectron spectroscopy studies[2,16] of oxidation state distributions for oxides formed in dry oxygen at room temperature indicate that the interface oxidation states are predominately $+1$ in accord with the $+1$ oxidation state of the oxidized dimer model. Modeling of O_2 adsorption on dimerized Si(001) surfaces indicates that O_2 dissociates on the dimer through charge transfer from the dimer dangling bond to the antibonding orbital of the O_2 molecule.[17] One possible resulting (meta)stable structure preserves the dimer bond yielding a structure very similar to that depicted in Fig. 1.[17] We note that the oxidized dimer structure satisfies the steric constraint of matching the areal density of Si atoms in the terminated lattice with the areal density of Si in bulk SiO_2 (half that of the lattice termination) without introducing energetically costly dangling bonds.

An intriguing aspect of the room temperature, dry oxide data is the low interface coverage. Approximately 10% of the interfacial area has 2×1 symmetry[18] while the remaining 90% exhibits the 1×1 symmetry of an abruptly truncated Si crystal.[8] Two plausible explanations for the low coverage are (1) an energetic barrier inhibits formation of the 2×1 order for room-temperature oxidation or (2) the observed order is not the most stable interface configuration. While dry oxidation at elevated temperature provides a critical test of these hypotheses, oxidation at elevated temperatures was incompatible with our apparatus. Instead, a second wafer (2a) was prepared identically to wafer 1 but a post-oxidation thermal anneal was included. RHEED data collected before and after the anneal indicate substantial loss of 2×1 order accompanied the anneal. X-ray data confirm this observation. While the correlation lengths remain comparable to those of wafer 1, scattering intensities are substantially reduced. No fractional order GID peaks were observed with momentum transfers greater than [3/2, 3/2, 0]. This reduction in the scattering at the larger momentum transfer implies increased disorder in the unit cell. Representing this disorder as a Debye–Waller factor, acceptable fits to the GID and rod data were obtained using the oxidized dimer model with u fixed at 0.65 Å (model 3, $\chi^2_{GID} = 2.2$ and $\chi^2_{rod} = 1.0$). Evidently, the 2×1 interfacial order is *not* thermally stable. We interpret this thermal instability and the low interface coverage as indications that the observed 2×1 interfacial order is associated with a metastable structure which is presumably an intermediate state of the dry oxidation process rather than a stable interfacial phase.

Many investigations of the SiO_2/Si interface structure involve exposure of the sample to moist air. In order to compare our results to those obtained in other investigations, wafer 2a was exposed to humid air for 2.5 h (wafer 2b) and 1 month (wafer 2c). Following each of these air exposures x-ray scattering data were collected. The 2×1 interfacial order is substantially weaker for the oxide exposed to air for 2.5 h, although the correlation lengths remain comparable to those of wafer 1 implying the residual 2×1 order retains epitaxy with the host Si lattice. The GID data collected for this wafer are comparable to data

collected for similarly prepared samples of Ref. 7. The residual 2×1 interfacial order all but disappeared after a one month exposure to moist air. Clearly, long range 2×1 interfacial order is not characteristic of equilibrium "native" oxides. The instability of the 2×1 order to humid air provides indirect support for dimer based models of this structure. Upon saturation exposures of room-temperature hydrogen, the dimer bond of the bare Si(001) surface is broken and the 2×1 surface reconstruction is replaced by a 1×1 dihydride phase.[19] We speculate that a similar dimer instability is responsible for the observed loss of 2×1 interfacial order with increasing exposure to humid air.

To recapitulate, x-ray scattering data provide evidence of long-range 2×1 epitaxial order at the SiO_2/Si interface for dry oxides grown at room temperature on Si(001) surfaces. The scattering is described by distorted dimer models of the interfacial structure. The observed 2×1 interfacial order is characteristic of only a small fraction of the interfacial area and is *not* stable upon thermal annealing. Long ranged 2×1 interfacial order does not survive prolonged exposure to humid air.

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