Atomic Structure of the Epitaxial BaO/Si(001) Interface

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We present the structure of the interface responsible for epitaxy of crystalline oxides on silicon. Using synchrotron x-ray diffraction, we observe a 2×1 unit cell reconstruction at the interface of BaO grown on Si(001) terminated with 1/2 ML of Sr. Since this symmetry is not present in bulk BaO or Si, only the interface contributes to diffracted intensity. First principles calculations accurately predict the observed diffraction and identify the structure of the BaO/Si interface, including the elemental composition and a sub-Å rumpling due to epitaxial strain of the 7 adjacent BaO and Si layers.

The interface formed between dissimilar materials is a subject of widespread technical importance and scientific interest. The study of the interface between amorphous SiO_2 and Si has been particularly intense because of its central role in modern electronic devices. However, transistors based on this interface will soon reach their performance limits. In recent years, the crystalline oxide-Si system has emerged as a promising platform for scientific and technical applications [1–4]. Unlike amorphous SiO_2 or HfO_2, crystalline oxides can be deposited on Si with an atomically abrupt interface formed between the two crystal lattices. Compared to amorphous systems, theoretical calculations for such a fully crystalline interface structure have the advantage that they can be performed using the physical interface structure. Since crystal oxide-Si interfaces, like all semiconductor interfaces, are expected to strongly influence key properties, such as the energy barrier and the mobility for charge transport, detailed comparisons between theoretical and experimental results for these structures promise to enhance our understanding of the oxide-semiconductor interface.

We use the BaO/Si interface as a model system to demonstrate this interplay between theory and experiment for a fully crystalline oxide-Si heterostructure. BaO is the simplest crystalline oxide that can be grown on Si. Despite this simplicity, the BaO/Si interface exhibits a complex structure because of the marked transitions in chemistry, coordination, bonding, and symmetry. Currently, there are a number of competing theoretical proposals for the structure of this interface, which differ fundamentally on issues as basic as the elemental composition of the interface. In addition, the inherently complex chemistry and nanoscale length scales of the interface present a serious challenge for experimental structure determination. Experimental probes of crystalline oxide-Si interfaces, such as transmission electron microscopy (TEM) and x-ray diffraction (XRD), have failed to provide conclusive results on interface structure because of a lack of either resolution or sensitivity.

Here, we use a combination of synchrotron XRD and first principles density functional theory (DFT) to overcome these difficulties and fully determine the structure and composition of the BaO/Si interface. Experimentally, we measure diffracted intensity by synchrotron XRD that exhibits a 2×1 unit cell reconstruction. This scattering is only from the interface region, since bulk Si and bulk BaO do not have this in-plane periodicity. By focusing on this diffraction, we are able to address questions concerning interface structure and composition far more precisely than would be possible with diffraction from the entire structure. This diffraction reveals a sub-Å rumpling of BaO and Si layers adjacent to the interface.

Despite the interface sensitivity of the diffraction data, it is not possible from the XRD data alone to determine the precise nature of this rumpling and the elemental composition of the interface; due to the low scattering cross-section of O and Si atoms relative to Ba and Sr, many different possible interface structures can lead to the same XRD. However, DFT calculations for several classes of interface structure reveal only one that is consistent with the observed XRD data. The predicted XRD from this theoretical structure matches, with only three adjustable parameters, all of the features we observe in the experimental XRD results. Having determined the BaO/Si interface structure in this way, we also find based on DFT calculations that the observed BaO/Si 2×1 interfacial reconstruction is driven by the bonding configuration of the first monolayer of O in the BaO, that an additional monolayer of O is bonded to the surface Si atoms, and that the two BaO layers and four Si layers adjacent to the interface are significantly rumpled by the interface epitaxial strain.

Epitaxial BaO layers were grown on Si(001) surfaces by a layer-by-layer approach using molecular beam epitaxy (MBE). Crystalline oxide growth on the Si(001) surface begins with a 1/2 monolayer (ML) of Sr [1,5]; this layer exhibits 2×1 symmetry, as established by reflection high
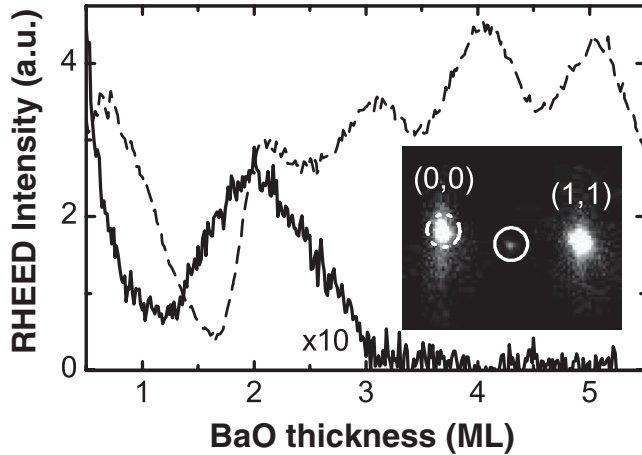
FIG. 1. RHEED intensity associated with 2×1 symmetry during the growth of BaO (solid line). The 2×1 symmetry is present for 1 ML and 2 ML of BaO. The oscillations of the (0,0) specular beam (dashed) indicate layer-by-layer growth of the oxide. The inset shows a RHEED image collected at 2 ML showing where the intensity was measured (white circles).

energy electron diffraction (RHEED). Previous experimental searches have found this 1/2 ML Sr to be required for the epitaxial growth of alkaline earth oxides on Si [1,5–7]. The "$2\times$" refers to a doubling of the lattice periodicity along the dimer bonds in the [110] direction of the Si(001) surface; the "$\times 1$" refers to the bulk periodicity in the [$\bar{1}$10] direction. During growth, we observed the surface structure of each layer and found that the 2×1 symmetry of the dimerized Si surface persists in the oxide until 2 ML of BaO were deposited (see Fig. 1) [6]. A total of 10 ML of BaO were grown at a Si temperature of 100 °C and rate of 1 ML/min by depositing Ba in an O_2 background of 10^{-7} Torr. During BaO deposition, strong RHEED oscillations of the specular beam were observed starting at 2 ML, allowing a precise determination of the growth

rate and film thickness. The rate deduced from RHEED oscillations agrees with that measured using a quartz crystal microbalance. The films were capped with a Al_2O_3 layer to protect them from ambient water vapor.

We performed synchrotron XRD on these samples at the Advanced Photon Source. A large area CCD detector was used to record the diffracted x-rays at a photon energy of 15.9 keV. The area in reciprocal space covered by this detector is $\sim 0.1 \times 0.1$ Si reciprocal lattice units (r.l.u.), which is larger than the diffraction peak (see Fig. 2 inset), allowing both the background and the shape of the diffraction to be determined for a single setting of the diffractometer angles [8–10].

These XRD measurements reveal a coherent, strained BaO/Si structure. Finite thickness oscillations observed in x-ray scans along $(1, 1, L)$ show that the BaO is coherently strained in-plane to the Si lattice constant, $a = 5.43$ Å. The BaO film out-of-plane lattice constant, based on scans along $(0, 0, L)$, is $c = 5.71 \pm 0.01$ Å, indicating that the BaO is tetragonal, with a c/a ratio of 1.05 ± 0.005. The x-ray results confirm that the 2×1 symmetry observed in the oxide during the BaO deposition persists in the final structure; we observe diffracted x-ray intensity at half-order Si reciprocal lattice points, $(n + 1/2, m + 1/2, L)$, where n and m are integers (see Fig. 2). Bulk BaO and Si lattices contribute no intensity to these rods of diffraction, so the observed intensity in these scans is exclusively due to structures at the interface. In order to collect the information necessary for a detailed determination of the interface structure, we measure a set of four rods along L up to $L = 3.5$, which are shown in Fig. 2. These four rods represent the largest momentum transfer for which the signal can be distinguished from the background. From the width of the diffracted signal in reciprocal space, we find an in-plane coherence length of 150 nm for the 2×1 structure. The observed intensity in each of the plots in Fig. 2 oscillates with a period of 1 Si r.l.u., indicating that multiple layers at the interface possess 2×1 in-plane symmetry.
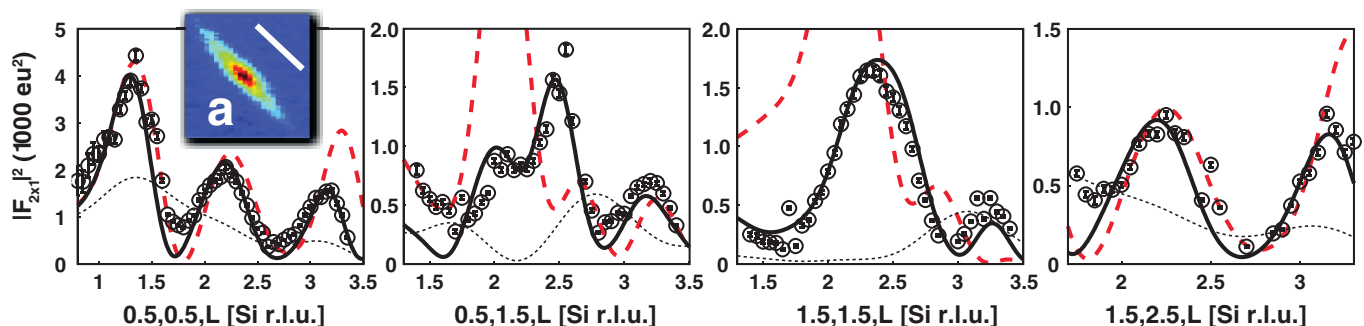

FIG. 2 (color).   Diffraction data and DFT predictions. Synchrotron x-ray diffraction data of the scattering cross section normalized to a 2×1 surface unit mesh, $\mathbf{F}_{2\times1}$, along 4 rods of the 2×1 BaO/Si(001) reconstructed interface (circles). The lines show the predicted intensity based on DFT structures with 1 ML of oxygen (solid black) and without oxygen (dashed red) at the interface, and based on a structure with 1 ML O but no BaO rumpling (dotted line). The inset (a) is a CCD image of the diffracted intensity at (0.5,0.5,2.0) of the Si reciprocal lattice. The white line is a 0.0025 Si r.l.u. scale bar aligned along the [001] direction.

We first fit the XRD data presented in Fig. 2 in the kinematic approximation [11] with a structure that features four atomic layers: the top layer of Si, the 1/2 ML of Sr, and the first two layers of the BaO. The 1/2 ML of Sr fully occupy surface sites between dimer rows of the original clean Si surface with a 2×1 symmetry and the Si and BaO layers are displaced from the bulk periodicity with a $p2mm$ plane symmetry. The correspondence between the model fit and the diffraction data is partial, with some areas of agreement but significant deviations. While fitting to a larger model would lead to better agreement, it is unlikely to accurately locate Si or O at the interface since these atoms contribute little to the XRD because they scatter x-rays far more weakly than Ba.

While the x-ray data and model fit above suggest a 2×1 rumpling of the first two layers of BaO, determining the full BaO/Si interface structures requires additional tools. Crystalline oxide-Si interfaces have been studied by TEM, but the results lack the resolution to decisively resolve questions of interface composition and structures [12]. DFT calculations have been performed for three candidate models that predict a 2×1 interface reconstruction as observed with XRD. For the first of these structures, referred to as (a) and shown in Fig. 3, the 1/2 ML Sr is adsorbed onto the surface and has no O bonded to the top layer of Si [13,14]. The second structure, referred to as (b) and also shown in Fig. 3, is the same as (a) except that 1 ML of oxygen is bonded to the silicon surface [13,15]. A third structure, referred to as (c), differs from (a) by the addition of 1/2 ML of Si at the BaO/Si interface (not shown) [1]. Other crystal oxide-Si structures with a 1×1 interface have been proposed based on DFT calculations [16], but are not considered here because they are inconsistent with the 2×1 interface observed by synchrotron XRD.

We are able to address the unresolved questions of the BaO/Si interface structure by comparing the diffraction expected from DFT relaxed ground states with the experimentally obs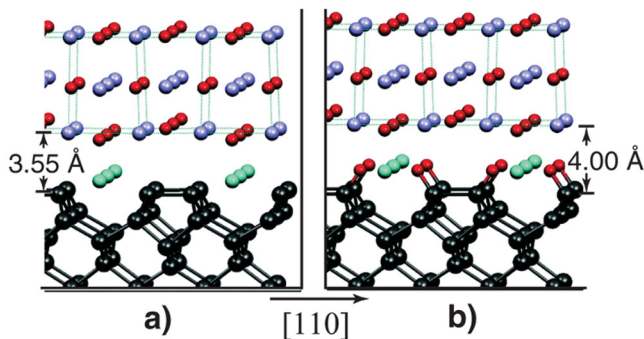erved XRD data. This approach has a number of advantages over structure refinement from XRD data only. The DFT relaxed ground states are sensitive to the position and composition of the interface, including weakly scattering elements such as O and Si that make little direct contribution to the diffracted intensity. Also, predictions for XRD from the DFT relaxed structures can be compared to experimental XRD results for important regions of reciprocal space only, i.e., those related to the 2×1 interface reconstruction. These advantages flow from the ability of DFT to identify physically realistic ground states that represent local minima in the atomic position energy landscape. However, DFT calculations cannot make a unique prediction for the physical interface structure because the absolute stability of each interface depends on assumed values for the chemical potentials of the elements that make up the structure, which are difficult to derive from the experimental conditions. Also, kinetic barriers may trap the physical interface into a structure that is different from the equilibrium structure. By combining the synchrotron XRD and DFT results, we can overcome the ambiguities that exist when these techniques are used independently to find the interface structure of our physical BaO/Si sample.

We compute ground state structures using DFT under the generalized gradient approximation (GGA-PW91) [17]. The band structure and energy were well-converged with a 30 Ry energy cutoff and an $8 \times 8 \times 8$ Monkhorst-Pack k-point mesh. The structural slabs are formed of 7 atomic layers of Si, an interfacial layer, and 4 atomic layers of BaO. A 2×1 surface unit cell is used, with in-plane lattice parameters corresponding to the theoretical Si lattice constant. The slab is terminated with H at the bottom surface, with a vacuum of 12 Å separated periodic copies out-of-plane. The bottom 3 atomic layers of Si are held fixed in the computed bulk positions. The other Si atoms, the interface atoms, and the BaO are relaxed completely.

The results of these calculations for structures (a) and (b) are shown in Fig. 3 and enable a quantitative comparison with the experimental x-ray data. In order to distinguish between the three proposed structures, we compare directly the measured x-ray scattering with that predicted for the DFT relaxed structures. We find that we can accurately model the measured x-ray data only with structure (b). This model of the diffracted intensity, shown as the solid line in Fig. 2, uses the atomic coordinates from the DFT relaxed structure with a single modification. Since our DFT calculations underestimate the epitaxial compressive strain on the BaO film [18], we allow a 3% out-of-plane expansion of the BaO structure. In modeling the diffraction from this BaO/Si structure, we have two adjustable parameters. The first parameter is an overall intensity scaling factor. The second parameter is a single Debye-Waller factor of 0.5 Å rms displacement to account for statically and thermally induced disorder, which exponentially reduces the expected intensity as the square of the momen-

FIG. 3 (color).   (a) The interface phase is predicted by DFT to be an adsorbed 1/2 ML Sr on top of dimerized Si with a rumpled BaO layer on top, (b) O is added to the structure of panel (a). O—red, Ba—blue, Sr—cyan, Si—black.

tum transfer. Comparing the predictions of this model with the x-ray data results in an *r* factor of 8%. Finally, we note that structure (a) does not reproduce many features of the measured scattering (dashed line of Fig. 2) and the diffraction predicted for structure (c) is unlike the measured diffraction in almost every way (not shown).

Insight into why the structure (b), with 1 ML O at the interface, provides an excellent fit to the x-ray data can be gained by comparing the calculated DFT structures. The Ba-Ba dilation or expansion for structures (a) and (b) are both 9% (0.013 nm), while for structure (c) it is less than 1%. This rumpling for (a) and (b) is due to the asymmetric charge distribution at the interface related to Sr-O bonding and is largely eliminated when all O anions in the first BaO layer form direct bonds to cations (Sr and Si) in the interfacial layer, as happens only in structure (c). A comparison of diffraction from the rumpled and unrumpled configurations is shown in Fig. 2. The real space differences between structures (a) and (b) that lead to structure (b) being a far superior match to the x-ray data are more subtle. For both structures (a) and (b), DFT predicts that the Si and BaO rumpling decays exponentially away from the interface. We find that the major difference is that the gap between the BaO and Si is 0.5 Å larger with the 1 ML O present. This extra distance has a strong effect on the measured x-ray intensity in Fig. 2 and allows us to identify the physical BaO/Si interface as containing both 1 ML of O and 1/2 ML of Sr.

The experimental identification of the interface between BaO/Si is a critical step in understanding the origin of key electronic properties, such as the conduction band offset [19]. Previous DFT calculations have found that the conduction band offset is increased by the inclusion of O at the interface for SrTiO$_3$ on Si [13], resulting in properties that are more suitable for device applications. For the BaO/Si structure, we calculate an increase of 0.7 eV in the conduction band offset for interfaces with 1 ML O. The inclusion of O serves to reduce the dipole at the interface by moving a sheet of negative charge from the top Si layer to the O layer, which is closer to the sheet of positive charge in the strontium layer.

In summary, we have determined the interface structure responsible for crystalline oxide growth of BaO on Si. We use the existence of an epitaxial strain-induced reconstruction at a buried interface to transform XRD into an interface specific technique. Diffraction from the interface reconstruction is dominated by a rumpling of the BaO layer having a 2×1 symmetry. We note that the absence of a RHEED oscillation at 1 ML BaO may indicate that the rumpled structure forms only after 2 ML BaO are deposited. With the XRD data only, we cannot determine the Si and O composition of the interface due to their insignificant contribution to scattered intensity. We are able to fully solve the BaO/Si interface structure by combining these XRD results with DFT calculations. The XRD results match those predicted for a DFT relaxed interface structure with only three adjustable parameters: an overall scaling, a Debye-Waller factor and a BaO out-of-plane expansion. We find that the physical BaO/Si interface contains 1/2 ML Sr and 1 ML O bonded to dimerized Si surface atoms. This collaboration of first principles DFT, high quality crystalline oxide on Si MBE growth, and interface XRD is a powerful paradigm for understanding these heteroepitaxial interfaces and provides a model system for understanding the properties of oxide-Si interfaces.

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