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Abstract
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Evolution of the Structure and Thermodynamic Stability of the $\text{BaTiO}_3(001)$ Surface

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We report a series of new surface reconstructions on $\text{BaTiO}_3(001)$ as a function of environmental conditions, determined via scanning tunneling microscopy and low energy electron diffraction. Using density functional theory calculations and thermodynamic modeling, we construct a surface phase diagram and determine the atomic structures of the thermodynamically stable phases. Excellent agreement is found between the predicted phase diagram and experiment. The results enable prediction of surface structures and properties under the entire range of accessible environmental conditions.

Oxides play a vital role in numerous applications, including electronic ceramics, semiconductor technology, and catalysis. Knowledge of the atomic structure and properties of oxide surfaces is essential in understanding and predicting the behavior of such systems, particularly as novel integrated nanodevices are developed. Surfaces are highly sensitive to environmental conditions, resulting in a large number of atomic structures (reconstructions). Such reconstructions are often produced by thermochemical conditions that are not entirely controlled; consequently, it is not easy to distinguish between stable and metastable conditions.

Much research has focused on the $\text{SrTiO}_3(001)$ surface [1–11], which has been shown to adopt reconstructions with $(1 \times 1)$, $(2 \times 1)$, $(4 \times 2)$, $(4 \times 4)$, $(6 \times 2)$, $(\sqrt{5} \times \sqrt{5})R_{26.6}^\circ$, and $(2 \times 2)$ symmetries. Larger superstructures have also been observed [11–14]. Even for this well-studied surface, variation in experimental conditions has resulted in conflicting observations, and only a limited number of structures, primarily $(1 \times 1)$ and $(2 \times 1)$ surfaces, have been treated theoretically [15–18]. Evidence suggests that $\text{BaTiO}_3$ surfaces will also adopt complex surface reconstructions: both $(2 \times 1)$ [19] and $(\sqrt{5} \times \sqrt{5})R_{26.6}^\circ$ reconstructions have been observed on the $(001)$ surface [20,21], and various superstructures were found on the $(111)$ surface [22]. Theoretical studies of the $\text{BaTiO}_3(001)$ surfaces have focused on stoichiometric $(1 \times 1)$ BaO- and TiO$_2$-terminated surfaces [23,24] and a few O-vacancy reconstructions [25].

Here, we experimentally and theoretically determine the surface structure of $\text{BaTiO}_3(001)$ over a wide range of environmental conditions, quantifying stability limits of each reconstruction. Using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED), a series of surface reconstructions including $(1 \times 1)$, $(2 \times 1)$, $(2 \times 2)$, $(\sqrt{5} \times \sqrt{5})R_{26.6}^\circ$, $(3 \times 1)$, $(3 \times 2)$, and $(6 \times 1)$ surfaces, are observed here, most for the first time. Using density functional theory (DFT) and $ab$ initio thermodynamics, we compute the atomic structures and free energies of $>70$ possible $\text{BaTiO}_3(001)$ reconstructions, and predict the phase diagram of the $\text{BaTiO}_3(001)$ surface. Excellent agreement between theory and experiment provides a coherent explanation for surface evolution.

Single crystal $\text{BaTiO}_3(001)$ substrates were preannealed in a tube furnace at 1223–1273 K in high purity oxygen, and then in reducing $\text{H}_2$ or ultrahigh vacuum (UHV) environment; the latter step creates bulk oxygen vacancies, giving rise to electrical conductivity enabling STM, LEED and AES. Samples were introduced into the UHV chamber (Omicron, VT-AFM), where they were annealed at temperatures ranging from 973 K to 1573 K. Sample heating was conducted by passing a current through the substrate, and surface temperatures were measured with an optical pyrometer. The STM measurements were performed with etched tungsten tips in constant current mode with biases $=1–2$ V and currents of 0.1–0.2 nA. The base pressure of the system was $10^{-8}$–$10^{-9}$ Torr during sample heating and $10^{-10}$ Torr during imaging. Images were obtained at room temperature.

DFT calculations were performed with ultrasoft pseudopotentials [26] and the generalized gradient approximation as implemented in the $ab$ initio code DCAPO [27], with a 50 Ry plane wave cutoff and a $4 \times 4 \times 1$ Monkhorst-Pack $k$-point mesh. To simulate the surface of a thick film, the systems were composed of 5–6 layers of bulk paraelectric $\text{BaTiO}_3$ (for BaO and TiO$_2$ surface terminations, respectively), capped on one end by three layers of Pt metal [28]. The capping Pt layers and the bottom 3–4 atomic layers of $\text{BaTiO}_3$ were held fixed in the bulk paraelectric structure. The top $\text{BaTiO}_3$ stoichiometric unit, plus any adsorbed species were relaxed completely until forces were $<1$ meV/Å. A dipole correction was included in the 1.2 nm vacuum separating the film from its periodic image. The in-plane lattice constant was fixed to the theoretical bulk $\text{BaTiO}_3$ value ($a = 0.399$ nm). $(1 \times 1)$, $(2 \times 1)$, $(2 \times 2)$, and $(3 \times 1)$ surface supercells were
considered, with various coverages and patterns composed of O vacancies, Ba, Ti, or O ad-atoms, or additional TiO₂ or BaO layers.

A diagram of the annealing temperatures and observed reconstructions is shown in Fig. 2(a). All surfaces exhibit atomically flat terraces, with unit-cell (0.4 nm) step heights, indicating the presence of a single surface termination. The (1 × 1), (2 × 1), c(2 × 2), (2 × 2), (\(\sqrt{5} \times \sqrt{5}\)) R26.6°, (3 × 1), (3 × 2), and (6 × 1) reconstructions were characterized by LEED and several were imaged by STM. Except for the (2 × 1) and (\(\sqrt{5} \times \sqrt{5}\)) R26.6° reconstructions, these reconstructions, and more importantly, the relationships between them, are reported here for the first time.

Preamnealed crystals exhibit faint (1 × 1) LEED patterns, with no contaminants detectable by Auger electron spectroscopy (AES). Heating between 873–973 K for 30 min in UHV results in (2 × 1) or c(2 × 2) reconstructions. Higher \(T\) annealing at 973–1073 K for 30 min leads to weak (\(\frac{1}{2} \times \frac{1}{2}\)) spots in the LEED pattern, indicative of a c(4 × 4) reconstruction. For initial UHV annealing temperatures of 1273 K, (2 × 2), (\(\sqrt{5} \times \sqrt{5}\)) R26.6°, and (3 × 1) superstructures develop as \(T\) is increased to 1473 K. Interestingly, the (\(\sqrt{5} \times \sqrt{5}\)) R26.6° and (3 × 1) reconstructions coexist for short times at 1323–1373 K. Figure 1 illustrates the structural characterization of the (\(\sqrt{5} \times \sqrt{5}\)) R26.6° and (3 × 1) reconstructions. The dimensions of the unit cells determined by LEED and STM agree. The STM image of the (\(\sqrt{5} \times \sqrt{5}\)) R26.6° reconstruction in Fig. 1(a) consists of two domains rotated by 36.5° with respect to each other. Multiple domain orientations are also identified in the LEED pattern. Figure 1(b) shows the STM image of the (3 × 1) surface, exhibiting bright rows believed to be adatoms along the [100] direction. The average spacing between adjacent rows is 1.2 nm, in agreement with the (3 × 1) unit-cell dimension.

Aggressive annealing above 1373–1473 K results in continuously evolving surface morphologies on microscopic as well as nanoscopic length scales. The changing nature of the surface indicates that some of the structures are not thermodynamically stable. Below 1273 K, where the reconstructions appear to be thermodynamically stable, the surface is atomically flat with single-unit-cell high steps running along the [100] directions. Based on findings for SrTiO₃ surfaces, this [100] step alignment is suggestive of the dominance of TiO₂ surface planes; our DFT calculations also find that TiO₂ surfaces are more favorable than BaO surfaces under most conditions. With annealing above 1373 K, a stripe phase oriented along the [100] direction develops subsequent to the (3 × 1) reconstruction, increasing in coverage with time and temperature [Fig. 1(e)]. Continued annealing at 1473 K results in the development of a (1 × 1) surface. At some locations macroscopic precipitates occur, as can be seen in Fig. 1(f).

DFT was used to model more than 70 possible BaO- and TiO₂-terminated surface structures, the details of which are reported elsewhere. The Gibbs free energy of each structure, \(\gamma(T, p) = G_{surf} - n_{Ba}μ_{Ba} - n_{Ti}μ_{Ti} - n_{O}μ_{O}\), was computed, where \(G_{surf}\) is the free energy of the slab, \(μ_{Ba}\), \(μ_{Ti}\), and \(μ_{O}\) are the chemical potentials of Ba, Ti, and O, respectively, and \(n_{Ba}\), \(n_{Ti}\), and \(n_{O}\) are the number of Ba, Ti, and O atoms in the surface [29]. \(G_{surf}\) is well approximated from DFT total energies [30], assuming the entropy change of the slab is approximately the same as that of its components in bulk form: \(G_{surf} = F_{surf} - n_{Ba}F_{Ba} - n_{Ti}F_{Ti} - n_{O}F_{O}\), where \(F_{surf} = F_{tot} - F_{base} - F_{bulk}\), \(F_{tot}\) and \(F_{base}\) are the total energies of the slab and the fixed base, \(F_{bulk}\) are the total energies per unit cell of bulk BaTiO₃, Ba, and Ti, respectively, and \(F_{O}\) is the total energy of an isolated O molecule [31].

The effect of \(μ_{O}\) and \(μ_{Ba}\) on structural stability is illustrated in the theoretical surface phase diagram in Fig. 2. The diagram defines stabilities for the lowest energy surface structures; superimposed are the stability limits of bulk BaTiO₃ at relevant \(T\). The figure shows seven thermodynamically stable surface structures in five different symmetries in the region of BaTiO₃ stability. The boundaries of this region are defined by the equilibria of bulk BaTiO₃ with BaO, O, and TiO₂ and the following constraints: (i) Bulk BaTiO₃ is in equilibrium with the surface,
so the Gibbs free energy of bulk BaTiO$_3$ is always
\[ g_{\text{BaTiO}_3}(T, p) = \mu_{\text{Ba}}(T, p) + \mu_{\text{Ti}}(T, p) + 3\mu_O(T, p); \]
(iii) a small amount of water is always present (as is the case in
UHV), so \( \mu_O(T, p) + \mu_{\text{H}}(T, p) \approx g_{\text{H}_2\text{O}}(T, p) \); and (iii) as
a result of preannealing in H$_2$, \( \mu_{\text{H}} = 0 \), giving the lower
bound of the oxygen chemical potential as \( \mu_{O_{\text{min}}} = g_{\text{H}_2\text{O}}(T) \).

The temperature dependence of the Gibbs free energies
is explicitly included via experimentally tabulated values.
Previous studies have neglected this \( T \) dependence [16, 17].
However, as Fig. 2 indicates, including the \( T \)-dependence
significantly extends the region of BaTiO$_3$ stability, and
is crucial to understanding the evolution of the surface.

Knowledge of the oxygen partial pressure defines the
value of \( \mu_{O} \) at every \( T \). The equilibrium partial pressures
of Ba and Ti with their respective binary oxides, along with
the time scale of the experiments, suggest that in the
experimental temperature range the system will reside at
the boundary between BaO and BaTiO$_3$ stability.
Consequently, \( \mu_{\text{Ba}} \) is also defined, providing sufficient
information to determine the trajectory of the system
through phase space and to relate each experimental
observation to a point in the surface phase diagram.
The yellow arrow in Fig. 2 shows the computed trajectory for
\( p_{O_2} = 10^{-10} \text{ torr} \) (the upper limit of the oxygen partial
pressure in the UHV chamber), while the black arrow gives
the trajectory at \( p_{O_2} = 10^{-22} \text{ torr} \) (the lower limit of the
oxygen partial pressure, corresponding \( \mu_{O_{\text{min}}}(T, p) \). The
actual pathway is expected to be somewhere in between
the two limits, in good agreement with the experimental
observations.

The phase diagram can be used to explain the relationships
between various equilibrium phases and nonequilibrium
morphologies. Following the black arrow in Fig. 2, \( \mu_{O} \) decreases
and the surface goes through a series of reconstructions with increasing Ti coverage, \( \theta \), as the
temperature is increased: \( (2 \times 2) \rightarrow (2 \times 2) \rightarrow (3 \times 1) \rightarrow (2 \times 2) \rightarrow (1 \times 1) \) \( (\theta = \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, 1) \). On the
other hand, at lower \( \mu_{\text{Ba}} \) the surface reconstructs directly from the \( (2 \times 1) \) to the \( (1 \times 1) \) phase under the same range
of \( \mu_{O} \). The low temperature \( c(2 \times 2) \) and \( (2 \times 1) \) and the
high temperature \( (2 \times 2) \) and \( (3 \times 1) \) phases occur within the
BaTiO$_3$ stability region as predicted. Two other phases,
\( c(4 \times 4) \) and \( (\sqrt{5} \times \sqrt{5})R26.6^\circ \), are observed experimentally
but have not been calculated due to computational
time constraints. Following the stability trends, the theo-
retical phase fields of these structures would be located in
the region between \( c(2 \times 2) \) and \( (3 \times 1) \), exactly the region
indicated by experiment.

Under high temperature conditions in which BaTiO$_3$ is
not stable, i.e., outside of the dashed lines in Fig. 2, the
surface undergoes a decomposition reaction: Evaporation
of BaO drives the rearrangement of Ti and O atoms on the
surface to form some energetically stable Ti$_2$O$_3$-rich
surface phase. The ordered nanostripes occurring at the highly
annealed surfaces shown in Fig. 1(e) are attributed to this
mechanism. Returning from such an excursion (lowering
T) results in BaO precipitation. These precipitates cannot
find the BaTiO$_3$ structure without considerable annealing
and therefore aggregate in micrometer-sized BaO clusters,
Fig. 1(f).

The phase relations in Fig. 2 explain the order of ex-
perimentally observed reconstructions and the surface
phase composition, but STM images alone cannot deter-
mine the atomic structure of the surfaces. To relate the
image contrast to atom positions we computed the local
density of states (LDOS) with energy between the Fermi
level and 2 eV above the conduction band edge, summing
over all \( z \) to obtain an image of the xy plane [32]. The
atomic structure of the only thermodynamically stable
\( (3 \times 1) \) phase determined from a wide array of computed
\( (3 \times 1) \) surfaces is shown in Fig. 3(c). The reconstruction
consists of Ti atoms at 2/3 of the empty hollow sites in the
oxygen lattice (i.e., above the Ba atoms in the subsurface
layer) and the upward shift of 1/2 of the surface oxygen
atoms (see supplementary material [33]). Because of the Ti
d character of the conduction band edge, the Ti adatoms,
which are \( \approx 1 \text{ Å} \) higher than the Ti atoms in the stoichio-
metric Ti$_2$O$_3$ plane, are responsible for the bright spots in
the STM image [Fig. 3(b)]. At lower resolution [Fig. 3(a)],
these spots appear as stripes twice the width of the dark

FIG. 2 (color online). (a) Schematic of annealing sequence and
observed phases. (b) Computed surface phase diagram of
BaTiO$_3$. The black and blue dashed lines show the boundaries
of BaTiO$_3$ bulk stability \( T = 1000 \text{ K} \) and \( T = 1400 \text{ K} \),
respectively. The black and yellow arrows show the computed
trajectories through phase space for the lower and upper limits of
\( p_{O_2} \), respectively, (see text). The white X’s correspond to ex-
perimental observations along the low \( p_{O_2} \) trajectory.
FIG. 3 (color online). (a) Comparison of STM and the computed LDOS of the predicted \((3 \times 1)\) phase. (b) Atomic scale detail of the computed LDOS and (c) surface atomic structure for the same phase. Ba: cyan, Ti: blue, O: red. The color bar in (b) gives the intensity in arbitrary units.