# Surface-hydrogen-induced metallization and rumpling in thin BaTiO<sub>3</sub> films

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We study theoretically metallization and polarization enhancement effects of H adsorption at the  $TiO_2$ terminated (001) BaTiO<sub>3</sub> (BTO) surface. The clean BTO slab does not polarize because the slab is too thin to support a ferroelectric state. We find that the metallization of the surface is a strong function of hydrogen coverage and that the insulating surfaces do not support a rumpling or polarization in BTO films, whereas all metallic surfaces do so. The donated charge from the adsorbed H transforms the  $TiO_2$  into a metallic capping layer, stabilizing the ferroelectric state.

DOI: 10.1103/PhysRevB.94.245425

#### I. INTRODUCTION

BaTiO<sub>3</sub> (BTO) is a ferroelectric perovskite with many applications; for example, epitaxial BTO films grown on semiconductors have gained interest as a high- $\kappa$  dielectric [1–3] for field-effect transistors (FETs) [4]. As BTO is ferroelectric, its integration with Si or Ge adds additional versatility in the construction of a ferroelectric FET [5-7], in microwave device applications [8], or as a nonlinear optical material for Si nanophotonic devices [9]. Due to this interest in utilizing ferroelectricity of BTO, it is crucial that the polarization of BTO is kept intact during growth and processing, and so the understanding of the effects of defects on the polarization is essential. Hydrogen is always present in growth chambers, especially those used for atomic layer deposition (ALD), where water is often used as an oxidizer [10], and so its effect on the materials properties of grown films is an important consideration. Interstitial hydrogen increases the polarization of bulk BTO by increasing the Ti-O separation and thus increasing the polarization of the nearby TiO<sub>2</sub> layers [11,12]; however, other theoretical studies have shown that interstitial hydrogen creates OH<sup>-</sup> groups that pin the polarization and prevent the material from switching [13]. Conversely, annealing in hydrogen gas has been shown to cause unwanted reaction with ferroelectric oxides by reducing the remnant polarization, causing O vacancies, and ejecting A-site ions, resulting in severe structural and chemical damage [14-16]; hydrogen also acts as a donor, causing the oxide to become conducting [17–19]. In contrast, annealing O-deficient SrTiO<sub>3</sub>(STO) in H<sub>2</sub> gas resulted in a decrease of conductivity. This has been possibly attributed to H substituting in O vacancy sites and acting as an acceptor [20], as has been seen in  $SrTi_{1-x}Fe_xO_{3-x/2}$  [21]. In bulk BTO crystals, theoretical calculations show that H acts as either an electron donor (interstitial defect) or acceptor (substituted for O), depending on the site [22], with experiment confirming the existence of BTO "oxyhydrides" containing up to 20% of O substituted by hydrogen [23]. Experimental results indicate that the formation of OH groups in Pb(Zr,Ti)O<sub>3</sub> pins the polarization and prevents the local Ti atoms from switching, leading to a degradation in hysteresis

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of the sample [24]. The formation of OH groups caused by H absorption has also been suggested as a source of resistivity degradation in bulk BTO [19].

The adsorption of atoms and molecules on BTO surfaces is an important topic; perovskites have been shown to be effective catalysts for removing CO and CH<sub>4</sub> [25], and BTO is a particularly effective catalyst for the combustion of  $CH_4$  [26]. Prior research shows that the adsorption of  $H_2O$  on the TiO<sub>2</sub>-terminated (001)BTO surface leads to disassociation into  $H^+$  and  $OH^-$  groups [27,28], and ~20% of Ti surface atoms have these OH<sup>-</sup> groups; the OH<sup>-</sup> adsorbed on Ti is enough to reverse the polarization of the surface TiO<sub>2</sub> layer [27]. Adsorption of H<sub>2</sub>O on the BaO-terminated surface leads to surface O vacancies, Ba(OH)<sub>2</sub> groups, and reversal of the surface polarization [29]. Hydrogen adsorption has been widely studied in other semiconductors and oxides; H adsorption on the Si-terminated (001)SiC surface leads to a metallic surface [30], and theoretical calculations show that the adsorbed hydrogen donates an electron to the system via a Si-H-Si bridge bond [31]. Interestingly, this metallization is only found at a certain H (high) coverage; with less H coverage, the surface remains insulating. The same behavior is seen at the  $(10\overline{1}0)$  ZnO surface [32] and the (001) STO surface [33–36], where the degree of H coverage causes either a metallic surface, or the surface remains insulating; experimental reports also show that H donates 0.3 electrons to the surface of STO by binding to O sites [37]. A recent theoretical study has also shown that H adsorption on the STO surface induces an antiferrodistortive octahedral tilting that is different than in bulk STO [38].

Here, we report a first principles study of the effect of hydrogen adsorption on the BTO surface. As we will show, the topic deserves serious consideration as adsorbed hydrogen causes significant changes on both the electronic and ionic structure of BTO.

### **II. COMPUTATIONAL DETAILS**

Density functional theory (DFT) was used to model the bulk and (001) surface of BTO. All calculations were done using the local density approximation and projector augmented-wave pseudopotentials as included in the Vienna *Ab initio* Simulation Package (VASP) code [39–44]. We used the Perdew-Zunger form of the exchange-correlation potential [45]. The valence configuration of  $3p^{6}4s^{2}3d^{2}$  was

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FIG. 1. The surface projection band of the bulk BTO onto BZ corresponding to (a)  $1 \times 1$  surface cell and (b)  $\sqrt{2} \times \sqrt{2} \times 1$  surface cell.

used for Ti,  $5s^25p^66s^2$  for Ba,  $2s^22p^4$  for O, and  $1s^1$  for H. A kinetic energy cutoff of  $E_{\text{cutoff}} = 600 \text{ eV}$  was used. For the Brillouin zone integration, the following Monkhorst-Pack [46] *k*-point meshes were used:  $8 \times 8 \times 8$  for bulk BTO,  $8 \times 8 \times 1$  for the  $(1 \times 1)$ -terminated TiO<sub>2</sub> surface, and  $6 \times 6 \times 1$  for the  $(\sqrt{2} \times \sqrt{2})$  surface. Bulk BTO structure was fully optimized, and all structures were optimized with respect to the ionic positions until the forces on all atoms were less than 50 meV/Å. The energy was converged to  $10^{-3}$ meV per atom.

The lattice constant a of tetragonal BTO was calculated to be 3.96 Å, with a c/a ratio of 1.005, in good agreement with the experimental 3.99 Å and 1.011, respectively [47], and with previously reported theoretical values of 4.00 Å and c/a = 1.010 [48]. All slabs were symmetrically terminated with TiO<sub>2</sub>, with the slabs being 10.5 unit cells thick, augmented by 15 Å of vacuum. Following previous work on the STO(001) surface [33,34], we consider O and Ti as possible adsorption sites for H. On a stoichiometric  $TiO_2$ -terminated  $(1 \times 1)$ surface, there are three possible adsorption sites: One on each O, and one on Ti (this will be elaborated further in Sec. III). For the  $(1 \times 1)$  surface, we consider coverages of 0, 1/3, 2/3, and 1 monolayer (ML), which corresponds to zero, one, two, and three adsorbed hydrogen atoms, respectively; for the larger  $(\sqrt{2} \times \sqrt{2})$  surface, we consider coverages of 0, 1/6, 1/3, 1/2, and 2/3 ML, which corresponds to zero, one, two, three, and four adsorbed hydrogens, respectively.

### **III. ELECTRONIC STRUCTURE**

To compare the electronic structure of the  $(1 \times 1)$  surface with bulk BTO, we project the bulk electronic structure onto the surface Brillouin zone as shown in Fig. 1(a). Electronic structure for all surface calculations is plotted along this projection, in order to distinguish the surface-related and bulk electronic states. The electronic structure of the  $(1 \times 1)$  surface is given in Fig. 2; the size of the dot in all band structure plots to follow indicates the size of the contribution of the surface atom in question. In Fig. 2(a), we see that the states



FIG. 2. The band structure of the clean  $TiO_2$ -terminated surface. The Fermi energy is indicated with a dotted line. (a) The contribution of the surface Ti atom is shown in blue. (b) The contribution of the surface O atoms is shown in red.

projected on the surface Ti atom are located in the middle of the conduction band and are not particularly distinct from them, with the exception of the two midgap bands. In Fig. 2(b), we show the surface-oxygen-projected states; we see the same two midgap bands, and they are dominated by the surface O. This is very similar to what happens at the STO surface [49], except the surface states of BTO are deeper in the band gap. These bands extend to ~1.5 eV above the top of the valence band of the bulk O state. Although these surface bands are higher in energy than the bulk, they are below the Fermi level, and the surface remains insulating. This is in good agreement with prior calculations of the BTO(001) surface [50–53].

This surface cell offers three possible adsorption sites, one Ti and two inequivalent O sites. The order of adsorption is given in Fig. 3. First, we show the 1/3 ML H coverage, where the H adsorbs on one of the O sites, creating an OH complex. The electronic structure for this adsorption is shown in Fig. 4. Immediately, we see a large change in the electronic structure; we note that the Fermi level is now in the conduction band, indicating that the surface is metallic. We also notice that the midgap surface state of the clean surface has disappeared; this is in contrast with the coverage of STO, where the surface state of O is altered but still distinct from the rest of the valence band [33,34]. In Fig. 4(a), we see that the charge obtained from the adsorbed H is present mostly on the surface Ti state, which has been lowered from the middle of the conduction band



FIG. 3. (a) The  $TiO_2$ -terminated surface, with 3 H adsorbed. (b) The order of adsorption. (1) H adsorbs on one of the O sites. (2) H adsorbs on the Ti site. (3) H adsorbs on the remaining O site.



FIG. 4. The band structure for the H adsorbed  $(1 \times 1)$  surface. (a) The surface Ti contribution in blue. (b) The O of the OH complex contribution in red. (c) The adsorbed H contribution in green.

and now forms its bottom; the reason for this drop in energy will be discussed in Sec. IV. Although all of the surface Ti dstates are occupied from the local density of states (LDOS), the majority of the charge is located in the  $d_{xy}$  band, with a lesser amount in the  $d_{yz}$  and  $d_{xz}$  bands, and a smaller amount still in the  $e_g$  bands. At first glance, this result is surprising; due to crystal field splitting, the  $t_{2g}$  and  $e_g$  bands are separated by  $\sim 2.5$  eV, so it would not be expected that any of the  $e_g$  states should be occupied, due to the large crystal field splitting. However, when we examine the LDOS of a slab of BTO, with no hydrogen adsorbed, we see that the  $d_{7^2}$  state is lowered and becomes comparable in energy to that of the  $t_{2g}$  bands; this is due to the reduced symmetry. The lowering of symmetry due to the surface causes strong hybridization between the Ti 4pand Ti3 $d_{7^2}$  states, just as occurs in SrTiO<sub>3</sub> [54]. Although the  $d_{x^2-y^2}$  is also partially occupied, this is because the orientation of the Ti orbitals to the crystal axes have changed due to uneven rumpling in the system; in other words, the TiO<sub>6</sub> octahedron is distorted because the O are no longer at the same z coordinate due to the adsorbed H pulling one of the O away from the surface, and therefore some spurious  $d_{x^2-y^2}$ occupation appears at the Fermi level.



FIG. 5. The charge density difference plots for the (a) 1/3 ML H, (b) 2/3 ML H, and (c) 1 ML H coverages. The red indicates an increase in charge density, and the blue indicates a decrease in charge density.

In Fig. 4(b), we see the contribution of O in the O-H complex; we see that this state has been lowered from the midgap and is now a weakly dispersive state below the valence band edge. In Fig. 4(c), we see that the H contribution is mostly due to this subvalence band state, indicating that some charge is forming an O-H bond; however, due to the metallicity of the surface, we also conclude that not all charge remains on the O-H complex. We see that the excess charge, beyond that adsorbed by the O-H bond, is transferred to the bottom of the conduction band and is distributed over the Ti states. We can view the change in charge density in the system [Fig. 5(a)] in the charge difference plot: We take the charge density of the 1/3 ML H adsorbed system and subtract the charge density of the isolated slab and isolated H atoms (we use the same relaxed atomic positions as for the H-adsorbed coverage). We see that there is a gain in charge between the O and H, indicating a bond, and that there is also a gain in charge on the surface titanium, indicating metallization. From integrating the LDOS of the occupied states in the conduction band, we see that there are 0.324 electrons present in the conduction band, giving us a surface charge density of  $2.1 \times 10^{14}$  electrons/cm<sup>2</sup>; for comparison, this is an order of magnitude higher than the electron surface density found at the SrTiO<sub>3</sub>/LaAlO<sub>3</sub> interface [55].

Now, when we add the second H to the BTO surface, it prefers to adsorb on the Ti site (the Ti-H bond length is 1.76 Å), giving us the 2/3 ML H coverage. In Fig. 6, we plot the corresponding band structure. Again, there are obvious differences for the adsorption of two H atoms than for the adsorption of only one. While the surface is now insulating like the clean slab, the Fermi level is pinned by a nondispersive midgap state. Examination of Fig. 6(a) shows that the surface Ti contribution is in the conduction band, where the states are again moved up in the middle of the conduction band; there is also some contribution to the midgap state. Figure 6(b) shows that there is no significant change for the O in the OH group in comparison with the surface with one adsorbed H. Finally, Fig. 6(c) shows that the H contribution is in the midgap state and the subvalence band state, corresponding to the Ti-H and







FIG. 6. The band structure for the 2/3 ML H adsorbed  $(1 \times 1)$  surface. (a) The surface Ti contribution in blue. (b) The O of the OH group contribution in red. (c) The adsorbed H contribution in green.

O-H bonds. The return of an insulating surface, simultaneous with the essentially unchanged condition of the O-H group, shows that any charge donated to the system from the O-H complex must be balanced by any charge accepted by the Ti-H complex. Indeed, in Fig. 5(b), we see an increase in charge density on the H in the Ti-H complex. This can be explained by back-donation [34,56]; the H adsorbed by O in the 1/3 ML H coverage donates charge to the system, which settles in the surface Ti *d* states. This allows Ti to become more chemically active, which attracts H; the adsorbed H in the Ti-H complex then appropriates the charge from Ti, causing the system to become insulating.

For the 1 ML H coverage, we fill the last O site, and the surface is fully hydrogenated. We show the electronic structure of the system in Fig. 7. The system again becomes metallic, and the overall band structure looks quite similar to that of the 1/3 ML H coverage with the exception that now there are two subvalence states. The third H bonding with O again donates charge to the system, which goes to the conduction band, consisting of mostly Ti states. From the integrated LDOS, we see that there are 0.36 electrons present in the conduction band, which gives a surface charge

FIG. 7. The band structure for the 1 ML H adsorbed  $(1 \times 1)$  surface. (a) The surface Ti contribution in blue. (b) The surface O contribution in red. (c) The H contribution in green.

density of  $2.1 \times 10^{14}$  electrons/cm<sup>2</sup>, which is very similar to that of the 1/3 ML H coverage  $(2.1 \times 10^{14} \text{electrons/cm}^2)$ . In Fig. 7(a), we see that the Ti-related states are at the bottom of the conduction band. Figures 7(b) and 7(c) look essentially the same as for the one adsorbed hydrogen, except for the doubling of O and H subvalence states. The Ti-H bond length is increased to 1.94 Å, a 0.18 Å change from the Ti-H complex for the 2/3 ML H coverage, and the O-H bond length increases to 1.09 Å, a 0.09 Å change from the 2/3 ML H coverage. Even though H is adsorbed on both H, they are not identical; in one case, the H is bent perpendicular to Ti (O-perp), and for the other O (O-par), the H tilts toward the Ti. Interestingly, the H adsorbed on Ti and the H adsorbed on O-par bend toward each other; the H-H distance for the 2/3 ML H coverage is 1.91 Å, but for the 1 ML H coverage the H-H distance is 1.26 Å. There is a peak at the top of the valence band, consisting mostly of O states in the O-H complex, and H states in the Ti-H complex, but not from H in the O-H complex and Ti in the Ti-H complex; this means that the H and O must be interacting indirectly. This can be explained by the electron present in the Ti conduction band, which allows indirect coupling between O in the O-H complex and H in the Ti-H complex.

Finally, we also investigate the possibility that more than one H can adsorb on a given Ti or O atom; in other words,



FIG. 8. The order of adsorption for the  $(\sqrt{2} \times \sqrt{2})$  surface. (1) The H adsorbs on an O site. (2) The H adsorbs on another O site, farthest from the original OH complex. (3) The H adsorbs on one of the Ti sites. (4) The H adsorbs on one of the other free O sites.

is having all O and all Ti present at the surface with one H each really the maximum coverage possible? To check this, we try placing another H on either Ti or O, which already has an adsorbed H bonded to it. In both coverages, the H simply combines with the adsorbed H to make  $H_2$ , which then moves away from the surface; thus, the assumption that 1 ML of adsorbed H coincides with three adsorbed H for the  $(1 \times 1)$ 



FIG. 9. The band structure for the 1 ML H adsorbed ( $\sqrt{2} \times \sqrt{2}$ ) surface. (a) The surface Ti contribution in blue. (b) The surface O contribution in red. (c) The H contribution in green.



FIG. 10. The band structure for the 1 ML H adsorbed ( $\sqrt{2} \times \sqrt{2}$ ) surface. (a) The surface Ti contribution in blue. (b) The surface O contribution in red. (c) The H contribution in green.

 $TiO_2$ -terminated surface is correct. We see that the order of H adsorption is O, Ti, O, and any further addition of H creates H<sub>2</sub> that desorbs from the surface, so that three adsorbed H is the maximum H coverage possible.

Now, we will examine the adsorption of H on a larger surface area; a larger cell is needed to consider octahedral tilting, which is important in many perovskites [57]. We use a  $(\sqrt{2} \times \sqrt{2})$  surface, which allows for six distinct adsorption sites, two Ti and four O. We consider up to four H atoms on the surface; the order of adsorption is shown in Fig. 8. The bulk band structure projected on the surface Brillouin zone of the  $\sqrt{2} \times \sqrt{2}$  cell is shown in Fig. 1(b).

The band plots for the 1/6 ML H and 1/3 ML H adsorption are essentially the same as those for the 1/3 ML H coverage on the  $(1 \times 1)$  surface and are not shown here. An interesting note is the lack of a Peierls transition on the surface; the adsorbed H has the possibility of relaxing away and destroying the  $(1 \times 1)$ periodicity of the surface, but instead they maintain the  $(1 \times 1)$ periodicity. We argue that the absence of the Peierls transition is due to the charge primarily being located on Ti states, which is coupled only weakly to the periodicity of H, so that the positions of the H atoms are not important. The 1/2 ML H coverage is shown in Fig. 9; in this coverage, there are two H adsorbed on O and one on Ti. We see that this is different than the 2/3 ML H coverage with the Ti-H complex because the system remains metallic and does not become insulating as in the previous coverage. This is due to the fact that there is a 2:1 ratio of O-H complexes versus Ti-H complexes, in contrast to the  $(1 \times 1)$  surface, where the charge donated by the OH complex is balanced by the charge accepted by the Ti-H complex. Thus, as we can see in Fig. 8(a), the electronic structure is a mix of the 1/3 ML H and 2/3 ML H coverages on the  $(1 \times 1)$  surface; the Fermi level is in the conduction band, but there is still a strongly localized Ti-H midgap state.

Finally, we add a fourth hydrogen atom to get the 2/3 ML H coverage. From the previous  $(1 \times 1)$  calculation, we expect to have two OH complexes and two Ti-H complexes; however, this is not the coverage for the  $(\sqrt{2} \times \sqrt{2})$  surface, where we form three OH complexes and one Ti-H complex. In Fig. 10, we see that the system essentially resembles that of the  $(1 \times 1)$  1 ML H surface; the Fermi level is in the conduction band, and Fig. 10(a) shows that the surface Ti states are brought down in energy and occupied, as before. The Ti-H bond length increased to 1.91 Å, indicating the same charging mechanism as for the  $(1 \times 1)$  coverage. The key difference between the  $(1 \times 1)$  and the  $(\sqrt{2} \times \sqrt{2})$  surface is that the insulating surface does not occur, as it does for the  $(1 \times 1)$  surface; the system always stays metallic, due there being an uneven number of Ti-H and OH complexes.

# **IV. ATOMIC STRUCTURE**

We now consider the effect of H adsorption on the polarization of BTO. The rumpling is defined by a relative shift in the *z* direction (normal to the surface) of the Ti and O atoms. To a good approximation, the polarization is linear with respect to the rumpling [58], so examining the rumpling is a simple way of approximating the effects of adsorbed atoms on the system polarization. The rumpling for the clean surface and the surface with adsorbed H are given in Fig. 11(a). We see that the rumpling of the surface layer is roughly equal to that of the bulk, but it dies very rapidly, and the majority of the system shows no rumpling; the polarization is limited to the vicinity of the surface, which forms an effective depolarizing field due to the change in surface charge density caused by the surface [59].

Now, we see the effect of adsorbed H on the atomic structure of the slab. We will begin by discussing the rumpling of the  $(1 \times 1)$  surface. The rumpling is shown for 1/3 ML H coverage in Fig. 11(b). We see that the rumpling for the O with H adsorbed is massively enhanced at the surface (red line), reaching roughly four times the bulk value. Although the rumpling for the O without H adsorbed (blue line) is increased near the surface, it is not as large. Three layers away from the surface, the rumpling for both O becomes that of bulk, until finally the rumpling dies in the middle of the slab (as it must due to the symmetry of the simulation). In Fig. 11(c),



FIG. 11. The rumpling of the  $TiO_2$  layers for (a) the clean BTO(001) surface, (b) the 1/3 ML H adsorbed surface, (c) the 2/3 ML H adsorbed surface, and (d) the 1 ML H adsorbed surface. The green dotted line is the rumpling of bulk BTO. In (b) and (c), the red represents the rumpling between the O with adsorbed H and Ti, and the blue represents the rumpling between the O without adsorbed H and Ti. In (d), although both O have adsorbed H, their rumpling is inequivalent near the surface.



FIG. 12. (a) The polarization of a traditional ferroelectric with a metal capping layer. The system polarizes itself so that the positively charged ion  $(Ti^+)$  moves towards the electrons in the metal, stabilizing the ferroelectricity. (b) In our system, there is an additional electric field caused by the positively charged adsorbed H<sup>+</sup>ion and the electron in the TiO<sub>2</sub> conduction band. This additional field in the BTO is killed by increasing the rumpling of the ferroelectric, increasing the polarization of the sample.

we plot the rumpling of the 2/3 ML H coverage surface; we see that, although the rumpling is increased at the surface, it dies quickly and the rest of the TiO<sub>2</sub> layers become flat, essentially the same as the clean surface. Also, the first two layers of this slab show mixed rumpling (the rumpling for the different O are opposite). Finally, in Fig. 11(d), we plot the rumpling of the 1 ML coverage, and we see that the rumpling is again increased with respect to the clean surface, similarly to the coverage with one adsorbed H. We also see that, even though the entire surface is hydrogenated, the two O atoms do not show equal rumpling. An important observation is that the 1/3 ML H and 1 ML H adsorbed systems have rumpling enhancements that penetrate the entire slab (the center of the slab is flat, as it must be due to symmetry). In other words, the rumpling enhancement of H is not purely a surface effect.

The reason for the rumpling can be explained by an electrostatic argument. The slab with no H adsorbed is essentially unrumpled because polarizing a slab would cost a large amount of energy, due to having an electric field in the material. However, for the 1/3 ML H coverage, when the electron from the H pours into the system, it is localized at the surface  $TiO_2$  layer, causing it to become metallic. This provides the necessary screening to allow the development of a polarization in the BTO slab. The same enhancement of the ferroelectric stability has been shown to occur in BTO slabs with metallic capping layers; these layers help screen the depolarizing field in the slab and allow the occurrence of rumpling/ferroelectricity [Fig. 12(a)] [60-62]. In essence, the adsorbed H causes the surface  $TiO_2$  layer to essentially become a metallic capping layer, stabilizing the ferroelectricity of the BTO slab. In a typical metal/BTO heterostructure, we see that the polarization of the slab is decreased with respect to bulk [60]. However, in contrast to the metal film, the adsorbed H actually increases the rumpling and polarization of the slab. This is because the positively charged proton and negatively charged TiO<sub>2</sub> layer form an electric dipolar layer that creates an additional electric field in the BTO slab. The



FIG. 13. The rumpling of the  $TiO_2$  layers for the 1/3 ML H coverage (red), in comparison to that of the same slab, with no adsorbed H, but with two extra electrons added to the system (blue).

BTO slab polarizes even more in response to this additional field [Fig. 12(b)]. To show that the presence of the proton adsorbed on the surface is important, we also simulate a BTO slab as before, but without the adsorbed H, instead we add two electrons to the system to mimic the charge added by the adsorbed H atoms (the excess negative charge is balanced by a uniform positive background charge). The comparison of rumpling in this system is shown in Fig. 13. We can see that, while the system is indeed rumpled, the rumpling is significantly less throughout the entire slab in comparison with the 1/3 ML H coverage. This shows that only adding the extra electrons is not sufficient to explain the rumpling of the system.

For the 2/3 ML H coverage, all the charge remains at the adsorbed H (the charge donated by the OH group is accepted by that of the Ti-H group), so that there is no bare H charge and no field, and the metallic capping layer is not created; therefore, no polarization of the BTO develops. The 1 ML H coverage is essentially the same as the 1/3 ML H coverage. So we see that there are two cases: (1) There are more O-H complexes than Ti-H complexes (1/3 H ML and 1 H ML coverages). In this case, a metallic capping layer is formed by the adsorbed H, and the slab can stabilize a ferroelectric state. (2) There are equal numbers of O-H and Ti-H complexes (0 H ML and 2/3 H ML coverages). In this case, there is no free charge; all charge introduced to the system by H is localized through bonding within Ti-H and O-H complexes, no metallic capping layer is formed, and therefore, the system cannot sustain a ferroelectric state. Thus, we see that the polarization developed by BTO only exists when there are an unequal number of O-H and Ti-H complexes, so that the surface TiO<sub>2</sub> layer becomes metallic.

Next, we examine the rumpling of the  $(\sqrt{2} \times \sqrt{2})$  surface, shown in Fig. 14. Due to the large amount of inequivalent rumplings on the surfaces (O-Ti-O with H, O-Ti-O, O-Ti with-H to O, etc.), the rumpling near the surface varies greatly with the specific placement of H. However, by the third layer of TiO<sub>2</sub>, the rumplings are the same at any coverage of H. In all coverages considered for the  $(\sqrt{2} \times \sqrt{2})$  surface, there is free charge located in the conduction band, which causes the surface to become metallic, stabilizing the polarization of the



FIG. 14. The rumpling of the ( $\sqrt{2} \times \sqrt{2}$ )TiO<sub>2</sub> layers for (a) the 1/3 ML H adsorbed surface, (b) the 2/3 ML H adsorbed surface, (c) the 1 ML H adsorbed surface, and (d) the 4H adsorbed surface. The green dotted line is the rumpling of bulk BTO. The red line indicates rumpling between a pair of Ti and O where both have adsorbed H, the green line indicates rumpling between a pair of Ti and H where one of the atoms has an adsorbed H, and blue indicates rumpling between a pair of Ti and H with no adsorbed H.

sample, as is seen in all coverages in Fig. 14. In all coverages, the rumpling is massively enhanced near the surface, and the system remains rumpled until the very center of the slab.

This enables stabilizing ferroelectricity in very thin BTO films. The O-H surface complexes, unbalanced by Ti-H complexes, result in a net electron transfer to the TiO<sub>2</sub> surface layer, in which the donated electrons remain in the conduction band, producing a metallic capping layer. This capping layer stabilizes the ferroelectricity in the slab. Calculations on the larger surface cell show that the system prefers to have unequal amounts of O-H and Ti-H surface complexes, which ensures that the surface has uncompensated electrons and forms a metallic capping layer. The adsorbed H also increases the rumpling of the slab with respect to bulk, due to the dipole electric field created by the adsorbed proton and metallic TiO<sub>2</sub> surface layer.

### V. CONCLUSIONS

We studied the effect of H adsorption on both the  $(1 \times 1)$ and  $(\sqrt{2} \times \sqrt{2})$  TiO<sub>2</sub>-terminated (001)BTO surfaces. For the  $(1 \times 1)$  surface, 1/3 ML H and 1 ML H adsorption led to a metallic surface, whereas no adsorption and 2/3 ML H adsorption led to an insulating surface, in agreement with prior DFT calculations of the STO(001) surface. The 1/3 ML H and 1 ML H surfaces have the Fermi energy located near the bottom of the conduction band, primarily comprised of Ti d states. The 2/3 ML H surface have a highly localized midgap state which is the Ti-H bond; the Fermi level is pinned by this state, and the system is insulating. We also show the weakening of the Ti-H bond due to excess adsorption of charge donated by the O-H complexes. We show that, once each O and Ti is occupied, additional H adsorption leads to formation of H<sub>2</sub>, so that the maximum coverage is one H for each surface O and Ti. For the  $(\sqrt{2} \times \sqrt{2})$  surface, we see that the system remains metallic up to 4H adsorption, due to the imbalance of Ti-H and O-H complexes, in contrast with the  $(1 \times 1)$  surface, which is either insulating or metallic depending on the coverage of H. We see that, in all coverages, for either surface, the insulating systems do not support a rumpling or polarization in BTO, whereas all metallic systems support a polarization in BTO. The addition of electrons from adsorbed H transforms the surface TiO<sub>2</sub> layer into a metallic capping layer, stabilizing the ferroelectricity of the slab without a metal electrode. The polarization is increased with respect to bulk by the adsorbed H.

#### ACKNOWLEDGMENTS

We thank Chungwei Lin and Agham Posadas for critically reading the paper and Lingyuan Gao for many insightful discussions. This paper was supported by the National Science Foundation (Award No. DMR-1207342), the Air Force Office of Scientific Research (Grants No. FA9550-12-10494

and No. FA9550-14-0090), and Texas Advanced Computing Center.

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