

# Humidity effects on (001) BaTiO<sub>3</sub> single crystal surface water adsorption

D. Y. He,<sup>1</sup> L. J. Qiao,<sup>1,a)</sup> Alex A. Volinsky,<sup>2</sup> Y. Bai,<sup>1</sup> M. Wu,<sup>1</sup> and W. Y. Chu<sup>1</sup>

<sup>1</sup>Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE),

University of Science and Technology Beijing, Beijing 100083, People's Republic of China

<sup>2</sup>Department of Mechanical Engineering, University of South Florida, Tampa, Florida 33620, USA

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Water adsorption on (001) BaTiO<sub>3</sub> single crystal surface under varying relative humidity conditions was studied by *ab initio* calculations and scanning probe microscopy utilizing different operation modes. At 95% relative humidity water droplets nucleated only on *c* domains, preferential adsorption location for water dipoles. BaTiO<sub>3</sub> (001) surface long 65% relative humidity exposure lead to no contrast between *a* and *c* domains observed by electrostatic force microscopy. *Ab initio* calculations confirm that water molecules prefer to adsorb on *c* domains due to their higher surface energy. © 2011 American Institute of Physics. [doi:10.1063/1.3544586]

Multiple efforts studied ferroelectrics performance in humid air,<sup>1–5</sup> which causes delayed cracking and fracture of ferroelectric ceramics under sustained electric field,<sup>1</sup> stress,<sup>2</sup> or mechanical-electrical coupling.<sup>3</sup> Under mechanical stress or electric field in BaTiO<sub>3</sub> single crystal, humidity can promote domain switching from *a* to *c*, but retard switching from *c* to *a*.<sup>4,5</sup> Humidity affects ferroelectrics performance. Several studies reported surface water film and adsorbates present on perovskite surfaces.<sup>6–11</sup> Scanning probe microscopy (SPM) is a convenient method for characterizing ferroelectric surfaces.<sup>12–19</sup> This paper aims to study water adsorption on ferroelectric surfaces using SPM. Ac atomic force microscopy (AFM) and electrostatic force microscopy (EFM) can be used to detect water droplets and characterize surface electrical properties under varying humidity.<sup>20,21</sup> *Ab initio* calculations were employed to reveal water adsorption mechanism on ferroelectrics.<sup>22,23</sup>

BaTiO<sub>3</sub> single crystal with 5 × 5 × 1 mm<sup>3</sup> dimensions was used in this study. Crystal was poled along [100] direction to get *a* domains on the (001) plane and then partially poled along the [001] direction to achieve some regions with 90° *a*–*c* domain structures. The sample was kept at 100 °C in dry Ar for 30 min to remove surface adsorbates and then slowly cooled to room temperature. Experiments were carried out with environmental chamber-equipped Agilent 5500 SPM (Agilent Technologies, USA). Relative humidity (RH) in the chamber was measured by a digital hygrometer and controlled by circulating Ar and water vapor. The instrument was operated in ac and EFM modes using both conventional (PPP-NCH, Nanosensors, Switzerland) and Pt–Ir coated silicon tips (PPP-EFM). For EFM 80 kHz cantilever frequency was used, just below 85 kHz resonance, while in ac mode 280 kHz cantilever frequency was used, close to its 300 kHz resonance frequency.

*Ab initio* density-functional theory calculations were conducted with commercial CASTEP code (UK), aided by MATERIALS STUDIO (Accelrys, USA) graphical front-end interface.<sup>24</sup> Exchange correlation interactions were described by the generalized gradient approximation in the Perdew–Burke–Ernzerhof form.<sup>25</sup> Ultrasoft Vanderbilt pseudopotentials were used in the treatment of core electrons<sup>26</sup> with

kinetic cutoff energy of 380 eV. A 6 × 6 × 3 mesh of special *k*-points in irreducible Brillouin zone was employed for *k*-space integrations. Calculation accuracy is as follows: stress ≤ 0.02 GPa, atomic displacement ≤ 5 × 10<sup>−4</sup> Å, energy per atom ≤ 5 × 10<sup>−6</sup> eV, and atomic forces ≤ 0.01 eV/Å.

Ac AFM mode was used to characterize water distribution on the (001) BaTiO<sub>3</sub> single crystal surface at 85% RH. Nucleation and growth of water droplets on the *a* domain surface are shown in Fig. 1. Humid air exposure duration had a pronounced effect on droplets' growth. After 8 min a few small water droplets nucleated on the (001) surface [Fig. 1(a)]. Nucleated water droplets grew in size with new droplets emerging with time [Fig. 1(b)]. After 120 min, an equilibrium state was reached with lateral droplet size ranging from 100 to 500 nm [Fig. 1(b)]. Droplet height increased continuously with time, growing fast during the first 20 min and then slowing down in Fig. 2. After 120 min droplets no longer grew and achieved saturation. Water droplets strongly adsorb on BaTiO<sub>3</sub> (001) surface. During humidity exposure interfacial force decrease is a spontaneous process associated with the surface energy change  $\Delta E = (E_{\text{Bulk}} + E_{\text{H}_2\text{O}} - E_{\text{Bulk,H}_2\text{O}}) > 0$ . After long humidity exposure sample surface is already saturated with H<sub>2</sub>O with no significant surface energy change. For the nucleation sites, Geneste and Dkhil found through density-functional calculations that in-plane-polarized BaTiO<sub>3</sub> (001) surface has strong interactions with water chemisorbed on both BaO and TiO<sub>2</sub> terminations.<sup>27</sup> Oxygen sites of both terminations have

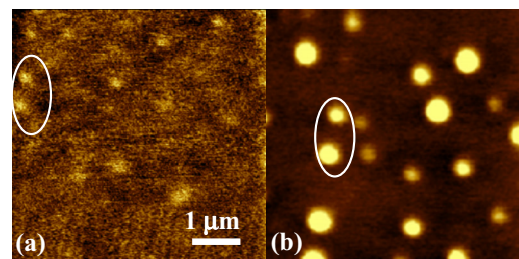


FIG. 1. (Color online) ac mode AFM images of water droplets nucleation and growth on (001) BaTiO<sub>3</sub> single crystal *a* domain surface at 85% RH after: (a) 16 min (3 nm Z scale) and (b) 120 min exposure (12 nm Z scale). The same region is outlined in both images.

<sup>a)</sup>Electronic mail: lqiao@ustb.edu.cn.

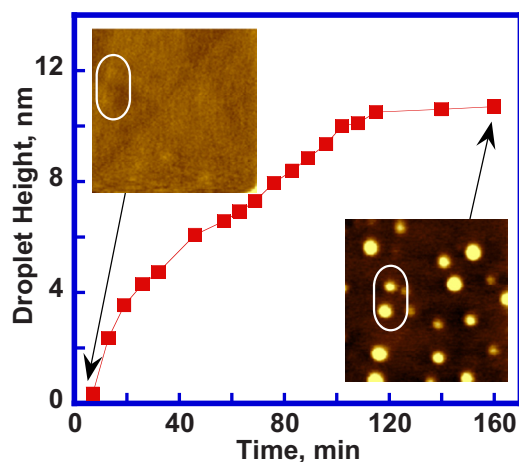


FIG. 2. (Color online) Water droplet height time dependence at 85% RH. Inserts show surface topography with the same area outlined.

strong intrinsic ability to attract and dissociate water and retain protons. It was concluded that water adsorption localized at certain sites on ferroelectric surfaces.

To characterize relationship between water adsorption and domains configuration, (001) surface with *a*–*c* domain structures was investigated. Figures 3(a) and 3(b) show topography and amplitude images obtained in dry Ar with surface topography corrugations attributed to adjacent *a* and *c* domains. As shown in previous work,<sup>4</sup> bright stripes in Fig. 3(b) are *c* domains and dark zones are *a* domains. Ferroelectric single crystal *a* and *c* domain surfaces have different electrical properties.<sup>28</sup> Based on the surface potential section profile in Fig. 3(b), *c* domain has higher potential, indicating positive polarization charge on its surface, while *a* domain has no surface charge. When humidity in the chamber increased to 95% RH, the surface conditions changed remarkably, as seen in Figs. 3(c) and 3(d). Water droplets assembled and spread along almost the whole *c* domain stripes, but no droplets were observed on *a* domains. Polarization charge supplies *c* domain surface with additional electrostatic energy, thus *c* domain has higher surface energy than *a* domain, demonstrated by *ab initio* local density calculations.<sup>29</sup> Be-

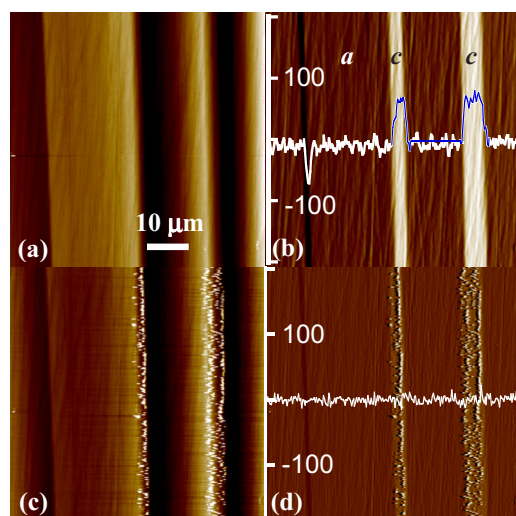


FIG. 3. (Color online) (001) BaTiO<sub>3</sub> surface topography images (80 nm Z scale) of *a*–*c* domain corrugations in (a) dry Ar and (c) at 95% RH; (b) and (d) are corresponding amplitude images with potential profiles in mV superimposed.

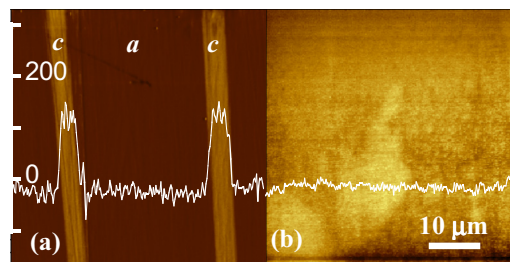


FIG. 4. (Color online) EFM images of original *a* and *c* domain corrugations on (001) BaTiO<sub>3</sub> surface acquired in (a) dry Ar (1 V Z scale), (b) after 30 min 65% RH exposure with corresponding potential profiles in mV superimposed (50 mV Z scale).

cause of higher surface energy polar H<sub>2</sub>O molecules prefer to adsorb on the *c* domain to neutralize its surface charge. Due to the strong interaction between electric dipoles, *c* domain surface charge promotes nucleation of adsorbed H<sub>2</sub>O molecules into droplets, so tiny water droplets assembled on the *c* domain surface leading to potential difference between *a* and *c* domains drops significantly, as shown in Fig. 3(d).

Figure 4 shows EFM images of (001) BaTiO<sub>3</sub> single crystal surface potential profiles under dry and humid conditions. In dry Ar *a* and *c* domains exhibit a large difference in surface potential with obvious domain boundaries present in EFM images, as shown in Figs. 4(a) and 4(b). As humidity was increased to 65% RH, image contrast decreased and the domain boundaries became less pronounced with time. After 30 min of 65% RH exposure, contrast became too low to be distinguished and the potential was almost zero. As a result the Z scale was adjusted from 1 V to 50 mV, showing slight texture in Fig. 4(b), but flat overall potential distribution. Electric field difference between *a* and *c* domains gradually disappeared with time because water molecules were continually adsorbed on the surface and neutralized *c* domains surface charge. Surface charge screening by polar water molecules determines surface electric performance.

*Ab initio* calculations were used to investigate water adsorption effect on BaTiO<sub>3</sub> surfaces. A supercell containing two BaTiO<sub>3</sub> cells was constructed along the *z* axis and optimized to obtain stable structure. (100) surface corresponding to *a* domain was created by cleaving the surface and inserting a vacuum slab at 15 Å depth. By releasing the top surface layer and constraining the bottom layer, (100) surface structure was relaxed to minimize the energy assuming stable state. Similarly, stable (001) surface *c* domain structure was obtained using this approach. After long relaxation time, minimal energies of (001) and (100) surfaces,  $U_1(001)$  and  $U_1(100)$ , were calculated. Higher  $U_1(001)$  energy compared with  $U_1(100)$  indicates that *a* domain is more stable than *c* domain. Then stable H<sub>2</sub>O molecule was placed into the vacuum slab to form initial adsorption model. By fixing the distance and angle between O and H atoms in H<sub>2</sub>O molecule, an optimization was carried out to obtain stable state of adsorbed *c* and *a* domain surfaces. The energy change in the adsorption process was calculated as  $U_{\text{ads}} = U_1 + U(\text{H}_2\text{O}) - U_2$ . Energy decrease by water adsorption was larger for the (001) surface than for the (100) surface, shown in Table I. This means that interaction between water molecule and *c* domain is stronger compared with *a* domain, thus water prefers to adsorb on *c* domains.

TABLE I. (100) and (001) surface energy before ( $U_1$ ) and after ( $U_2$ ) water adsorption with corresponding adsorption energy ( $U_{\text{ads}}$ ).  $U(\text{H}_2\text{O})$  is  $\text{H}_2\text{O}$  molecule energy.

| Energy (eV)             | (100)    | (001)    |
|-------------------------|----------|----------|
| $U_1$                   | -7241.46 | -7236.58 |
| $U(\text{H}_2\text{O})$ | -468.77  | -468.77  |
| $U_2$                   | -7710.31 | -7705.9  |
| $U_{\text{ads}}$        | 0.08     | 0.55     |

In summary, water interacts strongly with  $\text{BaTiO}_3$  (001) surface. Ferroelectrics adsorb water causing changes in their surface electric performance. Adsorption difference between *a* and *c* domains is due to their surface energy. Polar water molecules initially adsorb on *c* domains to neutralize surface charge. Water adsorption behavior is determined by relative humidity and exposure duration. If relative humidity is suddenly increased to 95%, water droplets form preferentially on *c* domain surfaces. If the sample is exposed to relatively low 65% RH for a long time, a large contrast decrease appears in EFM images. Adsorbed water neutralizes surface charges, thus electric potential difference between *a* and *c* domains gradually disappears with exposure time in humid environment.

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