

## Characteristics of the low electron density surface layer on BaTiO<sub>3</sub> thin films

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The surfaces of epitaxial BaTiO<sub>3</sub> films on SrTiO<sub>3</sub> substrates were investigated by x-ray reflectivity (XRR) and angle-resolved x-ray photoelectron spectroscopy (ARXPS). It was shown by XRR analysis that there exists a low electron density surface layer (about 87%–93% of the electron density of the underneath BaTiO<sub>3</sub> layer) of 15 Å on top of the film. Moreover, ARXPS results revealed a surface core-level shift of Ba in layer of about 11 Å, a value which is in agreement with the thickness obtained by XRR, indicating that the surface core-level shift of Ba stems from the low electron density surface layer. © 2008 American Institute of Physics. [DOI: 10.1063/1.2828339]

BaTiO<sub>3</sub> (BTO) as a typical perovskite ferroelectric material has been extensively investigated owing to the prospective applications in integrated capacitors, sensors, and high-density memories.<sup>1,2</sup> Most of these applications are oriented toward thin film geometries, where the surface/interface properties are of most important.<sup>3–7</sup> However, the near surface/interface structure of BTO remains not clear and needs better understanding.

Previous studies by x-ray photoelectron spectroscopy have revealed two sets of barium (Ba) core levels in the near surface region of BTO.<sup>8–10</sup> The lower-binding-energy component is assigned to Ba in BTO bulk environment and the higher-binding-energy one can be denoted as Ba surface state or the surface core-level shift of Ba. This Ba surface state is also found at the Pt/BTO interface<sup>11</sup> and Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> surface.<sup>12</sup> The existence of the layer containing Ba surface state might be a possible explanation of the “dead layer” effect.<sup>11,13</sup> However, none of the previous reports provided the thickness information of this layer; also no experimental evidence has been reported of the intrinsic structural difference near the surface region of the BTO films. In this work, we investigate the surface of the epitaxial BTO films on SrTiO<sub>3</sub> (STO) substrate by x-ray reflectivity (XRR) and angle-resolved x-ray photoelectron spectroscopy (ARXPS). We found that there is a low electron density surface layer on top of the BTO films; this surface layer contributes to the surface core-level shift of Ba.

The BTO films were deposited on single crystal STO (100) substrates by the laser molecular beam epitaxy equipped with reflection high-energy electron diffraction (RHEED). BTO films were deposited at 630 °C under an oxygen pressure of  $2 \times 10^{-2}$  Pa. After deposition, the samples were *in situ* annealed under the active oxygen for 20 min to reduce the oxygen vacancies. The stoichiometry ratio of Ba, Ti, and O of the sample is about 1:1:3 obtained

from Rutherford backscattering spectrometry using 3.06 MeV He<sup>2+</sup> ions as a probe beam (at this energy, the backscattering cross section for oxygen is greatly enhanced due to resonant scattering,<sup>14</sup> the uncertainty of the oxygen content is less than 3%), which suggests that there should be very few oxygen vacancies in the film. The detailed deposition conditions have been described elsewhere.<sup>15</sup> The sample of thickness 3000 Å estimated by counting the RHEED intensity oscillations was used for the analysis.

The x-ray reflectivity and high-resolution x-ray diffraction measurements were performed on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation. The incident beam in vertical direction was defined by a 0.1 mm slit at 300 mm before the sample and the scattered beam was collected by a 0.2 mm slit in vertical direction. The grazing incidence x-ray diffraction (GID) was performed at the diffuse scattering station of the Beijing Synchrotron Radiation Facility. The ARXPS was performed on a PHI-5300/ESCA surface analysis system using K $\alpha$  of Al ( $E=1486.6$  eV) at different take-off angles. The position of the C 1s peak was taken as a standard (with a binding energy of 285.0 eV).

The x-ray diffraction profile of the sample is shown in Fig. 1. The BTO film is found to be single phased and well oriented along the (00 $l$ ) direction. The out-of-plane lattice

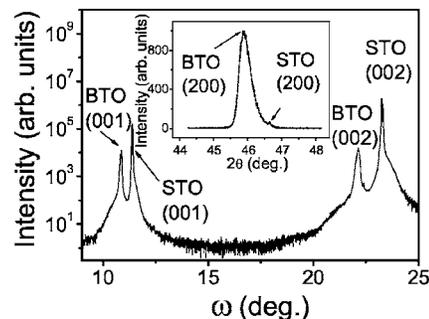


FIG. 1. X-ray diffraction profile of the sample. Inset: the grazing incidence x-ray (200) diffraction (GID) profile taken at the incident angle of 0.3°.

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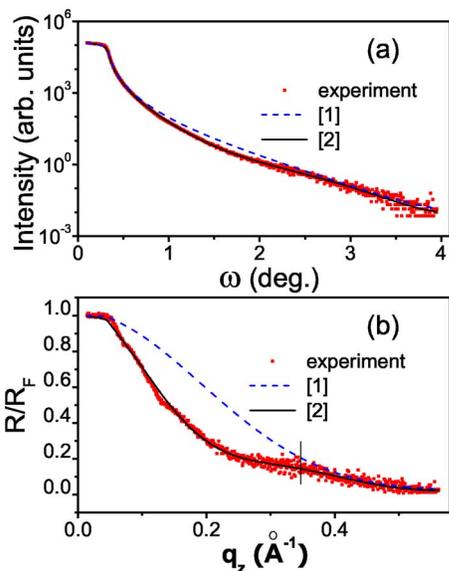


FIG. 2. (Color online) (a) X-ray reflectivity profiles of the sample. (b)  $R/R_F$  vs  $q_z$  to show the oscillations clearly. [1] fitting without surface layer (dashed line) and [2] fitting with surface layer (solid line).

constant is calculated to be  $4.08 \text{ \AA}$  and the in-plane lattice constant obtained from the GID (shown in the inset) is  $3.96 \text{ \AA}$ . It is very close to the tetragonal structure of bulk BTO ( $a=3.99 \text{ \AA}$  and  $c=4.04 \text{ \AA}$ ). Therefore, the BTO film is considered to be of tetragonal structure with small distortion.

Figure 2(a) shows the XRR result of the sample measured in air at  $115 \text{ }^\circ\text{C}$ . At this temperature, the physical adsorbed water on BTO surface could be removed.<sup>16</sup> The curves have been corrected for illumination. To present the interference fringes more clearly, we plotted the reflectivity data as  $R/R_F$  versus  $q_z$  in Fig. 2(b), where  $R_F$  denotes the Fresnel reflectivity of an ideally smooth surface;  $q_z = 4\pi \sin \omega / \lambda$  is the vertical wave-vector transfer with the incident angle  $\omega$  of the radiation with respect to the surface. The nominal thickness of the sample is  $3000 \text{ \AA}$ , which can be considered as infinitely thick layer for the XRR measurement. A bump is seen at  $q_z \approx 0.35 \text{ \AA}^{-1}$ , indicating that a surface layer is present on top of the film with an electron density different from the underlying BTO layer. We simulated the XRR profiles using the matrix formalism corrected by a Croce-Nevot factor.<sup>17,18</sup> From Fig. 2, we found that the model including only the BTO layer fails to reproduce the experimental data. However, the model, which includes a surface layer on the BTO layer, fits the experimental data best. From the fitting, we obtain that the BTO layer has an electron density of  $1.50 e^-/\text{\AA}^3$ ; this value is very close to the electron density of bulk tetragonal BTO phase (about  $1.56 e^-/\text{\AA}^3$ ), indicating that the film has a dense structure. The surface layer has a thickness of  $15 \text{ \AA}$  and a graded electron density ranging from  $1.31$  to  $1.40 e^-/\text{\AA}^3$ .

Figure 3 shows the electron density profile (EDP) obtained from the fitting data. From the EDP, one finds clearly that there are two regions in the curve, the surface layer and the BTO layer. This low electron density surface layer is expected to be a layer including Ba, which is originated from the BTO film itself. This enforces us to assume that the surface core-level shift of Ba may be due to the surface layer. To convince this assumption, we performed ARXPS analysis on this sample.

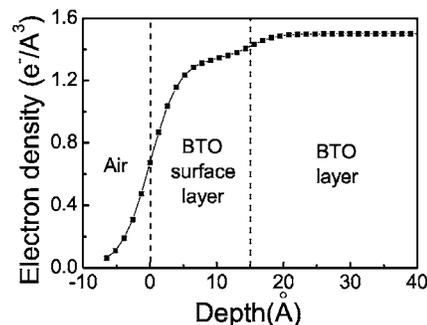


FIG. 3. The electron density profile (EDP) derived from the best fit to the experimental data.

Figure 4 shows the Ba  $3d$  core-level spectra of the sample taken at the takeoff angle of  $15^\circ$  (surface sensitive),  $30^\circ$ ,  $45^\circ$ , and  $90^\circ$  (interface sensitive). From Fig. 4, it is evident that the Ba  $3d_{3/2}$  and Ba  $3d_{5/2}$  peaks taken at different takeoff angles are composed of two components, the lower-binding-energy ones (Ba I) at  $778.1$  and  $793.4 \text{ eV}$  and the higher-binding-energy ones (Ba II) at  $779.5$  and  $794.8 \text{ eV}$ . With the decreasing of the takeoff angle, the intensity of Ba I decreases, whereas the intensity of Ba II increases, indicating that Ba II is originated from the surface (Ba surface state) and Ba I is from the interior BTO phase.<sup>10</sup>

We can estimate the thickness of the layer containing the Ba surface state by the formula  $d = \lambda \sin \alpha \times \ln(R/R_\infty + 1)$ ,<sup>19</sup> where  $\lambda$  is the mean attenuation length (about  $20 \text{ \AA}$ ),<sup>20</sup>  $\alpha$  is the takeoff angle,  $R$  is the intensity ratio of  $I_{\text{surface}}/I_{\text{bulk}}$ , and  $R_\infty$  is the ratio  $I_{\text{surface}}/I_{\text{bulk}}$  in the case of infinitely thick surface layer and bulk sample. The value of  $R_\infty$  is approximately 1 in the calculation. The formula is less accurate at the take-off angle lower than  $22.5^\circ$  due to the elastic electric scattering and the surface roughness. The plot of  $\ln(R/R_\infty + 1)$  versus  $1/\sin \alpha$  will produce a straight line through zero whose slope is  $d/\lambda$ , and then we obtain the thickness  $d$  to be about  $11 \text{ \AA}$ . This value is in the same order of magnitude as the thickness of the low electron density surface layer. From the above results, we conclude that the Ba surface state stems from the low electron density surface layer.

Let us now discuss the reason for the formation of the low electron density surface layer. One possible explanation is that the BTO on the surface reacts with the environment to form  $\text{BaCO}_3$  phase,<sup>21</sup> which has a lower electron density than that of the BTO film. However, XPS results of C  $1s$  (not shown) convince that there is no  $\text{BaCO}_3$  on the surface. Another possibility is that the top layer of BTO has rough sur-

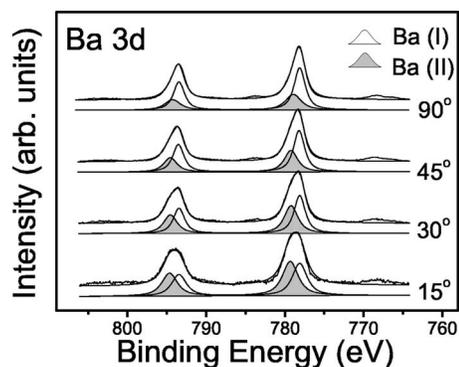


FIG. 4. Angle-resolved XPS spectra of Ba  $3d$  core level taken at the takeoff angle of  $15^\circ$  (surface sensitive),  $30^\circ$ ,  $45^\circ$ , and  $90^\circ$  (interface sensitive).

face, causing the decrease of the electron density. However, atomic force microscopy surface morphology (not shown) indicates that the surface is flat and compact. The root-mean-square surface roughness is 1.7 Å and the maximum height fluctuation is 6.4 Å.<sup>11</sup> The surface roughness is far smaller than the thickness of the surface layer. Therefore, this possibility can be excluded. The most possible reason is the surface lattice expansion due to the surface relaxation of BTO, which decreases the electron density of the surface layer.

Many authors investigated the surface relaxation of BTO ferroelectrics and suggested that there exists lattice expansion in the near surface region. Ishikawa and Uemori estimated that the magnitude of the relaxation is about 3.8% and its thickness is about eight layers in BTO.<sup>22</sup> Jian *et al.* also reported that there might be a surface relaxation of 10% outward in the BTO (100) plane.<sup>23</sup> The surface relaxation of BTO is also considered to exist in our films. Therefore, the surface layer will have less electron density than that of the underneath BTO layer. This might be the reason for the formation of the low electron density surface layer.

Because of the lattice relaxation of BTO, the ionic spatial distribution in the surface layer is different with the bulk BTO, which would influence the binding energy of Ba.<sup>24</sup> In addition, oxygen vacancies might exist in the air/BTO interface.<sup>8,25</sup> In this case, Ba cannot be fully coordinated, consequently causing the positive shift of Ba core level. Lattice relaxation of BTO and possible oxygen vacancies in the surface would be the origin of the surface core-level shift of Ba.

In summary, the surfaces of epitaxial BTO films grown on STO substrates were investigated by XRR and ARXPS. It was shown that there exists a low electron density surface layer of 15 Å on top of the BTO films. This layer contributes to the surface core-level shift of Ba. The surface relaxation of BTO is considered to be the reason for the formation of the surface layer. Lattice relaxation and possible oxygen vacancies in the surface might be the origin of the surface core-level shift of Ba.

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