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doi:10.1017/S1431927617008807

Microsc. Microanal. 23 (Suppl 1), 2017

In-situ STEM-EELS observation of ferroelectric switching of $BaTiO_3$ film on GaAs

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Ferroelectric metal-oxide thin films grown on semiconductor substrates are being studied due to their potential applications in non-volatile single transistor memory elements [1]. Epitaxial single-crystalline $BaTiO_3$ (BTO) thin film was successfully grown on polar GaAs substrate with a $SrTiO_3$ (STO) interlayer using molecular beam epitaxy method [2]. The spontaneous polarization of the BTO film was characterized using scanning transmission electron microscope (STEM) along with electron energy-loss spectroscopy (EELS) [3], and the macroscopic ferroelectric switching under coercive electrical biases was measured using piezoresponse force microscopy [4]. However, the microscopic ferroelectric behavior and the switching mechanism at the interfaces have yet to be demonstrated. In this work, we performed an atomic-scale STEM-EELS study of the ferroelectric switching of BTO film on STO-buffered GaAs substrate with *in-situ* electrical biasing.

The BTO/STO/GaAs cross-section sample is prepared by focused ion beam method and attached on the ProtoChips electrical E-chip using Pt as electrode. The Z-contrast images and EEL spectra are acquired using aberration-corrected JEOL ARM200CF STEM equipped with a cold field-emission source at 200 kV. The atomic-resolution Z-contrast image of the sample without electrical bias is shown in Figure 1(a). A 15-unit-cell thick BTO film is observed to be epitaxially grown on 2-unit-cell STO buffer layer on As-terminated GaAs substrate with an abrupt STO/GaAs interface. Atomic-resolution EEL spectra of Ti $L_{3,2}$-edge are taken from first four TiO_2 monolayers from the STO/GaAs interface as shown in Figure 1(b). The Ti L-edge in the BTO interfacial layers exhibits four prominent peaks originating from the $3d^0$ states splitting into t_{2g} and e_g components, which corresponds to a Ti^{4+} valence. However, the intensity of the third peak decreases in the STO layers, indicating a decrease of Ti valence from 4+ to a mixture of 3+ and 4+, due to interfacial O vacancies. Thus, the STO/GaAs interface is polarized by the interfacial dipole in the [001] direction, creating a spontaneous polarization of the BTO film in the [001] direction.

In-situ electrical bias (±3 V) is then applied to the sample to study the ferroelectric behavior of the BTO film. The positions of the atomic columns in the Z-contrast images are determined using the center-of-mass method as illustrated in the insets in Figure 2. The polarization is then quantified by the displacement of Ti columns with respect to the center of four neighboring Ba columns in an averaged section from the Z-contrast image. From Figure 2(a), we can directly observe that, upon application of -3 V, Ti columns are displaced downwards with respect to the Ba columns, indicating the switching of polarization from [001] to [00-1] direction. The average displacement of Ti columns is measured as -0.16 Å. Upon application of +3 V, as shown in Figure 2(b), the polarization reverses with an Ti average displacement of +0.39 Å. EEL spectra of O K-edge are measured within the BTO film under different electrical biases as shown in Figure 2(c). It is observed that peak a shifts towards higher energy by 0.4 eV after application of -3 V while shifts back to lower energy by 0.7 eV upon following application of +3 V. The energy shift confirms the structural change of TiO_6 octahedral under different external biases as we observed in the Z-contrast images. The charge accumulation and depletion at the STO/GaAs interface under external biases, which is important to understand the microscopic ferroelectric behavior, will be further studied.

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[5] This work was supported by the National Science Foundation (Grant No. DMR-1408427).

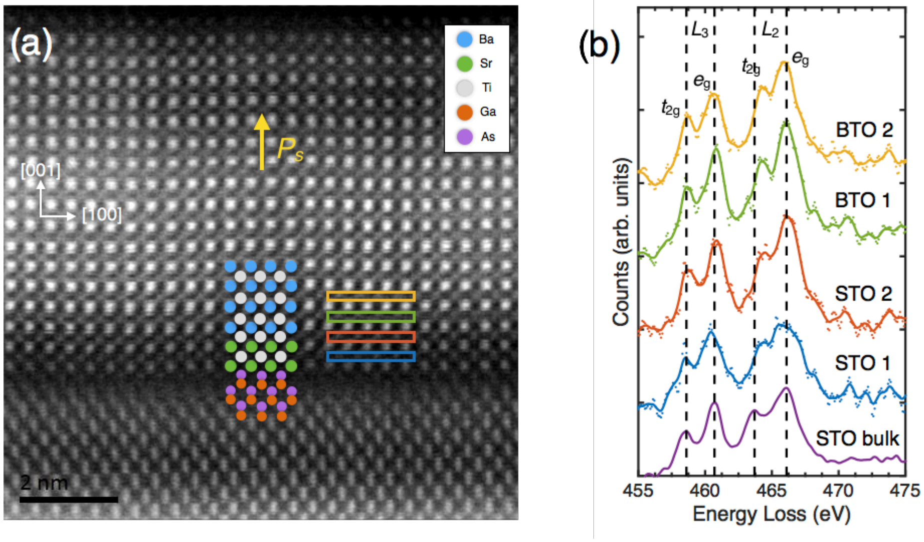

Figure 1. (a) Atomic-resolution Z-contrast image of the BTO/STO/GaAs sample without electrical bias. The proposed atomic columns are shown as inset. The spontaneous polarization P_s is in the [001] direction. (b) EEL spectra of Ti $L_{3,2}$-edge fine structure taken from the first four TiO_2 monolayers at the interface, corresponding to the colored rectangles in (a), along with that from STO bulk as reference. The spectra are aligned using L_3-t_{2g} peak and smoothed by Gaussian function with raw data shown by dotted curves.

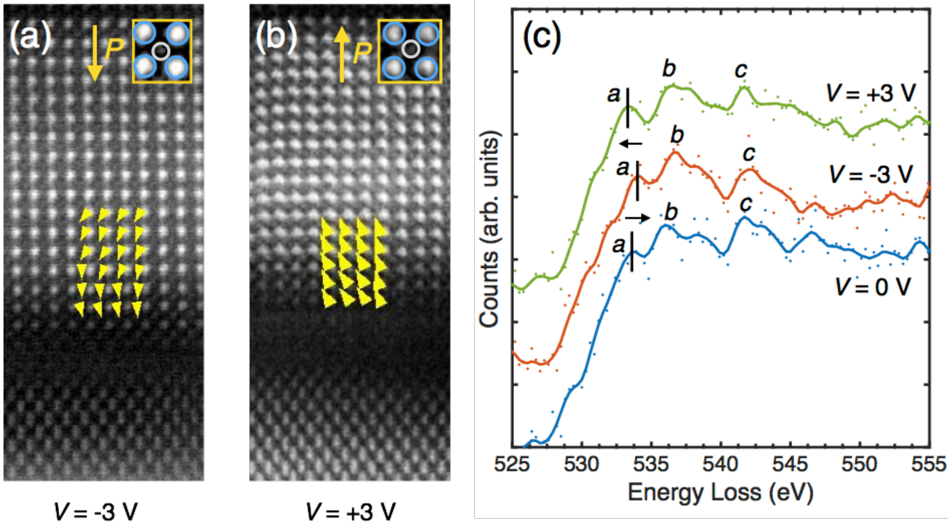

Figure 2. (a) and (b) Atomic-resolution Z-contrast images of the sample under -3 V and +3 V external biases, respectively. The polarization is measures by the displacement of Ti column with respect to Ba columns as shown in the insets. The direction of polarization in the calculated area is marked by the yellow triangles. (c) EEL spectra of O *K*-edge fine structure taken from the BTO film under $V = 0$, -3 and +3 V. The spectra are aligned with respect to Ba $M_{5,4}$-edge (not shown) and smoothed by Gaussian function with raw data shown by dotted curves. The three featured peaks are marked by *a*, *b* and *c*.

https://doi.org/10.1017/S1431927617008807