Soft X-ray photoemission study of Ba adsorption on the ceramic multiferroic BiFeO$_3$

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Abstract. Electronic structure of the ceramic multiferroic BiFeO$_3$ and ultrathin Ba/BiFeO$_3$ interface was studied in situ using photoelectron spectroscopy with energies in the range of 120–900 eV. The photoemission from the Bi 4$f$, O 1$s$, Fe 2$p$, and Ba 4$d$ core levels was studied. An effect of Ba adsorption is found to induce a significant change in all spectra that is originated from the strong interaction with the charge transfer between Fe, O, Bi surface atoms and Ba adatoms. The recharge between Fe$^{3+}$ ↔ Fe$^{2+}$ ions in surface region induced by Ba adsorption is found that provide enhancing the ferroelectric polarization gain.

1. Introduction

Multiferroics are the arresting group of materials with combining ferroelectric and magnetic properties. Multiferroics produce a lot of attention due to their potential application in spintronic and data storage devices. Multiferroic BiFeO$_3$ (BFO) is a suitable candidate for attaining ferroelectric and antiferromagnetic domain coupling owing to its high Curie temperature of ~1100 K and high Neel temperature of ~643 K [1, 2]. BFO has attracted much attention on account of simultaneously exhibiting magnetic and ferroelectric ordering. BiFeO$_3$ is characterized by a relatively simple crystal structure as the rhombohedrally distorted perovskite. Large ferroelectric polarization was predicted and observed in the BFO thin film in recent publications [3-6]. Electronic properties of BFO studied by X-ray photoelectron spectroscopy have been discussed in a series of experimental works [7-11]. The fine structure of the Fe 2$p_{3/2}$ core level was reveal to be on account of both the Fe$^{2+}$ and Fe$^{3+}$ ions [4, 9, 11]. It was found that ferroelectric polarization tends to grow with increasing Fe$^{2+}$ ions [4, 11]. Most of the works focused on study of the BFO core levels, and no works are devoted to the valence band spectra at low excitation energies, when surface and near-surface layers can be studied.

Applications of multiferroic materials in nanoscale devices necessitate studies of electronic properties of both the surface and interface. Studies of these systems provide insight into fundamental mechanisms of coupling between the lattice, spin, and electronic degrees of freedom and resulting order parameters in the bulk and at the interfaces. However, metal/BFO interfaces are still not investigated.

Recently, photoelectron spectroscopy (PES) experiments for the clean BFO have been carried out [1-4]. Most of BFO works focused on core level spectra, and no study is devoted to the valence band. This work present first PES study of Ba/BFO interface.

This paper reports PES studies of evolution in the electronic structure of the Ba/BiFeO$_3$ interface relevant to charge transfer and to exist of the Fe$^{2+}$ ions connected with the ferroelectric polarization. The data obtained through change in the valence band, Fe 2$p$, Bi 4$f$, O 1$s$, Ba 4$d$ core levels spectra show some mechanisms of interface formation and significant interaction between adatoms (Ba) and...
surface atoms (Bi, Fe, O). We demonstrate that a mechanism of the Ba/BiFeO interface formation is originated from the excited charge transfer in surface region that leads to effect of recharge of \( \text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+} \) ions and increase in amount of the \( \text{Fe}^{2+} \) ions.

2. Experimental

Photoemission studies were carried out at BESSY II (Helmholtz Zentrum, Berlin) via synchrotron radiation with photon energies in the range of 120–900 eV. Experiments were performed \textit{in situ} in an ultrahigh vacuum of \( 5 \times 10^{-10} \) Torr. Ceramic polycrystalline sample of BFO was obtained from initial fine-dispersed powder by sintering processing at a temperature of \( \sim 1200 \) K. The BFO sample was preliminary heated \textit{in situ} at a temperature of \( \sim 1000 \) K. Photoelectrons in a cone oriented along the normal to the surface were detected. The normal photoemission spectra from the valence band (VB) and from Bi 4f, O 1s, Fe 2p, Ba 4d core levels were recorded. The total energy resolution was 50 meV.

Step-by-step deposition of Ba submonolayer coverage up to 2 monolayers (ML) was performed onto the BFO surface. To ascertain the Ba coverage, the amount of 1 ML of Ba atoms can be analyzed from the intensity saturation of the Ba 4d core level peak. This made possible to determine the Ba dosage deposited onto the sample to better than 25%. The Ba overlayer is presented in monolayer units because of Ba sticking coefficient is equal to one at least up to 1 ML. Note that 1 ML is defined as one complete layer of Ba atoms and equal to \( 6.5 \times 10^{14} \) atoms/cm\(^2\). The normal photoemission spectra from the Bi 4f, O 1s, Fe 2p, Ba 4d core levels were recorded.

3. Results and discussion

Overview of the normal photoemission spectrum for the clean BiFeO\(_3\) ceramic sample at excitation energy of \( h\nu = 400 \) eV is presented in Figure 1a, curve 1. The spectrum clearly shows the principal Bi 4f peak and denotes a lack of foreign contaminations. As can been seen, the photoemission in the valence band region (VB) has too little intensity and could be measured at lower excitation energies (see Figure 1b).

![Figure 1(a, b). (a) Normal photoemission spectrum for the clean BiFeO\(_3\) (curve 1) ceramic sample and after 0.9 ML of Ba adsorption (curve 2). Excitation energy \( h\nu = 400 \) eV; (b) Normal photoemission spectra in the valence band region of the BiFeO\(_3\) ceramic sample at different Ba coverages: 1 – clean sample, 2 – 0.9 ML of Ba. Excitation energy \( h\nu = 120 \) eV.](image)

The normal photoemission spectrum of the ceramic BFO sample in the VB region and Bi 5d core level is shown in Fig. 1b, curve 1. The excitation energy is 120 eV. The position of the valence band maximum \( E_{\text{VBM}} = 0 \) eV is determined by extrapolating a linear fit to the leading edge of the VB photoemission. A broad band between binding energies of 0 and 10 eV below the \( E_{\text{VBM}} \) is obtained.
Calculations show that the width of the VB is about 8 eV [4, 8]. It is slightly less than obtained experimentally. Two small features located at binding energies of ~4 eV and ~6 eV can be related to the photoemission from the O 2p and Fe 3d core levels [5, 8, 12]. The broad feature between 20 and 30 eV is believed to consist of two separate structures, of which at least one is due to Bi 5d core level. It is evident that the Bi 5d are composed of two components, the lower-binding energy ones Bi 5d$_{3/2}$ at 26 eV and the higher-binding energy ones Bi 5d$_{5/2}$ at 29 eV. An unresolved shoulder at about 22 eV can be attributed to the O–related state, namely, O 2s as shown in [13].

Figure 2a presents photoemission spectra for the Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ core levels doublet. Shape of Bi 4f spectrum for the clean BFO (curve 1) coincides well with the data known from literature, for example [2]. The Ba adsorption on BFO surface is found to cause splitting the double structured spectrum of Bi 4f into two double structured ones, Figure 2a, curve 2. The initial Bi 4f core level peaks are shifted slightly to higher binding energy. The appearance of extra fine structure demonstrates the obvious chemical shift of the Bi 4f core level peaks corresponding to the photoemission from Bi atoms in the interface area.

![Figure 2(a, b).](a) Normal photoemission spectra of Bi 4f core level: 1 – clean BFO, 2 – Ba/BFO interface at Ba coverage 0.5 ML. Excitation energy $h\nu = 400$ eV; (b) Normal photoemission spectra of O 1s core level: 1 – clean BFO, 2 – Ba/BFO interface at Ba coverage 0.9 ML. Excitation energy $h\nu = 900$ eV.

A pronounced change induced by Ba adsorption is found to occur in the O 1s core level spectrum, as illustrated in Figure 2b. For the clean BFO surface the O 1s core level spectrum becomes a single peak at binding energy of 527 eV, Figure 2b, curve 1. The result characterizes the oxygen-metal bond in a single chemical state and the BFO surface without contaminations. Upon Ba adsorption, additional structure is found to appear on the high-binding-energy side of the O 1s peak at binding energy of about 530 eV, Figure 2b, curve 2. The emerge of the additional peak may be assigned to Ba adsorption providing interaction of oxygen surface atoms with Ba adatoms that leads to the appreciable chemical shift [9, 14, 15]. The energy shift of ~1 eV for the initial key component of
the O 1s peak to the lower binding energy indicates that the leading contribution to the chemical shift is the charge transfer, so the character of oxygen covalency is increased [9]. Besides, it should be considered that after Ba deposition oxygen atoms interact with modified Fe ions.

![Figure 3(a, b). Decomposition of normal photoemission spectra of Fe 2p_{3/2} core level for clean ceramic BFO (a) and for Ba/BiFeO$_3$ interface at Ba coverage of 0.9 ML (b). Thin red lines represent experimental data and thick black lines represent fitting results with fitting components. Excitation energy $h\nu = 850$ eV.](image)

The magnetic and ferroelectric properties of BFO are due to the Fe ions octahedrically surrounded with the oxygen ions, and due to not only Fe$^{3+}$ ions but especially also due to Fe$^{2+}$ ions [4, 7, 8]. So, studies of the photoemission from the Fe 2p core level can be used diagnostically to reliably identify the presence both the Fe$^{3+}$ and Fe$^{2+}$ ions. Figure 3 represents photoemission from the Fe 2p$_{3/2}$ core level for the clean BFO surface. The broad band Fe 2p$_{3/2}$ was decoupled into two subbands using Gaussian function. According to the fitting result, the atomic ratio of Fe$^{2+}$ and Fe$^{3+}$ ions corresponds to Fe$^{2+}$/Fe$^{3+} \approx 1$ in clean BFO. The Ba adsorption on BFO surface is found to cause significant change in the Fe 2p$_{3/2}$ spectrum (Figure 3). As can been seen, the atomic ratio is increased up to the value of Fe$^{2+}$/Fe$^{3+} \approx 1.5$ for Ba/BFO interface at Ba coverage of 0.9 ML. The observed effect of Ba adsorption signifies the improving ferroelectric polarization. The Ba ultrathin layer on the BFO surface is found to produce the strong interaction between Ba adatoms and Fe ions in interface area that leads to increase the ratio Fe$^{2+}$/Fe$^{3+} \approx 1.5$. The Fe 2p$_{3/2}$ core level evolution is obviously caused by the recharge between Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ ions and may be one of the reasons for enhanced ferroelectric and magnetic properties of BFO due to increasing in the amount of the Fe$^{2+}$ ions.

4. Conclusions

To summarize, the effect of Ba adsorption on the ceramic BFO surface was studied by PES using different excitation energy 120-900 eV. The Ba adsorption is found to modify the valence band spectrum as well as the Fe 2p, O 1s, Bi 4f core level spectra. It is found that the atomic ratio of the Fe$^{2+}$/Fe$^{3+}$ ions increases from ~1 up to ~1.5 in the process of the Ba/BFO interface formation. The data point out that the BFO ferroelectric polarization could be enhanced due to increase in the amount of the Fe$^{2+}$ ions under Ba adsorption. The appearance of additional shoulder on the high-binding-energy side of the O 1s photoemission peak is found that cause strong interaction of surface oxygen atoms with Ba adatoms. The negative energy shift of the key O 1s photoemission component indicates increasing the covalence of oxygen atoms. The Ba adsorption is found to induce splitting of the double structured spectrum of Bi 4f core level into two double structured ones accompanied by the chemical
shift. It could be attributed to the charge transfer from the Ba adsorbed atoms to the Bi surface atoms with increasing both the Bi-ionicity and electron density in the interface area. The data point out that the complex process of the charge transfer between Ba-Fe, Ba-Bi, Ba-O, Bi-O induced by Ba adsorption occurs in the condition of recharge between Fe$^{3+}$ ↔ Fe$^{2+}$ ions in the interface area that provide enhancing the ferroelectric polarization gain.

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