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Fe/BaTiO₃ interface: Band alignment and chemical properties

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Ultrathin BaTiO₃/Fe bi-layers were synthesized on MgO(001) and SrTiO₃(001) substrates by pulsed laser deposition in a single vacuum cycle. The full electronic band structure at the Fe/BaTiO₃ interface has been determined by hard x-ray photoemission spectroscopy measurements. Depending on the growth conditions, the valence and conduction band offsets are found 3.05–3.26 eV and 0.9–1.2 eV, respectively. Interface sensitive conversion electron Mößbauer spectroscopy demonstrates the absence of any magnetically dead layer thus proving that the determined band alignment is related to a sharp Fe/BaTiO₃ interface structure down to the atomic scale. © 2011 American Institute of Physics. [doi:10.1063/1.3657769]

The heterointerfaces between ferromagnetic (FM) and ferroelectric (FE) thin films have recently attracted much attention due to the magnetoelectric effects and their potential for the development of multifunctional devices. Among composite FM/FE multiferroics, the Fe/BaTiO₃ (BTO) system is one of the most popular.^{1–7} The magnetoelectric effect at the Fe/BTO interface was first predicted by Duan *et al.*¹ and attributed to changes of the interface magnetization upon the BTO electric polarization reversal. Electric manipulation of the Fe magnetic state was later observed in 10 nm Fe thin films deposited by pulsed laser deposition (PLD) on top of a BTO (100) single crystal, with a reported 20% change in the Fe coercive fields following the application of a 10 kV/cm electric field across the Fe/BTO structure.⁴ The inclusion of an ultrathin BTO tunnel barrier into Fe/BTO/La_xSr_{1-x}MnO₃ magnetic tunnel junctions has been used to manipulate the FM magnetization by switching the FE polarization through the magnetoelectric coupling at the FM/BTO interface,^{6,7} thus providing the unique opportunity of controlling the spin-dependent transport properties with electric rather than magnetic fields. The Fe/BaTiO₃ system also allows the control of the magneto-crystalline anisotropy that determines the Fe magnetization orientation.² Despite the high interest in the composite Fe/BTO multiferroic system, a full knowledge of the structural, chemical, and electronic interfacial structure is still lacking. In particular, the experimentally determined electronic band alignment for the Fe/BTO system has never been reported so far. In addition, the presence of magnetic "dead layers" has been reported at the Fe/BTO interface,⁵ which can directly affect the spin polarization of tunneling electrons in functional devices including the Fe/BTO stack.

In the present paper, the full electronic band alignment at the Fe/BTO interface has been determined utilizing x-ray photoemission spectroscopy (HAXPES), and the band gap

values for the employed ultrathin BTO layers was directly measured by reflection electron energy loss spectroscopy (REELS).⁸ Atomic-scale and interface sensitive ⁵⁷Fe conversion electron Mößbauer spectroscopy (CEMS) demonstrates the absence of any magnetically dead layer at the Fe/BTO interface, thus proving that the proposed band structure is intrinsically related to a chemically pure Fe/BTO system.

Fe/BTO heterostructures were grown by PLD in a home-made setup with a base pressure of $p \approx 10^{-6}$ Pa on MgO (001) and SrTiO₃ (001) (STO) single-crystal substrates by using a YAG:Nd laser ($\lambda = 1064$ nm) operating in the Q-switched regime ($\tau = 15$ ns) with the variable output energy $E = 50 \div 200$ mJ and repetition rate $\nu = 5\text{--}50$ Hz. Both Fe/BTO and BTO/Fe types of interfaces were formed in order to investigate the effect of the growth conditions on the interface properties. The BTO films (2–15 nm) were grown from the sintered stoichiometric BTO target at $T = 450^\circ\text{C}$ and further annealed at $T = 450^\circ\text{C}$ either in residual vacuum ($\sim 5 \times 10^{-6}$ Pa) or under ≈ 1 Pa of oxygen pressure, indicated in the following with BTO_v and BTO_o, respectively. Epitaxial ~ 10 nm thick Fe layers were grown in ultrahigh vacuum (UHV) at $T = 250^\circ\text{C}$ on MgO (001) substrates. In order to perform an interface-sensitive CEMS analysis, isotopically enriched ⁵⁷Fe and ⁵⁴Fe targets were used during PLD to form an ultrathin (~ 2 nm) ⁵⁷Fe Mossbauer-active tracer layer in contact with BTO. Alternatively, Fe was deposited on top of epitaxial/polycrystalline BTO film grown on STO(001). The structural properties as well as the ferroelectric nature of as-grown ultrathin BTO layers in contact with Fe have been reported elsewhere.⁸

The electronic band line-up at the Fe/BTO interface is determined from synchrotron HAXPES data obtained using instruments at beamlines BW2 (DORIS III) and P09 (PETRA III) at DESY (Hamburg, Germany). The adopted photon energy of $E = 6$ keV enables to probe layers up to 20 nm depth, thus providing the opportunity to investigate the electronic properties at the buried Fe/BTO interfaces, even in the presence of a continuous capping metal layer.

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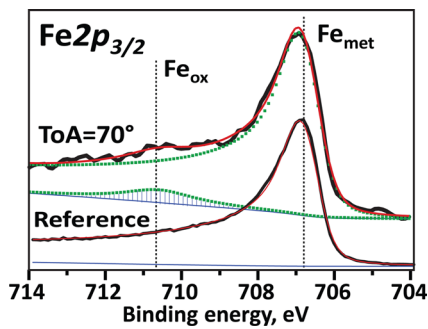


FIG. 1. (Color online) HAXPES Fe $2p_{3/2}$ core level spectrum of a BTO_v(5 nm)/Fe(12 nm)/MgO sample at 70° electron take-off angle fitted with the asymmetric line of a bulk Fe also given as a reference.

Photoemission spectra at variable take-off angle (ToA) are taken in order to analyze the chemical state of the Fe underlayer in contact with BTO. The spectrometers were calibrated with the Au4f line at $BE_{Au4f} = 84.0$ eV. The UNIFIT software is used to fit the experimental data.

Figure 1 shows the HAXPES Fe_{2p_{3/2}} lines acquired from BTO_v(5 nm)/Fe(12 nm)/MgO sample at 70° ToA along with the reference spectrum from the surface of a bulk Fe sample cleaned *in situ* by the Ar⁺ ion sputtering for 90 min. in UHV. The typical Fe line centered at 706.76 ± 0.05 eV is observed at the BTO_v/Fe interface. In order to account for its intrinsic asymmetry,⁹ the Fe2p line was fitted with the Doniac-Sunjic function.¹⁰ The Tougaard background model¹¹ has been employed as an alternative to the Shirley background for transition metals and is, therefore, especially suited for asymmetrical signals. The asymmetry parameter $\alpha \approx 0.38$ was thus deduced from the fitting of the recorded reference bulk Fe line. Only few percent area contribution of the oxidized fraction with the binding energy $BE = 710.7 \pm 0.1$ eV is found in the Fe 2p spectrum taken at the glancing (70°) take-off angle most sensitive to the Fe adjacent to the BTO layer on top (Fig. 1, upper spectrum). Therefore, based on the HAXPES analysis, we conclude a chemically sharp Fe/BTO interface. It is of interest to compare our results with the recently reported chemical properties of Fe/BTO interface, where a ~2 nm thick iron oxide (presumably FeO) layer has been concluded at the Fe/BTO single crystal interface from *in situ* XPS analysis.⁵ The different conclusions made by analyzing very similar XPS spectra result from the fact that in our analysis the core level Fe2p line shape is assumed to be *intrinsically* asymmetric as was pointed above.

In order to rule out the presence of any magnetically dead layer at the buried BTO/Fe interface, CEMS has been performed

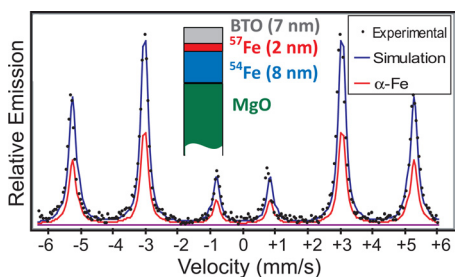


FIG. 2. (Color online) CEMS spectrum taken from BTO_v(7 nm)/⁵⁷Fe(2 nm)/⁵⁴Fe(8 nm)/MgO(100) sample fitted with the characteristic α -Fe magnetically split sextet.

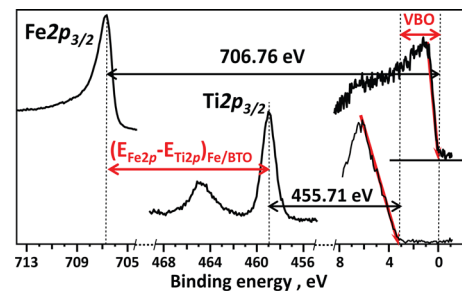


FIG. 3. (Color online) HAXPES spectra of a ~15 nm thick BTO film grown in oxygen on a highly doped STO substrate, of a bulk Fe sample, as well as the illustration of VBO determination in a Fe/BTO bi-layer.

at room temperature by using a ⁵⁷Co radioactive source embedded in an Rh matrix, which is moved by a standard constant acceleration drive. A BTO_v(7 nm)/⁵⁷Fe(2 nm)/⁵⁴Fe(8 nm)/MgO(001) sample is incorporated as an electrode in a He-CH₄ filled parallel-plate avalanche detector, which operates at ~700 V.¹² As clearly shown in Fig. 2, no other contributions than the magnetically split sextet relative to α -Fe (isomer shift of 0 mm/s) are observed at the Fe/BTO interface. The Fe magnetic moments at the interface are aligned parallel to the sample's plane, as evidenced by the nearly perfect 3:4:1:1:4:3 line intensity ratio. The Fe magnetic moment is not changed when compared to the bulk Fe value, showing a hyperfine magnetic field value of $B_{hf} \sim 33$ T for the ⁵⁷Fe sites in contact with BTO. At room temperature, paramagnetic phases such as FeO should be readily observed at the interface by CEMS, since they are represented by well-distinguishable doublets in a Mößbauer spectrum.¹³ By combining CEMS with HAXPES, we conclude that the chemical bonding at the BTO_v/Fe interface is characterized by the absence of either any magnetically dead layer or iron oxide, thus proving an abrupt Fe/BTO interfacial chemical structure down to the atomic scale. In order to determine the band line-up at the Fe/BTO interface, a well-known XPS-based technique has been employed by using the Kraut methodology.¹⁴ The valence band offset (VBO) in the Fe/BTO heterojunction is calculated according to Eq. (1):

$$VBO = (E_{Fe2p} - E_{Ti2p})_{Fe/BTO} - (E_{Fe2p} - E_F)_{Fe} + (E_{Ti2p} - VBM)_{BTO}. \quad (1)$$

The energy difference $E_{Fe2p} - E_F$ is measured on the clean surface of a Fe bulk sample and is found $E_{Fe2p} - E_F$

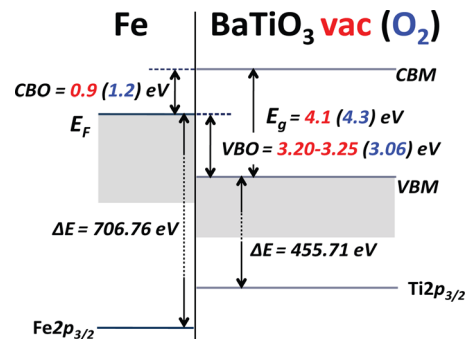


FIG. 4. (Color online) Summarized electronic band alignment diagram for Fe in contact with BTO_v and BTO_o (values in brackets).

TABLE I. Measured XPS line separations, E_g values, and calculated valence/conduction band offsets for different types of Fe/BTO heterojunctions.

	$(E_{Fe2p} - E_{Ti2p})_{Fe/BTO}$ ± 0.05 eV	VBO, ± 0.05 eV	E_g , ± 0.1 eV (Ref. 8)	CBO, ± 0.1 eV
MgO/Fe/BTO _V	247.85	3.20	4.1	0.9
STO/BTO _V /Fe	247.81	3.25	4.1	0.9
STO/BTO _O /Fe	248.00	3.06	4.3	1.2

$= 706.76 \pm 0.05$ eV as shown in Figure 3. In the same figure, the E_{Ti2p} line separation with respect to valence band maximum (VBM), as determined in a pure BTO film grown on a conducting (highly doped) STO substrate, is $(E_{Ti2p} - VBM)_{BTO} = 455.71 \pm 0.05$ eV. This value is in excellent agreement with previously reported data.¹⁵ We note that for BTO films grown in vacuum the line separations are found to be the same within the experimental error (not shown). The line separation $(E_{Fe2p} - E_{Ti2p})$ is determined from the spectra measured on a Fe/BTO bi-layer. Equation (1) can then be used to determine the VBO at different Fe/BTO interfaces. These values are given in Table I. The band gap of the employed ultra-thin BTO films has been previously determined by *in situ* REELS,⁸ and values $E_g = 4.1$ and 4.3 eV are found for the films grown in vacuum and in O₂, respectively. The obtained E_g is much larger compared to the bulk BTO single crystal¹⁶ and consistent with the earlier reported effects of the BTO film thickness¹⁷ and/or grain size.¹⁸ By combining the HAXPES and REELS (Ref. 8) data (Table I), we can construct the full electronic band structure for the different types of Fe/BTO interfaces. The summarized Fe/BTO electronic band line-up is shown in Figure 4.

Let us briefly discuss the observed differences in the electronic structure of Fe/BTO interface depending on the growth conditions. First, we notice that the VBO in case of Fe in contact with BTO_V is larger compared to that with BTO_O. This result corroborates the model describing the formation of the electric dipole at the metal/dielectric interface in terms of the charge (electron) transfer across the interface from the oxygen vacancies (V_O) in the ferroelectric acting as donors to the metal once the work function of the metal is sufficiently large.¹⁹ Hence, the presumably very high V_O concentration in BTO_V results in a decrease of the "effective" work function of Fe in contact with BTO_V giving rise to the larger VBO. Up to 0.3 eV, the change in the Pt/STO Schottky barrier height was predicted depending on the amount of V_O ,¹⁹ while similar calculations reveal up to 1 eV for Pt/PZT system as a function of V_O concentration.²⁰ The obtained VBO difference between Fe/BTO_V and Fe/BTO_O of ~ 0.2 eV is well within this range. The smaller bandgap in BTO_V compared to BTO_O can also originate from the high V_O concentration in the former. Assuming the energy levels of (both neutral and charged) oxygen vacancies lie in the

upper part of the gap, and suggesting their very high concentration in BTO_V, they can eventually form a sub-band thus effectively decreasing the bandgap by 0.2 eV compared to BTO_O. On the other hand, we observe no major differences between the VBO in Fe/BTO_V and the reversed BTO_V/Fe stack, thus confirming that the V_O abundance in BTO is mainly responsible for setting the VBO at the Fe/BTO interface.

In summary, we have determined the band line-up for the Fe/BaTiO₃ system. The absence of any spurious phase at the interface assures that the experimentally determined band alignment is related to a chemically pure Fe/BaTiO₃ interface structure. The experimental results reported here could help to calculate more precisely the tunneling probability in composite multiferroic systems including Fe/BTO, being of use for predicting the transport properties (i.e., the tunneling electroresistance) of ferroelectric and multiferroic tunnel junctions. The current data were obtained for non-polarized BaTiO₃ films. Further experiments are in progress in order to investigate the effect of the BTO polarization on the band alignment evolution at the Fe/BTO interface.

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