Pulsed laser deposition of ultrathin BaTiO₃/Fe bi-layers: Structural characterization and piezoelectric response

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ABSTRACT

Ferroelectric ultrathin BaTiO₃ (BTO) films in contact with Fe underlayer have been grown by pulsed laser deposition onto MgO (100) substrates in a single vacuum cycle. The structural properties of the composite system are investigated by Rutherford backscattering spectrometry/channeling and cross-sectional transmission electron microscopy. The BTO band gap is measured by in situ reflection electron energy loss spectroscopy to be Eg = 4.1–4.3 eV depending on the growth conditions. The ferroelectric nature of BTO (thickness down to 3 nm) on top of Fe is demonstrated by piezoresponse force microscopy, which shows an out-of-plane piezoelectric coefficient of 17±4 pm/V. The obtained results are promising in the view of integrating BTO/Fe stacks in functional ferroelectric tunnel junctions.

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1. Introduction

The non-volatile random access memory concept of ferroelectric tunnel junction (FTJ) takes advantage of an ultrathin ferroelectric (FE) layer sandwiched between two metal electrodes, where the tunneling resistance (TER) is defined by the potential barrier profile across FE is controlled by flipping its polarization direction. Giant TER effects in FTJs have been theoretically predicted [1,2] and recently experimentally observed, particularly employing a 3-nm thick BaTiO₃ (BTO) ferroelectric barrier [3,4]. Furthermore, by replacing the normal metal electrode with a ferromagnetic (FM) one in a metal–ferroelectric system, a magnetoelectric effect is expected as well [5,6], where the interplay between electronic and magnetic properties at FE/FM interfaces can affect both the electric polarization state of FE barrier and the spin polarization of the tunneling current, therefore providing a unique opportunity to control the transport properties of a magnetic tunnel junction by using magnetic and/or electric field [7].

In particular, Fe and BTO thin films are ideal materials displaying well known and robust FM and FE properties, and Fe/BTO is a model system that has been predicted [5] to show magnetoelectric coupling confined at structurally perfect Fe/BTO interface, once ferroelectrically functional FE/FM heterostructures are formed.

In this paper, the growth of ultrathin BTO/Fe bi-layers on single-crystal substrates by pulsed laser deposition (PLD) technique in a single vacuum cycle is reported. We discuss the structural properties of the Fe/BTO interface, as investigated by the combination of transmission electron microscopy and ion channeling techniques. Piezoresponse force microscopy (PFM) data demonstrate the ferroelectric nature of the ultrathin (down to 3 nm) BTO layer in contact with Fe.

2. Experimental details

BTO/Fe bi-layers were grown by PLD in a homemade setup with the base pressure of p ≈ 10⁻⁶ Pa on (001)-oriented single crystal MgO and STO substrates using YAG: Nd laser (λ = 1064 nm) operating in the Q-switched regime (τ = 15 ns) with the variable output energy E = 50–200 mJ and repetition rate ν = 50–50 Hz. The BTO films (2–15 nm) were grown from the sintered polycrystalline stoichiometric BTO target (ν = 5 Hz, the deposition rate is 0.005 nm per pulse) at T = 450 °C and further annealed at T = 450 °C either in residual vacuum (p ≈ 10⁻⁶ Pa) or under ≈ 1 Pa of oxygen pressure, indicated in the following with BTOV and BTOO, respectively. Both Fe/BTO (Fe on top) and BTO/Fe (BTO on top) types of interfaces were formed, in order to investigate the effect of the growth conditions on the interface properties. In the latter case, epitaxial ~10 nm thick Fe layers were first grown in ultra high vacuum (UHV) at T = 250 °C on MgO (001) substrates subjected to UHV annealing at T = 600 °C prior to deposition, and BTOV layer was grown on top without breaking
vacuum. Alternatively, Fe/BTO bi-layers were formed by depositing Fe (T = 250 °C, UHV) on top of BTOV or BTOO film grown on epitaxial Pt underlayer (T = 450 °C, UHV) on MgO(001) in a single vacuum cycle. The deposition rates, and the actual composition and the thickness of Fe/BTO bi-layers were measured by Rutherford backscattering spectrometry (RBS) with 2 MeV He\(^{++}\) ions. The orientational effects in the grown films were analyzed employing the channeling mode in RBS.

The cross-sectional high resolution electron microscopy (HRTEM) employing Zeiss Libra 200FE HR microscope was used to analyze structural properties of the Fe/BTO and BTO/Fe interfaces which are non-equivalent in terms of the growth conditions.

The band gap of ultrathin BTO films, which is known to depend on the growth conditions \[8,9\], was measured in situ by reflection electron energy loss spectroscopy (REELS) technique in XSAM-800 spectrometer employing electrons at the incident energy \( E = 500 \) eV. In this case, BTO\(_x\) and BTO\(_y\) films were grown at the same conditions directly on MgO(001) and STO(001) substrates.

Functional properties of BTO\(_x\)/Fe bilayers have been studied at ambient conditions and in low vacuum (~5 ∙ 10\(^{-1}\) Pa). Local BTO polarization was performed and PFM images were obtained using a commercial atomic force microscope NTegra Aura (NT-MDT) and conductive PtIr-, TiN-coated rectangular silicon cantilevers NSG03 (NT-MDT) with typical tip radius, length and stiffness ~30–40 nm, 130–140 μm and 0.3–6.1 N/m, respectively. Free oscillation resonance frequency of the cantilever was 90 kHz. Square patterns (1 × 1 μm\(^2\)) in BTO\(_x\) film were polarized up- and downward by applying positive and negative DC voltage between conductive tip and the Fe bottom electrode. Phase and amplitude maps of polarized patterns were obtained by resonant-enhanced piezoresponse force microscopy (RE-PFM) \[10\]. Despite the fact that RE-PFM is prone to many artifacts it has been utilized because of the low piezoresponse from ultrathin (nanocrystalline) BTO layers. To excite PFM response an alternating current (AC) voltage with amplitude \( U_{ac} = 2 \) V was applied between atomic force microscope (AFM) tip and Fe bottom electrode. Its frequency was chosen equal to contact resonance frequency of cantilever (750 kHz). An effective out-of-plane piezoelectric coefficient can be determined from \( d_{33}^* = A_{ac}/U_{ac} \) \[11\], where \( A_{ac} \) is the average amplitude of the tip vibration at polarized region. In RE-PFM the PFM response at resonance (A) is \( k \) times higher than \( A_{ac} \), where \( k \) is the effective contact quality factor of the cantilever (\( k \approx 2.5 \)).

### 3. Results and discussion

![Fig. 1. RBS/channeling spectra taken from: a) BTO(4 nm)/Fe(12 nm)/MgO(100) and b) BTO(4 nm)/Pt(5 nm)/MgO(100) samples.](image)

![Fig. 2. HRTEM bright-field image of PLD grown Fe/BTO\(_x\)/Pt/MgO(100) sample; FFT images in the insets are taken at MgO/Pt and Pt/BTO interfaces.](image)
Reels/Channeling analysis of Fe/BTO/Pt/MgO(001) heterostructure reveals epitaxy of BTO/Pt (Fig. 1,b) and no macroscopic orientation for Fe on top (spectrum not shown).

The cross-sectional TEM analysis of both types of Fe/BTO interfaces was performed. In case of BTO on top of Fe, the growth of continuous, crystalline, oriented barium titanate layer for the thickness as low as 2 nm has been found (images not shown). An abrupt BTO/Fe interface with no other chemical phase than Fe is detected at this interface as evidenced also by hard X-ray photoemission spectroscopy and conversion electron Mossbauer spectroscopy (reported elsewhere [12]) is concluded. Further growth of BTO on top of (epitaxial) Fe gives rise to nanocrystalline structure with grains 1–5 nm in size. For the alternative case of Fe grown in a single vacuum cycle on top of BTO film (on Pt underlayer), HRTEM is presented in Fig. 2. The epitaxy in BTO/Pt/MgO structure is established by performing fast Fourier transforms (FFT) on HRTEM image, which reveal the following orientation relationships: [100]_{BTO} || [100]_{MgO}, (001)_{Pt} || (001)_{MgO}, [100]_{BTO} || [100]_{Pt}, (001)_{BTO} || (001)_{Pt}. The Fe layer on top of BTO is polycrystalline. No intermediate phase at Fe/BTO interface has been found in this case either.

Reels spectra taken in situ from the surface of ultrathin (2–10 nm) BTO films grown on MgO(100) and STO(100) substrates are shown in Fig. 3. The extracted band gap of BTO is \( E_g = 4.1 \) and 4.3 eV for the films grown in vacuum and in O\(_2\) respectively. The obtained gap values are much larger compared to the bulk BTO \( E_g \approx 3.3 \) eV found in the literature [13]. Earlier [8], the band gap in ultrathin BTO films was found to vary in the range \( E_g \approx 3.7 \pm 3.9 \) eV depending on the thickness of the film. The drift of the band gap was explained by the compressive stress and the shrinkage of both the lowest conduction and the highest valence bands caused by the increasing number of the boundary atoms in an ultrathin layer. Similar results were obtained also in [9], where the band gap in BTO films was found to be larger the smaller the grain size (depending on the growth temperature). In particular, BTO films with the nanocrystalline (\(~20\) nm) structure prepared at \( T = 450^\circ\) C exhibited \( E_g \approx 4.2 \) eV, in exact agreement with our data, and the band gap decreased dramatically as a function of growth temperature (\( E_g \approx 3.4 \) eV for \( T = 600^\circ\) C). According to Reels data (Fig. 3), \( E_g \) appears the same for (nanocrystalline) BTO films grown in the same conditions on MgO and STO (100) oriented single-crystal substrates which have opposite lattice mismatch with respect to BTO. We therefore conclude that it is not the strain but the thickness of and the grain size in the film that contribute to the larger band gap in our ultrathin BTO films.

Fig. 4 demonstrates the results of polarization experiments by applying a DC voltage of \(+4\) V and \(-4\) V on a \( 1 \times 1 \mu m^2 \) regions of a 3 nm thick BTO film grown on Fe(10 nm)/MgO(100). First of all, the polarizing voltage does not affect the surface topography (Fig. 4a) (the root mean square roughness of BTO surface is \( \approx 0.72 \) nm). After polarizing an out-of-plane piezoresponse phase contrast is observed (Fig. 4c). It is worth noting that the phase contrast is quite small (\(-3.5^\circ\)), which we ascribe to the nanocrystalline structure of BTO layer. According to [14], in each point the phase shift depends on the number of nanocrystalline domains with upward and downward polarization located under an AFM tip. As a result, for nanocrystalline ferroelectric thin films the phase contrast is expected to be rather small since the overall phase shift variations are much smaller than 0–180° range. (Note that epitaxial ultrathin BTO films grown on Pt underlayer exhibit phase contrast \(-100^\circ\) in similar PFM analysis– the data to be reported elsewhere). The polarization in these domains can be switched back and forth by applying a \( \pm 4 \) V voltage of the opposite polarity. An average effective out-of-plane piezoelectric coefficient \( d_{33}^* \approx 17 \) pm/V has been estimated from RE-PFM amplitude map (Fig. 4b).

Phase contrast observed at ambient conditions is stable for at least 16 h which excludes charging effects as a possible origin of PFM contrast and strongly indicates that BTO layer on Fe as thin as 3 nm is indeed ferroelectric.

4. Conclusion

We have grown BTO/Fe bi-layers on MgO(100) substrates by infrared pulsed laser deposition in a single vacuum cycle. The structure of BTO layer in contact with Fe depends on the underlayer surface structure as well as on the growth conditions. The ferroelectric functionality of BTO films down to 3 nm thickness and in contact with Fe is of importance in the view of integrating such systems into functional devices.

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