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Multiferroic PbZrxTi1−xO3/Fe3O4 epitaxial sub-micron sized structures

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Large range well ordered epitaxial ferrimagnetic nominally Fe3O4 structures were fabricated by pulsed-laser deposition and embedded in ferroelectric PbZrxTi1−xO3 (x = 0.2, 0.52) epitaxial films. Magnetite dots were investigated by magnetoresistive microscopy and exhibited magnetic domain contrast at room temperature (RT). Embedding ferroelectric PbZrxTi1−xO3 layers exhibit remnant polarization values close to the values of single epitaxial layers. Transmission electron microscopy demonstrated the epitaxial growth of the composites and the formation of the ferrimagnetic and ferroelectric phases. Physical and structural properties of these composites recommend them for investigations of stress mediated magneto-electric coupling at room temperature. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3692583]

Multiferroic materials are currently being devoted a great deal of attention, in the intensive pursuit of sizable magneto-electric effects that can be applied in future devices.1,2 Along with the investigation of possible magneto-electric responses and mechanisms, both in single phase multiferroic materials and composite type of multiferroics, the demands for miniaturization require development of methods for top-down patterning or bottom-up synthesis of epitaxial nanostructures.3–5

We report on the fabrication of arrays of epitaxial nominally Fe3O4 structures of circular shape and size below 500 nm. Magnetite is a ferrimagnetic material with high Curie temperature, large room temperature (RT) magnetization and, very important for magneto-electric composites where the coupling should occur via elastic deformations, has large positive linear saturation magnetostriction, λS = 40 × 10−6.6 For reference, ferromagnetic metals such as Fe and Co have negative linear saturation magnetostriction, λS = −7 × 10−6 and λS = −60 × 10−6, respectively.6 Other ferrimagnetic ferrites with large (negative) linear saturation magnetostriction, such as CoFe2O4 (λS = −110 × 10−6) or NiFe2O4 (λS = −25 × 10−6),6,7 have been often employed in combination with piezoelectric materials, such as BaTiO3, BiFeO3, or PbZrxTi1−xO3 (PZT).1,2,4,5 Moreover, Kato and Ida demonstrated that Fe3O4 thin films exhibited ferroelectric switching and, thus, ferroelectric order at low temperatures7 and, a recent study8 reported relaxor ferroelectricity in magnetite single crystals. Combining piezoelectric materials epitaxially with a magnetostrictive material such as magnetite, Fe3O4, with positive magnetostriction and relatively low magneto-crystalline anisotropy (compared with CoFe2O4, for instance), is nevertheless very appealing; the effects of mechanical stress may lead to the changes of the magnetization chiefly in the direction of the applied stress. However, the combination of magnetite dot-like structures with any of these ferroelectrics has been neglected, most likely because of the difficulties of fabricating high quality magnetite structures.9 The epitaxial growth of films or sub-micron structures of the right phase, Fe3O4, which is in competition with the α-Fe2O3 and γ-Fe2O3 and FeO-like phases, requires special precautions. Moreover, magnetite thin films and probably structures should have low electrical resistance, which would make piezoelectric/electrical measurements quite difficult.

We grew magnetite structures by pulsed-laser deposition on a bottom epitaxial PbZrxTi1−xO3 (x = 0.2, 0.52, in brief PZT20/80 and PZT52/48, respectively) layer, and then covered by a top PbZrxTi1−xO3 layer of the same composition. Structural investigations by high resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS) proved that these composite structures were epitaxial and enabled the investigation of the oxidation state of iron in the magnetite structures, respectively. Magnetic force microscopy (MFM) investigations proved that the magnetite structures were magnetic at room temperature. Piezoresponse force microscopy (PFM) performed simultaneously with MFM proved that the embedding PZT layers had piezoelectric response.

SrRuO3 covered SrTiO3 (100)-oriented crystals were used as substrates. For the growth of the magnetite dots, stencil masks were applied on the substrates. The stencils consisted of amorphous SiN membranes on Si wafers, with circular apertures of about 400 nm diameter.10 Epitaxial dot-like structures were grown in situ with the stencil attached mechanically to the substrates, at temperatures of about 575 °C. After removing the stencil mask, the substrate with the Fe3O4 dots was reheated to 585 °C and the top PZT film was deposited.10

MFM and PFM were performed with a MFP-3D Asylum Research. For MFM, ASYMMFM silicon cantilevers with 50 nm CoCr coating were used. Macroscopic ferroelectric measurements were made with a Precision Multiferroic 200 V Test System (Radiant Technology) and with a TF2000 Analyzer (AixACCT). Cross section specimens for transmission electron microscopy were prepared by focused ion beam milling (FEI Nova NanoLab 600) of thin lamellae. HAADF-STEM and EELS analyses were performed in a FEI Titan 80-300 microscope with a spherical aberration corrected probe forming system.11

Figures 1(a) and 1(b) show topography and MFM phase images (5 μm × 5 μm areas) of magnetite dots (of about
400 nm diameter and 60 nm height) grown on Nb-doped SrTiO$_3$(100), this sample being used as reference. The MFM phase image (Fig. 1(b)) evidences that the magnetite dots have multiple domain state at RT. Figures 1(c) and 1(d) show topography and MFM phase images (5 μm × 5 μm areas) of a sample in which magnetite dots (of about 400 nm diameter and 50 nm height) are sandwiched between two epitaxial ferroelectric PZT20/80 layers. Despite the about 45 nm thick top PZT20/80 layer covering the magnetite dots, the signal generated by the magnetic domains of the dots is detectable and magnetic contrast is visible in the dot areas. This indicates that the embedded Fe$_3$O$_4$ dots are strongly magnetic at RT and can be probed by MFM through the capping PZT layer.

Figure 2 illustrates the HAADF-STEM, HRTEM, and EELS analyses performed on the same sample as the one investigated by MFM (Fig. 1). The micrographs show that the heterostructures of 75 nm thick bottom PZT20/80/magnetite/40 nm thick top PZT20/80 have relatively sharp interfaces and are epitaxial, despite the large in-plane lattice mismatch between magnetite ($d_{\text{bulk}} = 8.40$ Å at RT) (Ref. 6) and PZT20/80 ($d_{\text{bulk}} = 3.935$ Å, $c_{\text{bulk}} = 4.15$ Å at RT). HRTEM imaging (Fig. 2(d)) and the corresponding Fourier transforms (FFTs) of the micrographs (see Fig. 2(e)) indicated that the dot had spinel structure. Quantitative analysis of the FFT yielded a lattice spacing of ~0.290 nm for the (220) plane family, value that slightly deviates from 0.2967 nm (Ref. 9) for the same in the case of bulk Fe$_3$O$_4$. However, the dot structures have extended structural defects, formation of antiphase boundaries being notorious in the case of epitaxial magnetite films. Also magnetic field induced distortions affect the quality of both STEM and HRTEM images of the magnetic dot structures (see for instance, the dark contrast with no visible lattice fringes, in Figs. 2(a) and 2(b)). Hence, evaluation of the lattice parameter of the nominally magnetite dot is affected by large errors. The EELS spectrum acquired on a magnetite dot, based on the value of the intensity ratio of the Fe L$_{3,2}$ white lines (i.e., ~4.65, for our dots) and the features of the O K-edge fine structure, indicated that the oxidation state of iron corresponds most likely to Fe$_3$O$_4$ stoichiometry (see Fig. 2(c)). However, we cannot rule out the possibility that the dots are actually a rather disordered mixture of Fe$_3$O$_4$ and γ-Fe$_2$O$_3$. The spinel structure of ferrimagnetic γ-Fe$_2$O$_3$ ($d_{\text{bulk}} = 8.34$ Å at RT) (Ref. 6) is quite similar to that of Fe$_3$O$_4$ in terms of RT lattice parameters, so it is difficult to distinguish between them by indexations of electron diffraction patterns or XRD, especially when epitaxial strain imposed by the substrate and extended structural defects may severely distort the lattice. Refined EELS measurements with determination of exact peak positions ought to be performed and shall enable the discrimination, provided that EELS spectra are recorded either in dual EELS mode or with a separate low loss spectrum immediately after the core loss. A quite large energy shift between γ-Fe$_2$O$_3$ and Fe$_3$O$_4$ should be detected. Also x-ray absorption spectroscopy (XAS) would give more reliable information about the valency of Fe ions, whether indeed mixed Fe$^{2+}$ and Fe$^{3+}$ exist in the dot, as expected for Fe$_3$O$_4$. However, one has to keep in mind that this cannot be done through the capping PZT layer, therefore only slightly different samples, with different fabrication history, can be compared.

We measured ferroelectric hysteresis loops through platinum electrodes (about 60 μm × 60 μm), sputtered on top of the areas where the PZT-embedded magnetite dots are, as shown in photograph inset in the right lower corner of Fig. 3. Figure 3 summarizes the results for two samples, one with PZT20/80/magnetite/PZT20/80 (Fig. 3(a)) and one with PZT52/48/magnetite/PZT52/48 (Fig. 3(b)) heterostructures that differ in the composition of the epitaxial PZT layers. Among the PZT solid solution compositions, PZT52/48 has the highest piezoelectric coefficients and electromechanical coupling constants and remnant polarization of ~50 μC/cm$^2$, whereas for tetragonal fully c-axis grown PZT20/80 epitaxial films, we reported
record values of polarization of about 100 μC/cm². The remnant polarization was about $P_r = 70 \mu$C/cm² for the PZT20/80/magnetite/PZT20/80 sample (Fig. 3(a)) and $P_r = 40 \mu$C/cm² for the PZT52/48/magnetite/PZT52/48 sample (Fig. 3(b)), both measured at 1 kHz and RT. The hysteresis loops of both samples prove very good ferroelectric behavior and sharp polarization switching peaks and low leakage currents.

These nanostructured multiferroic composites with epitaxial interfaces hold promise for further studies, devoted to investigate the effects of the out-of-plane polarization switching in the embedding PZT layers upon the magnetic domains of the embedded magnetite. This will be performed in a consecutive MFM and PFM study with the MFP-3D Asylum Research scanning probe microscope. We have performed preliminary RT measurements of the out-of-plane piezoelectric response, before (pristine state) and after an in-plane magnetic field was applied ($\pm 2500$ gauss), using a variable field module (Asylum Research) to apply the magnetic field. No striking changes in the piezoelectric response of the ferroelectric PZT on top of the magnetic dots have been observed after application of the magnetic field. Figure 4 summarizes our PFM investigations: images of the phase (upper row) and amplitude (middle row) of the piezoresponse in the as-grown state (a and d), after application of $\pm 2500$ gauss (b and e), and $-2500$ gauss (c and f) in-plane magnetic field. However, no striking effects were observed upon application of the in-plane static magnetic field. The images in the lowest row are zoom-ins on a single structure. Polarization switching in the ferroelectric PZT could be achieved both on top of the magnetic dot and in between the dots, as seen from the piezoelectric phase hysteresis loops shown in the graph of Fig. 4(i). We shall continue the investigations by taking in situ MFM images of the magnetic domains of the dots, while the structures are subjected to an electric field. Interdigital top electrodes shall be deposited for applying in-plane electric fields on the PZT52/48/magnetite/PZT52/48 sample on the insulating substrate.

Summarizing, epitaxial multiferroic composites consisting of ferrimagnetic magnetostrictive Fe₃O₄ dot structures...
and ferroelectric PbZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} layers were fabricated by pulsed-laser deposition. The magnetite dots were investigated by magnetic force microscopy and proved to be ferromagnetic at room temperature. The embedding ferroelectric PbZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} layers exhibit remnant polarization values close to the values of the single epitaxial layers. The structural investigations by transmission electron microscopy demonstrated the high structural quality of the composites with epitaxial interfaces. Future studies will be dedicated to the stress mediated magneto-electric coupling of these multiferroic composites.

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