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Preparation of epitaxial $Eu_{0.65}Y_{0.35}MnO_3$ thin film on Nb:$SrTiO_3$(111) substrate

S.Z. Li, K.F. Wang, S.J. Luo, T. Wei, Y.Y. Guo, J.-M. Liu *

Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
International Center for Materials Physics, Chinese Academy of Sciences, Shenyang, China

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ABSTRACT

The (202) epitaxial $Eu_{0.65}Y_{0.35}MnO_3$ (EYMO) thin films on (111) Nb:$SrTiO_3$(NSTO) substrates are prepared by pulsed laser deposition. The structural, dielectric, and magnetic properties of EYMO thin films are characterized. The temperature dependent magnetization clearly shows an antiferromagnetic ordering at ~30 K. The weak ferromagnetism at low temperature, probably ascribed to the strain resulting from the mismatch between the substrate and thin film, is identified. The measured polarization–electric field loop and dielectric data demonstrate that the as-prepared EYMO thin film is weakly ferroelectric, and the dielectric anomaly at ~30 K indicates clearly the spin–phonon (magnetoelectric) coupling.

1. Introduction

Magnetism can control electric polarization in multiferroics, in which (anti)ferromagnetic and (anti)ferroelectric orders coexist. This effect has been investigated extensively. The multiferroicity not only promises potential applications in magnetoelectric devices but also poses exciting challenges in understanding the underlying physics [1–4]. Up to now, many studies reported the existence of different multiferroic behaviors. Among the multiferroics discovered, magnetic frustration induced ferroelectricity, such as $RMnO_3$ and RMn_2O_5, where R represents rare-earth species, has been of great interest for the intrinsic coupling between the two orders. The magnetic frustration as an important ingredient to the magnetoelectric coupling [5–9], and the colossal magnetocapacitive effects in such as spinel $CdCr_2S_4$ [10], have been emphasized. Typical examples are perovskite manganites Tb(Dy)MnO_3 where the spiral/helical spin order induces ferroelectric polarization [11–14]. The spin structure of Tb(Dy)MnO_3 favors an incommensurate collinear sinusoidal antiferromagnetic (AFM) order of Mn^{3+} spins along the b-axis, taking place at $T_N = 41$ K with a wave vector $q = (0, k_s \sim 0.29, 1)$ in the Pbnm orthorhombic cell, which is paraelectric. The nonzero polarization parallel to the c-axis appears only below ~30 K ($T_{lock\text{-}in}$) where an incommensurate–commensurate (or lock-in) transition occurs, generating a helicoidal spin structure with the magnetic modulation wave vector k_s locked at a constant value ~0.28 [11].

On the other hand, the ferroelectric transition and polarization flop by magnetic field are also observed in mixed-crystal system $Eu_{1-x}Y_xMnO_3$ with comparable lattice distortions with respect to Tb ion in $TbMnO_3$. Since $Eu^{3+}(4f^6)$ and $Y^{3+}(4f^0)$ have no magnetic moment, the magnetic behaviors from Mn 3d spins in $Eu_{1-x}Y_xMnO_3$ series may not be very complicated, different from $TbMnO_3$ where Tb ions contribute magnetic moment. Furthermore, the Mn spins form a spiral structure in the ab plane, resulting in a spontaneous polarization parallel to the a-axis [15–17]. In order to investigate the influence of Mn3d spins on multiferroics with no other magnetic ions, and also evaluate the effect of thin film strain, an investigation of the multiferroicity of $Eu_{0.65}Y_{0.35}MnO_3$ (EYMO) epitaxial thin films is interesting. As well known, EYMO in bulk form has an orthorhombic structure (*Pbnm*), and exhibits presumably the spiral magnetic structure coexisting with a ferroelectric component. In this work, we report the preparation of epitaxial EYMO thin films on (111)-oriented Nb:$SrTiO_3$ (NSTO) substrates using a bulk target of the same composition by pulsed laser deposition (PLD).

2. Experimental details

The PLD experiment was performed using a KrF excimer laser with wavelength of 248 nm and pulse width of 25 ns. Ceramic EYMO disk was used as the target and commercially available (111)-oriented NSTO single crystal wafers ($5 \times 10 \times 0.5$ mm^3) were used as substrates. We employed a laser beam of ~3 Hz in frequency and ~1.5 J/cm^2 in energy density. During the deposition, the substrate temperature was 900 °C with an ambient of oxygen of ~20 Pa in pressure. The post-annealing was done by aligning the samples at 500 °C for half an hour in an oxygen ambient of 0.1 atm. The as-prepared thin films are ~60 nm in thickness.

For the crystallinity characterization, X-ray θ–2θ and ϕ-scan diffractions with asymmetrical reflections using CuK_α were performed. Electron microscopy observations were carried out in an aberration-corrected transmission electron microscopy (TEM) (JEM4000). The specimen for the TEM analysis was prepared by conventional methods, grinding and Ar ion milling at room temperature. For electrical property evaluation, the top Au electrodes, each

* Corresponding author.
E-mail address: liujm@nju.edu.cn (J.-M. Liu).

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200 μm in diameter, were sputtered. The electric polarization P and capacitance C as a function of electric field E (voltage V) in the hysteresis mode were measured by RT66A (Radiant Inc., NM) and HP4294A impedance analyzer, respectively, with the samples inserted into the Quantum Design physical property measurement system (PPMS). The magnetism was tested using superconducting quantum interference device system (SQUID, Quantum Design Inc.).

3. Results and discussion

3.1. Epitaxial growth of EYMO thin film

First of all, we look at the crystallinity of the as-prepared EYMO thin films. The X-ray θ–2θ diffraction spectrum, as shown in Fig. 1(a), indicates that only the (202) peak of EYMO thin films is identified besides the reflections from the NSTO substrate, using the *Pbnm* setting with lattice constants $a=0.5336$ nm, $b=0.5842$ nm and $c=0.7451$ nm, demonstrating that the EYMO thin film is single-oriented with distorted perovskite structure. The epitaxial nature of the thin film is established by the ϕ-spectrum scan, referring to the (112) orientation of the EYMO thin film, as shown in Fig. 1(b). The three relatively narrow (112) reflections with the inter-separation of 120° are observed, indicating the epitaxial structure of the thin film on the substrate. The identified epitaxial relationship is EYMO(202)// NSTO(111).

For more detailed identification of the thin film structure, the selected area electron diffraction (SAED), cross-section and corresponding high-resolution TEM imaging are used to investigate the crystal structure and strain contribution. Fig. 2(a) shows the typical SAED pattern from a small area of the thin film along the [0$\bar{1}$0] axis, giving clear evidence of the single crystallinity of the thin film. Fig. 2(b) shows the cross-section image of the sample, indicating the interface between the EYMO thin film and substrate. The thin film appears flat, homogeneous and the microstructure is columnar-aligned in normal to the substrate surface. In various regions, one identifies the stripe-like contrast with the stripes parallel to the substrate surface. These stripes are the twinned domain structures associated with the strain effect. Furthermore, the accumulated strain regions, with brighter contrast due to the lattice mismatch between the film and substrate to some extent, are identified. It should be mentioned that the contrast resulting from the strain is more likely due to the halos appearing on the interface. Fig. 2(c) shows the high-resolution TEM image of the thin film, illustrating the microstructure of the interfacial region with some waving and distortion, which could arise from the strain in the thin film.

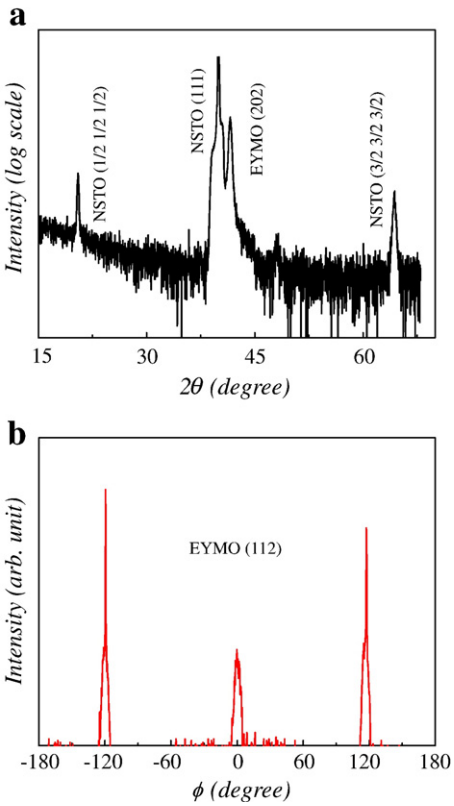

Fig. 1. (color online) (a) Measured θ–2θ and (b) ϕ-scan of the epitaxial EYMO on (111) Nb:$SrTiO_3$ substrate.

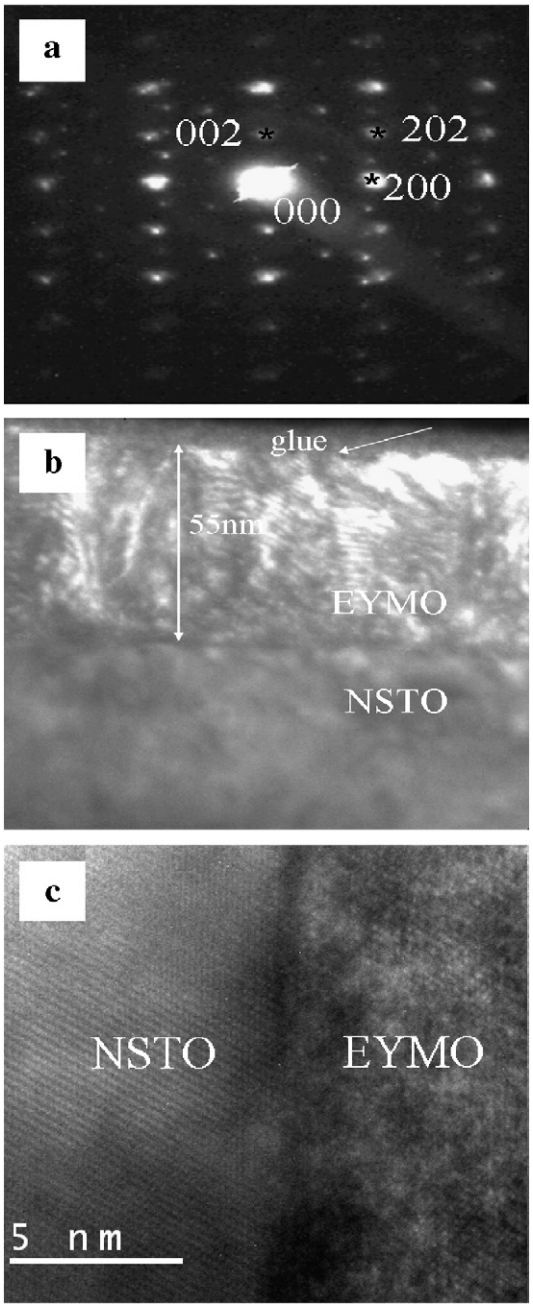

Fig. 2. (a) SEAD image of the EYMO thin film taken along the [0$\bar{1}$0] axis, (b) cross-section TEM image, and (c) high-resolution TEM image of the cross-section region.

3.2. Weak ferromagnetism

For the magnetism measurement, careful data processing was performed by subtracting the magnetic signals of the thin film from