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Tuning of magnetic properties for epitaxial Y_2NiMnO_6 thin film: Substrate is crucial

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ABSTRACT

The effects of epitaxial strain induced by lattice mismatch and substrate type on the structure and magnetic properties of Y_2NiMnO_6 thin films have been systematically investigated. Y_2NiMnO_6 thin films grown on (001)-oriented $LaAlO_3$ (LAO), (La,Sr)(Al,Ta)O_3 (LSAT), and $SrTiO_3$ (STO) substrates with varying film thickness are obtained by a simple polymer assisted deposition method. X-ray diffraction and Raman scattering observations indicate that the single-phase epitaxial films are successfully obtained. By magnetic measurements, it is found that all the films show an obvious ferromagnetic transition with a lower transition temperatures (Tc) than that of the Y_2NiMnO_6 bulk. With the biaxial tensile strain decreasing or the film thickness increasing, the Tc of the film increases. Besides, due to the different strain states of the films and the different surface migrations of the substrates, the structure and magnetic properties show a strong dependence on the type of substrate. It is suggested that the biaxial tensile strain and substrate type have crucial effects on the structure, magnetic properties and the related Tc of the thin film, which can be utilized to engineer the magnetic properties of the films and the related ferroelectricity.

1. Introduction

Recently, magnetoelectric (ME) multiferroics, simultaneously possess ferromagnetic and ferroelectric order, have attracted much attention due to their potential applications in memory and magnetic storage devices [1,2]. The ME materials with magnetically induced ferroelectric order are particularly interesting due to the electric control of magnetism or vice versa. Su et al. have reported magnetism driven ferroelectricity in Y_2NiMnO_6, which is confirmed by the appearance of ferroelectric polarization accompanying by the magnetic phase transition and the strong magnetoelectric (ME) effect [3]. Therefore, controlling of the magnetism may be an effective way to tune the ferroelectricity in Y_2NiMnO_6 and the related double perovskites. On the other hand, for potential device applications, the ferroelectric films play an even more important role. It has been reported that the electronic and magnetic properties can be adjusted by structural modifications [4–6]. The modifications in the Ni—O—Mn bond length and bond angle can directly influence the intensity of superexchange interaction. The structural modifications can be easily induced by the film-substrate lattice mismatch. Thus, it is feasible to manipulate physical properties of materials through rigid compression or extension of their chemical bonds via epitaxial strain. Moreover, because of the strong ME in Y_2NiMnO_6 [3], it is plausible to expect that the epitaxial strain is an effective way to tune the magnetism driven ferroelectricity in this system. These have motivated our present study on magnetic property of Y_2NiMnO_6 film under epitaxial strain.

In addition, for further application in industry, development of a simple and low-cost technology to prepare the uniform and thickness-controllable large area film material is very important. In this work, the Y_2NiMnO_6 (YNMO) thin epitaxial films are grown via a simple polymer assisted deposition (PAD) method [7–12]. The PAD technique, as a surfactant assisted sol-gel process, is suitable for film deposition by spin and dip coating. Therefore, it is suitable for coatings over large areas and complex-shaped objects avoiding the use of high-vacuum chambers in the film deposition process [13]. Besides, the desired thickness of the film can be easily controlled by the solution concentration, the molecular weight of the soluble polymer and the speed of coating [14–16]. By X-ray diffraction and Raman scattering observations, it is conformed that the single-phase epitaxial YNMO films are obtained successfully at a related lower annealing temperature compared to the previous reports [17,18]. The effects of film thickness and substrate type on the structure and magnetic properties of YNMO thin films are discussed in details. It is found that the magnetic transition tem-

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perature and low-temperature moment are increased with biaxial tensile strain reduced. In addition, the choosing of substrate provides another way to engineer the property of film.

2. Experimental

A precursor solution containing metal ions was prepared as follows. High purity (>99.99%) metal salts $Y(NO_3)_3{\cdot}6H_2O$ (0.5 mmol) and $Ni(NO_3)_2{\cdot}6H_2O$ (0.25 mmol) and $Mn(NO_3)_2$ (0.25 mmol,AR,50 wt.% in H_2O) were mixed and dissolved in 5 mL of H_2O. Then 0.2922 g of EDTA (Ethylene Diamine Tetraacetic Acid) and 0.2922 g of PEI (polyethyleneimine) with molecular weight of 70,000 were dissolved in 10 mL of H_2O and stirred at room temperature for 1 h. After 1 h chelating-reaction, 10 mL of PEI and EDTA transparent aqueous solution was slowly added into the 5 mL of nitrate solution by a dropper. Finally, the mixed solution was stirred by a magnetic stirring apparatus for 10 h at room temperature, and then concentrated to ~5 mL in a 60 °C oil bath.

The polymeric films were deposited on single-crystal substrates with different lattice parameters, including (001) $LaAlO_3$ (LAO, a_{LAO} = 3.792 Å), (001) (La,Sr)(Al,Ta)O_3 (LSAT, a_{LSAT} = 3.868 Å), and (001) $SrTiO_3$ (STO, a_{STO} = 3.905 Å) by a spin coating technique. The precursor solutions were deposited on single-crystal substrate at 3000 rpm (revolutions per minute), 5000 rpm, and 7000 rpm over 50 s to obtain YNMO films with different thickness. Then the coated substrates were placed in a muffle furnace. A low ramp rate of 1 °C min^{-1} was used from room temperature to 700 °C to make sure the water evaporated and polymers burned up to avoid the formation of voids in the bulk of the films. The samples were then rapidly heated (5 °C min^{-1}) to a temperature of 900 °C. After 2 h heat treatment, the films were cooled down to room temperature at 1 °C min^{-1}. The morphological properties of the deposited YNMO samples were observed by the atomic force microscopy (AFM, Auto Probe Pc; in contact mode, with low stress silicon nitride tip of less than 200 Å radius). All the images were obtained with a scanning area of 2.0 μm × 2.0 μm. A Philip's X'Pert X-ray diffraction system was used to characterize the crystallization and epitaxial quality of YNMO films. Besides, the morphological characteristics and thickness of YNMO films is also obtained by an FEI Sirion 200 field emission scanning electron microscope (SEM). The Raman backward scattering spectrum was measured on a JY LABRAMHR Raman spectroscopy, with an Ar^+ (514 nm line) laser as an excitation light source. In addition, the temperature-dependent magnetization (M-T) curve under a constant applied magnetic field was measured via a Quantum Design MPMS-7 superconducting quantum interference device (SQUID) magnetometer. The field-cooled (FC) magnetization curve was measured with an external magnetic field of H = 100 Oe applied parallel to the film surface in the temperature range 10 K–300 K.

3. Result and discussion

The morphological characteristics of the YNMO epitaxial thin films deposited on STO, LSAT, and LAO substrates at 5000 rpm are characterized via a SEM as shown in Fig. 1. It is found that the thickness of YNMO films obtained at 5000 rpm is about 50 nm (as a typical example, the cross-sectional image of YNMO/STO is shown in Fig. 1d). Besides, the surface morphologies and roughness are found to be different for the YNMO films grown on different substrates. To further confirm this result, an atomic force microscope (AFM) is involved to observe the surface morphology, which is a very effective method to explore the surface roughness in nanometer scale and surface morphology of thin films. The two-dimensional (2D) and three-dimensional (3D) surface topography of the 50 nm YNMO thin films deposited on LAO, LSAT, and STO substrates are presented in Fig. 2, which show obvious 3D island topography. However, the obvious difference of micrographs can be found for YNMO films with different substrates, which is consistent with the results of SEM observation. Compared with those of the YNMO films on LSAT and STO substrate, larger grains and more holes are shown in the surface of the film on LAO substrate. The average roughness (Ra) of the surface for the YNMO films on LAO, LSAT, and STO substrates are 25.3 nm, 20.1 nm and 19.0 nm, respectively. It is surprised to find that the average Ra of YNMO films on LSAT and STO substrates, which have larger film-substrate lattice mismatch, are smaller than that of YNMO/LAO film. This may indicate that the epitaxial film grown on cubic STO and LSAT substrates is superior to that on orthorhombic LAO substrate. Furthermore, the substrate effect may also be responsible for this result [19,20]. In this work, the different 3D morphology and average roughness indicate that the mode of substrate-surface migration is dependent on the substrate type.

To verify the crystallinity and epitaxial quality of YNMO films, the X-ray diffraction (XRD) θ/2θ scans and ω scans (rocking curve) are carried out. The XRD patterns for the 50-nm YNMO films grown on (001)-oriented LAO, LSAT, and STO substrates are shown in Fig. 3. It can be found that only (*00l*) peaks for YNMO films are observed along with the (*00l*) peaks of the substrates without any undesirable peak from XRD patterns, indicating that the YNMO films have a preferential c-axis orientation. The FWHM (full width at half maximum) of the rocking curves for (002) peaks of the films are less than 0.3, which indicates a high degree of crystallite orientation for all the YNMO films.

Fig. 4(a)–(c) show the substrate dependence of reciprocal space mappings around the (103) reflection for the YNMO thin films deposited on STO, LSAT, and LAO substrates, respectively. The in-plane lattice constant of the YNMO/LAO film matches with that of LAO substrate, confirming coherent epitaxial growth of the YNMO/LAO film. In contrast, as can be seen from Fig. 4(a) and (b), the peak position of (103) reflection of the YNMO films has been slightly shifted from those of the STO and LSAT substrates along the Q_{100} axis. In addition, the full width at half maximum of the peak for the YNMO film on LAO is apparently smaller than those of the films on STO and LSAT, which is consist with the full width at half maximum of rocking curves. Since the similarity between the lattice parameters of the pseudocubic bulk YNMO and LAO substrate, epitaxial YNMO thin films are coherently grown on LAO substrate. Although the YNMO films are also grown epitaxially on the LSAT and STO substrates, the large lattice mismatch between the films and the substrates will cause relaxation in the YNMO structure. The similar results have been reported by Hashisaka et al. in the La_2NiMnO_6 film system [26]. In La_2NiMnO_6 film system [26], since the lattice parameter of pseudocubic bulk La_2NiMnO_6 is close to lattice parameters of STO and LSAT substrates, epitaxial La_2NiMnO_6 thin films are coherently grown on these substrates. However, the large lattice mismatch between the La_2NiMnO_6 film and LAO substrate causes relaxation in the La_2NiMnO_6/LAO structure, which can be seen from the slight shift between La_2NiMnO_6 film and LAO substrate [26].

Raman spectroscopy is an excellent tool to obtain the information on the local structure of the different microphases or macrophases present simultaneously in many manganites. To detect the structural characteristics of the YNMO films, the Raman spectra for the YNMO films on different substrates were measured at room temperature, as shown in Fig. 5. It is found that the Raman spectra are dominated by two main peaks at around 512 cm^{-1} and 649 cm^{-1}, which can be assigned to the antisymmetric stretching (AS)/bending and symmetric stretching (S) vibrations of $Ni(Mn)O_6$ octahedra, respectively [21]. Moreover, in addition to these two peaks, two high-frequency scattering peaks are observed at around 1180 cm^{-1} and 1295 cm^{-1}. No obvious difference in peak shape is