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High-quality antiferromagnetic EuTiO$_3$ epitaxial thin films on SrTiO$_3$ prepared by pulsed laser deposition and postannealing

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We report on epitaxial growth and magnetic properties of EuTiO$_3$ thin films with a perovskite structure. Single crystalline EuTiO$_3$ films with atomically flat surface are grown on (001) surface of SrTiO$_3$ by pulsed laser deposition (PLD) and subsequent annealing in reducing atmosphere. The as-deposited films possess the crystal structure with an elongated $c$-axis and tend to stabilize ferromagnetically ordered Eu$^{2+}$ spins at low temperatures. Postannealing at 1000 °C relaxes the out-of-plane lattice strain, and brings about a drastic change in magnetic structure; the annealed film becomes an antiferromagnet below Néel temperature of 5.1 K. The change in magnetic properties accompanied by the modification in lattice constant is discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072598]

An interest in multiferroics, where ferroelectric and ferromagnetic (FM) or antiferromagnetic (AFM) orderings co-exist, has been recently revived because of their potential applications to multifunctional magnetoelectric and magneto-optical devices. In particular, the discovery of new multiferroics such as TbMnO$_3$, BiFeO$_3$, and BiMnO$_3$ triggered rapid developments in the exploration of materials with a strong dielectric-magnetic coupling so that a small modulation in magnetic (electric) field can induce a large change in electric polarization (magnetization). One strategy to achieve the strong dielectric-magnetic coupling is to select a system where magnetization couples to a specific infrared-allowed optical phonon mode with low frequency, i.e., a soft phonon mode. In such a case, a gigantic change in dielectric constant is expected to occur by an ordering of magnetic moments, since the energy scale of soft mode is comparable to that of magnetic interaction.

EuTiO$_3$ is a unique material having a strong coupling between magnetic ordering and soft phonon mode. Bulk EuTiO$_3$ adopts a cubic perovskite structure (Eu$^{2+}$Ti$^{4+}$O$_3$, space group $Pm\bar{3}m$) at room temperature. The absence of electrons in Ti 3$d$ orbital means that EuTiO$_3$ is a band insulator. Large magnetic moments localized on Eu sites ($J=5/2$) order below the Néel temperature ($T_N=5.5$ K) to form a $G$-type antiferromagnet. Interestingly, the dielectric constant varies in response to the ordering states of Eu spins due to the coupling between the localized spins and a soft phonon mode.

Another important aspect of the coupling between phonon and magnetic moments appears when a soft phonon mode is sensitive to lattice strains. This effect can be the most prominent in the form of thin film; an epitaxial strain due to the lattice mismatch between film and substrate has a great impact on the dielectric and magnetic properties. Recently, Fennie and Rabe calculated the dielectric properties of EuTiO$_3$ in FM or AFM phases under biaxial compressive strain and showed that the most stable magnetic phase can be tuned by experimentally attainable lattice strain. A similar attempt was performed by Ranjan et al. to calculate the stability of several magnetic phases as a function of lattice volume.

In spite of such interesting theoretical predictions and of practical importance in making devices, the fabrication of EuTiO$_3$ epitaxial thin film has been rarely reported. Recently, we have fabricated the thin films of EuTiO$_3$ on SrTiO$_3$ (001) substrates by PLD under the different deposition conditions from those in Ref. 11 and reported their magnetic properties. Although the as-deposited films could be obtained as a single phase of EuTiO$_3$, the out-of-plane lattice constant was larger (typically ~2.6%) than the bulk value, and an FM-like behavior was observed at low temperatures, in contrast to the AFM behavior of bulk EuTiO$_3$, which is in good agreement with recent theoretical studies.

EuTiO$_3$ thin films were grown on atomically flat SrTiO$_3$ (001) substrates (Shinkosha Co. Ltd.) by PLD. A KrF excimer laser (248 nm, 5 Hz) was focused on a sintered Eu$_2$Ti$_2$O$_7$ ceramic target at a fluence of 2 J/cm$^2$. The substrate temperature was maintained at 650 °C and the oxygen pressure was 1.0 × 10$^{-5}$ Pa. After the deposition, the film was annealed at 1000 °C under a flowing gas of 95 vol% Ar+5 vol% H$_2$ for 8.5 h to prevent the oxidation of Eu$^{2+}$. The thickness and chemical composition of films were characterized by the Rutherford backscattering using a 2.0 MeV He$^+$ beam. The analysis of the annealed film revealed a stoichiometric cation ratio (1:1) of Eu and Ti. The film thickness was evaluated to be about 200 nm.

The crystal structure of the films was estimated by high-resolution XRD measurements using Cu $K\alpha$ radiation. The 2$\theta$-ω XRD patterns for as-deposited and annealed films are shown in Fig. 1(a). For the as-deposited film, sharp Bragg

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peaks for EuTiO$_3$ 00$_n$ ($n=1, 2, 3$) are observed together with SrTiO$_3$ 00$_n$ peaks, indicating the epitaxial growth of EuTiO$_3$ oriented along the c-axis. The out-of-plane lattice constant calculated from the 003 peak is 0.3993 nm, which is much larger than the reported bulk value of 0.3905 nm. Upon postannealing, EuTiO$_3$ peaks shift toward higher angle side and are superimposed on the SrTiO$_3$ peaks without yielding any impurity phases. Namely, the crystal lattice of the as-deposited film shrinks along the c-axis by postannealing so that the out-of-plane lattice constant (0.3900 nm) is almost the same as the bulk value.

To fully examine the strain states, x-ray reciprocal space mapping (RSM) was measured for the 301 diffraction using a four-circle XRD apparatus. Figures 1(b) and 1(c) show the RSMs for the as-deposited and annealed films, respectively. Two Bragg spots from film and substrate are observed for the as-deposited film. These two spots have the same $Q_z$, while $Q_y$ of EuTiO$_3$ is smaller than that of SrTiO$_3$. This result indicates that the crystal lattice of the as-deposited film elongates unidirectionally along the c-axis, as implied by 2θ-ω scan. For the annealed film, in contrast, $Q_x$ and $Q_z$ of EuTiO$_3$ coincide well with those of SrTiO$_3$, meaning that the crystal structure of EuTiO$_3$ is relaxed by postannealing.

Surface morphology of the films was observed by an atomic force microscope. A stepped and terraced structure is clearly seen for the annealed film [Fig. 2(a)], the step height is approximately 0.4 nm [Fig. 2(b)], corresponding to the size of one unit cell of bulk EuTiO$_3$. The as-deposited film exhibited the characteristic of two-dimensional growth (not shown), reflecting the atomically flat surface of substrates. We believe that the postannealing of the as-deposited films on nearly perfectly lattice-matched SrTiO$_3$ substrates serves to reduce the lattice constant of c-axis without yielding defects such as grain boundaries and pits, leading to the single crystalline films with atomically flat and smooth surfaces.

Valence states of europium ions in the as-deposited and annealed films were characterized by room-temperature $^{151}$Eu CEMS spectra, as shown in Fig. 3(a), using $^{151}$Sm$_2$O$_3$ as a γ-ray source. Calibration of Doppler velocity was made by using a spectrum of α-Fe, which was also used as a standard for isomer shift. It is seen that the spectra are mainly composed of absorption due to Eu$^{2+}$ at around $-13$ mm s$^{-1}$, the fractions of the absorption area of Eu$^{2+}$ are estimated to be 0.96 and 0.98 for the as-deposited and annealed films, respectively. The remaining Eu$^{3+}$ ions in the as-deposited film are slightly reduced to Eu$^{2+}$ ions by postannealing. The impurity Eu$^{3+}$ ions are probably accompanied by the formation of Ti$^{3+}$ or interstitial O$^{2-}$ to compensate for the excess positive charge. In Fig. 3(b), the magnetization ($M$) of the as-deposited and annealed films is plotted as a function of temperature ($T$). Field cooling (FC) and zero field cooling (ZFC) were performed using a superconducting quantum interference device magnetometer, while a dc magnetic field ($H_d$) of 100 Oe was applied parallel to the film surface. One can see a large difference in magnetism between these two films; $M$ of the as-deposited film increases monotonically with decreasing $T$, while the annealed film exhibits a distinct AFM transition at 5.1 K, in reasonable agreement with the value reported for bulk single-crystalline EuTiO$_3$. No divergence between ZFC and FC conditions was observed for both the as-deposited and annealed films.

Figure 4 compares the magnetic properties between the as-deposited and annealed films in more detail. Figure 4(a) depicted the $M$–$T$ curves at varied $H_d$ for the annealed film. The AFM transition is evident when $H_d$ is low like 100 and 1000 Oe, whereas the FM behavior is observed when $H_d$ = 20 kOe. In other words, the stable spin structure in the annealed film is converted from AFM to FM as $H_d$ applied...
FIG. 4. (Color online) (a) M–T curves for annealed EuTiO$_3$ thin film at $H_{dc}=100$ (open squares), 1000 (open circles), and 20 000 Oe (open triangles) applied along the (100) direction. (b) $\chi$–T curves for the as-deposited EuTiO$_3$ thin film at $H_{dc}=3$ Oe and $H_{dc}=0$ Oe. The ac frequencies are 1, 10, 100, and 300 Hz. The inset represents the low-temperature data of the $M$–T curve for as-deposited film as shown in Fig. 3(b). The arrow denotes an inflection point. (c) Magnetic field ($\mu_0H$) dependence of $M$ at 2 K for the as-deposited (closed circles) and annealed (open squares) EuTiO$_3$ thin films. (d) Enlarged view of (c).

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