FEROMAGNETISM IN CRYSTALLINE AND AMORPHOUS THIN FILMS OF OXIDES CONTAINING DIVALENT EUROPIUM

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Introduction

It is known that some crystalline oxides containing Eu^{2+} show ferromagnetic properties. For instance, EuO is a ferromagnet having a Curie temperature of 69 K, and magnetic polaron is suggested as a mechanism to explain the ferromagnetism. Eu_2TiO_4 is a ferromagnet as well, and its Curie temperature is 7.8 K.

In contrast, $EuTiO_3$ and $EuZrO_3$ are antiferromagnetic, and the Néel temperatures of these compounds are 5.3 and 4.1 K, respectively. The crystal structure and magnetic properties of the latter compound have been unambiguously determined by our recent work [1]. Both $EuTiO_3$ and $EuZrO_3$ are interesting materials because of a strong coupling between magnetic ordering and phonon mode. With decreasing temperature, the dielectric constant decreases accompanied with an antiparallel ordering of magnetic moments of Eu^{2+} below the Néel temperature, due to the coupling between the localized spins and a soft phonon mode [2]. A similar phenomenon has been observed in $EuZrO_3$ very recently [3]. The soft phonon mode is sensitive to a lattice strain, and such an effect can be the most pronounced in a thin film form; an epitaxial strain due to the lattice mismatch between a film and a substrate has great influence on the dielectric and magnetic properties [4,5].

In the present study, we have prepared $EuTiO_3$ thin films deposited on single-crystalline substrates and found that as-deposited thin films exhibit ferromagnetic properties [6] in contrast to the bulk $EuTiO_3$, which is antiferromagnetic as mentioned above. We have also prepared amorphous thin films of EuO-TiO_2 and EuO-ZrO_2 systems. Surprisingly, amorphous $EuTiO_3$ and $EuZrO_3$ exhibit ferromagnetic transition although their crystalline counterparts are antiferromagnetic. Furthermore, amorphous Eu_2TiO_4 thin film is also ferromagnetic, and its Curie temperature is higher than that of its crystalline counterpart. These are very rare phenomena, considering that amorphization of ferro- or ferrimagnetic oxides often leads to spin glass phase accompanied with a drastic decrease in magnetic transition temperature. We discuss the mechanism that brings about the exotic ferromagnetism in these oxide thin films.

Experimental

Crystalline $EuTiO_3$ thin films were grown on $SrTiO_3$ and $LaAlO_3$ substrates by using a pulsed laser deposition method. The substrate temperature was maintained at 650°C during the deposition. For amorphous EuO-TiO_2 and EuO-ZrO_2 systems, silica glass was used as a substrate, which was kept at room temperature. The oxygen pressure was 1.0×10^{-5} and 10^{-6} Pa for the deposition of crystalline $EuTiO_3$ and amorphous EuO-TiO_2 and EuO-ZrO_2, respectively. The chemical composition of the resultant thin films was estimated by using Rutherford backscattering (RBS) measurements.

For the $EuTiO_3$ thin films grown on the single-crystalline substrates, X-ray diffraction (XRD) analysis was carried out to identify the crystalline phase and to obtain information about the orientation of the thin films as well as the lattice parameter. Both out-of-plane and in-plane XRD measurements were performed. The surface morphology of the thin films was examined by using atomic force microscopy (AFM). For the amorphous thin films, high-resolution transmission electron microscopy (HRTEM) as well as XRD analysis was carried out to confirm that the thin films were amorphous.

For both crystalline and amorphous thin films, ^{151}Eu conversion-electron Mössbauer spectroscopy was

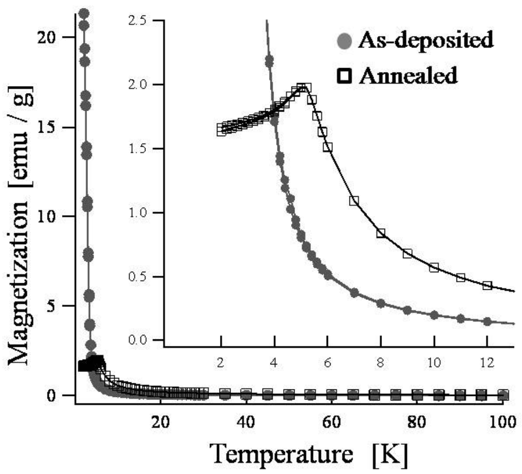

Fig. 1 Temperature dependence of magnetization for the as-deposited (closed circles) and annealed (open squares) $EuTiO_3$ thin films under H_{dc} =100 Oe applied along the <100> direction [6].

performed at room temperature to evaluate the valence state of europium ion in the thin films. As a 21.5 keV γ-ray source, $^{151}Sm_2O_3$ with activity of 1.85 GBq was used. Measurements of magnetic properties were carried out by using a superconducting quantum interference device (SQUID) magnetometer. The temperature dependence of magnetization and magnetic susceptibility as well as the magnetic field dependence of magnetization was obtained.

Results and discussion

The out-of-plane and in-plane XRD patterns of crystalline $EuTiO_3$ thin films clearly indicate that the thin films are epitaxially grown on the single-crystalline substrates. The reciprocal space mapping obtained from the XRD analysis as well as the XRD pattern itself shows that the lattice of the as-deposited $EuTiO_3$ thin films is elongated in direction perpendicular to the surface of the thin film. On the other hand, the thin film deposited on $SrTiO_3$ substrate obtained by annealing the as-deposited thin film at 1000°C in a reducing atmosphere (95 vol% Ar + 5 vol% H_2) has the same lattice parameter as the bulk $EuTiO_3$ with cubic perovskite structure.

Figure 1 depicts the magnetization as a function of temperature for the as-deposited and annealed $EuTiO_3$ thin films grown on the $SrTiO_3$ substrates. The annealed $EuTiO_3$ thin film exhibits antiferromagnetic transition with a Néel temperature of 5.1 K. In contrast, the magnetization of as-deposited thin film drastically increases at around 6 K with decreasing the temperature, suggesting that the as-deposited thin film manifests ferromagnetic transition. As demonstrated by the XRD analysis, the out-of-plane lattice parameter of the as-deposited thin film is longer than that of the bulk value. Some theoretical studies have been performed to deduce the effect of lattice volume or strain applied to the lattice on the dielectric and magnetic properties of $EuTiO_3$. Fennie and Rabe [4] carried out first principles density-functional calculations based on GGA+*U* for both ferromagnetic and antiferromagnetic states under biaxial compressive strain in *ab*-plane of the $EuTiO_3$ lattice. They found that the G-type antiferromagnetic phase is stable without the strain but that the ferromagnetic phase becomes more stable when the strain is larger than 1.2%. Since the lattice volume was kept constant in their calculations, the compression in *ab*-plane leads to a tensile strain in *c*-axis. Ranjan *et al.* [5] theoretically clarified that the magnetic structure changes from G-type antiferromagnetic to ferromagnetic with an increase in the lattice volume when *U*=6 eV. Our experimental results, which indicate that the elongation of *c*-axis is apt to stabilize the ferromagnetic order of magnetic moments of Eu^{2+} ions, is in agreement with the theoretical calculations.

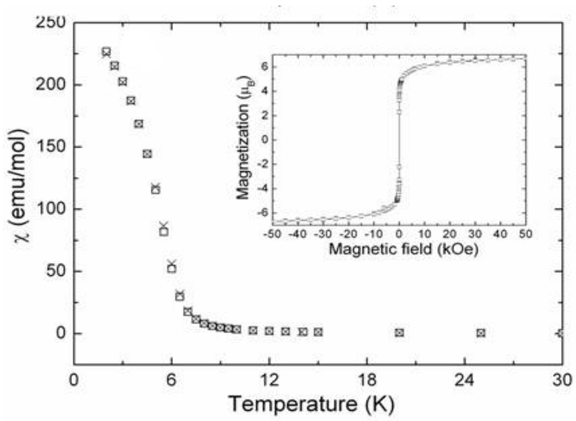

Fig.2 Temperature dependence of susceptibility for amorphous $EuTiO_3$ thin film. The measurement was carried out at an external magnetic field of 100 Oe. The crosses and open squares stands for the field-cooled and zero-field-cooled processes, respectively. The inset denotes magnetic field dependence of magnetization at 2 K (open squares) and a guide for the eye (solid line).

On the other hand, XRD analysis and HRTEM observation of $EuTiO_3$, Eu_2TiO_4, and $EuZrO_3$ thin films deposited on silica glass substrates indicate that these thin films are amorphous. Figure 2 illustrates the temperature dependence of magnetic susceptibility for amorphous $EuTiO_3$ thin film. The measurement was carried out at an external magnetic field of 100 Oe. The magnetic susceptibility abruptly increases at around 7 K with a decrease in temperature. The inset of Fig. 2 shows magnetic field dependence of magnetization at 2 K. The magnetization increases rapidly at a low magnetic field and tends to be saturated at a field higher than 1 T. The saturation magnetization is about $6.7\mu_B$ per Eu ion, and is almost the same as the magnetic moment of Eu^{2+} ($7\mu_B$). These facts clearly indicate that the amorphous $EuTiO_3$ shows ferromagnetic transition. Similar phenomena are observed in amorphous Eu_2TiO_4, and $EuZrO_3$ thin films as well.

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