論文の内容の要旨

論文題目　Electrical and Magnetic Properties of Rare Earth Monoxide Epitaxial Thin Films

（希土類単酸化物エピタキシャル薄膜の電気・磁気特性）

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I. Introduction

Rare earth elements form insulating sesquioxides (RE_2O_3, *RE*: Sc, Y, and lanthanides) because their trivalent ions have highly closed shell states. Only a few elements such as Eu and Yb form thermodynamically stable rocksalt monoxides with divalent ions. Rare earth monoxides (*RE*O), LaO, CeO, PrO, NdO, and SmO were obtained several decades ago by high pressure synthesis in the bulk polycrystalline form [1]. Since then, almost no report has been made probably due to their poor chemical stability. YO and GdO are known only in gaseous phases [2].

Recently, thin film growth technology has achieved significant progress. In particular, pulsed laser deposition (PLD) method, in which highly energetic ablated species are used for deposition, has enabled the synthesis of metastable materials in non-equilibrium conditions. Furthermore, epitaxial force from single crystalline substrate could stabilized the lattice of metastable compounds. Thus, it would be possible to synthesize unknown *RE*Os of epitaxial thin film form by using PLD.

In this study, I have fabricated YO, LaO, and GdO epitaxial thin films by PLD method and

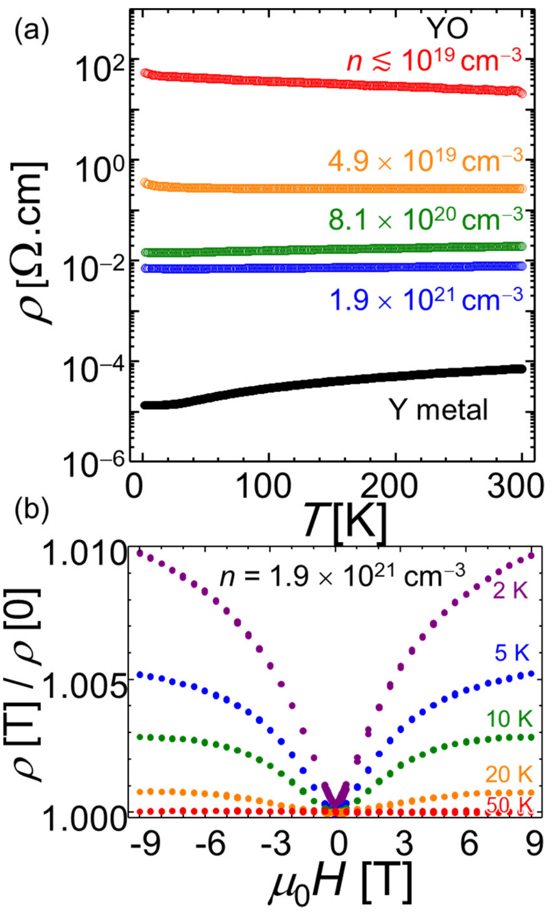

Fig. 1. (a) Temperature dependence of resistivity for YO films with different carrier density at 300 K. Y metal is shown as reference. (b) Isothermal magnetoresistance of YO film ($n = 1.9 \times 10^{21}$ cm^{-3}).

investigated their unique electronic and magnetic functionalities.

II. Experimental

YO and GdO epitaxial thin films were prepared on the (001) plane of CaF_2 single crystal substrates by PLD. Polycrystalline sesquioxides were used as the PLD target. Oxygen partial pressure (P_{O2}) monitored with a quadrupole mass analyzer was tuned by introducing Ar/O_2 1% gas during thin film growth. LaO epitaxial thin films were grown on the (110) plane of perovskite $YAlO_3$ (YAP) single crystal substrate and the (001) plane of $LaAlO_3$ (LAO) single crystal substrate by PLD, where P_{O2} was tuned by introducing pure O_2 gas. La metal was used as the PLD target. Lattice constants and crystal structures of the films were examined with XRD. XPS measurements confirmed that the *RE* ions existed in divalent states. Absorption spectra were obtained from transmittance and reflectance. Resistivity was evaluated with four-probe method. Hall effect was measured using Hall bar shaped samples, where magnetic field was applied perpendicular to the film surfaces. Magnetic susceptibility was characterized by a SQUID magnetometer.

III. Mott transition in YO epitaxial thin film

X-ray diffraction revealed coherent growth of YO with Y^{2+} ([Kr]$4d^1$)) on CaF_2 (001) substrate. Generally, oxygen vacancies in metal oxides behave as electron donors. In this study, I tried to tune the electrical resistivity of YO by controlling the oxygen partial pressure during PLD growth. In addition, the relation between electrical conductivity and electron carrier density was systematically investigated. As a result, it was found that the carrier density (n) and lattice constants of the YO thin film monotonically increased with decreasing P_{O2}. The resistivity (ρ) was tunable in a wide range of 10^{-3}-10^1 Ω.cm. The films with $n \geq 10^{20}$ cm^{-3} showed metallic conduction with positive dρ/dT slopes, whereas those with $n \leq 10^{20}$ cm^{-3} were found to be semiconducting with negative dρ/dT (Fig.1(a)). The semiconducting YO films exhibited a kink in absorption spectra, which is characteristic of Mott-Hubbard insulators [3]. These results suggest that the stoichiometric YO film is a Mott-Hubbard insulator and undergoes an insulator-to-metal transition by doping carrier electrons.

As shown in Fig.1(b), the metallic YO film ($n = 1.9 \times 10^{21}$ cm^{-3}) showed positive magnetoresistance with a sharp dip around 0 T originating from the weak antilocalization effect, suggesting the significant spin-orbit interaction.

IV. Superconductivity in LaO epitaxial thin film

LaO thin films grew coherently on YAP substrates with compressive strain regardless of P_{O2}. LaO possesses La^{2+}:[Xe]$5d^1$, whose delocalized $5d^1$ electron leads to high carrier density of ~10^{22} cm^{-3}. The tetragonal distortion c/a and electron carrier density at 300 K n_{300K} increased with decreasing P_{O2} and reached to 1.019 and 1.58 $\times$ 10^{22} cm^{-3},

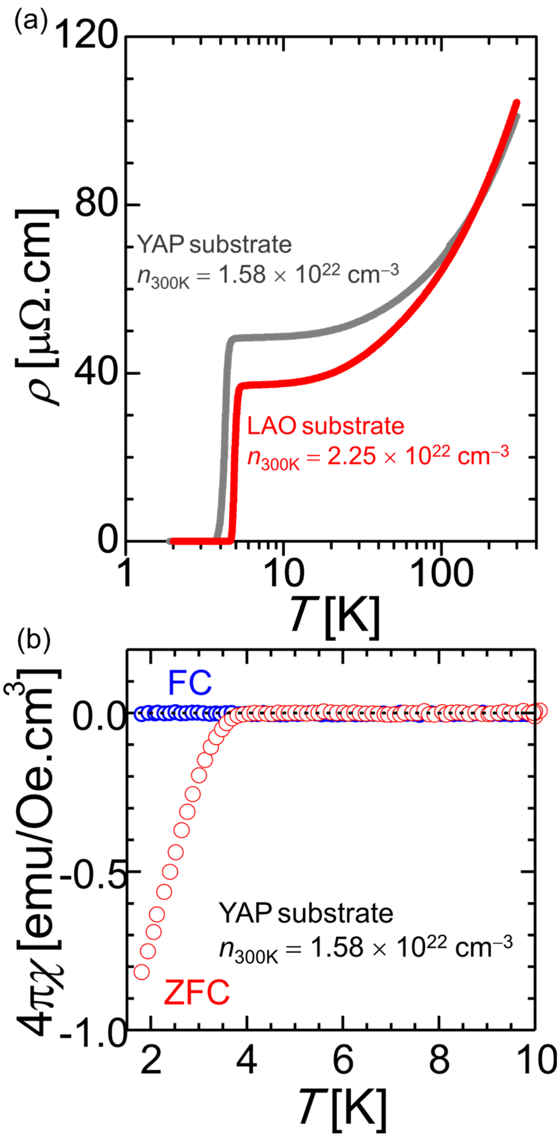

Fig. 2. (a) Temperature dependence of resistivity for LaO films on YAP and LAO substrates. (b) Temperature dependence of magnetization for LaO film on YAP substrate at 10 Oe in zero-field cooling (ZFC) and field-cooling(FC) processes.

respectively, at P_{O2} = 1 × 10^{-8} Torr. As shown in Fig.2(a), the resistivity vs temperature (ρ-T) curve of the LaO (001) epitaxial thin film showed not only metallic conduction but also superconductivity with onset T_c^{onset} of 4.56 K and zero resistance T_c^{zero} of 3.70 K. The superconductivity completely disappeared at 9 T. Magnetization measurements proved almost full volume fraction, implying "bulk" superconductivity (Fig.2(b)). Considering from the chemical trend of LaX, the transition temperature of LaO should be below 1 K. To understand the higher T_c superconductivity of LaO among LaX, I evaluated the density of state at the Fermi level ($N(E_F)$) from T_c *vs*. upper critical field plot. The obtained $N(E_F)$ was 1.06 states $eV^{-1}f.u.^{-1}spin^{-1}$, which is four times as large as the theoretical values of LaX series [4]. According to the BCS theory, T_c is proportional to $\exp(-1/N(E_F)V)$, where V is the electron phonon interaction. Thus, the relatively high Tc of LaO can be rationalized by high $N(E_F)$.

The tensilely strained LaO thin film on $LaAlO_3$ substrate showed higher T_c (T_c^{onset} = 5.24 K and T_c^{zero} = 4.59 K) than that of compressively strained film on $YAlO_3$ substrate (Fig.2(a)). n_{300K} of the tensilely strained film was 2.25 × 10^{22} cm^{-3}, which was larger than that of the compressively strained film. However, $N(E_F)$ and Debye temperature θ_D of the tensilely strained film were almost comparable to those of compressively strained film. On the other hand, the electron-phonon coupling parameter $\lambda_{e\text{-}ph}$ was the largest for the tensilely strained film, suggesting that an influence of lattice strain on T_c through the electron-phonon interaction.

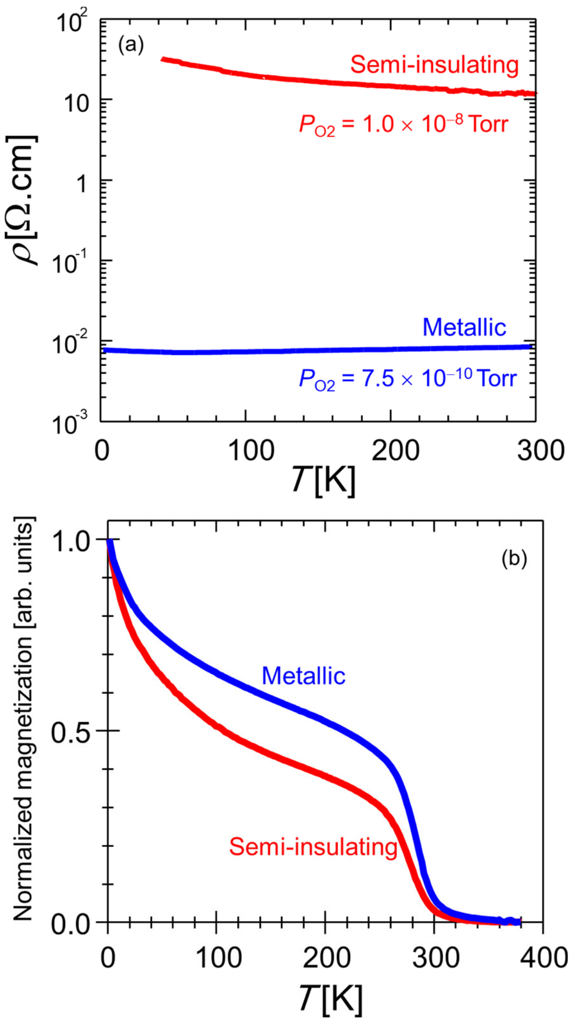

Fig. 3. (a) Temperature dependence of resistivity for GdO films synthesized under P_{O2} = 1.0 × 10^{-8} Torr (semi-insulating) and 7.5 × 10^{-10} Torr (metallic). (b) Temperature dependence of in-plane normalized magnetization for semi-insulating and metallic GdO films under 0.3 T in FC process.

V. Room temperature ferromagnetism in GdO epitaxial thin film

GdO grew coherently on CaF_2 (001) substrate. GdO possesses Gd^{2+} with half-filled 4f orbital ([Xe]$4f^7 5d^1$) similar to ferromagnetic semiconductor EuO. As shown in Fig.3(a), the electrical transport properties can be controlled from semi-insulating to metallic state by P_{O2}. Both semi-insulating to metallic GdO films showed ferromagnetism with Curie temperature (T_C) of ~320 K (Fig.3(b)), which is the highest value among Gd binary compounds reported so far. Electron carrier doping by introducing oxygen vacancies was ineffective to increase T_C. The electron configuration of GdO possibly contributes to such high T_C through e.g. RKKY interaction. The rapid increase in magnetization below around 50 K could be due to overlapping of magnetic polarons [5].

The field dependent magnetization (M-H curve) of metallic GdO thin film showed hysteresis with saturation magnetization of approximately 1 μ_B/Gd at 5 K (Fig. 4(a)). The semi-insulating GdO thin film also exhibited similar M-H curve. The shape of M-H curve corresponds well to that of anomalous Hall effect (AHE) (Fig.4(a)). The anomalous Hall resistivity was maximized at 100 K, suggesting the presence of a Berry-phase contribution to the AHE, similar to Gd thin film [6]. Hysteresis was observed in both M-H loop and AHE even at 300 K.

VI. Conclusion

I have synthesized *RE*O epitaxial thin films (*RE* = Y, La and Gd) with unusual valence states of RE^{2+} by PLD and investigated their electrical and magnetic properties. YO was found to be a Mott-Hubbard insulator with $4d^1$ configuration and the electrical transport properties could be tuned from semi-insulating to metallic states by electron doping. The compressively strained LaO thin film on YAP substrate exhibited superconductivity with onset T_c of 4.56 K, which is highest among rocksalt La*X* due to the large density of state at the Fermi level. Higher onset T_c of 5.24 K was observed in the tensilely strained LaO thin film on LAO substrate, probably reflecting the effect off lattice strain on the superconductivity through electron-phonon interaction. GdO was proved to be a room temperature ferromagnetic semiconductor from the hysteretic *M*-*H* and AHE-*H* loops observed at 300 K.

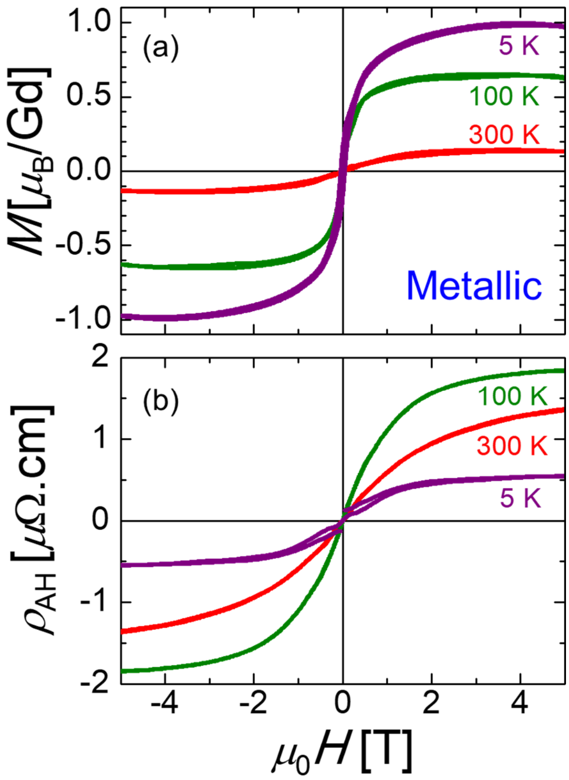

Fig. 4. (a) Applied magnetic field dependence of in-plane magnetization at 5, 100, 300 K for metallic GdO thin film. (b) Anomalous Hall resistivity of metallic GdO thin film at 5, 100, 300 K.

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