Study on itinerant ferromagnetism in rocksalt-type neodymium monoxide epitaxial thin film and heterostructure

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博士論文

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（岩塩型ネオジム単酸化物エピタキシャル薄膜とヘテロ構造における遍歴強磁性の研究）

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Contents

1 Introduction

In this chapter, the electrical and magnetic properties expected for neodymium monoxide NdO were introduced. Among the rare earth (*RE*) oxides, the most stable compound is the rare earth sesquioxides RE_2O_3, which have trivalent rare-earth ions. RE_2O_3 are mainly paramagnetic insulators and electrically and magnetically inactive. In contrast, rare-earth monoxides *RE*O with unusual divalent rare-earth ions show various magnetism and electrical conductivity. For example, in europium (Eu) oxides, Eu_2O_3 is a paramagnetic insulator, while EuO is a ferromagnetic insulator originating from localized 4f electrons.

About 40 years ago, *RE*O were synthesized by reacting *RE* metals and their sesquioxides under high temperature and high pressure. However, it was not easy to obtain high-quality *RE*O samples by this method, and the physical properties have scarcely been investigated. Recently, our group has succeeded in synthesizing *RE*O as a thin film. In this method, high-quality *RE*O samples are obtained by structural stabilization. Then, various physical properties of *RE*Os have been revealed by the measurements of the thin films.

In this study, I focused on neodymium monoxide NdO. NdO is expected to have magnetism derived from the 4f electrons and electrical conductivity derived from the 5d electrons. As for the magnetism, there are two magnetic interactions between the 4f electrons in NdO. One is a ferromagnetic direct exchange interaction between the nearest neighbor neodymium ions, and the other is an antiferromagnetic superexchange interaction between the next nearest neighbor neodymium ions. In addition to these interactions, there is a possible contribution from the RKKY interaction mediated by the 5d electrons. Among these three interactions, the ferromagnetic interaction intensifies with decreasing interionic distance, but the antiferromagnetic interaction is almost independent of distance. So, the ferromagnetic interaction dominates in NdO with a small oxide ion, and NdO is expected to show ferromagnetism. The purpose of this study is the synthesis of NdO in the form of high-quality epitaxial thin film and the investigation of its electrical and physical properties. Application of NdO for a ferromagnetic heterostructure is also demonstrated.

2 Experimental techniques

In this chapter, the techniques used for the synthesis and physical characterization of the samples were described. For the synthesis of *RE*O thin films, pulsed laser deposition (PLD) was adopted. During the thin film deposition, the sample surface was observed by a reflective high-energy electron diffraction system equipped on the PLD system. The crystal structure and film orientation of the synthesized samples were analyzed by an X-ray diffractometer equipped with a four-axis diffractometer. The electronic configuration of NdO was determined by X-ray absorption spectroscopy and X-ray photoelectron spectroscopy. The surface topography of substrates and thin films was observed by the atomic force microscopy system. Local crystal structures of NdO thin film were observed with transmission electron microscopy (TEM). Besides, fast Fourier transform processing of TEM images and the simulation of reciprocal lattice patterns were performed. The electrical measurements were performed by the four-terminal method, and the magnetization measurements were performed by a superconducting quantum interference device magnetometer.

3 Synthesis of NdO epitaxial thin film

In this chapter, the results of optimization on the synthesis conditions for NdO epitaxial thin films by mean of PLD was shown. NdO (001) epitaxial thin films were synthesized on $YAlO_3$ (110) single crystal substrate by PLD for the first time (Fig. 1), where the synthesis parameters were precisely optimized to obtain pure phase and single orientation. From XRD, the lattice constant of NdO thin film was calculated to be about 5.1 Å, which was close to that of 4.994 Å reported for bulk NdO. By TEM measurements, the local crystal structure of NdO epitaxial thin film was investigated, where the origin of the two kinds of lattice constants was revealed to be the lattice relaxation. By synchrotron XAS and PES measurements, the the anomalous valence state with the $4f^3 5d^1$ electron configuration for the Nd^{2+} ion was confirmed.

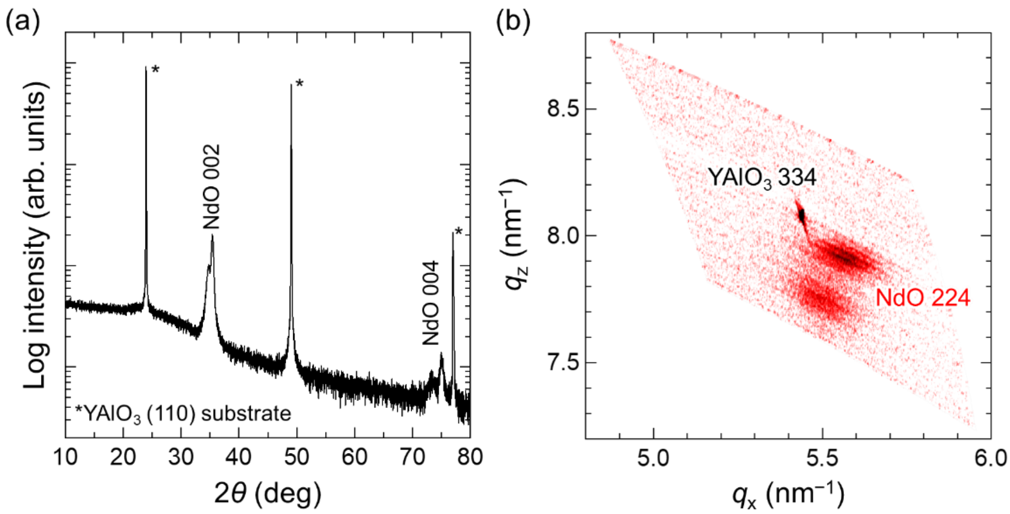

Figure 1 (a) XRD θ-2θ pattern and (b) reciprocal space map at around 224 diffractions for NdO (001) epitaxial thin film on $YAlO_3$ (110) substrate.

4 Physical properties of NdO epitaxial thin films

In this chapter, the electrical and magnetic properties of NdO were investigated using the synthesized NdO epitaxial thin films. Magnetic measurements showed that NdO exhibits ferromagnetism with T_C = 19.1 ± 1.8 K (Fig. 2). The ferromagnetism of NdO with a relatively high T_C was derived from the dominance of the 4f direct exchange interaction by the small ionic radius of the oxide ion. Besides, the magnetic anisotropy and large coercivity of NdO were attributed to the localized $4f^3$ electronic state. In the electrical measurements, metallic electrical conduction due to itinerant $5d^1$ electrons was observed (Fig. 3a). Around T_C, the resistivity decreased abruptly due to the formation of ferromagnetic ordering. Below T_C, the AHE corresponding to the magnetic hysteresis appeared, and the coercivity of the AHE was consistent with the magnetization hysteresis (Fig. 3b). These results indicated that itinerant ferromagnetism arises from the strong magnetic interaction between 4f-5d electrons in NdO.

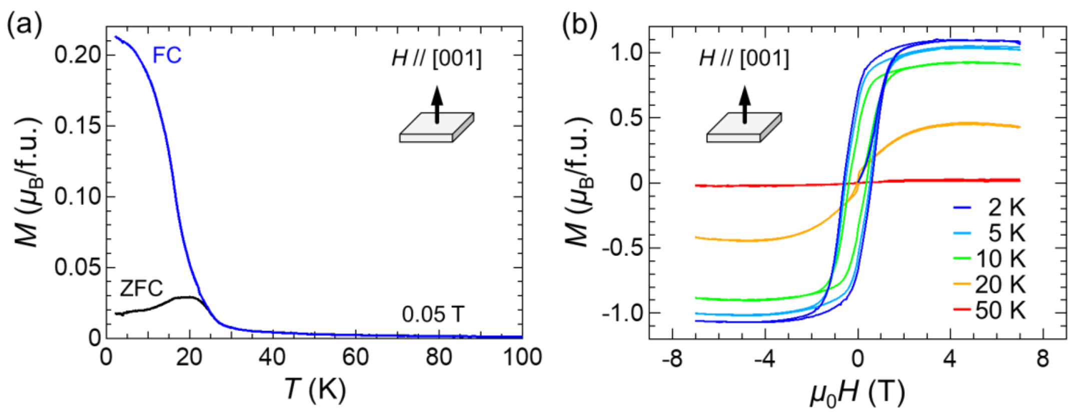

Figure 2 (a) Temperature dependence of magnetization for NdO epitaxial thin film at 0.05 T (FC: blue; ZFC: black). (b) Magnetic field dependences of magnetization at different temperatures from 2 to 50 K. Magnetic field was applied along the out-of-plane [001] direction.

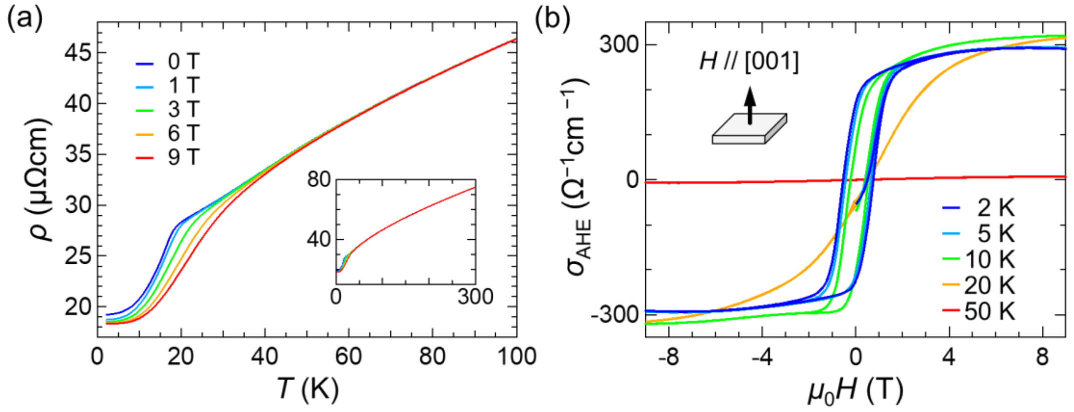

Figure 3 (a) Temperature dependence of resistivity for NdO epitaxial thin film at various magnetic fields. Inset shows overall view of 2–300 K. (b) Magnetic field dependence of anomalous Hall conductivity at different temperatures from 2 to 50 K. The magnetic field was applied to the out-of-plane [001] direction.

5 Thickness dependence of physical properties in NdO epitaxial thin films

Prior to the synthesis of NdO/EuO heterostructures in the next chapter, I synthesized NdO thin films with thicknesses of 3–40 nm and investigated their physical properties in this chapter. X-ray diffraction showed that phase-pure NdO (001) epitaxial films were obtained in the whole thickness range. Electrical resistivity increased monotonically with decreasing thickness, and showed insulating temperature dependence for small thicknesses due to the localization of the 5d electrons. As for magnetism, T^{*}_{1} corresponding to the bulk T_{C} decreased monotonically with decreasing film thickness as a result of suppressed magnetic interaction at the surface and film/substrate interface. Meanwhile, the 9-nm and 12-nm-thick films showed a “weak ferromagnetic” phase above the bulk T_{C}. The origin of the “weak ferromagnetic” phase could be the surface magnetization, and its thickness dependence could reflect the change in surface flatness of NdO thin film.

6 Synthesis and physical properties of NdO/EuO heterostructures

In this chapter, the synthesis and physical properties of ferromagnetic NdO/EuO heteroepitaxial structures were described. A ferromagnetic heteroepitaxial structure of metallic NdO and insulating EuO with an atomically smooth interface was successfully synthesized. The magnetism was dominated by the EuO layer with in-plane magnetic anisotropy and T_C of 69 K. On the other hand, the electrical conduction in the NdO layer exhibited a large MR due to the strong coupling between the $4f^3 5d^1$ and $4f^7$ electrons in the NdO and EuO layers, respectively. The Hall conductivity also well corresponded to the in-plane magnetic anisotropy for the EuO layer. The sign change in the Hall conductivity suggested a formation of a non-trivial magnetic structure derived from the interfacial exchange coupling below T_C of NdO.

7 Conclusion

In this study, I synthesized rocksalt-type NdO epitaxial thin films and NdO/EuO heterostructures and investigated their electrical and magnetic properties. NdO showed characteristic physical properties owing to the localized 4f and itinerant 5d electron systems, such as the "weak ferromagnetic" phase above the bulk T_C of NdO thin films and the interfacial magnetotransport in the NdO/EuO heterostructure. These physical properties arising from the 4f-5d interaction have the potential for application in the field of spintronics, and the findings of this study be beneficial for the development of spintronic materials utilizing rare-earth compounds.