

論文内容の要旨

論文題目 **High-energy spectroscopic studies of functional oxide thin films and heterojunction**

(機能性酸化物薄膜およびヘテロ接合の高エネルギー分光による研究)

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Due to the advances in oxide thin film fabrications, one can now obtain oxide thin films with high qualities and/or unique properties. For example, ferromagnetism in diluted magnetic semiconductors (DMSs) is achieved in thin film samples, since incorporating magnetic ions into host semiconductors exceeding the solubility limit can be performed using thin film growths. It has also become possible to design atomically abrupt oxide junction interfaces to generate device functions or even new phenomena [1]. These features make oxide thin films and heterostructures worth investigating. Alternatively, one can investigate properties of materials in a qualitatively new way by exploiting the unique characteristics of oxide thin film samples. High-energy spectroscopy is a powerful tool to investigate electronic and magnetic properties of materials, and hence of oxide thin films. We have performed high-energy spectroscopy studies of Na_xCoO_2 thin film, $n\text{-ZnO}/p\text{-NiO}$ heterojunction, and $\text{Zn}_{1-x}\text{V}_x\text{O}$ thin film, as described below.

On the origin of large thermoelectric power in Na_xCoO_2

Na_xCoO_2 is a potential thermoelectric (TE) material, since it shows large TE power and low resistivity [2]. Since TE powers are generally small in low resistive materials, there have been attempts to understand the unusually large TE power in Na_xCoO_2 . There have been mainly two scenarios: (1) A scenario based on metallic Boltzmann transport theory, in which the large TE power is attributed to the large band mass (small band width) [3,4]. (2) A model based on correlated hopping, in which the large TE power at high temperatures is explained as due to the large spin-orbital entropy of localized $\text{Co}^{3+}/\text{Co}^{4+}$ mixed valence state [5].

In order to investigate the large TE power, we have performed a precise temperature dependent photoemission spectroscopy (PES) study on Na_xCoO_2 epitaxial thin films using the reactive-solid phase epitaxy method [6]. A single crystalline surface was obtained, as evidenced by dispersions in the angle-resolved PES spectra. We observed a temperature dependent shift of the Co $3d$ -derived peak, from which we derived the chemical potential shift $\Delta\mu(T)$ (Fig. 1). $\Delta\mu$ revealed a crossover from the low-temperature degenerate state to the high-temperature correlated hopping state at a

characteristic temperature $T^* \sim 200$ K. Therefore, we concluded that the transport properties including the TE power at high temperatures should be treated in the correlated hopping picture.

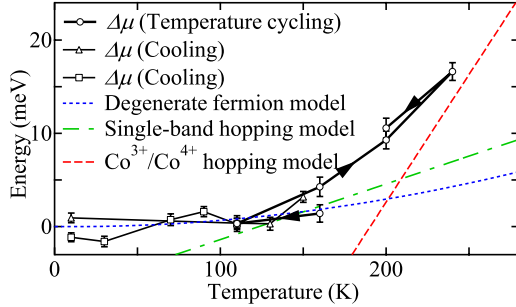


Fig.1 $\Delta\mu$ of Na_xCoO_2 . $\Delta\mu$'s estimated from the degenerate fermion model and correlated hopping models are plotted for comparison.

Potential profiling of an $n\text{-ZnO}/p\text{-NiO}$ junction interface

$n\text{-ZnO}/p\text{-NiO}$ is an atomically abrupt oxide heterojunction, and is a representative and promising transparent all-oxide diode for future oxide electronics [6]. Direct investigation of the charge depletion region (CDR) is important since it is the center of the device functions. Due to the generally high carrier concentrations in carrier doped oxides, the CDR widths in oxide junctions become as narrow as several nanometers, and thus, the investigation requires a spatial resolution of nanoscale.

We have performed a depth-profile analysis on an initially 10-nm thick ZnO overlayer using Ar-ion sputtering [Fig. 2(a)] and have studied the potential changes at surface and interface using PES. Systematic core-level shifts were observed below a critical ZnO thickness ~ 2.5 nm [Fig. 2(b)]. We described this behavior using a model based on charge conservation [Fig. 2(a)]. We deduced a potential profile across the junction, such as the CDR width of 2.3 nm on the ZnO side and the built-in potential of 0.54 eV.

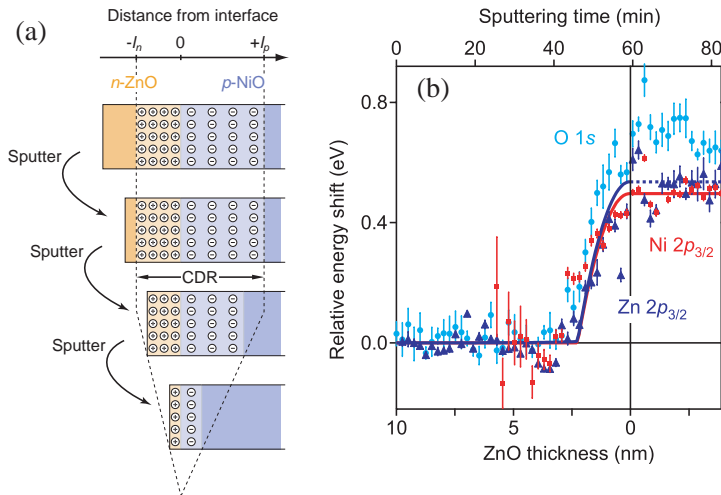


Fig.2 Depth-profile analysis of ZnO/NiO. (a) Removal of the ZnO overlayer by Ar-ion sputtering and evolution of the charge distribution in the CDR. (b) Core-level shifts as a function of sputtering time or ZnO thickness.

High energy spectroscopy study of Zn_{1-x}V_xO thin film

Ferromagnetic DMSs have attracted much interest for potential spintronics device materials. Zn_{1-x}V_xO thin film shows high-Curie-temperature ferromagnetism [8], which is attractive for applications. However, ferromagnetism in DMSs is controversial both on the mechanism and on the origin whether it is intrinsic or extrinsic. Therefore, electronic and magnetic structure studies of DMSs are highly required.

We have performed soft x-ray magnetic circular dichroism (XMCD) and valence-band PES studies on Zn_{1-x}V_xO. From the magnetic field and temperature dependences of the V 2*p* XMCD intensity, we estimated that ~10 % of the V ions contributed to the Curie-Weiss paramagnetism, while the others were coupled antiferromagnetically. The ferromagnetic component was below the detection limit, consistent with the magnetization measurements. Comparison with atomic multiplet calculation indicated that the V²⁺ ions were substituting for the Zn site. Orbital anisotropy of V 3*d* electrons due to elongation along the *c*-axis of ZnO explained both the suppressed orbital magnetic moment of 3*d* electrons and the XMCD line shape (Fig. 3).

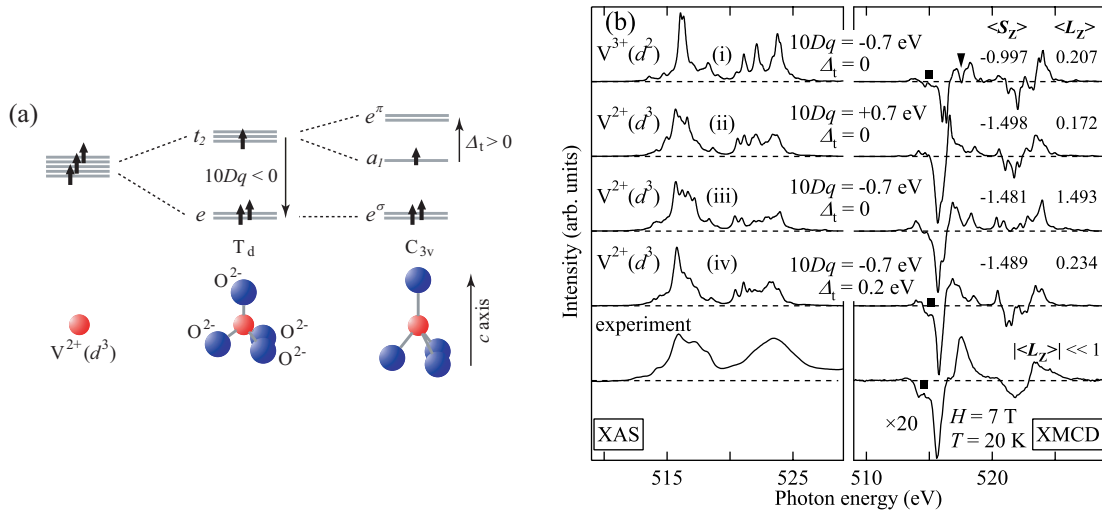


Fig.3 XAS and XMCD of Zn_{0.95}V_{0.05}O and comparison with atomic multiplet calculation. (a) Single-electron energy levels in the predominantly tetrahedral crystal field. The degeneracy of *t*₂ states is lifted by elongation of the tetrahedral along the *c*-axis. (b) Comparison of experiment with calculation.

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