

Valence States of Mn, Fe, Co, and Ni impurities in SnO films

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1 Introduction

Diluted magnetic semiconductors (DMSs) are considered as key materials in the spintronics field. While various candidates of room-temperature ferromagnetic DMSs have been developed, such as GaN:Mn[1], TiO₂:Co[2], ZnO:Mn[3], and Ga₂O₃:Mn[4,5], the origins of the ferromagnetism are still controversial. We have previously investigated the correlation between the magnetic properties and the electronic and atomic structures of GaN:Mn and Ga₂O₃:Mn using a combination of systematic X-ray absorption spectroscopy measurements with first-principles many-electron calculations. As a result, Mn ions are found to be located at the tetrahedrally-coordinated Ga sites mainly with a valence of +2 in ferromagnetic GaN:Mn[6,7]. We also found similar states of Mn ions in Ga₂O₃:Mn[4]. In this study, we examine transition metal (TM) doped SnO. SnO is considered to have an advantage in investigating the correlation between carrier transports and magnetism since the majority carrier type can be controlled from holes to electrons[8].

2 Experiment

TM-doped SnO thin films were prepared by pulsed laser deposition (PLD) using a KrF* excimer laser source on yttria stabilized zirconia (YSZ) (001) single crystal substrates. Compacts of SnO mixed with TM oxide powders was used as the PLD target whose dopant concentrations were designed to be 5 cation%. In this study, we chose Mn, Fe, Co, and Ni as TM. The substrate temperature was kept at 673 K during the deposition. After the deposition, the films were cooled to room temperature in the chamber pumped down to less than 2×10^{-4} Pa.

The crystal structures and crystallinity of the films were investigated by high-resolution five-axes X-ray diffraction (XRD) with Cu-K α radiation. Hall effect measurements were carried out by the van der Pauw method at room temperature to evaluate carrier types, mobilities, and concentrations.

TM-*L*_{2,3} X-ray absorption spectra were obtained at KEK-PF BL-11A by the total electron yield method with a 800 lines/mm grating monochromator. All measurements of the spectra were carried out in the vacuum chamber at room temperature.

3 Results and Discussion

Systematic XRD analyses indicated the epitaxial growth of single phase TM-doped SnO films. All samples showed *p*-type conductivity.

The valence states of TM ions are considered to be +2 when they simply substitute for the Sn sites in SnO.

Divalent TM oxides with TM = Mn, Fe, Co, and Ni exhibit rocksalt type structures with octahedral TM sites. Meanwhile, the Sn site in SnO is located at the apex of a pyramid with four O atoms. Therefore, the electronic structure of divalent TM ions at the Sn site is considered to be unique. Figure 1 shows TM-*L*_{2,3} X-ray absorption spectra of the TM-doped SnO films. While the characteristics of Mn-, Co-, and Ni-*L*_{2,3} edges spectra indicate that the valence state of each ion is +2, the Fe-*L*_{2,3} spectrum suggests that the Fe ions exist as Fe³⁺ in the SnO films, which implies that the 3*d*⁶ electronic configuration is not favorable in SnO.

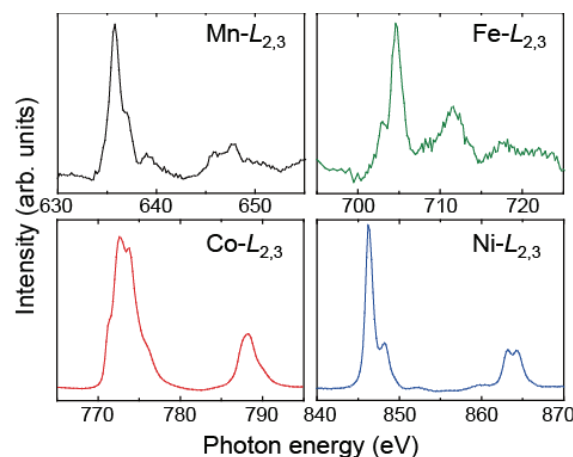


Fig. 1: TM-*L*_{2,3} X-ray absorption spectra of TM-doped SnO films.

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