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Electronic structure of $(Ga_{1-x}Mn_x)_2O_3$ diluted magnetic semiconductors

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Introduction

Diluted magnetic semiconductors (DMSs) with room-temperature ferromagnetism have attracted interests in terms of spintronic applications. However, the origin of the ferromagnetism is still controversial because of the lack of sufficient information on the local atomic, electronic and magnetic structures of the dopants. We have previously reported that the valence state of Mn ions in MBE-grown ferromagnetic Mn-doped GaN thin films is a mixture of +2 (majority) and +3 (minority), whereas it is +3 (majority) in paramagnetic films grown by the same technique but with slightly different conditions [1, 2]. In contrast, room temperature ferromagnetism was observed for Mn-doped Ga_2O_3 thin films with a dominance of Mn^{2+} [3]. The control of Mn valency can also be essential for the improvement of the magnetic properties of Mn-doped Ga_2O_3. In the present study, we have prepared Mn-doped Ga_2O_3 thin films under an oxidant atmosphere to control the valency of Mn. The local atomic and electronic structures of the Mn dopants were probed using Mn-$L_{2,3}$ XANES and comparatively discussed with those in Mn-doped GaN.

Methods

Previously we found that Mn-doped Ga_2O_3 thin films grown on sapphire substrates show γ-phase with the spinel structure [3]. In the present study, we used spinel ($MgAl_2O_4$) (100) substrates to obtain epitaxial films. The films were made by the pulsed laser deposition method using a KrF^* excimer laser (λ = 248 nm) with the pulse rate of 1 Hz and the laser energy density of 3.0 J/cm^2. Sintered Mn-doped Ga_2O_3 compact was used as a target. Substrate temperature was kept at 773 K. Oxygen gas was introduced to the vacuum chamber via an electron cyclotron resonance (ECR) ion source.

Mn-$L_{2,3}$ XANES spectra were obtained at KEK-PF BL-11A by the total electron yield method with 800 lines/mm grating monochromators. All measurements of XANES spectra were carried out in the vacuum chamber at room temperature.

Results and Discussion

Systematic x-ray diffraction analysis indicated the epitaxial growth of Mn-doped γ-Ga_2O_3 films. The Mn concentration of the films estimated from the x-ray energy-dispersive spectroscopy analysis on scanning and transmission electron microscopes was 7 cation%.

Figure 1 shows Mn-$L_{2,3}$ XANES spectra of the Mn-doped Ga_2O_3 thin films compared with the spectra of MnO (Mn^{2+}), Mn_3O_4 (Mn^{2+} : Mn^{3+} = 1 : 2), and Mn_2O_3 (Mn^{3+}). Since there are sharp peaks at the Mn-L_3 edge in the spectra of Mn-doped films as in the case of the spectrum of MnO, these films contain Mn^{2+}. In addition, a comparison with the spectra for Mn_3O_4 and Mn_2O_3 suggests that the Mn^{3+} content in the films increases as going from the top to the bottom. The Mn^{2+} ratio with respect to Mn^{3+} was evaluated by the branching ratio technique, yielding the values of ~100% to ~60% as presented in the figure. Thus, we demonstrate the mixed valence state of Mn by using ECR ion source. However, the mixed-valence Mn-doped Ga_2O_3 films were found to be paramagnetic at room temperature, in contrast to the case of Mn-doped GaN. This can be explained in terms of the difference in electronic structure, particularly the spatial distribution of Mn-3d – anion-2p hybridized states, between Mn-doped GaN and Ga_2O_3.

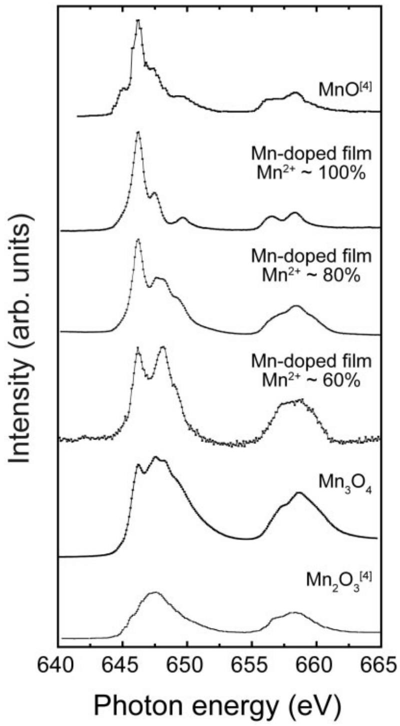

Fig. 1 Mn-$L_{2,3}$ XANES spectra of Mn-doped Ga_2O_3 films with various-mixed valence states, compared with those of MnO [4], Mn_3O_4, and Mn_2O_3 [4].

References

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