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Identification of local environment of Mn in γ-Ga_2O_3 using XANES and first-principles calculations

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Introduction

Diluted magnetic semiconductors (DMSs) have attracted keen interests recently. Several models on the ferromagnetism have been proposed and a lot of experiments and theoretical calculations have been done in order to examine them. However, the mechanism is still controversial because of the lack of sufficient information on local atomic, electronic and magnetic structures of the dopants.

We have already reported that the valence state of Mn in the MBE-grown ferromagnetic Mn-doped GaN thin films exhibit mixed +2 (majority) and +3 (minority), whereas it is +3 (majority) in paramagnetic film grown by the same technique but with slightly different conditions [1,2]. Valency control of Mn is thus found to be essential for them. In present study, we prepare Mn-doped Ga_2O_3 thin films and investigate the local environment of Mn.

Methods

The thin films were made by pulsed laser deposition (PLD) using a KrF* excimer laser (λ = 248 nm) on α-Al_2O_3(0001) substrate with pulse rate of 10Hz and laser power of 3 J/cm^2. Sintered Mn-doped Ga_2O_3 compact was used as a target. Substrate temperature was kept at 773 K and p_{O2} = 0.05 Pa during the deposition[3].

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

In order to interpret experimental spectra, a first-principles method using density functional theory and configuration interaction scheme was employed. Details of this computational method were described elsewhere [4]. There are two kind of cationic sites in the spinel structure, i.e., coordinate number (CN) = 4 site and CN = 6 site. Two kinds of model clusters, MnO_4^{6-} and MnO_6^{10-} were used for the calculation, which correspond to Mn^{2+} with CN = 4 and CN = 6, respectively.

Results and Discussion

Mn-doped Ga_2O_3 thin films shows γ-phase with the spinel structure. No secondary phase can be found by TEM and XRD. The concentration of Mn of deposited film was measured by energy dispersive x-ray spectroscopy equipped to a scanning electron microscope (SEM) and TEM. Both of them found that there are 7 cation% of Mn. The magnetic property of Mn-doped film was measured by the superconducting quantum interference device (Quantum Design MPMS-XL). *M-H* curve and *M-T* curve indicate that Mn-doped film is ferromagnet up to temperatures higher than 350K.

Figure 1 shows experimental XANES of the Mn-doped Ga_2O_3 thin film in comparison to theoretical spectra of Mn^{2+} (CN = 4) and Mn^{2+} (CN = 6). Since Mn-L_3 edge XANES of Mn^{2+} have a sharp peak as shown in theoretical spectra, Mn in the Mn-doped thin film is identified as 2+. Absence of a low-energy shoulder of the L_3 edge peak in the experimental XANES clearly implies that Mn is most likely present at the CN =4 site. This is quite natural, since $MnGa_2O_4$ is known to prefer a normal spinel structure[5]. The combination of experiment and theoretical calculation is a powerful tool to identify the valence state and cationic site as in the present study.

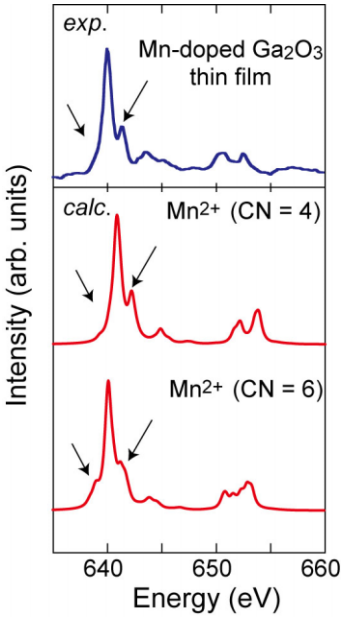

Fig. 1 Experimental Mn-$L_{2,3}$ XANES and corresponding theoretical spectra for Mn^{2+} (CN =4) and Mn^{2+} (CN =6).

References

[1] S. Sonoda et al., J. Phys.: Condens. Matter 18, 4615 (2006).
[2] S. Sonoda et al., Appl. Phys. Lett. 90, 012504 (2007).
[3] H. Hayashi et al., Appl. Phys. Lett. 89, 181903 (2006)
[4] H. Ikeno et al., Phys. Rev. B 72, 075123 (2005).
[5] B. Boucher et al., J. Appl. Phys. 37, 960 (1966).

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