XAFS measurement of Mn-doped ZnO semiconductor thin films

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Introduction

Transition metal (TM) doped semiconductors have long been studied for possible applications as spin-based fieldeffect transistors, spin-polarized lasers and nonvolatile magnetic semiconductor. Research in diluted magnetic semiconductors (DMS) has been stimulated by the discovery of materials with a Curie temperature. In recent, Mn-doped GaAs is on the order of 110K [1]. However, the penetration of spintronics as a technology depends upon the development of semiconductors that can support theoretical studies or above room temperature (RT). The prediction by Dietlet al. [2] showed that ZnO might exhibit a Curie temperature above RT when doped with TM, this led to a considerable research interest for these materials, especially with Mn.

In this report, we study on the local structure analysis of Mn ions doped in ZnO thin films.

Experimental

The ZnO:Mn thin films were formed on SiO/Si(100) substrates by laser ablating a ceramic target which was a mixture of ZnO and prescribed amounts of 10 wt% MnO₂. A QW-YAG laser ($4\omega_0 = 266 \text{ nm}, 1 \text{ J/cm}^2$) was used to ablate the target in a vacuum chamber with a background pressure of 1 x 10⁶ Torr. The ZnO:Mn thin film of 270 nm thick was formed on the SiO_y/Si(100) surface at RT. After the ablation the samples were annealed at 300 °C, 500 °C and 700 °C for 3 to 120 min in the O₂ atmosphere, to activate the doped Mn atoms to their ionized states. The crystal structure was investigated by the X-ray diffraction (XRD). We measured the Mn K-edge (6.55 keV). Detailed microstructure characterization was performed by X-ray absorption fine structure (XAFS) in the fluorescence yield mode at the BL-27B beamline of the Photon Factory synchrotron facility (KEK, Tsukuba, Japan) at the total ion beam current amounted to 400 mA, was monochromatic using a Si(111) double-crystal monochromator. Each sample was placed at a 45° angle to the incident X-ray beam and fluorescence yield was monitored using a 7-element Ge SSD.

Result and Discussion

Figure 1 shows the XAFS spectra of as-deposited and annealed ZnO:Mn thin films. The absorption edges of the K-shell shifted toward the high energies with the increased annealing temperature, indicating the valency change of the doped Mn ions. The vibration pattern also changed at the extended X-ray absorption region. There was a big change on the XAFS structure at annealing temperature of 700 °C. However, there was no significant change for different annealing time, which was also demonstrated in the case of XRD. These results indicated that the valency of Mn changed at 700 °C, which led to a spin orientation of the Mn atoms. Although we could not determine the exact valency of the doped Mn, a magnetic activation of Mn should occur at 700 °C, which gave rise to a large increase on the magnetic resistance.

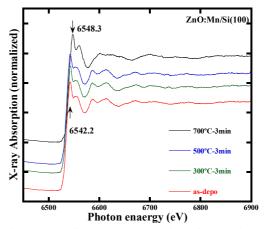


Fig.1. Annealing temperature dependence of X-ray absorption fine structure spectra.

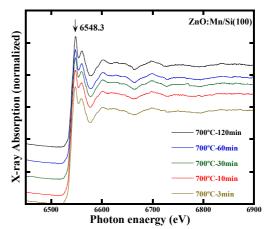


Fig.2. Annealing time dependence of X-ray absorption fine structure spectra.

References

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