Materials Science

9C/2010G024

Local structure of transition metals doped in ZnO nanoparticle

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Introduction

Diluted magnetic semiconductors (DMS) have attracted increased attention as promising ferromagnetic semiconductor with high-Curie temperature after recent theoretical predictions [1]. However there is a major scientific problem of explaining and understanding the contradicting magnetic results obtained from compositionally similar materials. Transition metal doped ZnO is one of the widely studied DMS, which has attracted a lot of scientific interest, but has also resulted in inconsistent data with respect to the magnetic properties.

Recently, microwave heating has been shown to be an efficient method for non-aqueous sol gel route offering direct and homogeneous heating conditions in comparison with conventional methods and allowing the preparation of materials at low temperature within short reaction time [2]. In this study, Fe or Co doped ZnO nanoparticles were synthesized by microwave assisted non-aqueous sol gel route, and their magnetic property and the local structure around the transition metal ions are investigated.

Experimental

Fe or Co doped ZnO were synthesized by microwave assisted non-aqueous sol gel route by adapting a procedure developed for binary and ternary oxides and published previously [3]. Phase identification was conducted by powder X-ray diffraction (XRD). Magnetic properties were investigated with SQUID magnetometer. X-ray absorption of Fe and Co K-edge was measured in transmission mode at the beam line 9C in Photon Factory.

Results and discussion

Single phase of hexagonal wurtzite structure was confirmed in both Fe or Co doped ZnO up to 30 or 20 at% doping concentration, respectively, by XRD method. Magnetization measurement revealed that the Co doped ZnO showed no ferromagnetic behaviors down to 2 K, and followed only Curie-Weiss behavior in their temperature dependence. On the other hand, Fe doped ZnO showed a ferromagnetic hysteresis only in 20% doped sample.

The XANES spectra of the Fe K-edge exhibit a main peak and visible pre-edge peak as shown in Fig. 1. The pre-edge positions in Fe = 2 and 5 % are slightly lower by ~ 1eV than those in the other sample and similar to that in the Fe_3O_4 reference. The shift of the pre-edge peak indicates that Fe in the products is a mixture of Fe^{2+} and Fe^{3+} ions, and the contribution of Fe^{3+} increases with increasing the doping concentration from 2 to 30%. There is an obvious shoulder in the Fe doped ZnO sample with Fe = 2 and 5%. Its intensity decreases with an increase in the doping level. The complete disappearance of the shoulder peak for doping concentration equal to or larger than 15% suggests that the local environment around the Fe ion changes for these high doping levels. The room temperature ferromagnetic behavior observed at 20% Fe doped ZnO might be attributed to the local structural changing around Fe in ZnO.

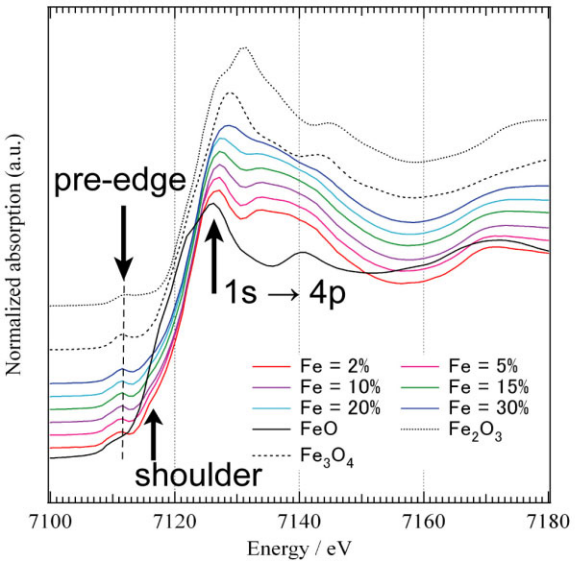

Fig. 1 Fe K-edge XANES spectra of the Fe doped ZnO products and references.

References

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