13B1/2008G703

Solubility of codoped Cu ions in $Zn_{0.95}Co_{0.05}O$ diluted magnetic semiconductors

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Introduction

Transition metal (TM) doped diluted magnetic semiconductors (DMSs) with room-temperature ferro-magnetism (RTFM) currently attract intense scientific interest because of their potential application in the spintronics devices [1]. Recently, a number of studies have suggested that Cu codoping in (Zn,Co)O DMS could improve the ferromagnetism, and the phenomenon is intrinsic [2]. However, the solubility of Cu in ZnO is usually quite low and remains in debate. In this report, the local structure around Co and Cu in $Zn_{0.95-x}Cu_xCo_{0.05}O$ were investigated by means of XAFS to determine the real solubility of Cu ions in the codoped ZnO based DMS.

Experimental

$Zn_{0.95-x}Cu_xCo_{0.05}O$ (x=0, 0.005, 0.02, 0.05, 0.08) were fabricated by the sol-gel method and then sintered at 1473K for 6 h in air atmosphere. The Co and Cu K-edge fluorescence XAFS spectra of $Zn_{0.95-x}Cu_xCo_{0.05}O$ were collected at the BL-13B1 beamline of Photon Factory, High Energy Accelerator Research Organization (PF, KEK), using a Si (111) double crystal monochromator.

Results and discussion

Fig. 1(a) and (b) display the Fourier transforms (FTs) of Co and Cu K-edge EXAFS functions for $Zn_{0.95-x}Cu_xCo_{0.05}O$ ($0 \le x \le 0.08$) sintered at 1473 K, respectively. Those of the ZnO, Co_3O_4, CoO, CuO, and Cu_2O are also shown as references. It can be seen from Fig. 1(a) that the existence of Co_3O_4 and CoO can be safely excluded. Furthermore, the FTs of $Zn_{0.95-x}Cu_xCo_{0.05}O$ shown in Fig.1(a) are very close to that of ZnO, presenting two strong peaks located at around 1.55 and 2.82 Å corresponding to the nearest Co–O and the next-nearest Co–Zn neighbors, respectively. The Co K-edge XAFS analysis indicates unambiguously that the doped Co ions are located substitutionally at the Zn sites for all the $Zn_{0.95-x}Cu_xCo_{0.05}O$ DMSs sintered at 1473 K. Fig. 1(b) clearly shows that the FTs of Cu K-edge EXAFS functions $Zn_{0.95-x}Cu_xCo_{0.05}O$ (x=0.005, 0.02) sintered at 1473 K are quite close to that of wurtzite ZnO, which indicates that all the Cu ions occupy the Zn sites in ZnO lattice at the low Cu codoped concentrations ($x \le 0.02$). However, as the Cu concentration x increases to 0.05, a small shoulder peak A marked by arrow appears at 2.39 Å as the characteristic peak of CuO. Increasing x to 0.08, the intensity of peak A increases obviously and the amplitude of the Cu-Zn peak B is damped strongly. These suggest that, for the $Zn_{0.95-x}Cu_xCo_{0.05}O$ sintered at 1473 K with high doping level $x \ge 0.05$, not all the Cu ions are incorporated into the wurtzite ZnO matrix but a part of CuO phase precipitated.

In order to determine the solubility limit of Cu in ZnO for the $Zn_{0.95-x}Cu_xCo_{0.05}O$ sintered at 1473 K, we quantitatively fit the main peaks (R=0.7~3.3 Å) including the first nearest Cu-O and the next-nearest Cu-Zn coordination shells. An adjustable parameter p ($0<p<1$) was denoted as the percentage of CuO phase in $Zn_{0.95-x}Cu_xCo_{0.05}O$ and the solubility of codoped Cu ions in $Zn_{0.95}Co_{0.05}O$ with different Cu doping concentration x can be obtained from the formula: solubility = x×(1-p). From the fitting results, we can obtain that the solubilities of Cu atoms in $Zn_{0.95-x}Cu_xCo_{0.05}O$ (x=0.05, 0.08) are about 0.036±0.003 and 0.039±0.004, respectively. The evolution of the Cu solubility in $Zn_{0.95}Co_{0.05}O$ as a function of Cu concentration (x) is plotted in Fig. 2. It can be clearly seen that, with the x further increasing, the fitting curve will approach the upper limit of 0.04. Therefore, we can estimate that the absolute value of the solubility for substitutional Cu is about 0.04.

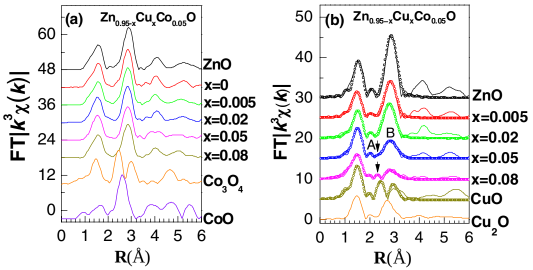

Fig.1. Fourier transform amplitude of EXAFS $k^3\chi(k)$ functions at the Co (a) and Cu (b) K-edge of $Zn_{0.95-x}Cu_xCo_{0.05}O$ with different Cu concentrations, Co_3O_4, CoO, CuO and Cu_2O as well as Zn K-edge of ZnO. The empty circles in (b) show the fitting results.

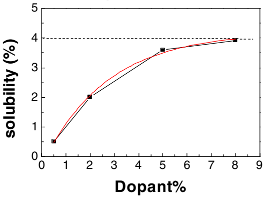

Fig.2. The Cu ions solubility as a function of Cu concentration in $Zn_{0.95-x}Cu_xCo_{0.05}O$ ($0 \le x \le 0.08$). The color line shows the fitting results of solubility.

References

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