Local structure of codoped Ag_x - $Zn_{0.92}Co_{0.08}O$ nanostructure studied by XAFS

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Introduction

Transition metals doped ZnO-based diluted magnetic semiconductors (DMS) have recently attracted considerable research interests for their promise applications in "spintronic" devices[1]. A number of experimental results on the magnetic behaviors and structures have been studied. More recently, Qiu *et al.* have reported that DMS nanostructures, especially for Ag⁺ hybrid nanostructure of surface modification, can provide unique functions in enhancing and stabilizing magnetism[2]. But it is not clear enough that the relationship between the local structure around Ag ions and magnetism of Ag-ZnCoO nanostructure. In this report, the local structure around Co and Ag in Ag_x-Zn_{0.92}Co_{0.08}O samples were determined by means of XAFS to clarify the structural detail of the doping atoms.

Experimental

The $Ag_x-Zn_{0.92}Co_{0.08}O$ nanostructures are prepared via solution chemistry method[2]. The Co K-edge EXAFS spectra of $Ag_x-Zn_{0.92}Co_{0.08}O$ samples were measured in fluorescence mode at BL-12C 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 Co K-edge EXAFS oscillation functions $k^3x(k)$ and the Fourier transforms (FT) of the $k^3 x(k)$ functions with those of the reference compounds ZnO, CoO, and Co_3O_4 . One can see that the existence of CoO and Co₃O₄ in Zn₀₀₂Co₀₀₈O and Ag-Zn₀₀₂Co₀₀₈O powder samples can be safely excluded, since their FT features are significantly different from those of $Zn_{0.92}Co_{0.08}O$ and Ag_x - $Zn_{0.92}Co_{0.08}O$ samples. Fig. 1(a) manifests the quite similar oscillation shapes of the Zn_{0.92}Co_{0.08}O nanorods as that of ZnO, but quite different from the curves of Co powders. Moreover, in Fig.1(b), the FTs for the samples also exhibit two peaks at 1.60 and 2.84 Å corresponding to the nearest Co-O and the next nearest Co-Zn coordinations at the same positions as those of ZnO, suggesting that Co ions are substitutionally doped into ZnO host in Zn_{0.92}Co_{0.08}O nanorods. Remarkably, it is evident that the FTs of Ag_x-Zn_{0.92}Co_{0.08}O has an obvious peak at 2.16 Å which is very similar to that of Co-metal characteristic peak. With further increasing the Ag concentration from 0.02 to 0.07, its intensity increases remarkably. However, we do not find any Co metal in our Co core-level XPS spectra. On the other hand, it is well known that the interstitial Ag widely exists in Ag doped ZnO host lattice. Therefore, we suppose that the peak at 2.16 Å in FTs corresponds to the interstitial Ag.



Fig.1 (a)EXAFS oscillation functions $k^3x(k)$; (b)Fourier transform amplitudes curves of Co K-edge for EXAFS functions of Ag_x-Zn_{0.92}Co_{0.08}O hybrid-nanorods with different Ag concentrations, CoO, Co_xO, and Co metal.

To verify our supposition, Fig.2 shows Fourier transform of Ag K-edge EXAFS for $Ag_x-Zn_{0.92}Co_{0.08}O$, the reference Ag foil and Ag_2O powder. It is found that the FTs for the samples show a primary peak at 2.68Å corresponding to Ag-Ag of Ag foil, indicates that Ag atoms mostly exist as metallic Ag. However, a shoulder peak at 2.15Å observed in Ag_x-Zn_{0.92}Co_{0.08}O can't be simply attributed to the nonlinearity of the phase shift function of back-scattering atom Ag, because the gap between shoulder and main peak in Ag_x-Zn_{0.92}Co_{0.08}O is obviously larger than that in Ag foil. Moreover, its site is quite similar with the peak at 2.16 Å in Co K-edge FTs for $Ag_x-Zn_{0.92}Co_{0.08}O$, suggesting that Ag atoms partially exist in interstitial site. Hence, we consider that besides main metallic Ag, numerous interstitial Ag atoms exist in $Ag_x-Zn_{0.92}Co_{0.08}O$.



Fig. 2 The RSFs of the Ag K-edge EXAFS for the Ag_x - $Zn_{0.02}Co_{0.08}O$ and the reference Ag foil.

References

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