Local Structures Around Co Atoms in Wurtzite ZnO Nano-Composites Probed by Fluorescence XAFS

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Abstract: The local structures around Co ions in the $Zn_{1-x}Co_xO$ nano-composites prepared by the sol-gel method have been investigated by fluorescence X-ray absorption fine structure (XAFS) technique. The results indicate that for dilute Co-doped ZnO (x=0.02, 0.05), the Co^{2+} ions are incorporated into the ZnO lattice, and are located at the position of the substitutional Zn^{2+} ions. As the Co content increases to 0.10 or higher, only part of the Co ions enter the lattice of the wurtzite and the others exist in the form of a Co_3O_4 phase whose content increases with the doped Co concentration. In the substitutional $Zn_{0.98}Co_{0.02}O$ sample, the bond length of the first shell $R_{Co\text{-}O}$ and the second shell $R_{Co\text{-}Zn}$ is smaller than the second shell Zn-Zn distance in ZnO by about 0.01~0.02 Å. These results imply that only small local lattice deformation is induced by dilute Co^{2+} substituting into the Zn^{2+} sites.

Keywords: Co-doped ZnO, fluorescence-XAFS.
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INTRODUCTION

Diluted magnetic semiconductors (DMS) have been of much interest and have been studied extensively for the purpose of the use of both charge and spin of electrons in semiconductors [1-2]. Especially, ZnO-based DMS have attracted much attention as ferromagnetic semiconductors with a high Curie temperature above 300K and large magnetization [3]. These materials are expected to be promising candidates for next generation spintronic devices utilizing electronically or optically controlled magnetism. Recently Wu *et al.* claimed that they have obtained a dilute magnetic semiconductor in $Zn_{1-x}Co_xO$ nanorods with a Curie temperature higher than 350k using a simple thermal chemical vapor deposition method [4]. Ramachandran *et al.* also reported that Co-doped ZnO films on sapphire substrates prepared by pulsed-laser deposition have a Curie temperature higher than 300K [5].

Diverse and apparently contradictory results and interpretations about the origin of ferromagnetism for Co-doped ZnO can often be found in the literatures [4-7], and the discrepancies are commonly attributed to the differences in the fabrication conditions and to second phases [8-9]. Although a great number of investigations have been performed on the ferromagnetism of Co-doped ZnO at room temperature as well as related structures, the behavior of the local structure around the Co atoms in ZnO and its dependence on the composition, *x,* of $Zn_{1-x}Co_xO$ is still not yet clearly understood for samples synthesized using the sol-gel method.

In the present work, we present a direct observation of the local structure around Co in $Zn_{1-x}Co_xO$(x=0.01, 0.02, 0.05, 0.10, 0.15, 0.20, 0.25), using Co-*K* edge fluorescence XAFS. The results show that Co enter the wurtzite lattice and substitute for Zn up to x=0.10, and the presence of Co_3O_4 is apparent for samples with higher concentration.

EXPERIMENTAL

Co-doped ZnO nano-composite samples were prepared by a sol-gel method using $Zn(CH_3COO)_2{\cdot}H_2O$ and $Co(CH_3COO)_2{\cdot}H_2O$ as starting precursors, de-ionized water as a solvent and Polyvinyl alcohol(PVA) as a stabilizing agent. After mixing at 80°C for two hours, the sol is formed and dried at 300°C to get the xerogel. The xerogel was heated at 800°C for an hour in O_2 atmosphere.

The X-ray absorption spectra of $Zn_{1-x}Co_xO$ samples at the Co K-edge were measured at the beamline of U7C of the National Synchrotron Radiation Laboratory (NSRL). The NSRL storage ring was operated at 0.8 GeV with maximum current of 300 mA. The x-ray beam is from a three-pole superconducting wiggler with a magnetic field

intensity of 6 Tesla. The XAFS spectra of the $Zn_{1-x}Co_xO$ samples were collected in fluorescence, with fluorescence ionization chamber filled with Ar at room temperature. A Keithley Model 6517 Electrometer was used to collect the electron charge directly. The x-ray absorption spectra of Co_2O_3 and ZnO powders were also measured by transmission model for reference. XAFS data were analyzed by UWXAFS3.0 [10] and USTCXAFS3.0 [11].

RESULTS AND DISCUSSION

The EXAFS functions $k^3\chi$ (k) for Co_3O_4, CoO, wurtzite ZnO and Co-doped ZnO nano-composites with different cobalt concentrations are shown in Fig.1. The oscillatory function of $Zn_{0.98}Co_{0.02}O$ as shown in Fig 1 is very close to that of the wurtzite ZnO powder. The region from k=8 to 12 Å^{-1} for the $Zn_{0.75}Co_{0.25}O$ nano-composite is similar to that of the Co_3O_4 powder. For k<8 Å^{-1}, the oscillatory function is similar to that of the ZnO powder. However, the oscillatory function of the CoO powder is quite different than that of Co-doped ZnO, demonstrating that there is no CoO particle within our nano-composites samples. These results show that the local structure of the Co ions is the same as that of Zn ions in the wurtzite lattice for the dilute Co-doped ZnO with x=0.02. With x increasing to 0.25, some of Co^{2+} ions still occupy the Zn^{2+} sites, and the Co^{3+} ions are in the Co_3O_4 phase.

There are two features labeled as A (k=3.5 Å^{-1}) and B (k=6.0 Å^{-1}), which are characteristic of the wurtzite structure. The intensities of both features gradually decrease with the Co-doping concentration. As the Co concentration increases to 20%, the feature B disappears completely, indicating that the content of Co_3O_4 the phase is enhanced with increasing Co concentration.

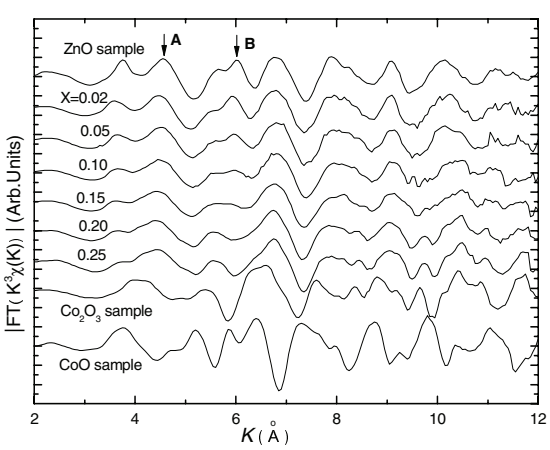

FIGURE 1. The $k^3\chi(k)$ functions of the CoO, Co_3O_4, ZnO powder and Co-doped ZnO composites with different cobalt concentration.

Fig. 2(a) shows the comparison of the radial distribution functions (RDF) of ZnO, $Zn_{1-x}Co_xO$ (x=0.02, 0.25), CoO, and Co_3O_4. The RDF of $Zn_{1-x}Co_xO$ nano-composite samples with different Co doping content are shown in Fig.3.b. There are two strong peaks located at 1.6 and 2.6 Å. The first peak is corresponding to the nearest four Co-O pairs with the bond length around 1.98Å. The position of this peak does not change significantly with increasing Co content because the Co-O bond changes only by 0.09Å when incorporated into the ZnO lattice as compared to the Co_3O_4 phase. The second peak is comes from the second shell of twelve Co-Zn pairs with a bond length around 2.7 Å. This peak moves from 2.8 Å (x≤0.10) to 2.6 Å (x≥0.15). Moreover, for x≥0.15, a peak appears at R= 3.1 Å. The intensity of this peak increases with increasing Co concentration. As seen from the Fig 2 (a), one can easily find that the third strong peak for Co_3O_4 is located nearly at 3.0 Å. Hence, the peak at 3.0 Å for x≥0.15 can be attributed to Co_3O_4. At the same time, the peak (R=4.8 Å) corresponding to the higher shell of Co_3O_4 can be found when x≥0.15. This peak is also strengthened with increasing Co concentration. Seen from Fig. 2(a) and Fig. 2(b), the RDF of $Zn_{0.75}Co_{0.25}O$ is similar to that of Co_3O_4. We, therefore, conclude that for higher Co concentrations (x≥0.15), the Co atoms tend to occupy the Zn sites in the ZnO wurtzite lattice. After the sample was heated at 800°C for an hour in an O_2 atmosphere, some Co ions aggregated and generated Co_3O_4.

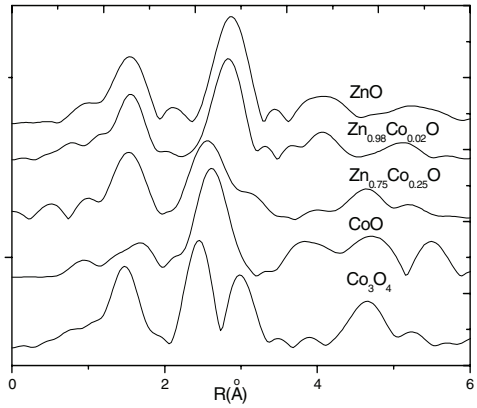

FIGURE 2(a). The RSF curve of the wurtzite ZnO, Co-doped ZnO with x=0.02 and x=0.25, CoO and Co_3O_4 sample.

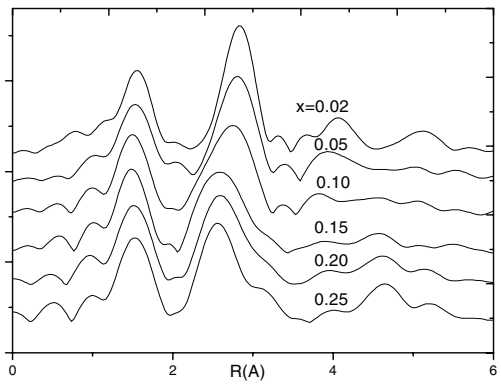

FIGURE 2(b). The RSF curve of the Co-doped ZnO composites with different iron concentration.

Fig. 2(b) shows that the second shell peak of $Zn_{0.90}Co_{0.10}O$ becomes broader for x<0.10. The fitting results for $Zn_{0.90}Co_{0.10}O$ shown in Table 1 reveal that there is a Co-Co bond, with the Co coordination number 4.7. It is clear that the Co ions are not isolated in the ZnO wurtzite lattice. They aggregate in the lattice, and some of them change from the wurtzite to the Co_3O_4 structure. This is why the corresponding peak is broadened. A striking feature is that the $Zn_{0.90}Co_{0.10}O$ is a turning point for the $Zn_{1-x}Co_xO$. For x<0.10, Co ions are all inclined to occupy the Zn sites in the ZnO wurtzite lattice. While for x>0.10, the Co ions have two forms: some Co ions are incorporated into the ZnO lattice, others in the second phase Co_3O_4.

To obtain the structural parameters of the $Zn_{1-x}Co_xO$ nano-composites, a least-squares fit was performed for the data analysis using the USTCXAFS3.0 code. The theoretical amplitude functions and phase shifts were calculated by FEFF8.2 [10]. For x≥0.10, two paths were used in fitting the curve. The Co-Zn bond is used in the model with Co substituting for Zn in the ZnO wurtzite lattice. We used the CoO wurtzite lattice with the structure parameters of ZnO to get the path of the Co-Co bond. S^2_0 was obtained from fitting the curve of Co_3O_4. The curve were performed in the R-range between 1.2 and 2.2Å for the first nearest Co-O shell (R=1.97Å). The range from 2.2 to 3.8 Å is for the two second shells Co-Zn and Co-Co (R=3.21Å). The fitting results are summarized in Table 1.

TABLE 1. Local structure parameters of Co-doped $Zn_{1-x}Co_xO$ (x = 0.02, 0.05, 0.10, 0.15), wurtzite ZnO, CoO and Co_3O_4.

X	*Pair*	*N*	*R*(Å)	σ^2(Å^2)
0.02	Co-O	3.8	1.98	0.0453
	Co-Zn	11.01	3.21	0.0851
0.05	Co-O	4.0	1.97	0.0587
	Co-Zn	12.07	3.21	0.0977
0.10	Co-O	3.71	1.95	0.0647
	Co-Co	4.69	3.10	0.0534
	Co-Zn	9.58	3.21	0.0688
0.15	Co-O	4.7	1.94	0.0806
	Co-Co	4.38	3.09	0.0443
	Co-Zn	3.54	3.22	0.0378
ZnO	Zn-O	4	1.98	-
	Zn-Zn	12	3.21	-
CoO	Co-O	6	2.13	-
	Co-Co	12	3.02	-
Co_3O_4	Co-O	4	1.94	-
	Co-Co	12	3.34	-

Table 1 shows that the bond length of Co-O is also decreasing with increasing x. For x≥0.10, a Co_3O_4 phase exists. The bond length of Co-O in this phase is about 1.94 Å, so the average bond length, R, decreases. The Debye-Waller factor, σ^2, becomes larger with the Co content, indicating that doping with Co ions distorts the local structure of the wurtzite lattice. However, the coordination number N of the first nearest shell is reduced with increasing Co content, which may be caused by the Co_3O_4 phase.

Lee *et al* claimed that the second phase of Co only exists for x≥20 [12] for $Zn_{1-x}Co_xO$ nano-composites. However, our result shows that the σ^2 of Co-Co bond in $Zn_{0.90}Co_{0.10}O$ is larger than that of $Zn_{0.85}Co_{0.15}O$. This indicates that the Co_3O_4 compound possibly exists in $Zn_{0.90}Co_{0.10}O$, and a considerable amount of second phase Co_3O_4 has been formed in $Zn_{0.85}Co_{0.15}O$. The length of the Co-Zn bond is expanded, in accordance with the X-ray diffraction (XRD) result reported by Ueda *et al.* [13] Our results further show that only a small local lattice deformation is induced by dilute Co^{2+} substituting into Zn^{2+} sites. The coordination number and the bond lengths are nearly equal to those of wurtzite ZnO.

CONCLUSIONS

The local structures around Co atoms for Co-doped wurtzite ZnO with different compositions are investigated using XAFS. We found that for samples with low cobalt content (x=0.02 and 0.05), the Co ions are incorporated into the wurtzite lattice, and substitute for the Zn ions. With the cobalt content increasing to x=0.10, only a part of the cobalt atoms are inclined to occupy the Zn sites in the lattice of wurtzite ZnO, and the rest form a Co_3O_4 phase. As the cobalt content reaches x=0.25, Co ions mainly exist in a Co_3O_4 phase. Only a small lattice distortion is induced for dilute Co^{2+} substituting into Zn^{2+} sites.

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