Magnetic Property and Spatial Occupation of Co Dopants in Zn_{0.98}Co_{0.02}O Nanowires

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Received: March 25, 2009; Revised Manuscript Received: June 24, 2009

Single phase Co-doped ZnO dilute magnetic semiconductor nanowire was synthesized by a chemical solution method and characterized by X-ray absorption fine structure (XAFS). The Co *K*-edge XAFS spectroscopy reveals that the doped Co ions are substantially incorporated into the ZnO host lattice. Moreover, the spatial occupation of Co dopants in $Zn_{0.98}Co_{0.02}O$ nanowire is resolved further by the detailed O *K*-edge XANES analysis. We suggest that the Co ions are randomly doped into the ZnO matrix and located at the Zn sites. The magnetization measurement of the Co-doped ZnO nanowire shows the room temperature ferromagnetic characteristic with a relatively larger saturation magnetization. Furthermore, we suggest that the enhanced ferromagnetism can be ascribed to the coeffect of the size effect and the homogeneity of Co dopants for $Zn_{0.98}Co_{0.02}O$ nanowire, which will make it useful in nanometer spintronic devices.

1. Introduction

Dilute magnetic semiconductors (DMSs) are envisioned as promising candidates for future spintronic technologies which would simultaneously utilize the spin and charge of the carriers.^{1,2} Zn_{1-x}Co_xO DMS has been thought to be one of the most important *n*-type DMS and has been extensively studied³ because of the initial theoretical prediction⁴ and experimental observation⁵ of room temperature ferromagnetism (RT-FM). However, both theoretical and experimental studies give numerous contradicting results about its magnetic properties, ranging from spin-glass behavior, paramagnetism to ferromagnetism (FM) with a $T_{\rm C}$ below or above room temperature (RT).^{6,7}

The current research of ZnO-based DMSs mostly focuses on the bulk materials, such as bulk crystals or thin films.^{6,7} However, in the past several years, increasing number of papers reported the RT-FM in the one-dimensional (1D) doped ZnO DMS nanowires.^{8–10} These interests are primarily stimulated by the fact that 1D DMS nanostructures are the potentially ideal functional components to the integration of DMSs toward a three-dimensional (3D) architecture of nanoscale electronic chips because of their superior properties such as low dimensionality and quantum confinement effect, etc.^{11,12} Xu et al.⁸ demonstrated the growth of well-aligned Zn_{1-x}Cr_xO nanorods using an in situ vapor transport method and achieved RT-FM ordering. Cui et al.9 prepared the Mn-doped ZnO nanowires through the method of an electrochemical process and found FM in the as-grown sample at 300 K. Because of the mismatch and rather limited solubility of magnetic impurities in the host semiconductor, the inhomogeneous doping may be a generic property of DMS. Additionally, some suggested that homogeneous Zn1-xCoxO DMSs exhibit a spin-glass behavior, and RT-FM was found in inhomogeneous samples.^{13–15} But, for the applications of a practical spintronics device, the homogeneous DMSs are necessary such as to accomplish the requirement of spin detection and manipulation.¹¹ Furthermore, considerable efforts to prepare the ZnO nanowires through the chemical method have achieved a homogeneous nature.^{16–18} Unfortunately, the argument of the distribution of Co ions in the Zn_{1-x}Co_xO nanostructures is not strong, and the magnetic property in these nanomaterials has been ambiguous until now. There are far fewer reports of the relationship between RT-FM and the size effect for Zn_{1-x}Co_xO nanowire DMS. Conventional methods such as compositional mapping can only give macroscopical results other than the atomic local structure. These intensively influence the judgment on the origin of the RT-FM for Zn_{1-x}Co_xO DMS nanomaterials.

In this work, we used a chemical solution process to synthesize Co-doped ZnO nanowire. The XAFS technique at both Co and O *K* edges was employed to study the spatial distribution of Co dopants in $Zn_{0.98}Co_{0.02}O$ nanowires. The experimental spectra combined with the theoretical calculations provided the experimental evidence for the highly ordered doping of substitutional Co atoms. Importantly, we show that the $Zn_{0.98}Co_{0.02}O$ nanowire exhibits a strong RT-FM characteristic which is due to the size effect and the random substitution.

2. Experimental Section

2.1. Synthesis. The $Zn_{0.98}Co_{0.02}O$ nanowire was synthesized by the thermal decomposition of transition metal acetate in refluxing trioctylamine. In a typical procedure, zinc acetate and the desired amount of cobalt(II) acetate were mixed in a roundbottomed flask with trioctylamine. Subsequently, this mixture was rapidly heated to 310 °C and reacted for 3 h. After the reactions completed, the green precipitates were washed several times with deionized water and ethanol. In this article, the referenced sample $Zn_{0.98}Co_{0.02}O$ thin film was synthesized by the pulsed laser deposition (PLD) method, which is a representative physics technique. The synthesis and the magnetic property have been described in detail in our previous work.^{19,20}

2.2. Characterization. The structural analysis of Co-doped ZnO nanowire was carried out by using X-ray diffraction

10.1021/jp902685k CCC: \$40.75 © XXXX American Chemical Society

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Figure 1. (a) Transmission electron microscopic image of the $Zn_{0.98}Co_{0.02}O$ nanowire. (b) X-ray diffraction pattern of $Zn_{0.98}Co_{0.02}O$ nanowire. All of the peaks noted in the figure match the XRD pattern of pure ZnO.

(XRD). The morphology and microstructure of the sample was investigated by transmission electron microscope (TEM). The magnetization was measured with a superconducting quantum interference device (SQUID) at 300 K under a magnetic field of 5 kOe. The Co K-edge XAFS measurements were measured in a grazing-incidence geometry at the beamline BL13B1 of Photon Factory (PF) of High Energy Accelerator Research Organization (KEK), Japan, and the beamline U7C of the National Synchrotron Radiation Facility (NSRL), China. The storage ring of PF was operated at 2.5 GeV with the maximum current of 450 mA. The electron-beam energy of NSRL was 0.8 GeV, and the maximum stored current was about 250 mA. A double crystal Si (111) monochromator was used. The O K-edge XAFS spectra were measured at beamline U19 of National Synchrotron Radiation Laboratory, China. The data were collected in a mode of sample drain current under a vacuum better than 5×10^{-7} Pa.

3. Results and Discussion

The TEM image (Figure 1a) shows that the $Zn_{0.98}Co_{0.02}O$ nanowire is single-crystalline with the average diameters of 45 \pm 5 nm and lengths ranging from 2 to 6 μ m. Figure 1b shows the θ -2 θ XRD pattern of Co-doped ZnO nanowire. The results indicate that the $Zn_{0.98}Co_{0.02}O$ nanowires show good crystallinity. Like pure ZnO, all of the diffraction peaks correspond to a single



Figure 2. Hysteresis loops for the $Zn_{0.98}Co_{0.02}O$ nanowire measured at 300 K. The inset is a magnified plot near zero field for better clarity. The M - H curve of the $Zn_{0.98}Co_{0.02}O$ thin film is shown as a comparison.



Figure 3. (a) Co *K*-edge EXAFS oscillation functions $k^3\chi(k)$ for the Zn_{0.98}Co_{0.02}O nanowire, Zn_{0.98}Co_{0.02}O thin film (PLD), Co foil, and the Zn *K*-edge function for reference ZnO powder. (b) Their Fourier transforms spectra (solid lines). The dashed lines show the fitting results.

phase with hexagonal wurtzite structure, and no extra diffraction peaks of cobalt metal or oxide impurities were observed within the detection limit.

Figure 2 displays the magnetic-field dependence of magnetization (M - H) at 300 K for the Zn_{0.98}Co_{0.02}O nanowire and thin film. The well-defined hysteresis loop (the insert in Figure 2) with a coercivity of approximately 70 Oe and the saturation magnetization of 0.95 $\mu_{\rm B}$ /Co can be observed, which indicates the obvious ferromagnetic behavior of the Zn_{0.98}Co_{0.02}O nanowire. However, from Figure 2, it can be clearly seen that the measured saturation magnetization $M_{\rm S}$ of 0.95 $\mu_{\rm B}$ /Co is much larger than that (0.16 $\mu_{\rm B}$ /Co) in the PLD-grown Zn_{0.98}Co_{0.02}O thin film and also much larger than that in the bulk samples which are generally reported to be intrinsic paramagnetic in nature in the Co-doped ZnO system.²¹ The underlying physics will be discussed later.

In order to obtain detailed structural information, Co *K*-edge extended-XAFS (EXAFS) $k^3\chi(k)$ function of Zn_{0.98}Co_{0.02}O and their Fourier transforms (FTs) are shown in Figure 3a and b, respectively. The Co and Zn *K*-edge function of PLD-grown Zn_{0.98}Co_{0.02}O thin film, Co foil, and wurtzite ZnO are also shown as references. First, the existence of the metallic Co cluster can be safely excluded since the $k^3\chi(k)$ and FT features of metallic Co are significantly different from those of the Zn_{0.98}Co_{0.02}O



Figure 4. O *K*-edge XANES spectra of the $Zn_{0.98}Co_{0.02}O$ nanowire and thin film, ZnO powder, and the calculated spectra for the model structure: $Co_{Zn} + V_{Zn}$, along with four representative model structures of replacing one, two, three, and four Zn nearest neighbors of the absorbing O atom by Co, denoted as O–Co₁, O–Co₂, O–Co₃, and O–Co₄.

nanowire and thin film. It can be seen from Figure 3a that both the Zn_{0.98}Co_{0.02}O nanowire and thin film exhibit similar oscillation shape, which is also very close to that of the wurtzite ZnO powder. In addition, the FTs of the Zn_{0.98}Co_{0.02}O nanowire and thin film shown in Figure 3b are both similar to that of the pure ZnO, presenting two strong peaks at around 1.6 and 2.8 Å, respectively. We have quantitatively fitted these two peaks assuming the Co substitution for Zn sites in the Zn_{0.98}Co_{0.02}O nanowire. This structure model can give a good fitting quality as shown by the empty circles in Figure 3b. The extracted interatomic distances of Zn_{0.98}Co_{0.02}O nanowire are $R_{Co-O} =$ 1.96 ± 0.01 Å and $R_{Co-Zn} = 3.22 \pm 0.01$ Å. These results confirm that all the Co ions occupy the Zn sites in the ZnO lattice in the Zn_{0.98}Co_{0.02}O nanowire, in agreement with previous reports.^{19,22}

In our previous studies,¹⁹ we proved that Co K-edge EXAFS is not able to distinguish whether the substitutional Co_{Zn} ions are homogeneously distributed or clustered together around oxygen atoms because of the similar atomic numbers between Co and Zn scatters. The information of Co distribution cannot be resolved through the analysis of Co K-edge XAFS. To check the influence of Co distribution on the spectral shape of the O K-edge XANES, we have compared in Figure 4 the O K-edge XANES of the Zn_{0.98}Co_{0.02}O nanowire with the calculated spectra for the model structures: $Co_{Zn}+V_{Zn}$, along with four model structures replacing one, two, three, and four Zn nearest neighbors of the absorbing O atom by Co, denoted as O-Co₁, O-Co₂, O-Co₃, and O-Co₄, respectively. All of these O K-edge XANES spectra were calculated by the FEFF8.4 code. Obviously, the $Zn_{0.98}Co_{0.02}O$ nanowire shows a strong peak A1 at 535 eV which can be assigned to the transition of O 1s electron to the unoccupied O 2p states in the conduction band, followed by the region between 539 and 545 eV which is due to the O 2p states hybridized with Zn and Co 4p states.²³ The spectral shape of the solution-grown Zn_{0.98}Co_{0.02}O nanowire exhibits quite identical features with those of pure ZnO powder and the calculated spectrum for undoped ZnO. However, the

XANES of the $Zn_{0.98}Co_{0.02}O$ nanowire is quite different from that of our PLD-prepared Zn_{0.98}Co_{0.02}O thin film and the calculated spectra for the model structures where a strong preedge peak B (530.6 eV) can be clearly observed. It is known that the pre-edge region of 530-535 eV for ZnO arises from O 2p-Zn 3d hybridized states in the band gap.²³ Because of the d¹⁰ configuration of Zn atom, the O K-edge of pure ZnO does not show any features that are related to the O 2p and Zn 3d hybridized orbital. When Co substitutes Zn in ZnO, the appearance of the strong pre-edge peak B in the Co clustering calculated models can be mainly attributed to the partially occupied Co 3d states and the strong hybridization between Co 3d states and O 2p states. However, this pre-edge B appears only as a shoulder in the spectra of our solution-grown Zn_{0.98}Co_{0.02}O nanowire. This is distinctly different from that of PLD-grown $Zn_{1-x}Co_xO$ thin films in which the prominent existence of Co_{Zn} clusters has been suggested previously.¹⁹ Furthermore, compared with the Zn_{0.98}Co_{0.02}O nanowire, the amplitude of peak A₁ is significantly damped for the $Zn_{0.98}Co_{0.02}O$ thin film. This may be ascribed to the formation of Cozn clusters which will lead to the broadening and dispersion of O 2p states in the ZnO lattice.²⁴ Therefore, the homogeneity and the clustering of Co dopants can be evidently distinguished from these characteristics. From the above results, we consider that in our nanowire the Co atoms are not in the clustering configurations $Co-O-Co_n$ ($n \ge 0$) and do not aggregate to form the Co-rich nanoscale region. This means that, in this solutionprepared nanowire, the Co dopants are likely to distribute homogenously in the host ZnO matrix. Moreover, the calculated spectrum of the O-Co₁ model cannot reproduce the experimental one of the Zn_{0.98}Co_{0.02}O nanowire as well. It is consistent with our previous work²⁵ in which the pre-edge B still remains for the model structure of Mn_{Zn} alone without any native defects. According to our first-principles calculations,²⁴ we suggest that the V_{Zn} along with Mn_{Zn} gives rise to a shoulder peak in the pre-edge region of the O K-edge XANES. Simultaneously, from the comparison of the spectra in Figure 4, the main features of the experimental O K-edge spectra of the Zn_{0.98}Co_{0.02}O nanowire can be reproduced well by the calculated spectrum for the model structure of $Co_{Zn} + V_{Zn}$, confirming the existence of Zn vacancy.

Recently, some authors reported that the ferromagnetism of many DMSs might be associated with spinodal decomposition, in which isostructural dopant-rich nanoscale domains are embedded within a dopant-poor host matrix because of the rather limited solubility of magnetic impurities in semiconductors.^{13,15,26} For example, Kuroda et al.²⁶ have found that the high- $T_{\rm C}$ (300 K) FM in Co-doped Zn_{0.95}Cr_{0.05}Te:I films can be traced to the decomposition of the material into nanoscale Cr-rich (Zn,Cr)Te nanoclusters (11< d <22 nm) embedded coherently within a Crpoor semiconductor lattice through the energy dispersive X-ray spectroscopy. It has been widely accepted that the effect of spinodal decomposition is maximized when the magnetic ions are in their neutral charge state (such as Co²⁺ in ZnO), whereas it is suppressed by the repulsive interaction between charged magnetic ions.^{13,15,26} Different from these reports, in the Zn_{0.98}Co_{0.02}O nanowire, the O K-edge has revealed the existence of V_{Zn}, which can act as a shallow acceptor. Therefore, the charge state of Co ions in our $Zn_{1-x}Co_xO$ nanowire may be deviated from its neutral charge state (+2) due to the presence of these acceptor defects. Consequently, the mutual Coulomb interactions of these charged Co ions will impede the spinodal decomposition and stabilize the growth of a uniform (Zn,Co)O nanowire. Very recently, it has been reported that in the highly doped II-VI semiconductor nanoparticles,²⁷⁻³⁰ the Mn²⁺ and Co²⁺ impurities tend to diffuse to and aggregate in the nearsurface region. For example, Meyerheim et al.²⁸ have found the wurtzite-type CoO nanocrystals coherently embedded within a hexagonal ZnO matrix for the Zn_{0.75}Co_{0.25}O films with high doping content. Li et al.²⁹ and Zhang et al.³⁰ have found that Co dopants in ZnO:Co have a tendency to assemble together forming the Co-related secondary phase at high Co concentration (≥ 0.05) , while isolated Co dopants dominate the distribution for low concentrations (≤ 0.02). For the Zn_{0.98}Co_{0.02}O nanowire under study in this work, the substitution of Co ions at the Zn site are found to occur randomly, consistent with those of low doping cases in the literature. Additionally, in the case of strong clustering of Co ions, peak B can be still clearly seen due to the tendency of out-diffusion of Co_{Zn} ions to the surface, even at the much lower Co concentration of 0.005.19 Therefore, in Zn_{0.98}Co_{0.02}O nanowire prepared by chemical solution, the Co ions are more likely to distribute themselves evenly in the ZnO matrix than to form the Co-rich (Zn,Co)O clusters.

With regard to the origin of the ferromagnetism, the Co dopants are substantially located at the Zn sites, and thus, the observed RT-FM is intrinsic and cannot be due to the Co cluster secondary phase. Besides the extrinsic origin of RTFM arising from FM secondary phases, several mechanisms have been proposed for intrinsic magnetic ordering, including carriermediated RKKY-type or related Zener mechanism,² and a bound magnetic polarons (BMP) model³ in terms of structural defects. For the former case, the high concentration of dopants and itinerant carriers are required to induce ferromagnetism. However, without codoping with other ions or further treatment such as annealing in the vacuum and Zn vapor environment, the carrier concentration in Co-doped ZnO is usually low.^{31,32} Moreover, on the basis of theoretical computation, Khanal et al.³³ have proposed that the effects of quantum confinement strongly limit maximum achievable carrier concentration for the ZnO nanowire, and the limit for ZnO with a diameter of about 40 nm is approximately 10¹⁸ cm⁻³, which is far below the threshold (10²⁰ cm⁻³) to mediate ferromagnetic ordering. Therefore, the carrier-mediated scenario cannot be simply applied here. A possible explanation for the intrinsic magnetism can be found involving a magnetic coupling interaction mechanism based on the BMP model.^{3,7} Within the BMP model, bound carriers associated with the structural defects occupy a volume γ^3 , where γ is the radius of the orbit, and are responsible for coupling remote Co²⁺ ions within this volume. Ferromagnetism is achieved when the BMPs start to overlap to form a continuous chain throughout the material, thus percolating FM in the DMS. In the Zn_{0.98}Co_{0.02}O nanowire, the Zn vacancies can be served as the acceptor holes as discussed earlier which are located throughout the lattice at arbitrary distances with respect to Co sites. For the case of a random distribution of Co dopants, we can estimate the average Co-Co interatomic distance to be about $3.61(2x)^{-1/3}$ or 10.6 Å at the concentration x = 0.02³⁴ According to refs 3 and 7, the orbital radius of polarons can be obtained from the relationship $\gamma = \varepsilon_r(m/m^*)a_0$, where ε_r is the dielectric constant, *m* is the electron mass, *m*^{*} is the effective mass of the donor electrons, and a_0 is the Bohr radius (0.53 Å). For highly insulating Co:ZnO, $m/m^* = 3.57$, and ε_r is in the range of 10–37. Then we can obtain that the polaron radius is in the range of 18.9–70 Å, which covers that (10.6 Å) of the average Co-Co interatomic distance. Therefore, it is quite possible that the Co-doped level of 0.02 for our homogeneous Zn_{0.98}Co_{0.02}O nanowire is sufficient to realize the ferromagnetic coupling and thus lead to the observed RT-FM.

From the description of magnetization, we have shown that the $Zn_{0.98}Co_{0.02}O$ nanowire exhibits the RT-FM property with a relatively large saturation magnetization. However, a number of studies have shown the intrinsically paramagnetic properties for the $Zn_{1-x}Co_xO$ bulk modality with a perfect single-crystal structure.^{21,35} Given the highly insulating nature and the characteristic of nanowire for the sample, we naturally relate the strong FM to the effect of size confinement. Recently, Peng et al.³⁶ have reported that the size effect can be used to enhance hole-induced magnetization in the ZnO nanowire. Using the first-principles methods, they have shown that the size effect can reduce critical hole concentration for stabilizing the magnetization and that the critical holes (acceptor doping) concentration needed to induce ferromagnetism is less than 1/8 of that needed in bulk materials. This means that the Zn vacancy will play an important role in our system and more Co dopants will be inside the BMPs radius easily due to the size effect, thus increasing the probability of the ferromagnetic coupling between two magnetic impurities within the same orbital. On the basis of BMP theory, accordingly, we can attribute the strong FM of the Zn_{0.98}Co_{0.02}O nanowire to the 1D size effect relevantly. Finally, we discuss the reason for the larger saturation magnetization of the $Zn_{0.98}Co_{0.02}O$ nanowire than that of the $Zn_{0.98}Co_{0.02}O$ thin film. This is reasonable because XANES spectroscopy indicates the random substitution of Co at the Zn site. Indirect superexchange interaction of these dispersive Co ions is expected to lead to ferromagnetism, whereas pairs or groups of Co ions separated by intervening oxygen atoms usually align antiferromagnetically because of short-range superexchange interaction, 2,3,37 and the strong antiferromagnetic coupling has been reported in $Zn_{1-x}Co_xO$ thin films.³⁸ This antiferromagnetic coupling will decrease the magnetic moment for the Zn_{0.98}Co_{0.02}O thin film. In fact, the measured magnetization of our sample is almost comparable with that of samples prepared by similar methods in refs 39 and 40, which have also reported the homogeneity of the Co dopants in ZnO nanostructures. Additionally, in ref 39, Yuhas et al. also observed a drop in the overall magnetic moment per Co dopant with increasing levels of Co concentration in the ZnCoO nanowire and ascribed this to the increased number of antiferromagnetic pairs of cations. Thus, the Zn_{0.98}Co_{0.02}O nanowire shows a relatively higher $M_{\rm S}$ compared with that of the thin film as expected. This nature makes the Zn_{0.98}Co_{0.02}O nanowire suitable for DMSs applications.

4. Conclusions

In summary, the Co-doped ZnO nanowire was synthesized through the method of chemical solution and possesses ferromagnetism at room temperature. We have employed the XAFS technique at both Co and O *K* edges to study Co distribution in the Zn_{0.98}Co_{0.02}O nanowire. The EXAFS analysis of the Co *K*-edge spectra revealed that the Co ions are incorporated into the Zn sites of the ZnO. The detailed O *K*-edge XANES analysis indicated that in the Zn_{0.98}Co_{0.02}O nanowire, the substitutional Co_{Zn} ions are likely to be distributed uniformly in the ZnO lattice. We propose that ferromagnetic ordering is induced by the Zn vacancy-derived impurity band and enhanced by the 1D size effect and the uniform nature in the Zn_{0.98}Co_{0.02}O nanowire. We expect that this DMS nanostructure with RT-FM will be rather significant in spintronic research and applications.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant Nos. 10605024,

10635060, 20621061, and 10725522). The authors would like to thank NSRL and Photon Factory for the synchrotron radiation beam time.

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(34) For the homogenous $Zn_{1-x}Co_xO$ matrix, the number of cobalt atoms in one unit cell is 2x, i.e., the amount of unit cell required to include one Co atom is 1/2x. Hence, the average Co–Co interatomic distance is about $3.61(2x)^{-1/3}$, where the 3.61 is the equivalent lattice constant.

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JP902685K