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Research paper

Morphological evolution of solution-grown cobalt-doped ZnO nanostructures and their properties

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ABSTRACT

It is demonstrated that the morphology of Co-doped ZnO nanostructures can be easily altered by controlling Co-doping concentration. A facile low-temperature solution method was employed for the nanosynthesis. The morphology of the nanostructures changed from nanorods to nanoparticles, and to needle-like structures as the molar ratio of Co^{2+} ions increased. No noticeable changes in structural and optical properties were caused by the low concentration of Co-doping, while a magnetic transition was observed. At the very low Co concentrations below 0.3 at%, the nanostructures showed diamagnetism, whereas a paramagnetic behavior was observed at a concentration of 2.5 at%.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted big interest as a potential matter to allow for the simultaneous control of electrical charges and magnetic spins [1–3]. Their application areas include data storage, spin electronics, and magneto-optoelectronics [4–6]. To synthesize DMSs, magnetic dopants like iron (Fe) [7], cobalt (Co) [8], nickel (Ni) [9], and manganese (Mn) [10] have been doped into non-magnetic semiconductor matrices. One of major goals with the DMS-related researches was to achieve the ferromagnetic behavior at room temperature. For that purpose, relatively large amount of magnetic dopants that have a Curie temperature (T_C) much higher than room temperature were necessary [11]. To this aim, Co that has a high T_C of 1388 K and large magnetic moment of 1.75 Bohr magneton/atom has been intensively investigated as a dopant [12].

In the matrix side, oxide-based semiconductors such as ZnO, TiO_2, and SnO_2 have been preferred because they make ferromagnetism sustain to room temperature [11,13–15]. A typical matrix material is ZnO. ZnO is a wide band-gap semiconductor (E_g = 3.37 eV) with many unique features, including large excitonic binding energy (60 meV), high optical transmittance, nontoxicity, and piezoelectricity [16–18]. Magnetic, electrical, and optical properties of Co-doped ZnO have been closely studied both in bulk and at nanoscale [19,20]. In particular, nanostructured Co-doped ZnO has been paid more attention since its large surface-to-volume ratio could provide the DMSs with additional functionalities. A variety of Co-doped ZnO nanostructures such as nanoparticles, nanorods, and nanowires have been synthesized and examined by the employment of differing methods [21–23]. From the previous reports, it may be stated that the properties of Co-doped ZnO nanostructures significantly depend on the morphology [23,24]. For the further study, however, it would be desirable to ensure an experimental method that can afford to produce various nanostructures with little change in synthesis conditions.

In this work, it is demonstrated that the morphology and doping concentration of Co-doped ZnO nanostructures can be simultaneously controlled in situ, using a facile low-temperature solution method. The standard condition for the synthesis of ZnO nanorods is kept constant for all experiments, while only the concentration of Co precursor added to the mixture solution is varied. To the best of our knowledge, this is the first report on the morphological evolution by the use of a single synthesis method. Furthermore, the Co-doping concentration is relatively low in this study, which is another dissimilarity to the conventional DMSs.

2. Materials and methods

2.1. Materials

Two precursors, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) were purchased from Sigma-Aldrich. Ethyl alcohol (C_2H_5OH), ethylenediamine ($C_2H_4(NH_2)_2$, EDA), and sodium hydroxide (NaOH) beads were

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purchased from Daejung Chem. All chemicals were used with no further treatment and deionized (DI) water was used as solvent.

2.2. Synthesis of Co-doped ZnO nanostructures

Co-doped ZnO nanostructures were synthesized by a low-temperature solution method. At first, a 0.297 g of $Zn(NO_3)_2{\cdot}6H_2O$ and varying amounts of $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 1 ml of DI water and stirred at 50 °C to prepare a salt solution containing both Zn^{2+} and Co^{2+} ions. Here, the amount of Co precursor was adjusted in the range of 1.46–29.1 mg to modulate the molar ratio of Zn^{2+} to Co^{2+} from 200:1 to 10:1. In the meantime, a 1.2 g of NaOH was dissolved in 1 ml of DI water to create NaOH solution. The NaOH solution was slowly added to the salt solution for 5 min under stirring, and then 4 ml of EDA was introduced into the mixture solution. At the next step, 20 ml of ethyl alcohol was put into the solution, and the reaction proceeded at 50 °C for 5 days. Also, pure ZnO nanorods were independently synthesized for comparison at the same conditions except no use of Co precursor. Finally, nanostructure powders were collected from the reaction solution through repeated centrifugation and washing. Detailed synthesis conditions and sample names are summarized in Table 1.

2.3. Characterization

The morphologies and dimensions of Co-doped ZnO nanostructures were analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7500F). Additional SEM analyses were performed to confirm the morphologies and estimate Co-doping concentration, using another FE-SEM (Hitachi SU-70) quipped with an energy-dispersive X-ray spectroscope (EDX). For the closer examination of the nanostructures, a transmission electron microscope (TEM, Tecnai G2 F30) was utilized. The crystal structures and qualities of Co-doped ZnO nanostructures were characterized by X-ray diffraction (XRD, Rigaku D/MAX 2200) with Cu K_α radiation. The optical property of the samples was examined using UV–Vis spectrophotometry (UV–Vis Cary 50 Bio). The magnetic measurements were conducted in the temperature range of 4.2 – 300 K, using superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM, Quantum Design MPMS 3).

3. Results and discussion

3.1. Morphologies and compositions

Fig. 1 shows SEM images of Co-doped ZnO nanostructures along with pure ZnO nanorods. As can be seen in Fig. 1(a), well-developed hexagonal ZnO nanorods are synthesized when no dopants are used. The morphology begins to change once cobalt nitrate is introduced into the solution as a doping chemical. Most interestingly, the morphology of the Co-doped ZnO nanostructures gradually evolves depending on the molar ratio of Zn^{2+} to Co^{2+} ions. When low concentrations of Co precursor are employed (Zn^{2+}:Co^{2+} = 200:1–100:1), resulting nanostructures resemble the morphology of pure ZnO nanorods, but both ends of individual nanorods are somewhat tapered (Fig. 1(b) and (c)). The average diameter and length of CZ2 samples are estimated at 440 nm and 5.1 μm, which are slightly thinner and longer than those of pure ZnO nanorods (500 nm and 3.1 μm). Provided that the cobalt nitrate concentration is raised, Co-doped ZnO nanostructures show the mixed morphology of short nanorods and nanoparticles (Zn^{2+}:Co^{2+} = 70:1, Fig. 1(d)) and become agglomerated nanoparticles at a higher concentration (Zn^{2+}:Co^{2+} = 20:1, Fig. 1(e)). Increasing the concentration further (Zn^{2+}:Co^{2+} = 10:1), the morphology turns to needle-like structures (Fig. 1(f)).

To verify the differing morphologies, TEM analyses were also conducted on the selected samples. Fig. 2 presents TEM images of CZ2 and CZ3 samples. It is clearly seen from Fig. 2(a) that CZ2 has nanorod morphology with tapered ends. On the other hand, CZ3 consists of a lot of nanoparticles and nanorods that have small aspect ratios (Fig. 2(b)), though image clarity is not good enough. These observations are in good agreement with those from SEM analyses. The experimental conditions for syntheses of all the nanostructures were the same except the concentration of Co precursor employed, signifying the important role of cobalt nitrate.

One possible way to alter the morphology is to hinder the one-dimensional (1D) growth of ZnO by the formation of pure Co or Co-rich phases. To diagnose this possibility, Co element mapping and concentration analyses were made using both TEM-EDX and SEM-EDX. For all the measured samples, neither Co agglomerates nor Co-rich phases were found. Fig. 3 exhibits SEM-EDX spectra of CZ2 and CZ4 samples. From the two spectra, Co concentrations in CZ2 and CZ4 are calculated to be 0.23 and 2.5 at%, respectively. Considering the accuracy of SEM-EDX is about 1 at%, these values represent that little Co atoms are actually incorporated into the ZnO matrix. Similar results were obtained from TEM-EDX analyses too. The very low Co-doping concentrations fall behind the Zn^{2+} to Co^{2+} molar ratios in the original mixture solutions. It is stated from these results that very low concentrations of Co atoms are distributed throughout ZnO nanostructures without forming Co-rich phases.

At the standard condition adopted in this study, 1D growth of ZnO is preferred since ZnO nuclei are homogeneously formed through the following reactions and EDA is preferentially coated onto the high-energy prismatic planes of ZnO nanocrystals.

$$Zn^{2+} + 4OH^- \leftrightarrow Zn(OH)_4{}^{2-} \quad (1)$$

$$Zn(OH)_4{}^{2-} \leftrightarrow ZnO + H_2O + 2OH^- \quad (2)$$

When cobalt nitrate is added to the zinc nitrate solution, similar reactions to the above are supposed to occur, leading to the formation of CoO and the substitution of Co cations into Zn^{2+} sites. However, it is inferred from the low Co-doping concentrations that the formation process of $Co(OH)_4^{2-}$ is not as efficient as in Eq. (1). Thus, at the low Zn^{2+} to Co^{2+} molar ratios (CZ1 and CZ2), the effect of Co precursor on the morphology is minimal. If the molar ratio is increased, a certain concentration of Co atoms are doped into

Table 1
Synthesis conditions of pure ZnO nanorods and Co-doped ZnO nanostructures.

Sample	Zn^{2+}:Co^{2+} molar ratio	$Co(NO_3)_2$ (mg)	$Zn(NO_3)_2$ (g)	NaOH (g)	EtOH (mL)	EDA (mL)	Temperature (°C)	Reaction time (days)
ZnO	NA	0	0.297	1.2	20	4	50	5
CZ1	200:1	1.455	0.297	1.2	20	4	50	5
CZ2	100:1	2.910	0.297	1.2	20	4	50	5
CZ3	70:1	4.150	0.297	1.2	20	4	50	5
CZ4	20:1	14.551	0.297	1.2	20	4	50	5
CZ5	10:1	29.103	0.297	1.2	20	4	50	5