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Ferromagnetic mechanism of (Co, Cu)-codoped ZnO films with different Co concentrations investigated by X-ray photoelectron spectroscopy

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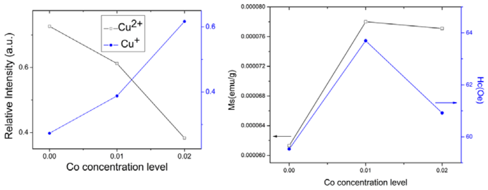
HIGHLIGHTS

- Cobalt/copper-codoped ZnO films show Cu valence from +2 to +1 as the Co concentration level exceeds 1% by XPS.
- The optical bandgap of $Zn_{0.95-x}Co_xCu_{0.05}O$ films shows a blue-shift from 3.01 to 3.13 eV with increasing Co concentration.
- The ferromagnetism of $Zn_{0.95-x}Co_xCu_{0.05}O$ films is correlated with the valence state of the Cu ions and oxygen vacancies.

GRAPHICAL ABSTRACT



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ABSTRACT

Cobalt/copper-codoped ZnO nanoparticles, synthesized with different Co concentrations by a sol–gel method using ethanol as solvent, were studied via XPS. Hexagonal wurtzite structure was found in all samples, with no evidence of any secondary phase. The average crystallite size of the samples was around 20–30 nm, altered significantly with increasing Co concentration. Copper ions and Cobalt ions are indeed substituted into the ZnO lattice at the Zn^{2+} site, as shown by XRD and XPS. Further studies showed dramatic changes of Cu valence from +2 to +1 as the Co concentration level exceeds 1%, accompanied by a blue-shift of the optical bandgap from 3.01 to 3.13 eV. Ferromagnetism of the Co-doped $Zn_{0.95}Cu_{0.05}O$ thin films was observed and found to be tunable – a phenomenon associated with the valence state of the Cu ions and the existence of some defects like oxygen vacancies in the films.

1. Introduction

Zinc oxide (ZnO) is a wide-bandgap semiconductor with wide bandgap energy of 3.37 eV in the near-UV spectral region and large free-exciton binding energy of 60 meV [1,2]. Owing to its amenability to doping, ZnO can be doped with a wide variety of ions to meet the demands of several application fields [3]. ZnO-based diluted magnetic semiconductors (DMSs) possess many attractive characteristics such as low cost and environment-friendliness [4]. The key question about the DMS materials is this: Is the Curie temperature compatible with junction temperatures [5]? Among the DMS materials reported so far, transition metal (TM) doped ZnO has emerged as an attractive example with a Curie temperature at or above room temperature, following the prediction of Dietl's group [6]. Among the TM-doped ZnO DMSs, the magnetism of Cu-doped ZnO is still controversial. In fact, the intrinsic property of the material has been shown in a Cu-based

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system, because the metallic copper and all possible Cu-based secondary phases are nonferromagnetic [7]. The Cu-doped ZnO system was at first rejected as a DMS system showing RTFM, in the initial theoretical studies [8], but later, Park's [9] theoretical prediction and Buchholz's [10] experimental report for ZnCuO showed room-temperature ferromagnetic properties. Thereafter, Hou et al. [5] reported that itinerant electrons play an important role in ferromagnetism in Cu-doped ZnO films prepared by direct current reactive magnetron sputtering. Based on theoretical calculations, Sluiter et al. [11] argued that Co has the best potential as a substitute for Zn in doping ZnO to produce a DMS when the Co is combined with a hole dopant or an electron dopant. While Song [12] demonstrated that room-temperature ferromagnetism of Co:ZnO films depends strongly on the substrate, Co^{2+} replaces Zn^{2+} in all Co:ZnO films. Chakraborti [13] reported systematic studies of the epitaxial growth and properties of (Co, Cu)-codoped ZnO thin films using pulsed-laser deposition. Also, Lin [14] synthesized ZnCoO that exhibited obvious ferromagnetic ordering above room temperature if prepared with a particular amount of Cu doping by a standard solid-state reaction method. Recently, we reported that (Co, Cu)-doped ZnO shows a red-shift compared to the case when either Co or Cu atoms alone are used to dope ZnO [4,15].

Some groups have investigated the luminescence characteristics of ZnO thin films based on XPS analysis [16,17], analyzing the relationship between UV emission and the stoichiometry of the film. And in our previous letter [18], we reported a significant change of Cu valence and varied chemical bonding of O1s with increasing Co doping in ZnCuO films, supported by XPS results. However, no one has explained in detail how the defects in (Co, Cu)-codoped ZnO thin films so dramatically affect the chemical bonds therein, which in turn alter the films' ferromagnetic and optical properties. This area of inquiry is of great interest because the ferromagnetic and optical properties of ZnO are known to be closely related to a sample's defects [11,13]. So in the present work we have further examined the ferromagnetic properties, using XPS measurements. Deeper understanding of such issues will help explore the possibility of practical applications of ZnO DMSs.

We report here the synthesis of (Co, Cu)-codoped ZnO films with a Cu concentration of 5% and a low Co doping level ($0 \leq [Co] \leq 2\%$) by a sol–gel method on glass substrate. The synthesized thin films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), UV–visible transmission spectrometer and vibrating sample magnetometry (VSM).

2. Experiment

The fabrication of the (Co, Cu)-codoped ZnO films were prepared from zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), cobalt acetate ($Co(CH_3COO)_2 \cdot H_2O$), and copper acetate ($Cu(CH_3COO)_2 \cdot H_2O$) as sources for Zn, Co, and Cu. These compounds were mixed and dissolved into ethanol with a little ethanolamine (C_2H_7NO) as stabilizer. The solution was stirred at 60 °C for 2 h to yield a stable and homogeneous precursor solution, until the sol pH value reached 8 with glacial acetic acid or ammonia. The coating solution was aged for 72 h at room temperature and then deposited on clean glass substrate by a spin coater (KW-4A). The as-deposited films were subsequently put into a furnace at 120 °C for 10 min after spin coating at 3000 rpm for 45 s. To obtain the desired thickness, the spinning-preheating procedure was repeated 10 times. Finally, the films were annealed at 450 °C for 2.5 h in a muffle furnace.

The surface morphology was checked by using a JSM-6360LV scanning electron microscope (SEM). The film thickness was measured to be about 400 nm by an XP-Plus Stylus Profilometer. X-ray powder diffraction with Cu K_α radiation (Rigaku D/max-2500) was used to characterize the microstructure of the (Co, Cu)-codoped ZnO films with a step size of 0.02°. The chemical bonding state and composition were analyzed by X-ray photoelectron spectroscopy (XPS) using the XSAM800 photoelectron spectroscope and a carbon source for calibration ($C_{1s}=285$ eV). Optical transmittance was recorded with a double beam UV–visible spectrophotometer made by Shimadzu in the wavelength range 200–800 nm. To check the magnetic property, the magnetic measurements were carried out using a vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Microstructures

Fig. 1 displays typical XRD patterns of $Zn_{0.95-x}Co_xCu_{0.05}O$ ($x=0$, 0.01, 0.20) thin films. The same peaks are observed for all samples whether Co is introduced or not, which indicates a hexagonal wurtzite structure with no Co- or Cu-related phase within its detection sensitivity, evidencing the incorporation of both Co and Cu into Zn sites. The films show a weak preferred orientation along the *c*-axis perpendicular to the glass substrate. Note that the diffraction intensity of the three peaks is almost unchanged, but further increasing the Co concentration causes a significant increase in the diffraction intensity, indicating that introducing Co into Cu-doped ZnO at a concentration of 2% achieves the best crystal quality for the samples. To check the effect of Co doping on

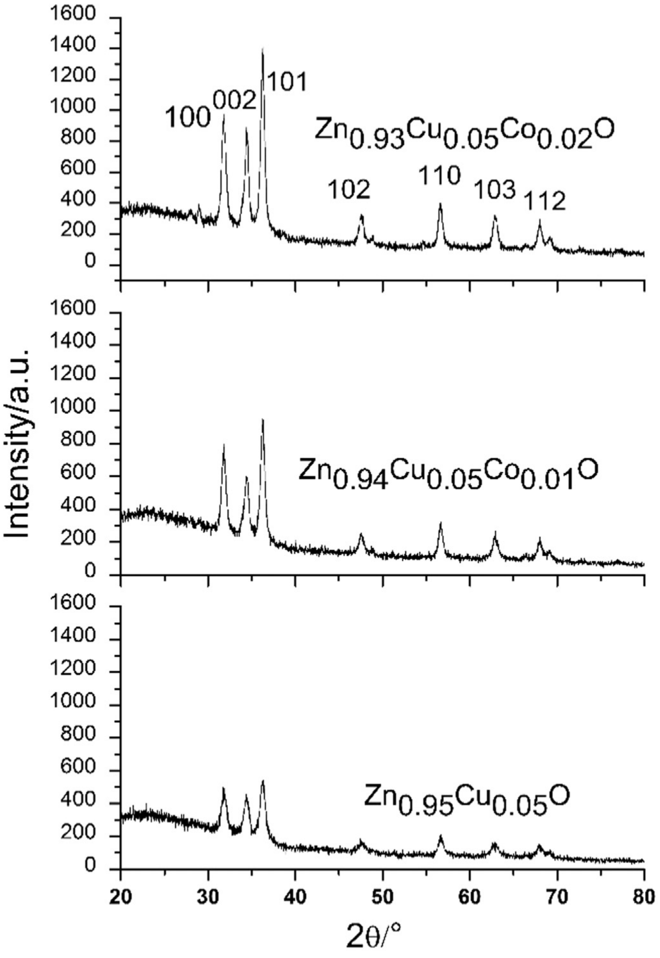

Fig. 1. XRD spectra of $Zn_{0.95-x}Co_xCu_{0.05}O$ films. ($x=0$, 0.01, 0.02).