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Fabrication and properties of Li-doped ZnCoO diluted magnetic semiconductor thin films

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ABSTRACT

Li-doped ZnCoO (ZnCoO:Li) diluted magnetic semiconductor thin films were prepared on SiO_2 substrates by pulsed laser deposition. In ZnCoO:Li films, Co^{2+} substituted Zn^{2+} and Li occupied the interstitial sites behaving as donors. The ZnCoO:Li films are of high electron concentration in the 10^{20} cm^{-3} order and acceptable crystal quality with a hexagonal wurtzite structure. No cluster, precipitate, or second phase was found from the X-ray diffraction pattern and Co *k*-edge X-ray absorption near-edge structure measurements. The *sp*–*d* exchange interactions between the band electrons and the localized *d* electrons of Co ions substituting Zn ions were observed. The magnetization of ZnCoO:Li film is 0.61 μB/Co, higher than that of the ZnCoO film (0.49 μB/Co). The enhanced defect density and electron concentration due to the introduced Li donors may answer for the improvement of ferromagnetism at room temperature.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted much attention because of their potential use in the spintronics field [1,2]. The main challenge in DMS materials is to obtain intrinsic ferromagnetism with Curie temperature above room temperature (RT). Dietl et al. [3] have theoretically predicted that ZnO-based DMSs would be able to realize RT ferromagnetism. For the Co-doped ZnO

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(ZnCoO) system, the RT ferromagnetism is a controversial issue and has been explained from the point of view of either microstructural details [4] or dopant defect [5]. Sato et al. [6,7] have shown that the *n*-type doping could realize RT ferromagnetism in ZnCoO. Whereas, Spaldin [8] and Jayakumar et al. [9] argued that the hole doping could enhance the ferromagnetism in ZnCoO. It seems that, regardless of the opinion, an impurity is necessary to improve the ferromagnetism in ZnCoO.

In this work, we introduced Li into ZnCoO to prepare DMS films. The behavior of Li in ZnO has been studied intensively. In previous study, Li atoms always had a larger possibility to form Li_{Zn} (Li substituting for Zn as an acceptor) than Li_i (Li occupying interstitial site as a donor), since it always decreases electron concentration of *n*-type ZnO and leads to either semi-insulating samples or *p*-type conduction in an oxygen-rich environment [10]. However, Li can also act as a shallow donor when it occupies an interstitial site, which may enhance the *n*-type conduction in some cases [11]. Besides, due to the formation of Li_2O and strongly bound Li–H complexes [12], the behaviors of Li in ZnO are still too complex to understand clearly. What is more, up to date and to the best of our knowledge, the behavior of Li in ZnCoO films is rarely reported. Thus, in this work we fabricated the Li-doped ZnCoO (ZnCoO:Li) DMS films and studied their properties in detail. Our motivation is to make clear the behavior of Li in ZnCoO films based on the structural, electrical, optical, and ferromagnetic properties.

2. Experiment

ZnCoO:Li thin films were deposited on quartz substrates by pulsed laser deposition (PLD). The targets were high-purity $ZnO–Co_2O_3–Li_2CO_3$ ceramic disks with the Li content of 0.1 at.% and Co content of 5 at.%. A KrF excimer laser (Compex102, 248 nm, 25 ns) was used as the ablation source. The chamber was evacuated to a base pressure of 4×10^{-4} Pa and then high-purity O_2 (99.999%) was introduced into it as the ambient gas with the working pressure of 0.02 Pa. The substrate temperatures were varied from 350 to 500 °C. All the films were grown for 30 min with the thicknesses of about 500 nm.

The film structure and crystalline quality were characterized by a Bede D1 X-ray diffraction (XRD) system with a Cu *Ka* source (λ = 0.15406 nm). The electrical properties were investigated by using a four-point probe van der Pauw configuration (HL5500PC) at RT. The field-emission scanning electron microscope (FE-SEM) and high-resolution transmission electron microscope (HR-TEM) were employed for morphological and microcosmic structures studies. Energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) were used to study the element contains. The transmission through film was investigated in the wavelength range from 300 to 800 nm by a Varian Cary-300 spectrophotometer. To determine the valence state and local geometry of the Co dopant in the host ZnO lattice, Co *k*-edge X-ray absorption near-edge structure (XANES) measurements were carried out. Magnetization studies were carried out using a superconducting quantum interference device (SQUID) magnetometer. Additionally, induced-coupled-plasma (ICP) atomic emission spectra were used to determine the Co contents in the samples after measuring the magnetic properties.

3. Results and discussion

The microscopic dopant contents in ZnCoO:Li films were analyzed by EDX. The results revealed that the Co contents in films are all around 4.5 at.%, regardless of the growth temperature. Fig. 1a shows the a typical EDX spectra of the ZnCoO:Li film grown at 400 °C. EDX data of Co taken at different locations throughout the specimens proved that its distribution was homogenous. Unfortunately, the Li content in films cannot be determined by EDX due to its limitation.

In order to further confirm the existence of Li dopant in ZnCoO:Li films, XPS was done. Fig. 1b shows the Li 1*s* core level spectra of the ZnCoO:Li film. The spectra consist of two components by the Gaussian deconvolution. The binding energy peak at 52.4 eV is related to Li interstitials (Li_i) and the peak at 55.6 eV to Li_{Zn}–O bonds [10]. The Li 1*s* spectra of ZnCoO:Li films are dominated by the 52.4 eV peak, which is very different from those reported of *p*-type ZnO:Li films [10]. The XPS results reveal that most Li atoms in ZnCoO:Li films occupy interstitial sites acting as donors. In this regard, the ZnCoO:Li films should be of *n*-type conductivity.