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Effect of In and N dopants on the structural and magnetic properties of ZnO:Mn thin films

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ABSTRACT

In this paper, indium (In) and nitrogen (N) doped ZnO:Mn thin films were fabricated and their structural and magnetic properties were investigated. X-ray diffraction and X-ray photoelectron spectroscopy measurements show that the samples possess typical wurtzite structure and have no other impurity phase. Magnetic measurements reveal that both Mn mono-doped and Mn–In codoped ZnO films show paramagnetic behavior, while room temperature ferromagnetism is achieved in weak *p*-type ZnO:Mn films by codoping with N. First-principles calculations further indicate that N codoping can change the ground state of ZnO:Mn system from antiferromagnetic to ferromagnetic while the Mn–In codoped ZnO is favored antiferromagnetic in energy. Therefore, N codoping is expected to be a promising technique to realize ferromagnetic ZnO:Mn semiconductors with high Curie temperature.

1. Introduction

In recent years, diluted magnetic semiconductors (DMSs), which involve the charge and spin degrees of freedom of electrons in a single substance, have attracted much attention due to their potential applications in spintronics [1]. By doping with magnetic ions, ferromagnetism has been

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realized in III–V semiconductors, but the highest reported Curie temperature (T_C) is only 200 K in Mn doped GaAs [2,3]. The main obstacle in DMS is the realization of room temperature (RT) ferromagnetism. Since Dietl et al. theoretically predicted that RT ferromagnetism might exist in wide-band-gap semiconductors [4], transition metals (TMs, e.g. Mn, Co, Fe, Ni, etc.) doped ZnO semiconductors have been studied extensively and in particular, to the Mn-doped and Co-doped ZnO system [5–9]. However, the reported experimental results have been inconsistent and sometimes controversial. Some groups have reported FM but with different T_C in *p*-type and even heavily *n*-type ZnO:Mn systems [8–10], whereas others have only observed paramagnetic or antiferromagnetic (AFM) behaviors [11]. Meanwhile, it is even surprising that RT ferromagnetism has been observed in pristine ZnO nanoparticles and thin films, structure defects such as oxygen or zinc vacancies have been considered as the origin of the diverse magnetic behaviors [12,13]. Thus the origin of RT FM is still a controversial issue and more research is needed for better understanding.

Based on first-principles calculations [14–17], it is predicted that doping with Mn atoms does not lead to a ferromagnetic (FM) ground state in ZnO and suggested the necessity of codoping, the presence of additional carrier plays an important role in stabilizing and/or enhancing the FM coupling by the codoping ions in ZnO:Mn^{2+}, which has been experimentally confirmed by recent works. However, considering the FM was been observed not only in Mn-doped ZnO by codoping *p*-type dopants (Na, N and P) [18–21], but also in highly *n*-type ZnO:Mn by codoping group III elements (Al, Ga, and In) [22,23], the circumstances under which ZnO:Mn^{2+} can be ferromagnetism is still debatable. In the present work, In and N dopants have been introduced into the ZnO:Mn^{2+} films. By combining the experiments and first-principles calculations, we systematically investigate the structural and magnetic properties of ZnO:Mn + In and ZnO:Mn + N systems and demonstrate that N codoping is expected to be a promising technique to realize ferromagnetic ZnO:Mn semiconductors with high T_C.

2. Experiments

ZnO:Mn thin films with thickness of 250 nm were deposited on unheated quartz substrates by RF magnetron sputtering. The target for sputtering was prepared using a solid state reaction method. ZnO (99.99%) and MnO (99.99%) powders mixed according to the nominal atomic ratios were mixed thoroughly and sintered at 1000 °C for 10 h in air. In this experiment, the Mn doping level was controlled at about 4 at.%. The ZnO:Mn + In films were deposited using the ZnO:Mn target with addition of 1.5 wt.% In_2O_3 (99.99%), while the N codoping was fulfilled by N^+-implantation (70 keV, doe of 1×10^{16} cm^{-2}) at 300 K. To activate the implanted ions and recover the crystallinity, the N^+-implanted samples were annealed at 600 °C for 60 min under a flowing N_2 ambient. The electrical properties of the films were obtained by van der Pauw Hall method using a Hall analyzer at RT. The crystal structure and surface morphology of the obtained films were characterized by X-ray diffractometer (XRD) with a Cu Kα radiation ($\lambda = 0.15406$ nm) and field-emission scanning electron microscopy (FE-SEM). Chemical bonding states and compositions of the films were analyzed by X-ray photoelectron spectroscopy (XPS) with Mg Kα X-ray source ($h\nu = 1253.6$ eV). The magnetic properties were measured by using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL). The magnetic field was applied parallel to the film plane.

Table 1
Room temperature electrical properties of the studied samples. The column at the far right lists the energy differences ΔE for the ZnO:Mn, ZnO:Mn + In and ZnO:Mn + N systems. Negative values of ΔE indicate stability of the ferromagnetism.

Sample	Carrier concentration (cm^{-3})	Hall mobility ($cm^2/V\,s$)	Resistivity (Ω cm)	Carrier type	$\Delta E = E_{FM} - E_{AFM}$ (meV)
ZnO:Mn	2.19×10^{18}	7.40	2.65×10^{-1}	*n*	74
ZnO:Mn + In	1.98×10^{20}	7.46	4.22×10^{-3}	*n*	48
ZnO:Mn + N	2.98×10^{16}	1.27	1.64×10^{2}	*p*	−372