



Post-annealing effects on structural and magnetic properties of Mn–N codoped ZnO thin films

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ABSTRACT

The sputtered ZnO:Mn thin films were implanted with nitrogen ions (N^+) and subsequently annealed at different temperatures up to 800 °C in N_2 atmosphere. The structural and magnetic properties of the samples were systematically investigated. Both x-ray diffraction and Raman analyses reveal that all the films are of the wurtzite structure of ZnO with no distinct evidence of secondary phases. X-ray photoelectron spectroscopy studies indicate that both Mn^{2+} and N^{3-} ions were incorporated into ZnO lattice successfully. While the films without nitrogen ions show paramagnetic behavior, ferromagnetism with clear hysteresis at 300 K is observed in Mn–N codoped ZnO films. Most importantly, we also found that the magnetic behavior of the codoped ZnO is very sensitive to the annealing temperature due to its effect on the activation of nitrogen ions. The strongest ferromagnetism is obtained in the films with the highest amount of nitrogen ions acceptors. Our results support the predication that the ferromagnetic ZnO: Mn^{2+} should be more stable of a hole-rich environment by theory.

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1. Introduction

Recently, there has been an intense researching for ferromagnetic ordering in diluted magnetic semiconductors (DMSs) focusing on possible spin-transport properties, which has many potentially interesting device applications such as spin-valve transistors, spin light-emitting diodes, non-volatile memory, logic devices and ultra-fast optical switches [1]. The main challenge in practical applications of the DMS materials is the attainment of Curie temperatures (T_C) around or preferably above room temperature (RT) to be compatible with junction temperatures. After

the theoretical prediction of RT ferromagnetism (FM) in Mn-doped ZnO by Dietl et al. [2], ZnO doped with magnetic transition metal (TM, e.g. Mn, Co, Fe, Ni, etc) ions has been intensively studied [3–5]. However, experimental results on Mn-doped ZnO DMS are quite controversial. FM above RT has been reported for both *n*-type and *p*-type Mn-doped ZnO thin films [6–9]. Thus the circumstance under which Mn-doped ZnO can be ferromagnetic is still debatable. Most recently, several theoretical approaches have concluded that Mn mono-doping does not lead to a FM ground state in ZnO suggesting the necessity of codoping, the presence of additional carriers plays an important role in stabilizing and enhancing the FM by codoping ions with Mn-doped ZnO [10–13]. In our previous study, we have found that RTFM can be achieved in ZnO:Mn films by codoping with nitrogen (N) [14]. But it is well known that

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the N element is widely regarded as the most promising candidate for the *p*-type doping of ZnO and post-annealing has strong effect on its chemical state and local structure, which would meanwhile affect the magnetic properties of Mn–N codoped ZnO films. Thus in this work, we systematically investigated the post-annealing effects on structural and magnetic properties of Mn–N codoped ZnO thin films. The results show that the magnetic behavior of the codoped ZnO samples is sensitive to the annealing temperature.

2. Experimental

The Zn_{0.96}Mn_{0.04}O target for sputtering was prepared using a solid state reaction method. ZnO (99.99%) and MnO (99.99%) powders were mixed thoroughly according to the nominal atomic ratios and then sintered at 1000 °C for 10 h in air. The ZnO:Mn thin films were deposited on unheated quartz substrate by RF magnetron sputtering. The Mn concentration of the ZnO:Mn films was determined to be 3.56% with a relative error of $\pm 10\%$ by using the energy dispersive x-ray spectroscopy. The thickness of the films was about 500 nm measured by a profiler meter. In order to obtain an almost homogeneous nitrogen profile in depth, four N⁺ ion implantations with energy 10 keV (of $2 \times 10^{15} \text{ cm}^{-2}$), 30 keV (of $5 \times 10^{15} \text{ cm}^{-2}$), 70 keV (of $9 \times 10^{15} \text{ cm}^{-2}$), and 150 keV (of $2.6 \times 10^{16} \text{ cm}^{-2}$) into the ZnO:Mn sample with a resulting box-like nitrogen distribution in the film were carried out at RT. The calculated profile (SRIM [15]) is depicted in Fig. 1. Then the samples were annealed at different temperatures up to 800 °C for 60 min under a flowing N₂ ambient to activate the implanted ions and recover the crystallinity. After optimizing the annealing condition, it was found that the *n*-type as-implanted ZnO:Mn–N films could convert to *p*-type conduction with a hole concentration of 10^{16} – 10^{17} cm^{-3} after annealing around 500 °C. However, the films are *n*-type again or showing semi-insulating characters with an uncertain conduction type with further increase in the annealing temperature. In this paper, we choose four representing samples: (a) sample A: the sputtered ZnO: Mn film, (b) sample B: the as-implanted ZnO:Mn–N film, (c) sample C: the ZnO:Mn–N film annealed at 500 °C; (d) sample D: the ZnO:Mn–N film annealed at 700 °C. Their RT electrical properties are listed in Table 1.

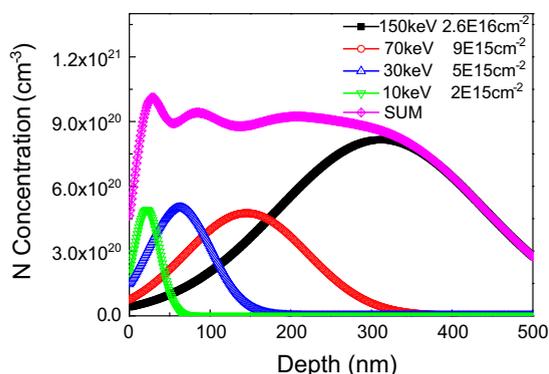


Fig. 1. N concentration profiles simulated with the SRIM software (Ref. [15]) for the as-implanted sample.

The electrical properties of the films were obtained by the van der Pauw Hall method using a Hall analyzer. The crystal structure of the films was identified with an x-ray diffractometer (XRD) using Cu K α radiation. Raman scattering measurements were performed in the backscattering geometry using 514.5 nm line of Ar⁺ laser as an excitation source. Chemical bonding states and compositions of the films were analyzed by x-ray photoelectron spectroscopy (XPS) with Mg K α as x-ray source ($h\nu = 1253.6 \text{ eV}$). Prior to measurement, the surface layer of the samples was cleaned by Ar⁺ ion bombardment for 2 min to avoid the effects of surface contamination. The magnetic properties were measured by using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL).

3. Results and discussion

Fig. 2(a) presents the XRD patterns of samples A–D. For all of the films, only one diffraction peak around 34.21° can be observed, which indicates that the samples are wurtzite structure with *c*-axis preferred orientation. No extra diffraction peaks attributed to Mn; N-related secondary phases or impurities are detected within the sensitivity of the XRD measurement, even for the samples after thermal treatment, implying that the doped Mn and N ions are of ZnO lattice. N⁺ ions-implantation induces severe microscopic structural disorder and lattice strain in ZnO: Mn films, as shown in Fig. 2(b), which causes the full width at half-maximum (FWHM) of the ZnO (002) peak to broaden markedly. After thermal annealing, as manifested by the XRD pattern remains unchanged except for a reduction in line-width, which means that the crystal quality of ZnO:Mn–N films has been improved significantly. Furthermore, we also find that N⁺ ion-implantation and post-annealing induce a change in lattice constant *c* for the codoped samples. By using the Bragg's formula, we calculate the lattice constant *c* of samples A–D and their values are also shown in Fig. 2(b).

Raman spectra collected from samples are shown in Fig. 3. In our measurement range of 200 – 1000 cm^{-1} , for all of the samples, we observed two intrinsic vibrational peaks at 437 and 575 cm^{-1} , which are corresponding to the high frequency branch of E₂ mode [E₂ (high)] and the A₁ longitudinal optical mode [A₁ (LO)] of ZnO, respectively [16]. The E₂ (high) mode is the characteristic of the wurtzite ZnO, while the A₁ (LO) mode is commonly related to the defects in the films. Besides the intrinsic Raman modes of ZnO, there also exists two additional modes (AMs), labeled as AM1 and AM2 [AM1 at $\sim 275 \text{ cm}^{-1}$

Table 1
RT electrical properties of samples A, B, C, and D, where n/p denotes an uncertain conduction type.

Samples	Carrier Concentration (cm ⁻³)	Hall mobility (cm ² V ⁻¹ s ⁻¹)	Resistance ($\Omega \text{ cm}$)	Carrier type
A	2.05×10^{18}	13.76	0.22	n
B	5.98×10^{17}	2.56	9.87	n
C	1.72×10^{17}	0.73	69.65	p
D	2.33×10^{14}	2.25	3471	n/p

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