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Full Length Research Paper

Room Temperature Ferromagnetism of Ni –doped ZnO Thin Films

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ABSTRACT

Ni-doped ZnO thin films (Ni concentration up to 10 mol%) were generated on Si (100) substrates by a sol-gel technique. The films showed wurtzite structure and no other phase was found. The chemical state of Ni was found to be bivalent by X-ray photoelectron spectroscopy. The results of magnetic measurements at room temperature indicated that the films were ferromagnetic, and magnetic moment decreased with rise of Ni concentration. The magnetization of Ni (10 mol%)-doped ZnO film annealed in nitrogen was lower than that annealed in argon, suggesting that the density of defects had an effect on ferromagnetism.

Keywords: Semiconductors, Thin films, Chemical synthesis, Electronic states.

INTRODUCTION

Zinc oxide (ZnO) which is a versatile semiconductor material, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions and it is a wurtzite-type semiconductor with band gap energy of 3.37 eV and very large excitation binding energy (60 meV) at room temperature. In view of the potential applications of spins and charges combination in carriers for what is now called “spintronics” devices [1], much attention has been devoted to diluted magnetic semiconductors (DMS). Among the transition-metal (TM) doped III-V and II-VI semiconductors, TM doped ZnO is the most common, likely to be a result of the prediction made by Dietl et al. [2]. The magnetic properties of TM-doped ZnO and the related mechanism have been widely studied both theoretically and experimentally [3,4]. There are many works on Mn- or Co-doping but few on Ni-doping, plausibly a result of the large driving force for NiO and ZnO segregation [5]. Despite much effort, a consensus on magnetic properties and origin of ferromagnetism has not been reached. Wakano et al. [6] reported the detection of ferromagnetism in Ni-doped ZnO thin films at 2 K. Recently, ferromagnetism has been found in Ni-doped ZnO nanorods, films, nanoparticles, and nanowires at room temperature [7]. Nonetheless, Yin et al. [8] found only paramagnetic behavior in Ni-doped ZnO, while Huang et al. [9] observed ferromagnetism below 2 mol% and paramagnetism above 5 mol% Ni concentration in Ni-doped ZnO nanoparticles. To elucidate the Ni-doped ZnO system

further, we prepared ZnO films with various levels of Ni doping (2, 5, 8 and 10 mol%). The films were annealed in nitrogen. For investigation of the effect of defect density, a Ni (10 mol%)-doped ZnO film was annealed in argon. The structure and magnetic properties of the films were examined and the mechanism of ferromagnetism was discussed.

EXPERIMENT

The Ni-doped ZnO thin films were generated on Si (100) substrates using a sol-gel technique followed by spin-coating at room temperature. The Si substrates were thoroughly cleaned with ethanol and acetone prior to deposition. First, $x\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $(1-x)\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (where $x = 0.02, 0.05, 0.08, 0.10$, giving Ni-doped ZnO films with Ni concentrations 2, 5, 8 and 10 mol%, respectively) were dissolved in ethylene glycol dimethylether ($\text{C}_2\text{H}_8\text{O}_2$). Then ethanalamine ($\text{C}_2\text{H}_7\text{NO}$) was added slowly with stirring at 70°C within a period of 1 h for the generation of a transparent and uniform solution. Deposition was carried out in air. The substrate was secured on a sample holder and was rotated at a speed of 4000 r/min for 40 s for spin coating. The coating process was repeated 5 times. After each spinning, the film was heated in a furnace at 100°C for 1 min for solvent evaporation and annealed in nitrogen at 500°C for 5 min for organic residue removal. Additionally, one sample with the Ni content of 10 mol% was annealed in argon atmosphere for comparison with the one annealed in nitrogen.

The crystal structure of films was characterized by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. The morphology of films was examined by atomic force microscopy (AFM). The valence states of surface elements were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS peaks were calibrated against the C1s peak of carbon contaminant at 284.6 eV. Magnetic measurements were performed using a quantum design superconducting quantum interference device (SQUID).

RESULTS AND DISCUSSION

According to the XRD results and within the detection of XRD, there was no phase other than that of wurtzite observed in the Ni-doped ZnO samples.

The XRD pattern of Ni (10 mol%)-doped ZnO film annealed in nitrogen as an example (Figure 1 (a)), all the peaks belong to the wurtzite phase of ZnO. In other words, the Ni atoms are well dispersed in the ZnO lattice.

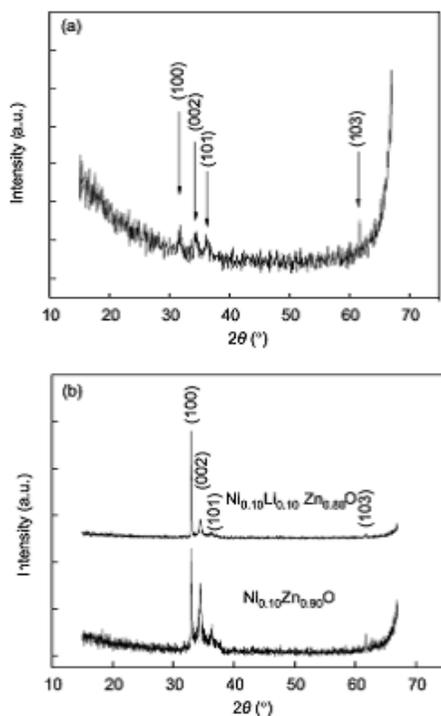


Figure 1 (a) XRD spectrum of $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.10$) thin film annealed in nitrogen at 500°C ; (b) XRD spectra of $\text{Zn}_{0.90}\text{Ni}_{0.10}\text{O}$ (bottom) and

$\text{Zn}_{0.80}\text{Ni}_{0.10}\text{Li}_{0.10}\text{O}$ (top) films annealed in argon at 600°C .

Figure 2 shows the AFM image of the film. One can see that the surface is smooth and roughness is limited to 4 nm. The images of the other films show similar characteristics.

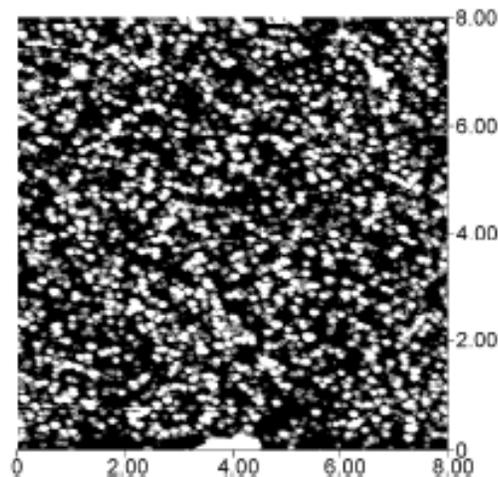


Figure 2 AFM image of $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.10$) thin film annealed in nitrogen.

The $\text{Ni}2p_{3/2}$, $\text{Zn}2p_{3/2}$ and ZnLMM spectra of the Ni (10 mol%)-doped ZnO film are shown in Figure 3. The $\text{Ni}2p_{3/2}$ peak is at ~ 853.12 eV binding energy. The $\text{Ni}2p_{3/2}$ binding energies of Ni⁰ (metallic), Ni²⁺ (NiO), and Ni³⁺ (Ni₂O₃) are 852.70, 853.50 and 857.30 eV, respectively [10]. We consider that the nickel of Ni (10 mol%)-doped ZnO is 2+ in valence. From the $\text{Zn}2p_{3/2}$ and ZnLMM spectra, the zinc is also in a valence state of 2+. Therefore, it is likely that there is replacement of Zn^{2+} by Ni^{2+} in the ZnO lattice.

Magnetic properties were investigated at room temperature. As shown in Figure 4, the M-H curves exhibit hysteresis loops, indicating ferromagnetism. The saturation moments per Ni²⁺ are approximately 0.39, 0.32, 0.26, 0.21 μB for Ni concentrations of 2, 5, 8 and 10 mol%, respectively, showing a larger magnetic moment at a lower nickel concentration, in consistent with the results of Liu *et al.* [11]. Due to compensation effect of oxygen vacancies, carrier density decreases with increasing Ni concentration. As a result, ferromagnetism decreases with rise of Ni concentration. In addition, antiferromagnetic interaction among Ni ions increases with increase of Ni concentration, a consequence of shortened

distance between Ni ions in the lattice. Hence, ferromagnetism weakening is expected when there is a rise of Ni concentration. We found that a Ni (10 mol%)-doped ZnO film annealed in argon was ferromagnetic and showed a slightly higher magnetization than that annealed in nitrogen (Figure 5). Due to the stability of nitrogen, the concentration of substituted nitrogen must be very small, thus the effect on magnetic properties is not evident. Since it is easy to conduct Li doping and just like nitrogen, lithium can act as an acceptor, we prepared $\text{Ni}_{0.10}\text{Zn}_{0.90}\text{O}$ and $\text{Ni}_{0.10}\text{Li}_{0.10}\text{Zn}_{0.80}\text{O}$ films in argon to confirm the influence of holes. The samples were annealed at 600°C for 5 min for better crystallinity. The XRD spectra of the two samples are shown in Figure 1 (b).

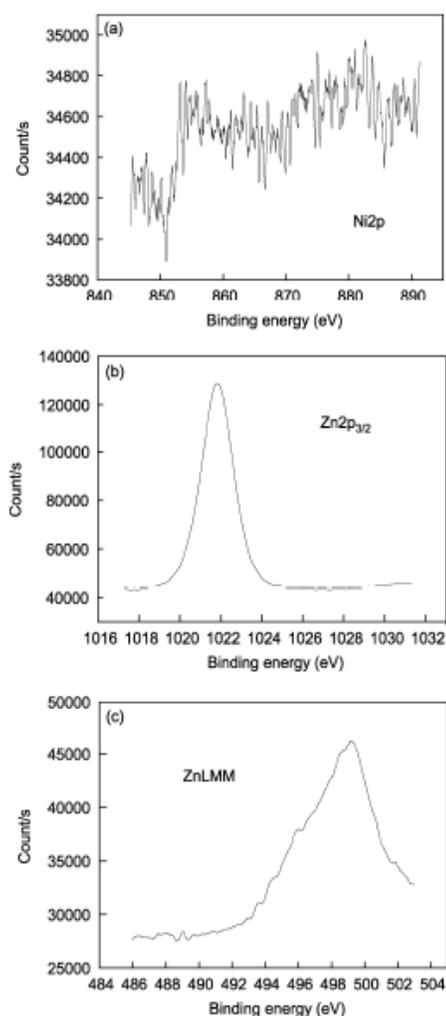


Figure 3 XPS spectra of Ni-doped (10 mol%) ZnO annealed in nitrogen.

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It can be seen that the samples annealed at a higher temperature have wurtzite structure. The M-H curves of both samples shown in Figure 6 exhibit hysteresis loops, indicating ferromagnetism. Additionally, the saturated magnetization of $\text{Ni}_{0.10}\text{Li}_{0.10}\text{Zn}_{0.80}\text{O}$ is much smaller than that of $\text{Ni}_{0.10}\text{Zn}_{0.90}\text{O}$. The ferromagnetism of Ni-doped ZnO could arise from either dopants or impurities. The possible impurities are metallic Ni and its oxide, such as NiO. Metallic Ni should not be a candidate because the films were generated in air and the presence of NiO was unlikely. NiO is antiferromagnetic with a Néel temperature of 520 K [12]. It has been reported that nanocrystalline NiO shows weak ferromagnetic behavior at low temperature. Therefore, despite that NiO impurity could be present but undetected in XRD analysis, the room temperature ferromagnetism in the Ni-doped ZnO films should not be ascribed to NiO. We consider that the trend of “larger magnetic moment at lower nickel concentration” is good enough to confirm that the origin of ferromagnetism is not Ni-related.

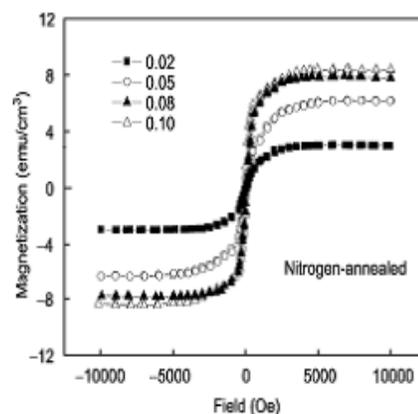


Figure 4 M-H curves of $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ ($x=0.02, 0.05, 0.08, 0.10$)

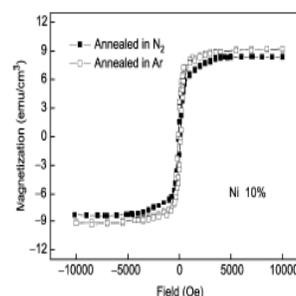


Figure 5 M-H curves of $\text{Zn}_{0.90}\text{Ni}_{0.10}\text{O}$

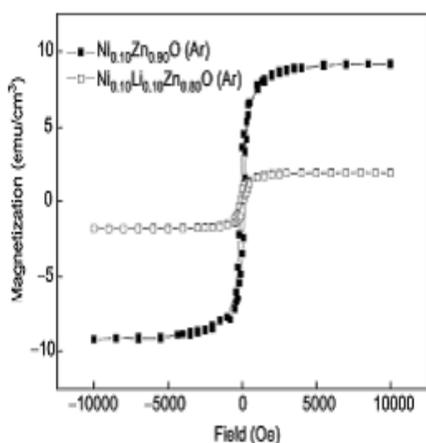


Figure 6 M-H curves of $\text{Zn}_{0.90}\text{Ni}_{0.10}$ and $\text{Zn}_{0.80}\text{Ni}_{0.10}\text{Li}_{0.10}\text{O}$ thin films annealed in argon at 600°C .

According to the Zener model, magnetic ordering of DMS is enhanced when there is a rise of the density of charge carriers. Recently, Hou *et al.* [13, 14] investigated ferromagnetism of ZnO-based DMS; they demonstrated that a carrier-mediated mechanism (especially the electron-mediated one) could appropriately explain the ferromagnetism of TM-doped ZnO DMS. They also showed that ferromagnetism could be significantly affected by growth condition and defects of DMS, and that the films treated in argon or vacuum had a large number of defects [15]. In case of annealing TM doped ZnO DMS in nitrogen, partial substitution of lattice oxygen and occupation of oxygen vacancies by nitrogen atoms occur, resulting in decline in electron as well as defect density. Therefore, the ferromagnetism of Ni doped ZnO could be a result of interaction between delocalized charge carriers (electrons) and localized *d* spins of Ni ions. This deduction is further supported by the weaker magnetic moment of Li-doped $\text{Ni}_{0.10}\text{Zn}_{0.90}\text{O}$ due to the holes induced by Li doping.

CONCLUSION

In summary, single-phase Ni co-doped ZnO films of different Ni concentrations were prepared by spin-coating. All the films were ferromagnetic at room temperature, and magnetic moment decreased with rise of Ni concentration. It was observed that the film annealed in nitrogen was lower in magnetic moment than the one annealed in argon, and the (Ni, Li)-

codoped sample exhibited weaker magnetic moment than Ni-doped ZnO (10 mol%). We propose that defect density has a significant effect on ferromagnetism, and that the ferromagnetic nature of Ni-doped ZnO films follows a carrier-mediated mechanism.

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