Ferromagnetic and Optical Properties of Partially Cu-Doped ZnO Films

Fan-Yong Ran[a], Masaki Tanemura[a], Yasuhiko Hayashi[a], Norihiro Ide[a], Masao Imaoka[a], Tun-Seng Herng[b], and Shu-Ping Lau[b]

[a] Department of Environmental Technology, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan 466-8555
[b] School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Republic of Singapore

Reprint requests to F.-Y. R.; E-mail: fyran80@gmail.com

Z. Naturforsch. **64a,** 765 – 768 (2009); received October 7, 2008 / revised February 18, 2009

Wurtzite structure ZnO films (3×3 mm^2) with a partial-area Cu doping were successfully prepared using a micro-area Ar^+-ion beam (~ 380 μm in diameter) and a simultaneous Cu supply at room temperature. A Cu_2O phase was formed in the ZnO films by Cu doping. The partially Cu-doped ZnO films exhibited room-temperature ferromagnetism (RTFM) with a saturation magnetization of 1.6×10^{-5} emu and a coercive field of 40 Oe. Since Zn, Cu, and their compounds are not ferromagnetic, the observed RTFM is attributed to the intrinsic property of Cu-doped ZnO films. As confirmed by the low temperature photoluminescence (PL) spectra, no serious optical damage was recognized in the region without Ar^+-ion irradiation. Thus, it was believed that the micro-area Ar^+-ion irradiation with a simultaneous Cu supply was promising to integrate the magnetic and optical properties of ZnO-based materials.

Key words: Cu-Doped ZnO Films; Ar^+-Ion Beam; Room-Temperature Ferromagnetism.
PACS numbers: 75.50.Pp, 79.20.Rf, 68.55.Ln, 78.55.Et

1. Introduction

ZnO-based diluted magnetic semiconductors (DMSs) have attracted extensive interests in recent years due to the prediction of a possible Curie temperature higher than room temperature, paving the way for spintronic applications [1, 2]. The room-temperature ferromagnetism (RTFM) has been reported mainly for ZnO films doped with Mn and Co [3 – 5]. However, these dopants are ferromagnetic materials and can easily form magnetic impurities, such as Mn_3O_4 and Co. Thus, a problem has always arisen on the origin of the ZnO-DMSs, whether the FM was intrinsic or from impurity phase [6]. Recently, RTFM in Cu-doped ZnO was demonstrated both theoretically and experimentally [7, 8]. Cu-doped ZnO was thought to be an unambiguous DMS, since Zn, Cu, and their compounds are not ferromagnetics [9].

ZnO is also an attractive optical semiconductor for visible and ultraviolet optoelectronic devices due to the wide band gap energy of 3.4 eV and large exciton binding energy of 60 meV (compared with GaN, ~ 25 meV) [10]. ZnO-based DMSs have been mainly prepared by substituting transition metals for Zn during ZnO film deposition, and the deposition has been carried out on the whole substrate surface without patterning. Although the ferromagnetism can be realized, the substitution would also induce defects and hence destroy the optical properties of the entire films [10, 11]. In the present work, in order to integrate both the optical and ferromagnetic properties, partial-area doping of Cu into a ZnO film was tackled.

ZnO films have conventionally been prepared by pulsed-laser deposition [8], magnetron sputtering [12], and molecular beam epitaxy [3]. In this work, the partial-area doped ZnO films were attempted by a post-treatment using a micro-area Ar^+-ion irradiation with a simultaneous Cu supply. The structural and magnetic properties of the films were characterized in detail. In addition, low temperature photoluminescence was measured to insight into the optical property of pure and doped ZnO films.

2. Experimental Details

Our experimental system comprises a differentially pumped micro-beam ion gun (JEOL; MIED) and an arc-plasma gun (ULVAC; APG-1000) serving as a dop-

ing source. The details of the system have been described elsewhere [13]. The ion gun and the arc-plasma gun are located on the same X, Z-plane, with their incidence angles at 55°, from the normal to the surface (Fig. 1). 3 keV Ar^+ ions focused into a microbeam of 380 μm in diameter were used for the ion irradiation. The simultaneous Cu supply to the whole sample surface was carried out with a frequency of 0.5 Hz.

A sample employed was a pure ZnO film, 550 nm thick, deposited on 3×3 mm^2 c-sapphire by helicon magnetron sputtering. Prior to the doping process, the sample was pre-irradiated by the Ar^+-ion beam for 5 min. Then, Ar^+-ion irradiation with a simultaneous Cu supply to the sample was carried out for 5 min to incorporate Cu into Zn sites. The chamber was pumped down to $\sim 10^{-7}$ Pa, and the pressure was maintained at 10^{-6} Pa during the experiments. The ion irradiation was carried out at room temperature (RT).

Due to the small diameter of the Ar^+-ion beam ($\sim$ 380 μm), only a small region of the ZnO film ($\sim$ 380 μm in diameter) was doped with Cu. This small region is referred to as R1. The other region in which Cu was deposited without Ar^+-ion irradiation is referred to as R2.

Phase and crystal structure of the whole sample (including both R1 and R2 regions) were characterized by X-ray diffraction (XRD; RINT2000, Rigaku). Surface morphology was observed by atomic force microscope (AFM, JSPM- 5200TM, JEOL). The magnetic property was investigated by an alternating gradient magnetometer with a maximum field of 10 kOe. Photoluminescence (PL) spectra were measured at 77 K using a SPEX 1702/04 spectrometer excited by a 325 nm He-Cd laser.

3. Results and Discussion

The XRD patterns of pure and irradiated ZnO films are shown in Figure 2. Both of the films mainly showed (002) peak of ZnO at $\sim$ 34.48° and (006) peak of sapphire substrate at $\sim$ 41.8°, implying that the films possessed a hexagonal wurtzite structure with a preferred c-axis orientation, and the co-irradiation did not affect the preferred orientation. After irradiation, a weak Cu_2O (111) peak appeared at about 36.2°, suggesting that a Cu_2O phase was formed in the ZnO film.

The effect of Cu-doping on the surface morphology was investigated by AFM with a carbon nanofiber cantilever [14]. Three- and two-dimensional AFM images of the pure ZnO as-deposited by magnetron sputtering

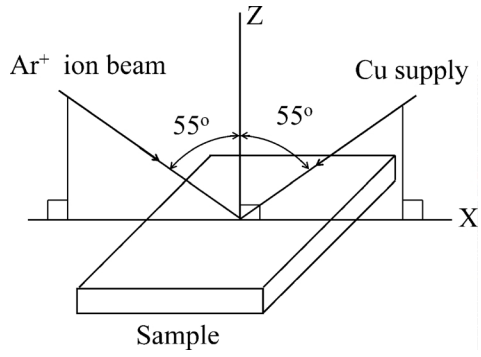

Fig. 1. Geometrical configuration of sample, ion beam, and Cu supply.

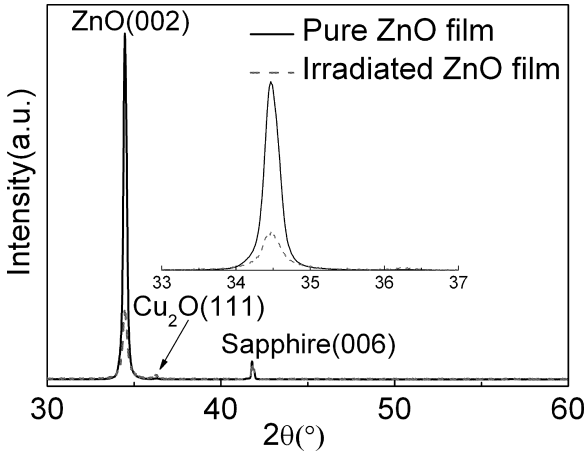

Fig. 2. XRD patterns of pure and irradiated ZnO films.

and R1 region of irradiated ZnO films are shown in Figure 3. The directions of incidence Ar^+ ions and a Cu supply are shown in Figure 3b. Individual grains were clearly observable in this figure. The grains were almost uniform in size distribution for respective films. The pure ZnO film was characterized by spherical grains with an average diameter of $\sim$ 200 nm, whereas the doped regions R1 was featured by the rod-like grains with cross-sectional diameter of $\sim$ 200 nm. The root mean square (RMS) roughness of pure ZnO was $\sim$ 27.4 nm. After irradiation, the RMS roughness was reduced to $\sim$ 10.5 nm.

Figure 4 shows the magnetization versus applied field (M-H) curves measured at 300 K for doped ZnO films, exhibiting the magnetic hysterisis. The saturation magnetization (M_s), coercive field (H_c) and remnant magnetization (M_r) was about 1.6×10^{-5} emu, 40 Oe and 2.0×10^{-6} emu, respectively. Zn, Cu, and their related compounds are not ferromagnetic materi-

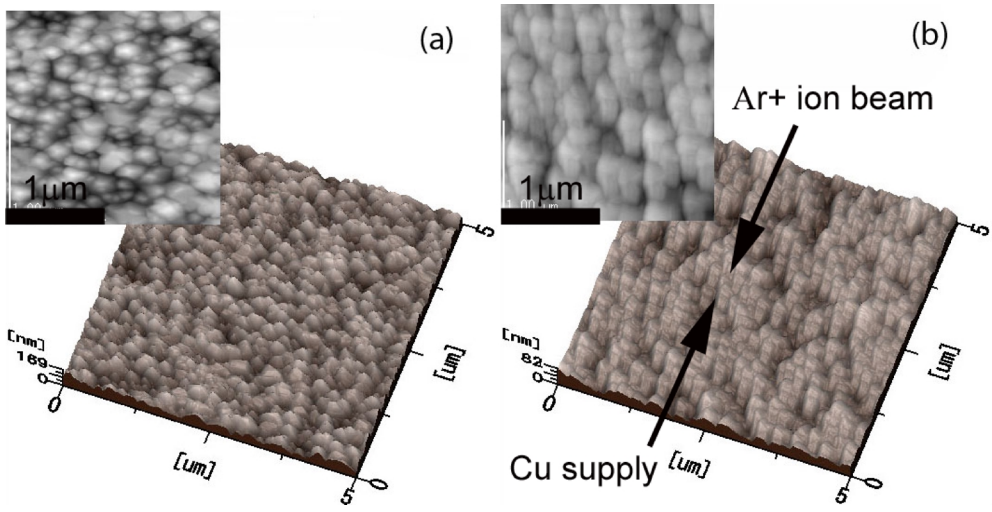

Fig. 3. Three- and two-dimensional AFM images of (a) pure ZnO film, and (b) R1 region of irradiated ZnO film.

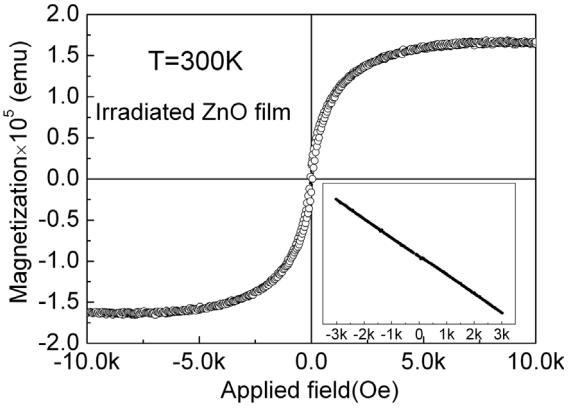

Fig. 4. Magnetization hysteresis curves of doped ZnO films measured at RT.

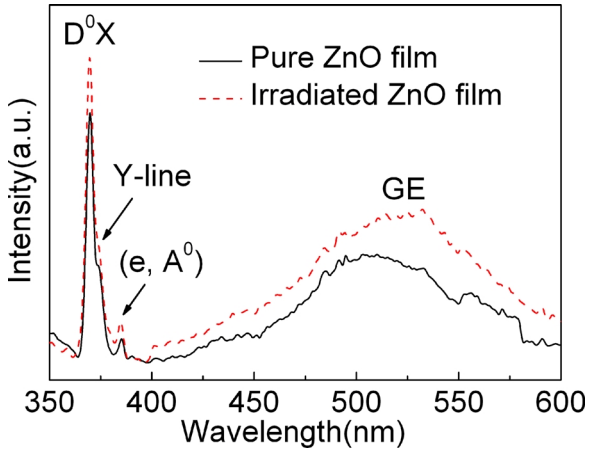

Fig. 5. PL spectra of pure ZnO and R2 region of irradiated ZnO film measured at 77 K.

als. And as can be seen in an inset of Figure 4, sapphire substrate showed diamagnetic behaviours, this ruled out the magnetization coming from the substrates. In addition, it was confirmed previously that no ferromagnetic impurity was detected by TEM for ZnO nanostructures fabricated by Ar^+-ion irradiation with a simultaneous Cu supply [9]. So the observed RTFM is thought to be an intrinsic property of Cu-doped ZnO film. Our research on Cu-doped ZnO films deposited by helicon magnetron sputtering suggested that the ferromagnetism might originate from defects related mechanisms [15].

Cu was supplied over the whole sample surface (R1 and R2 region), while micro-beam Ar^+-ion irradiation was done only at the small region R1, ~ 380 μm in diameter. As was demonstrated in the previous paper, Cu can be doped into ZnO nanostructures by Ar^+-ion irradiation with a simultaneous Cu supply [9]. Does Cu doping occur without Ar^+-ion irradiation? In order to answer this, PL measurement was carried out for the R2 region at 77 K. The result is shown in Figure 5, in which a PL spectrum for an as-deposited ZnO film is also shown for comparison. Neutral-donor-bound exciton (D^0X) peak was observed at about 370 nm (3.351 eV). The shoulder peak at about 374 nm (3.315 eV) should be due to the recombination of electrons localized at the Zni defects or the holes in the valence band (Y-line) [16]. There can be observed also a peak at around 385 nm (3.22 eV) which may attribute to (e, A^0) [17]. Beside these peaks, broad green emis-

sion (GE) peaks centered at around 500 nm also can be seen. Up to now, there is no consensus in the literature concerning the nature of the GE emission band. Several intrinsic defects, such as oxygen vacancies, zinc interstitials, and zinc vacancies, have been proposed. Extrinsic impurities such as Cu are also considered as possible candidates for the emission [18, 19]. The intensity ratio of D^0X and GE peak for both spectra was about 1.5. Our work found that Cu doping would dramatically decrease D^0X peak and increase the GE peak [15]. However, as is clear in Figure 5, the PL spectra are almost identical for the two films. This implied that the substitution of Cu into Zn sites was never induced by Cu supply without Ar^+-ion irradiation, and that no serious optical damage was induced by Cu deposition alone. Thus, Ar^+-ion irradiation with a simultaneous Cu supply was essential for the Cu substitution into Zn sites.

4. Conclusions

Partially Cu-doped ZnO films (3×3 mm^2) were successfully prepared by micro-area Ar^+-ion (~ 380 μm in diameter) irradiation with a simultaneous Cu supply. Both the non-doped and partially doped ZnO films showed the hexagonal wurtzite crystal structure with a preferred (002) orientation and a Cu_2O phase was formed in the ZnO films by Cu doping. The Cu-doped ZnO films exhibited RTFM due to the incorporation of Cu into Zn sites, and no serious optical damage was recognized in the non-ion-irradiated region. Thus, it is believed that the micro-area Ar^+-ion irradiation with a simultaneous Cu supply is promising for the integration of both optical and ferromagnetic properties of ZnO-based films.

[1] H. Ohno, Science **281**, 951 (1998).
[2] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[3] G. L. Liu, Q. Cao, J. X. Deng, P. F. Xing, Y. F. Tian, Y. X. Chen, S. S. Yan, and L. M. Mei, Appl. Phys. Lett. **90**, 052504 (2007).
[4] H. J. Lee, S. Y. Jeong, C. R. Cho, and C. H. Park, Appl. Phys. Lett. **81**, 4020 (2002).
[5] H. H. Huang, C. A. Yang, P. H. Huang, C. H. Lai, T. S. Chin, H. E. Huang, H. Y. Bor, and R. T. Huang, J. Appl. Phys. **101**, 09H116 (2007).
[6] R. M. Frazier, G. T. Thaler, J. Y. Leifer, J. K. Hite, B. P. Gila, C. R. Abernathy, and S. J. Pearton, Appl. Phys. Lett. **86**, 052101 (2005).
[7] X. B. Feng, J. Phys.: Condens. Matter **16**, 4251 (2004).
[8] D. B. Buchholz, R. P. H. Chang, J. H. Song, and J. B. Ketterson, Appl. Phys. Lett. **87**, 082504 (2005).
[9] T. S. Herng, S. P. Lau, S. F. Yu, H. Y. Yang, L. Wang, M. Tanemura, and J. S. Chen, Appl. Phys. Lett. **90**, 032509 (2007).
[10] S. J. Pearton, K. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, Prog. Mater. Sci. **50**, 293 (2005).
[11] H. T. Lin, T. S. Chin, J. C. Shih, S. H. Lin, T. M. Hong, R. T. Huang, F. R. Chen, and J. J. Kai, Appl. Phys. Lett. **85**, 621 (2004).
[12] D. L. Hou, X. J. Ye, H. J. Meng, H. J. Zhou, X. L. Li, C. M. Zhen, and G. D. Tang, Appl. Phys. Lett. **90**, 142502 (2007).
[13] M. Tanemura, T. Okita, H. Yamauchi, S. Tanemura, and R. Morishima, Appl. Phys. Lett. **84**, 3831 (2004).
[14] M. Tanemura, M. Kitazawa, J. Tanaka, R. Okita, L. Miao, and S. Tanemura, Jpn. J. Appl. Phys. **45**, 2004 (2006).
[15] F. Y. Ran, M. Imaoka, M. Tanemura, Y. Hayashi, T. S. Herng, and S. P. Lau, Physica Status Solidi (b), **246**(6), 1243 (2009).
[16] H. F. Liu, S. J. Chua, G. X. Hu, H. Gong, and N. Xiang, J. Appl. Phys. **102**, 063507 (2007).
[17] G. Xiong, K. B. Ucer, R. T. Williams, J. Lee, D. Bhattacharyya, J. Metson, and P. Evans, J. Appl. Phys. **97**, 043528 (2005).
[18] X. P. Peng, J. Z. Xu, H. Zang, B. Y. Wang, and Z. G. Wang, J. Luminescence **128**, 297 (2008).
[19] Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).