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Article *in* Applied Physics Letters · May 2006

DOI: 10.1063/1.2192577 · Source: IEEE Xplore

Ferromagnetism in 200-MeV Ag^{+15}-ion-irradiated Co-implanted ZnO thin films

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(Received 23 June 2005; accepted 13 March 2006; published online 4 April 2006)

Structural, electrical resistivity, and magnetization properties of 200-MeV Ag^{+15}-ion-irradiated Co-implanted ZnO thin films are presented. The structural studies show the presence of Co clusters whose size is found to increase with increase of Co implantation. The implanted films were irradiated with 200-MeV Ag^{+15} ions to fluence of 1×10^{12} ions/cm^2. The Co clusters on irradiation dissolve in the ZnO matrix. The electrical resistivity of the irradiated samples is lowered to half. The magnetization hysteresis measurements show ferromagnetic behavior at 300 K, and the coercive field increases with the Co implantation. The ferromagnetism at room temperature is confirmed by magnetic force microscopy measurements. The results are explained on the basis of the close interplay between the electrical and the magnetic properties. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2192577]

In the recent years, there has been a great interest to develop materials which exhibit semiconducting and ferromagnetic properties, known as diluted magnetic semiconductors (DMSs).[1,2] Besides their "charge," the ferromagnetic semiconductors possess an additional degree of freedom and functionality of "spin," which can be integrated into the existing semiconductor devices, important for applications. The ferromagnetism has been achieved in both II-VI and III-V semiconductors by the addition of 3*d* transition metal elements, which have Curie temperatures typically varying from low temperature (4.2 K) to above room temperature.[3] Dietle *et al.*[4] predicted theoretically, using mean-field model, the possibility of room temperature ferromagnetism in Mn doped ZnO and GaN, provided the hole doping is sufficiently high (3×10^{20}/cm^3). Around the same time, Sato and Katyama[5] made the density functional calculations and predicted the ferromagnetism in transition metal substituted ZnO through double exchange mechanism, which did not require free carrier for high concentration of the substituent. There are various reports on magnetic properties of transition metal doped ZnO,[6–8] but the main issue is the origin of ferromagnetism in this system. It may be possible that the ferromagnetism follows from the precipitate/clusters of the transition metal and their oxide phases, which are ferromagnetically ordered. However, if the ferromagnetism is due to the carrier-mediated exchange in ZnO matrix, it would be exciting to investigate properties for its use in semiconductor based spintronics devices. In most of the previous studies, the transition metals were incorporated by synthesizing the solid-state reaction of transition metal oxide and ZnO in bulk form and then the films were deposited. There are a few reports where the DMS materials have been synthesized by ion implantation in ZnO thin films and the single crystals.[9–11] In most of these implanted systems, the Co clusters were observed with a sizable amount. The main issue that still remains unsolved, however, is the dissolution of the clusters and putting them at an appropriate site in the ZnO matrix to avoid the possibility of ferromagnetism arising from the clusters.

Swift heavy ion (SHI) irradiation has been known for the deposition of large of amount energy to the lattice in a very short time through the electron-phonon interactions. The mechanisms of energy transfer are well explained in the literature through two well-known models such as Coulomb explosion[12] and thermal spike.[13] According to the thermal spike model during the passage of SHI the kinetic energy of the excited electrons is transmitted to the lattice by electron-phonon interaction in a way efficient enough to increase the local lattice temperature above the melting point of the material. The increase in temperature is followed by rapid thermal quenching (10^{13}–10^{14} K/s) that results in modifications of materials in controlled fashion. The SHI irradiation has been widely used for modifications of physical properties of various materials and has found immense utility in mixing two different materials,[14,15] creating structural strains/

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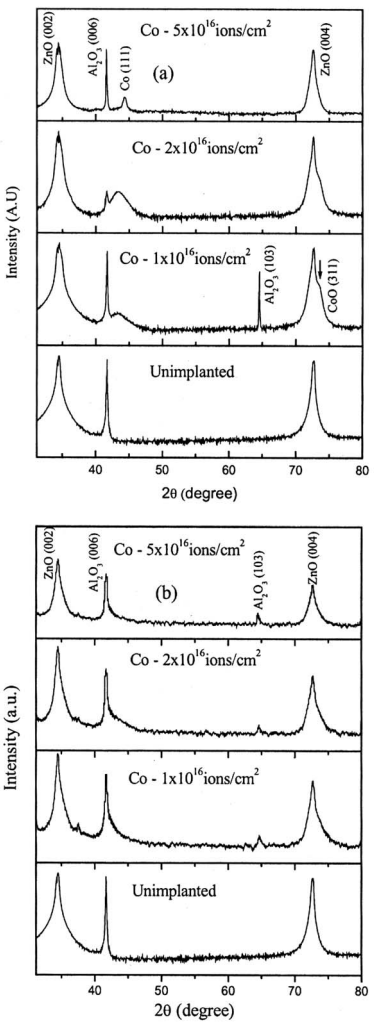

FIG. 1. X-ray diffraction patterns of (a) undoped and 80-keV Co ion implanted at 300 °C and (b) undoped and 200-MeV Ag^{+15} ion irradiated with 1×10^{12} ions/cm^2 Co-implanted ZnO thin films.

disorders and generating point/clusters and columnar defects in colossal magnetoresistance (CMR) materials,[16] ferrites, and other oxide materials. In this letter, we report on the use of SHI irradiation to dissolve the Co clusters in Co-ion-implanted ZnO thin films to synthesize the single phase Co doped ZnO to achieve the ferromagnetic semiconductor at room temperature.

The ZnO films of thickness of 400 nm were deposited on α-Al_2O_3 (0001) single crystal by plasma assisted molecular beam epitaxy (PAMBE). During the deposition the substrate temperature was maintained at 720 °C and the chamber base pressure was 2×10^{-9} Torr. The details of the film deposition can be found elsewhere.[17] The well-characterized films were implanted with 80-keV Co ions to doses of 1×10^{16} to 5×10^{16} ions/cm^2 at 300 °C to recover the implantation damage. Further, the Co-implanted ZnO thin films were irradiated with 200-MeV Ag^{+15} ions to fluence of 1×10^{12} ions/cm^2 at room temperature using the 15UD tandem accelerator at Nuclear Science Centre, New Delhi, India. Here onwards, we name our films as ZnO, ZnOCo1U, ZnOCo2U, and ZnOCo3U for pure, and 1×10^{16}, 2×10^{16}, and 5×10^{16} ions/cm^2 Co implanted, respectively, before SHI irradiation and ZnOCo1R, ZnOCo2R, and ZnOCo3R for respective films irradiated with 200-MeV Ag^{+15} ions. The structural characterization of Co doped ZnO thin films before and after SHI irradiation was performed by powder x-ray

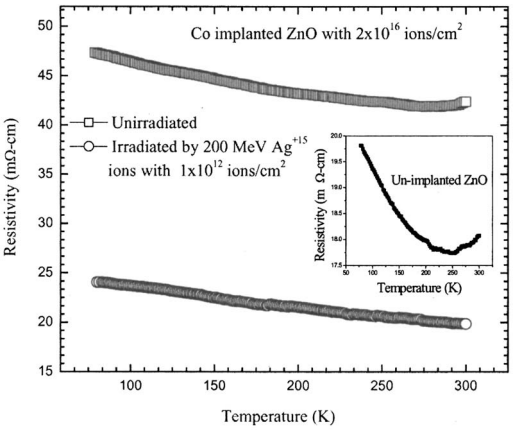

FIG. 2. Resistivity as a function temperature for unirradiated and 200 -MeV 1×10^{12} ions/cm^2 Ag^{+15} irradiated, 2×10^{16} ions/cm^2 Co implanted. ZnO thin films. The inset shows the resistivity as a function of temperature for pure ZnO.

diffraction (XRD) using Bruker D8 x-ray diffractometer. The electrical resistivity as a function of temperature of the films was performed using four-probe method in the temperature range of 77–300 K. The isothermal magnetization hysteresis measurements were performed at 300 K using alternating gradient force magnetometer (AGFM) (micromag-2900, Princeton Measurements Co.) with a sensitivity of 10^{-8} emu. In these measurements, the magnetic contribution from the substrate was subtracted from the measured data.

Figure 1(a) shows the x-ray diffraction pattern of ZnO, ZnOCo1U, ZnOCo2U, and ZnOCo3U thin films. The presence of Co clusters of nanosize is clearly evident by their (111) peak in Fig. 1(a) appearing at $2\theta=44.35$. A small shoulderlike structure at $2\theta=73.5$ along with the ZnO (004) peak is identified with CoO (311). The appearance of the Co clusters and other phases indicate that in the as implanted ZnO films Co does not go to the Zn site. Further, Fig. 1(a) also shows that the Co (111) peak width decreases with increase in implantation dose suggesting that the Co cluster size increases as the doping concentration is increased. To dissolve these Co clusters, the implanted films were irradiated with 200-MeV Ag^{+15} ions to fluence of 1×10^{12} ions/cm^2. The electronic stopping power S_e, nuclear stopping power S_n, and range R_p of the 200-MeV Ag^{+15} ions in ZnO calculated using SRIM-2003 code are 24 keV/nm, 69 eV/nm, and 13.65 μm respectively. S_e is three orders of magnitude higher than S_n and the range of the ions is very much larger than the film thickness (400 nm), which indicates that there is no implantation of Ag ions in the films. The large S_e in these films creates high local temperature due to the electron-phonon coupling as suggested by the thermal spike model and dissociates the Co clusters along the ion path. There may be some level of amorphization during this process. To confirm, the x-ray diffraction measurements of SHI irradiated implanted films were made and shown in Fig. 1(b). The Co (111) clusters peak at $2\theta=44.35$ and CoO (311) shoulder at $2\theta=73.5$ are absent in Fig. 1(b) which indicates that the Co clusters and other phases of Co oxide are dissolved with the ZnO matrix. It can also be seen that there is no significant change in their peak width and position. Unlike in conventional thermal annealing, where the sample is exposed to high temperature for a considerable amount of time, leading to the growth of the clusters[18] and also modifying the defects states such as oxygen vacancies, etc., SHI irradiation has been very effective in taking the sample to

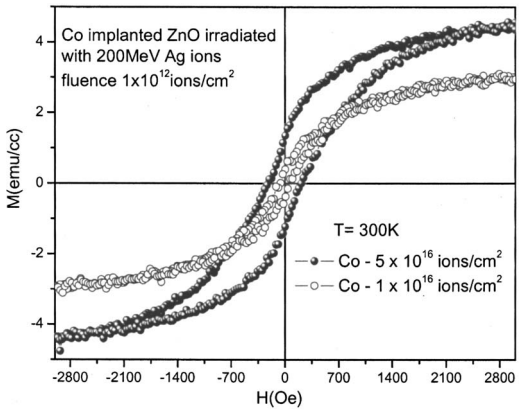

FIG. 3. Isothermal dc magnetization as a function of magnetic field for 200-MeV Ag^{+15}-irradiated Co-implanted ZnO thin films having Co dopings of 1×10^{16} and 5×10^{16} ions/cm^2.

very high temperature through electron-phonon coupling in a short span of time, which essentially dissolves the Co clusters and does not allow them to grow. Many efforts of dissolving Co clusters through the conventional annealing ended up with an increased cluster size or with a formation of oxide phases of cobalt.[18,19]

In order to understand the electrical transport behavior, the resistivity of the films was measured as a function of temperature before and after SHI irradiation. Figure 2 shows the resistivity as a function of temperature for ZnOCo2U and ZnOCo2R thin films. Before discussing the implanted films, we would like to discuss the resistivity of pure ZnO films (see inset of Fig. 2). The resistivity of pure ZnO film shows the metal insulator transition around 250 K. The resistivity shows metallic behavior up to 250 K and after that it follows the semiconductor nature, possibly due to the presence of oxygen vacancies in the films. A similar trend is observed in ZnOCo2U films with the metal insulator transition temperature at 285 K. The resistance, however, increases by a factor of 2.5 of that of pure ZnO film (see Fig. 2). Figure 2 also shows that after SHI irradiation the resistivity of the implanted film decreases by a factor of 2 and the metal insulator transition disappears. The Co clusters present in the implanted films act as scattering centers, leading to increase in resistivity. On SHI irradiation the clusters dissolve, making the film more ordered and hence decreasing the resistivity. Similar results were observed for other films. This is corroborated by our XRD results. The absence of Co cluster peak in XRD pattern and the decrease in resistivity emphasize the inference that the SHI irradiation transforms the Co clustered system into a Co substituted ZnO system.

As stated earlier, we are primarily interested in examining the ferromagnetism in the system. Figure 3 shows the isothermal magnetization hysteresis curves at 300 K for ZnOCo1R and ZnOCo3R thin films. Both the films show the ferromagnetism at 300 K and the magnetization and coercivity (H_c) increase with the increase of implantation dose. Further, to confirm the ferromagnetism in these materials, we have performed the magnetic force microscopy (MFM) measurements at room temperature. Figure 4 shows the MFM pictures of ZnO and ZnOCo3R films. From Fig. 4(a) it is clear that there is no magnetic contrast in ZnO film, whereas ZnOCo3R film shows a good contrast and the magnetic domains are uniformly distributed over the whole film area.

To summarize, we have synthesized Co doped ZnO thin films by 80-keV Co ion implantation at 300 °C with various

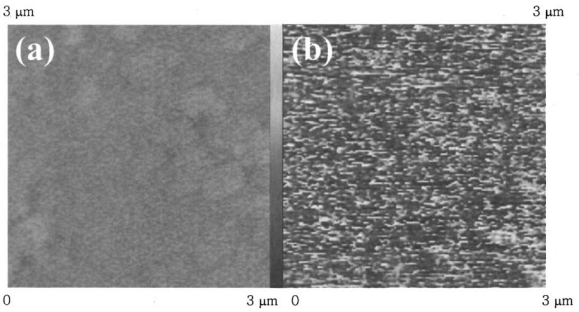

FIG. 4. Magnetic force microscopy (MFM) pictures for (a) pure ZnO film and (b) 200-MeV Ag^{+15}-ion-irradiated Co-implanted ZnO thin film having Co doping of 5×10^{16} ions/cm^2.

dose values followed by 200-MeV Ag^{+15} ion irradiation, which shows a single phase structure. These films are ferromagnetic at room temperature and exhibit the semiconductor behavior. The correlation between the electrical and magnetic properties in the present system formulates it to be a potential aspirant for the spintronics oriented devices wherein the communication between the charge and spin is highly desired.

This work is financially supported by KIST Future Resource Program (2E18510), R & D project for NT-IT Fusion Strategy of Advanced Technology, and KOSEF under Contract No. R01-2004-000-10715-0. The authors are thankful to IUAC Pelletron group for providing the 200-MeV Ag^{+15} ion beam.

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