Annealing temperature effect on optical properties of Cr-implanted ZnO nanostructure

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Room temperature ferromagnetism was observed in Cr-implanted ZnO nanowires annealed at 500, 600, and 700 °C. The implantation dose for Cr ions was 1 ×10¹⁶ cm⁻², while the implantation energies were 100 keV. Except for ZnO (100), (002), and (200) orientations, no extra diffraction peaks from Cr-related secondary phase or impurities were observed. With the increasing of annealing temperatures, the intensity of the peaks increased while the FWHM values decreased. The Cr 2p₁/₂ and 2p₃/₂ peaks, with a binding energy difference of 10.6 eV, appear at 586.3 and 575.7 eV, can be attributed to Cr³⁺ in ZnO nanowires. For the Cr-implanted ZnO nanowires without annealing, the band energy emission disappears and the defect related emission with wavelength of 500–700 nm dominates, which can be attributed to defects introduced by implantation. Cr-implanted ZnO nanowires annealed at 500 °C show a saturation magnetization value of over 11.4 × 10⁻⁵ emu and a positive coercive field of 67 Oe. The origin of ferromagnetism behavior can be explained on the basis of electrons and defects that form bound magnetic polarons, which overlap to create a spin-split impurity band.

Keywords: ZnO; Annealing temperature; Optical.

1. INTRODUCTION

Extensive studies have been carried out on ferromagnetism in dilute magnetic semiconductors (DMSs) because of their potential applications in spintronic devices such as magnetooptic switches, magnetic sensors, spin valve transistors, and spin light-emitting diodes, etc. [1–4]. A
key requirement in realizing most devices based on spin is that the host material should be ferromagnetic above room temperature. In addition, it is necessary to have both efficient spin-polarized carrier injection and transport. One approach to achieving spin injection into these materials is to apply ferromagnetic metals as the contacts. However, the reported spin injection efficiency is usually low due to formation of interfacial layers. For these reasons, there is interest in developing DMS and semiconductors which exhibit ferromagnetism [5]. Dietl et al. [6, 7] have applied Zener’s model which based on exchange interaction between carriers and localized spins, to explain the ferromagnetism transition temperature in compound semiconductors and find room temperature ferromagnetism in p-type wide band gap semiconductors GaN and ZnO with Mn concentrations of 5 at.%. The theory assumes ferromagnetic correlations mediated by holes from shallow acceptors in a matrix of localized spins in a magnetically doped semiconductor. Ex been reported in the Co-doped, V-doped, Fe-doped, and Mn-doped ZnO system [8–11]. Some experimental results provided evidence in support of intrinsic nature of the ferromagnetism in the MT-doped ZnO [12, 13]. However, some studies on the MT-doped ZnO suggested that the room temperature ferromagnetism is an extrinsic phenomenon caused by the presence of transition metal clusters [14].

However, a key aspect of the work is the need to achieve soluble concentrations of the transition metals well above the equilibrium solubility limit in ZnO or GaN, which requires the use of non-equilibrium methods such as low-temperature epitaxial growth or ion implantation. Ion implantation can be used to survey the magnetic properties of a number of transition metal dopants in various semiconducting oxide materials. Room temperature ferromagnetism was observed in ZnO implanted with Co, Mn, and Cr [15–17]. Recently, one-dimensional (1D) DMS nanostructures have received much attention for they could potentially be used as building blocks for fabricating 3D architecture of novel spintronics microchips [18]. Ferromagnetic DMS nanowires and nanorods are reported to have higher Curie temperature and a larger magnetic moment as compared to their bulk and film counterparts [19]. In this study, we report the direct observation of simultaneous room temperature ferromagnetism in Cr-implanted ZnO nanowire (ZNWs) grown by thermal evaporation, and investigate the effects of annealing temperature on the microstructure, photoluminescence, and ferromagnetism properties of Cr-implanted ZnO nanowires.

2. EXPERIMENTAL DETAILS

The synthesis of the ZNWs was carried out in a conventional horizontal tube furnace with a quartz working tube. Zn powder with purity of 99.99% was deposited on a quartz boat and placed in the center zone of the tube furnace, which acted as the source material. Silicon (111) substrates were placed in the low temperature zone, 10 cm upstream the source and acted as the substrate. After the quartz tube was pumped to the desired vacuum of 2 Pa, the temperature of the furnace was raised from room temperature to 500–700 °C at a ramping rate of 20 °C/min. When the tube temperature reached 400 °C, a gas mixture of O2 (60 sccm) and Ar (30 sccm) was then introduced.
into the system. The total gas pressure was kept at 20 Pa during deposition. After maintaining the high temperature for 2 h, the furnace was let cool naturally to room temperature before taking out the sample for characterization. The ZNWs were n type in conduction, with a Hall concentration of $6 \times 10^{15} \text{ cm}^{-3}$ and a mobility of $90 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Cr ion implantation was carried out in a Metal Vapor Vacuum Arc (MEVVA) source system. The metal source implanter is equipped with three ion sources, and hence can provide three beams of metal ions into a large target chamber. The anode of the discharge is located on-axis with respect to the cathode and has a central hole through which a pan of the plasma plume streams. At the target location, the ion beam is several cm wide. The implantation dose and energy for Cr ions was $1 \times 10^{16} \text{ cm}^{-2}$ and 100 keV, respectively. Rapid thermal annealing was carried out at temperatures of 500 °C, 600 °C, and 700 °C for 30 s in a flowing oxygen atmosphere.

The X-ray diffraction (XRD) analysis was carried out with a scanning rate 0.02 s$^{-1}$ with Cu Ka radiation. The Cr concentration in the nanowires was verified using an energy dispersive X-ray spectroscopy (EDX) system (EDAX gene- sis 7000) operated at 12 kV. The electron beam is scanned in a faster pattern over the surface for imaging. The beam was focused to a final probe diameter of about 50 Å. Some Cr ions may be dispersed in the underlying substrate and more accurate detection on an individual nanowire by TEM is under way. The chemical bonding states were investigated by X-ray photo electron spectroscopy (XPS, Kratos Ltd XSAM800) with Mg Ka excitation. An RM-1000 type Raman micro-spectrometer was used to measure the chemical bonding of the implanted samples. The excitation source was an Ar$^{+}$ laser working at a wavelength of 514.53 nm. Photoluminescence (PL) measurements were done at room temperature as well as at 10 K using a He–Cd laser as the excitation source, operating with a power of 50 mW and a wavelength of 325 nm. A 2010 JEOL JEM transmission electron microscopy (TEM) was used to characterize the crystalline structure at accelerating voltage of 200 kV. Magnetic characterization was performed by a superconducting quantum interference device (SQUID) from Quantum De- sign. The direction of the magnetic field for the measurement of the $M$–$H$ curve was in-plane.

3. RESULTS AND DISCUSSION

Figure 1a shows typical SEM images of ZNWs grown with high density. Typical diameters of the stem part and the sharp nanotip range between 150 and 40 nm, respectively, and the whole length of nanowire appears to be 500 nm to several μm. Figure 1b shows the EDX spectra for Cr-implanted ZnO nanowires annealed at 600 °C. The sample has an oxygen peak at 0.53 keV and Zn signals at 1.04, 8.65, and 9.58 keV. The Cr signal was observed and quantitative analysis yielded concentrations of 3 at.%. Figure 2 shows the typical XRD spectra of these Cr-implanted ZNWs with Cr implantation energy of 100 keV and annealed at temperatures of 500, 600, and 700 °C, respectively. Except for ZnO (002), (103), and (201) orientations, no extra diffraction peaks from Cr-related secondary phase or impurities were observed. It is shown that all the diffraction peaks in the pattern can be easily indexed as the pure hexagonal phase ZnO with calculated lattice parameters.
of $a = 3.245$ Å, $c = 5.199$ Å, which is in good agreement with the reported standard values (JCPDS No. 65-3411). Inset of Fig. 2 shows the enlarged patterns of Cr-implanted ZnO nanowires near (002) diffraction. With the increasing of annealing temperatures, the intensity of the peaks increased while the FWHM values decreased. This result indicates that Cr ion implantation has introduced defects in the ZnO nanowires and the microstructure and crystalline were greatly improved by annealing. The increase.

**Fig. 1** SEM image (a) and the corresponding EDAX spectrum (b) of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at 600 °C

**Fig. 2** XRD spectra of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at temperatures of 500, 600, and 700 °C, respectively
of the ZnO unit cell induced by implantation has been reported [20]. Fringes of the (002) peak indicate that nitrogen implantation in ZnO induces a deformed layer with a larger c parameter. Ferromagnetic behavior above room temperature in Fe-ion-implanted ZnO single crystals have also been studied [21]. The value of the full with at half maximum decreased from 0.24 to 0.17 with increasing the annealing temperature from 700 to 900 °C and could be due to recovery of the crystal structure.

Figure 3 shows O1s, Zn 2p3/2 and Cr 2p narrow scan spectra of the Cr implanted ZnO nanowires annealed at 600 °C. The typical O1s peak with binding energy of 532.5 eV can be ascribed to O2− ions on wurtzite structure of hexagonal Zn2+ ion array [22–24]. The Zn 2p3/2 peak is situated at 1022.3 eV, showing that Zn ions in the nanowires are mainly in the chemical states of Zn2+ [25, 26]. Figure 3d shows the XPS emission peak of Cr 2p. The binding energy located at 575.7 eV correspond to Cr3+ at Cr 2p3/2, clearly different from 574.0 eV of Cr metal and 576.0 eV of Cr2+ [27]. Likewise, the binding energy located at 586.3 eV corresponds to Cr3+ at Cr 2p1/2. The data reveal the presence of appearance of Cr3+ in the Cr-doped ZnO nanowires.

The Raman spectra of Cr-implanted ZnO nanowires are presented in Fig. 4. We can see an intense E2 peak at 436 cm−1 and a weak A1 LO mode at 574 cm−1 in the Raman spectrum, as expected from the Raman selection rules in semiconductors with wurtzite crystal structure [28]. The A1 LO mode at 574 cm−1 is attributed to disorder-activated Raman scattering while peaks at 520 cm−1 is attributed to scattering from the silicon substrate. It is interesting to note that the frequency of the A1 LO phonon mode of the annealed ZnO:Cr nanowires almost coincides that of the as-implanted ZnO as indicated by the dotted lines. The difference of Raman spectra between as-deposited and Cr-implanted samples reveals that the ion implantation has induced defects and disorder in ZnO nanowires. Figure 5 shows the PL spectra of as-deposited and Cr-implanted ZnO nanowires and annealed at different temperatures. The PL spectrum of ZnO consists of two distinct emissions: an intense and dominated peak at 383 nm and a broad band emission at 512 nm, which was assigned to the UV emission and green emission, respectively. For the Cr-implanted ZnO nanowires with Cr ion implantation energies of 100 keV, the band energy emission disappears and the defect related emission with wavelength of 500–700 nm dominates, which can be attributed to defects introduced by implantation.
Fig. 3 XPS spectra of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at 600 °C. (a) O 1s, (b) Zn 2p3/2, and (c) Cr 2p

Compared to as-implanted ZnO, The band energy emission intensity of annealed ZNWs increased while the full width at half maximum values decreased. The UV emission, also called near band-edge emission, originated from the free-exciton recombination [29]. Moreover, the enhancement in UV emission intensity of the room temperature PL in our result was due to the improvement in the crystal quality of the ZnO nanowires by annealing. It was reported that the improvement of crystal quality (decrease of impurities, and structure defects such as oxygen vacancies and zinc interstitials) can lead to a high near band-edge emission to deep-level emission ratio, resulting in the detectable UV emissions at room temperature [30, 31]. It was reported that the oxygen vacancies responsible for the green emission are mainly located at the surface [32] and the PL intensity ratio of the UV emission to deep-level emission decreases with increasing surface area [33] under the same preparation process. Therefore, it is likely that the strong green emission of ZNWs is related to their high surface-to-volume ratio.

We used TEM to further investigate the structural characteristics. The low-resolution TEM image for ZnO nanowires grown at 700 °C was shown in Fig. 6a. With a growth time of 60 min, the mean length was 1.4 μm and the diameter was 120 nm. The selected area electron diffraction
pattern (SAED) of a single ZNW (inset of Fig. 6b) can be indexed to wurtzite structure of hexagonal ZnO and indicates that the ZNW grows along the (002) direction. In the high resolution TEM (HRTEM) image (Fig. 6c), the lattice spacing of 0.52 nm also corresponds well to the interplanar distance of the (002) crystal plane of wurtzite ZnO.

**Fig. 4** Raman spectra of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at temperatures of 500, 600, and 700 °C

**Fig. 5** PL spectra of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at temperatures of 500, 600, and 700 °C, respectively

Figure 7 shows room temperature magnetization versus field curves for Cr-implanted ZnO
nanowires with Cr ion implantation energies of 100 keV and annealed at temperatures of 500, 600, and 700 °C, respectively. Nanowires annealed at 500 °C show a saturation magnetization value ($M_S$) of over $11.4 \times 10^{-5}$ emu and a positive coercive field of 67 Oe. In addition, the magnetization value of Cr-implanted nanowires shows a decrease trend with increasing annealing temperatures. The magnetization versus temperature curves shown in inset of Fig. 7 indicates that the Curie temperature for Cr-implanted ZNWs annealed at 700 °C is well above 400 K. The carrier concentration is not much improved after annealing and in the order of $10^{15} \text{ cm}^{-3}$, which suggests that FM does not depend upon the presence of a significant carrier concentration. The relative high resistivity and low electron concentrations of the Cr-implanted ZnO nanowires unambiguously rules out the possible carrier mediated exchange, such as the Rudermann–Kittel–Kasuga–Yosida (RKKY) [34] and double exchange mechanism [35]. Moreover, conventional super exchange interactions cannot produce long range magnetic order at concentrations of magnetic cation of only a few percent, i.e., 3 at.% Cr doped ZnO.

![TEM images of ZnO nanowires](image)

**Fig. 6** TEM (a), HRTEM (b) and SAED (c) images of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at 700 °C
Bound magnetic polarons (BMP) model for an oxide semiconductor as a function of doping and carrier density was predicted by Coey et al. [34]. The general formula for the oxide is, \((\text{A}(1-x)\text{M})_x(\text{O}0\delta)_n\), where A is a nonmagnetic cation, M is a magnetic cation, 0 represents a donor defect, and the occurrence of different magnetic phases is determined by the polaron and cation percolation threshold \(\delta_p\) and \(x_p\), respectively. It is predicated that in oxide, ferromagnetism occurs when \(\delta > \delta_p\) and \(x < x_p\) [36]. The critical defect concentrations for \((\text{NO})\) establishing percolation threshold for long range ferromagnetism order can be estimated from \(r_3(\text{NO}/\text{NO})\), where \(\text{NO}\) is the oxygen density for ZnO, and \(r\) is estimated to be about \(3.8 \times 10^{18}\) cm\(^{-3}\). From the SQUID measurements shown in Fig. 7, it is observed that the appearance of room temperature ferromagnetism compared to as-grown ZnO nanowires can be attributed to the larger defect density caused by Cr incorporation. For the as grown ZnO nanowires, the calculated defect concentration is about \(2 \times 10^{17}\) cm\(^{-3}\), whereas for the Cr implanted ZnO nanowires with implantation energies of 100 keV, the value is calculated to be greater than \(10^{18}\) cm\(^{-3}\). The presence of such a large concentration of defects present in the low temperature annealed nanowires allows for long range ferromagnetism in accordance with the BMP model. We propose that ferromagnetic exchange here in Cr-implanted ZnO nanowires, is mediated by electrons and defects that form bound magnetic polarons, which overlap to create a spin-split impurity band.

**Fig. 7** \(M–F\) (magnetization–field) plots of ZnO nanowires implanted with Cr implantation energies of 100 keV and annealed at temperatures of 500, 600, and 700 °C, respectively. *Inset* shows the \(M–T\) (magnetization–temperature) curves for ZnO nanowires implanted with Cr and annealed at 700 °C.
4. CONCLUSIONS

In conclusion, room temperature ferromagnetic behavior has been observed Cr-implanted ZnO nanowires annealed at 500, 600, and 700 °C. With the increasing of annealing temperatures, the intensity of the XRD and PL peaks increased while the FWHM values decreased. The relatively high resistivity and low electron concentrations of the Cr-implanted ZnO nanowires unambiguously rules out the possible carrier mediated exchange. For the as grown ZnO nanowires, the calculated defect concentration is about $2 \times 10^{17}$ cm$^{-3}$, whereas for the Cr implanted ZnO nanowires with implantation energies of 100 keV, the value is calculated to be greater than $10^{18}$ cm$^{-3}$. The presence of such a large concentration of defects present in the low temperature annealed nanowires allows for long range ferromagnetism in accordance with the bound magnetic polarons theory which mediated by electrons and defects.

REFERENCES
