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Magnetic Properties of Transition Metal-implanted ZnO Nanotips Grown on Sapphire and Quartz

Jeremy A. Raley[1], Yung Kee Yeo[1], Robert L. Hengehold[1], Mee-Yi Ryu[2]*, Yicheng Lu[3], and Pan Wu[3]

[1]*Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AFB, OH 45433, USA*
[2]*Department of Physics, Kangwon National University, Chuncheon, Kangwon-do 200-701, Korea*
[3]*Department of Electrical and Computer Engineering, Rutgers University, Piscataway, NJ 08854, USA*

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ZnO nanotips, grown on c-Al_2O_3 and quartz, were implanted variously with 200 keV Fe or Mn ions to a dose level of 5×10^{16} cm^{-2}. The magnetic properties of these samples were measured using a superconducting quantum interference device (SQUID) magnetometer. Fe-implanted ZnO nanotips grown on c-Al_2O_3 showed a coercive field width of 209 Oe and a remanent field of 12% of the saturation magnetization (2.3×10^{-5} emu) at 300 K for a sample annealed at 700 °C for 20 minutes. The field-cooled and the zero-field-cooled magnetization measurements also showed evidence of ferromagnetism in this sample with an estimated Curie temperature of around 350 K. The Mn-implanted ZnO nanotips grown on c-Al_2O_3 showed superparamagnetism resulting from the dominance of a spin-glass phase. The ZnO nanotips grown on quartz and implanted with Fe or Mn showed signs of ferromagnetism, but neither was consistent.

Keywords : ZnO nanotip, ferromagnetism, ion implantation, superconducting quantum interference device (SQUID)

1. Introduction

Zinc oxide (ZnO) semiconductor doped with transition metals (TMs) is one of the most promising materials for use in spintronic applications [1]. The pursuit of a room-temperature magnetic semiconductor has already led researchers to dope ZnO with several different TMs using various doping methods [2-5]. The ion implantation technique has been used to introduce TM ions into wide bandgap materials in order to achieve room temperature dilute magnetic semiconductor (DMS) [6-8]. ZnO is a radiation-hard material that remains crystalline even after ion bombardment with heavy doses at high energy. The implantation process, however, does induce damage in the semiconductor crystal, and thus proper annealing must be performed to remove this damage.

There have been many reports of magnetic hysteresis persisting well above room temperature, but the observation of ferromagnetism in bulk TM-doped ZnO is typically associated with secondary phase formation. The research reported here concentrates on the magnetic properties of TM-implanted ZnO nanotips grown on sapphire and quartz substrates by metal-organic chemical vapor deposition (MOCVD). Field emission scanning electron microscope (FESEM) images of ZnO nanotips grown on sapphire and quartz are shown in [9] and [10], respectively. Nanotips are tiny pillars of single crystal ZnO that rise from the substrate with little or no connection to one another. It is apparent from the lack of connection between pillars of ZnO that this sort of material cannot be easily used to make a device based upon charge carrier movement. However, the isolation between individual nanotips may prove to be beneficial in certain circumstances, such as a sensor applications. The vastly increased surface area of the nanotips compared to conventional thin films would allow for added sensitivity to substances in the ambient air. The effects of interesting airborne substances on the magnetic properties of the transition metal doped ZnO is a matter for further investigation. Another application is a data storage system based on magnetic writes and optical reads in order to leverage the speed advantages of each. For instance, a remanent field in the material induced by the magnetic write head could be optically read out by the Kerr rotation of a polarized beam. We report the room temperature ferromagnetism in TM-implanted ZnO nanotips grown on sapphire and quartz substrates.

*Corresponding author: Tel: +82-33-250-8474
Fax: +82-33-257-9689, e-mail: myryu@kangwon.ac.kr

2. Experiment

ZnO nanotips were grown on c-plane sapphire and quartz substrates using a vertical flow MOCVD system. Details of the ZnO nanotip growth using MOCVD have been described elsewhere [9, 10]. ZnO nanotips were implanted with 200 keV Fe or Mn ions at a dose level 5×10^{16} cm^{-2} at room temperature. After TM implantation, the samples were annealed at temperatures between 675 and 800 °C for periods of 5 to 20 minutes in an atmosphere of pure O_2 flowing at 25 sccm. FESEM images (not shown) indicate that the as-grown nanotips are about 500 nm in height and 40-60 nm in width. No morphological changes are observed after implantation and post annealing [9, 10]. The magnetic moment of each sample was measured using a superconducting quantum interference device (SQUID) magnetometer. The SQUID measurements involved both variable-field measurements and temperature-dependent magnetization. The temperature-dependent measurements have been made in both field-cooled (FC) and zero-field-cooled (ZFC) configurations. In FC measurements, the sample is cooled from room temperature to 5 K with a 500 Oe magnetic field applied to the sample, while in ZFC measurements, the samples is cooled to 5 K with no magnetic field applied before magnetic moment measurements begin.

3. Results and Discussion

The magnetic properties of Fe-implanted ZnO nanotips grown on c-sapphire have been investigated as a function of annealing time and annealing temperature (not shown here) by using a SQUID magnetometer. The results of magnetic moment measurements taken at 5 and 300 K are shown in Fig. 1 as a function of magnetic field, along with the as-grown and the as-implanted (not annealed) samples. For clarity, only data taken at 5 and 300 K are shown in the figure, although measurements were taken at other temperatures as well. The as-grown sample (Fig. 1(a)) clearly shows linear diamagnetic behavior at both 5 and 300 K, which is mainly attributable to the sapphire substrate. The as-implanted sample (Fig. 1(b)) also shows predominately diamagnetic behavior at 300 K, but at 5 K, it shows a ferromagnetic hysteresis loop. Upon annealing, all the samples are characterized as superparamagnetic at 5 K and diamagnetic at 300 K in variable field measurements except for the sample annealed at 700 °C for 20 min, showing the strongest signatures of ferromagnetism in terms of hysteretic separation and strong saturation magnetization (M_S). Since the diamagnetic component due mainly to the sapphire substrate significantly affects the magnetization curve, it was corrected in order to obtain the true magnetic properties of the annealed samples due to the Fe implantation. The corrected results are shown in Figs. 1(c)-1(d). Variable field measurements revealed that the sample annealed at 700 °C for 20 min only demonstrated ferromagnetism as well as strong saturation magnetization. The samples annealed under other conditions show almost no separation between the positive and negative legs of the hysteresis loop (small coercive field) and none have M_S values rivaling that of the sample annealed at 700 °C for 20 min.

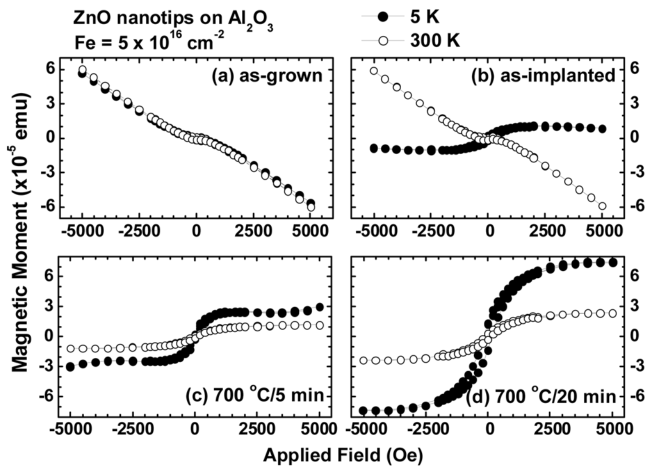

Fig. 1. Variable field magnetization measurements taken at 5 and 300 K for Fe-implanted ZnO nanotips grown on c-Al_2O_3. Raw data (diamagnetic background not subtracted) are presented for (a) as-grown and (b) as-implanted ZnO nanotips.

The coercive and the remanent fields for the measurements shown in Fig. 1 are detailed in Table 1. For these data, the linear diamagnetic influences were removed before determination of the coercive and the remanent fields. The values, especially from the 300-K measurement, taken

Table 1. Coercive (H_c) and remanent (B_R) fields at 5 and 300 K for various annealing conditions in Fe-implanted ZnO nanotips grown on c-Al_2O_3. Coercive fields given are averages of the positive- and the negative-going zero magnetization crossings. Remanent fields are reported as percentages of the saturation magnetization (M_S), which also varies with the annealing temperature.

Annealing Conditions		Coercive Fields (O_e)		Remanent Fields (% of M_S)	
Temp (C)	Time (min)	5 K	300 K	5 K	300 K
675	20	98	187	12	14
700	5	94	170	10	13
700	20	317	209	19	12
725	10	230		14	

from the sample annealed at 725 °C are anomalous due to their virtually non-magnetic hysteresis characteristics. The fact that the hysteresis loop lies almost flat along the x axis means that a measurement along the zero magnetization line will have a long distance inside the hysteresis loop. Thus, these data were not included in Table 1. According to the strength of the coercive field (H_c), the sample annealed at 700 °C for 20 min shows the strongest ferromagnetic behavior. This sample also displays the greatest remanent field (B_R) at 5 K. For this sample, the data presented in Fig. 1(c) and Table 1 shows an H_c width of 317 Oe at 5 K and 209 Oe at 300 K and the B_R values are 19% and 12%, respectively, as a fraction of M_S values at both 5 and 300 K. Expressed in terms of the Bohr magneton (μ_B), the M_S values for the sample annealed at 700 °C for 20 min are 0.56 and 0.18 μ_B per Fe atom when measured at 5 and 300 K, respectively. The calculated value of the effective magneton number for Fe^{2+} is 5.4 μ_B [11]. The results from variable field measurements point to annealing at 700 °C for 20 min as the best annealing condition. The fact that this sample alone demonstrates magnetic properties favorable for DMS fabrication suggests that a longer annealing time may be necessary to activate Fe implanted into ZnO nanotips on c-Al_2O_3.

Figure 2 shows the magnetic measurements of Fe-implanted ZnO nanotips as a function of the sample temperature under both FC and ZFC conditions. A probing field of 500 Oe was used during both measurements and during field cooling. For all samples implanted with Fe, the low temperature FC and ZFC magnetization tracks upward together, which is generally an indicator of ferromagnetism. However, the strength of ferromagnetism is generally indicated by the magnitude of the difference between the FC and ZFC magnetizations. For the as-grown sample, the separation between the FC and the ZFC magnetization curves increases with decreasing the sample temperature, where the FC magnetization increases steadily and the ZFC magnetization remains constant as the sample temperature decreases. The as-implanted sample shows clear FC-ZFC magnetization separation in the temperature-dependent measurements shown in Fig. 2(b). The sample annealed at 700 °C for 5 min shows almost no separation between the FC and the ZFC magnetization curves as seen in Fig. 2(c). The samples annealed at 675 °C for 20 min and 725 °C for 10 min also show the small FC-ZFC difference (less than for the as-implanted sample), indicating that they are paramagnetic (not shown here). The strongest ferromagnetism is present in the sample annealed at 700 °C for 20 min, which shows the largest FC-ZFC separation.

The Mn-implanted ZnO nanotips grown on quartz were annealed at temperatures between 675 and 800 °C for 10-20 min. The results of variable magnetic field measurements performed at both 5 and 300 K are shown in Fig. 3(a) and 3(b) for the Mn-implanted ZnO nanotips annealed at 675 and 750 °C, respectively. The data shown here have removed the linear diamagnetic influences arising from the substrate. The sample annealed at 675 °C for 20 min shows H_c values of ~150 Oe at both 5 and 300 K and B_R values of ~10% of M_S at both 5 and 300 K. The greatest coercive field width is obtained for the sample annealed at 750 °C for 10 min, showing H_c values of 344 and 267 Oe at 5 and 300 K, respectively. The value of M_S for the sample annealed at 750 °C is ~1.1 μ_B per Mn atom measured at both 5 and 300 K. The calculated maximum magnetic moment per Mn^{2+} is 5.9 μ_B [11]. The values of B_R for the sample annealed at 750 °C, as a percentage of M_S, are ~27% at both 5 and 300 K.

Figure 3(c) and 3(d) show the temperature-dependent magnetization measurements taken from the Mn-implant-

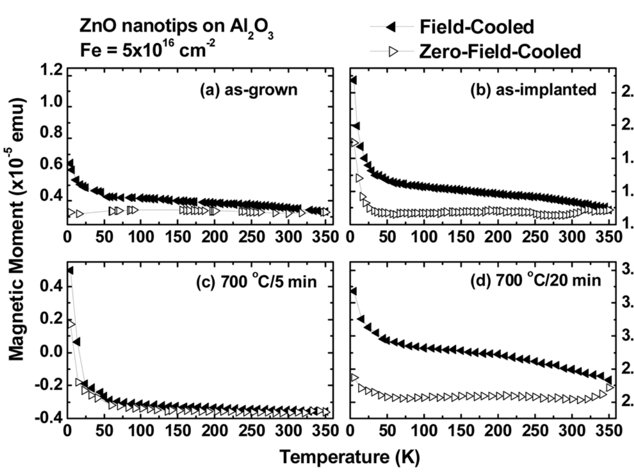

Fig. 2. Temperature-dependent magnetization measurements on Fe-implanted ZnO nanotip samples grown on c-Al_2O_3.

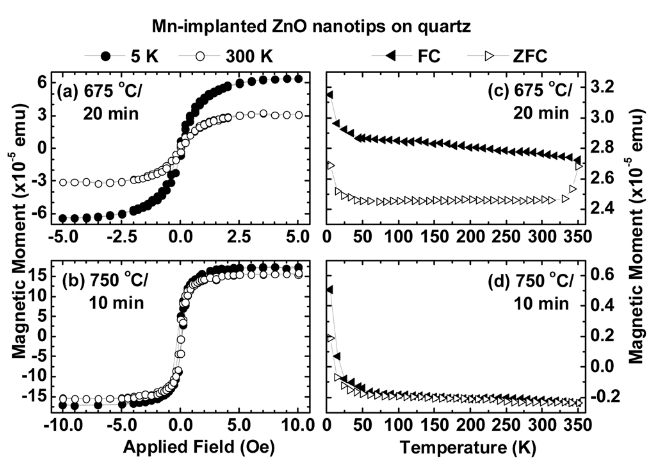

Fig. 3. Magnetic hysteresis and temperature-dependent magnetization measurements for Mn-implanted ZnO nanotips grown on quartz.

ed ZnO nanotips annealed at 675 and 750 °C, respectively, under both FC and ZFC conditions. Variable temperature SQUID measurements reveal the absence of spin-glass phase in all of the Mn-implanted ZnO nanotips grown on quartz. The sample annealed at 750 °C shows the lack of ferromagnetism indicated by the gap between the FC and the ZFC magnetization being smaller than even the gap in the as-implanted sample (not shown) in spite of the strong evidence of ferromagnetism in variable field measurements (highest H_c and B_R). The greatest separation between the FC and the ZFC magnetization occurs in the sample annealed at 675 °C for 20 min as shown in Fig. 3(c). Despite weaker signs of ferromagnetism in variable field measurements, the temperature-dependent magnetization and photoluminescence (not shown) show that the sample annealed at 675 °C for 20 min causes the implanted Mn to be well-incorporated into the ZnO crystal lattice.

4. Conclusions

Magnetic characterization studies have been conducted using a SQUID magnetometer on MOCVD-grown ZnO nanotip samples implanted with 200 keV Fe or Mn ions at room temperature to a dose level of 5×10^{16} cm^{-2} and annealed at various conditions in an oxygen flow. The ferromagnetic properties of ZnO nanotips were found to depend upon the annealing temperature and annealing time. The Mn-implanted ZnO nanotips grown on c-Al_2O_3 (not shown) showed superparamagnetism resulting from the dominance of a spin-glass phase across the range of annealing conditions. The Mn-implanted ZnO nanotips grown on quartz showed sings of ferromagnetism in variable field measurements with H_cs of 344 Oe (5 K) and 267 Oe (300 K) and B_Rs of ~27% of M_S at both 5 and 300 K. Unfortunately, in both Fe- and Mn-implanted ZnO grown on quartz, the temperature-dependent magnetization measurements do not confirm the findings of the variable field measurements.

One of the most promising materials found in this research is ZnO nanotips grown on c-Al_2O_3, doped with Fe, and annealed at 700 °C for 20 min. This sample showed a coercive field of 317 Oe at 5 K and 209 Oe at 300 K. The remanent fields in this sample are 19% and 12% of M_S measured at 5 and 300 K, respectively. Annealing 700 °C for 20 min also produced the greatest separation and low-temperature tracking in temperature-dependent measurements on Fe-implanted ZnO nanotips grown on c-Al_2O_3. ZnO nanotips will continue to play a role in DMS research because of their ease of growth, uniformity of implanted dopant concentration, and potential application in devices where electrical isolation is desired in a DMS.

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