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Crystalline Ni nanoparticles as the origin of ferromagnetism in Ni implanted ZnO crystals

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We report the structural and magnetic properties of ZnO single crystals implanted at 623 K with up to 10 at. % of Ni. As revealed by x-ray diffraction, crystalline fcc-Ni nanoparticles were formed inside ZnO. The magnetic behavior (magnetization with field reversal and with different temperature protocols) of all samples is well explained by a magnetic Ni-nanoparticle system. Although the formation of Ni:ZnO based diluted magnetic semiconductor cannot be ruled out, the major contribution to the magnetic properties stems from crystalline nanoparticles synthesized under these implantation conditions. © 2006 American Institute of Physics.
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I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have recently attracted huge research attention because of their potential application for spintronic devices.^{1,2} In DMS materials, transition or rare earth metal ions are substituted onto cation sites and are coupled with free carriers to yield ferromagnetism via indirect interaction.^{3,4} ZnO based DMS is particularly interesting since the room temperature ferromagnetism was reported for various dopants.^{3–7} However, the interpretation of the observed ferromagnetism is still controversial.^{8–11} A secondary phase (metal or compound nanoparticles) induced by magnetic doping can be responsible for the measured ferromagnetism as reported in Mn:ZnO,¹² Co:ZnO,^{13–15} and Co:TiO₂.¹⁶ Recently ferromagnetism was reported in Ni doped ZnO (Refs. 5 and 17–19) and TiO₂,²⁰ where, however, a careful characterization of structural (e.g., highly sensitive method) and magnetic characteristics (e.g., temperature dependent magnetization) was only partly performed. In contrast, Cho *et al.*, questioned the origin of the ferromagnetism in Ni doped TiO₂ by compositional analysis and transport measurements,²¹ while Zhu *et al.* reported Ni-nanoparticle formation in rutile TiO₂.²² In the present paper, we attempt to clarify the ferromagnetism in Ni implanted ZnO. X-ray diffraction (XRD) and zero field cooled magnetization/field cooled magnetization (ZFCM/FCM) were used to investigate the structural and magnetic properties.

II. EXPERIMENT

Hydrothermally grown ZnO single crystals from Crys-tec, Berlin were implanted with Ni ions at 623 K and with different fluences of 0.8×10^{16} , 4×10^{16} , and 8×10^{16} cm⁻², respectively. The implantation energy of 180 keV yielded a projected range of $R_p = 80 \pm 34$ nm and maximum atomic concentrations of 1%, 5%, and 10%, respectively (SRIM code²³). Virgin and implanted samples were investigated us-

ing Rutherford backscattering spectroscopy/channeling (RBS/C) spectrometry XRD, and superconducting quantum interference device (SQUID) [Quantum Design magnetic property measurement system (MPMS)] magnetometry. By SQUID, the virgin ZnO is found to be purely diamagnetic with a susceptibility of -1.48×10^{-6} emu/Oe cm³. That background has been subtracted in the following discussion. XRD was performed with a Siemens D5000 diffractometer using Cu $K\alpha$ radiation. The monochromator was removed to obtain higher x-ray intensity, which is required to detect a small amount of secondary phases. The RBS spectra were collected with a collimated 1.7 MeV He⁺ beam at a Van de Graaff accelerator with a surface barrier detector at 170°.

III. RESULTS AND DISCUSSION

RBS/C is used to check the lattice damage after implantation. Figure 1 shows RBS/C spectra for different fluences. The arrow labeled Zn indicates the energy for backscattering from surface Zn atoms. The implanted Ni ions cannot be

FIG. 1. (Color online) RBS random (ran.) and channeling (ch.) spectra for different samples (Ni fluence is indicated).

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TABLE I. Structural and magnetic properties for Ni implanted ZnO with different Ni fluences. Metallic Ni fraction corresponds to the percentage of crystalline Ni compared with all implanted Ni.

Fluence (10^{16} cm^{-2})	$\chi_{\min}$ (RBS/C) (%)	Crystallite size (nm)	Saturation moment at 10 K (μ_B/Ni)	Metallic Ni fraction (%)	Coercivity at 10 K (Oe)	$T_{\max}$ (ZFCM measured) (K)
0.8	45	...	0.05	8	10	≤ 5
4	57	5.8	0.16	27	30	16
8	69	8.0	0.22	37	120	44

detected for the very low fluence ($0.8 \times 10^{16} \text{ cm}^{-2}$, not shown); they are, however, more pronounced as a hump in the random spectrum for higher fluences of 4×10^{16} and $8 \times 10^{16} \text{ cm}^{-2}$ (not shown). The channeling spectra were collected by aligning the sample to make the impinging He^+ beam parallel with the $\text{ZnO}\langle 0001 \rangle$ axis. $\chi_{\min}$ is the channeling minimum yield in RBS/C, which is the ratio of the backscattering yield at channeling condition to that for a random beam incidence.²⁴ Therefore, the $\chi_{\min}$ labels the lattice disordering degree upon implantation, i.e., an amorphous sample shows a $\chi_{\min}$ of 100%, while a perfect single crystal corresponds to a $\chi_{\min}$ of 1%–2%. The humps in the channeling spectra mainly come from the lattice disordering due to implantation. The $\chi_{\min}$ (see Table I) increases with increasing fluence and quantitatively confirms the applied fluence. RBS/C measurement also revealed that the ZnO host material still partly remained in a crystalline state after irradiation by Ni ions up to a fluence of $8 \times 10^{16} \text{ cm}^{-2}$ ($\chi_{\min}$ of 69%).

By XRD, crystalline fcc-Ni nanoparticles were detected. Figure 2 shows the XRD patterns [focused on the Ni(111) peak] for all samples. At a low fluence ($0.8 \times 10^{16} \text{ cm}^{-2}$), no evident crystalline Ni nanoparticles could be detected due to their small grain size, while from a fluence of $4 \times 10^{16} \text{ cm}^{-2}$ the Ni(111) peak appeared and grew with the fluence. The inset shows a wide range scan for the highest fluence sample ($8 \times 10^{16} \text{ cm}^{-2}$). Ni nanoparticles were epi-

taxially embedded into the ZnO matrix with an orientation of $\text{Ni}(111)\parallel\text{ZnO}(0001)$, and no NiO particle was detected. The full width at half maximum (FWHM) of the Ni(111) peak decreased with fluence, indicating growing of the average diameter for these nanoparticles (Table I). The crystallite size is calculated using the Scherrer formula.²⁵

Magnetic properties were investigated using a SQUID magnetometer. Figure 3(a) shows the magnetization versus field reversal (M - H) of all samples measured at 10 K. Hysteretic behavior was observed for all three samples. The saturation moment and the coercivity increase with increasing fluence (Table I). Saturation behavior is also observed at 300 K for the sample with the highest fluence [Fig. 3(a) inset]. However, neither coercivity nor remanence can be ob-

FIG. 2. (Color online) XRD patterns of Ni(111) in Ni implanted ZnO crystals with different fluences. Inset shows the wide range XRD pattern for the highest fluence sample where Ni(111) parallel with ZnO(0002) is detected and no NiO is detectable, and those sharp peaks are from ZnO due to Cu $K\alpha_2$ or tungsten emission.

FIG. 3. (Color online) (a) M - H curves measured at 10 K for all samples with different Ni fluences. Inset shows the M - H curve measured at 300 K for the highest fluence sample. (b) Temperature dependent coercivity and remanence for the highest fluence sample.

FIG. 4. (Color online) ZFCM/FCM curves at 50 Oe for different fluence samples. Solid symbols are ZFCM curves, while open symbols are FCM curves. Inset shows a zoom of the low temperature part of the ZFCM/FCM for the fluence of $0.8 \times 10^{16} \text{ cm}^{-2}$, which reveals the same behavior as the higher fluence sample, but with a $T_{\text{max}} \leq 5 \text{ K}$.

served at 300 K. The temperature dependence of the coercivity and the remanence is shown in Fig. 3(b). Both values decrease drastically with increasing temperature. This is a strong indication of the superparamagnetism of a magnetic nanoparticle system. Knowing the formation of fcc-Ni from XRD, it is reasonable to assume that fcc-Ni nanoparticles are responsible for the magnetic behavior. For bulk Ni crystal (Curie temperature of $\sim 630 \text{ K}$), the magnetic moment is $0.6 \mu_B/\text{Ni}$ at 0 K. If assuming the same value for Ni nanoparticles, around 27% of implanted Ni ions are in the metallic state using the saturation moment at 10 K for the fluence of $4 \times 10^{16} \text{ cm}^{-2}$ (Table I). This fraction is much higher than that of Fe implanted ZnO, where only 13% of implanted Fe ions formed bcc-Fe nanoparticles at the same fluence and implantation energy.¹¹

In a solid matrix, the magnetic behavior for a single particle follows the Néel process.^{26,27} At high temperature, the system shows superparamagnetic behavior (Fig. 3), while at low temperature, the system exhibits a slow relaxation, which can be confirmed by ZFCM/FCM measurement using a small field. Figure 4 shows the ZFCM/FCM curves in a 50 Oe field for all samples. In order to obtain these curves, the sample was cooled in zero field from above room temperature to 5 K. Then a 50 Oe field was applied, the ZFC curve was measured with increasing temperature from 5 to 300 K, after which the FC curve was measured in the same field from 300 to 5 K with decreasing the temperature. After subtracting the diamagnetic background from the substrate, a distinct difference in ZFC/FC curves was observed. ZFC curves show a gradual increase (deblocking) at low temperature and reach a maximum at a temperature of T_{max} (for the sample with the lowest fluence of $0.8 \times 10^{16} \text{ cm}^{-2}$, T_{max} is around or below 5 K), while FC curves continue to increase with decreasing temperature. At a much higher temperature than T_{max} , the FC curves still depart from corresponding ZFC curves, which distinguish the Ni particle system from a conventional spin-glass system where the FC curve merges together with the ZFC curve just at T_{max} and

shows a plateau below T_{max} .²⁸ The ZFC/FC curves are general characteristics of magnetic nanoparticle systems.^{26–28} For a dc magnetization measurement in a small magnetic field by SQUID, the blocking temperature is given by $T_B(V) \sim K_{\text{eff}}V/k_B$, where K_{eff} is the anisotropy energy density, V is the particle volume, and k_B is the Boltzmann constant. The T_{max} is a measure of the blocking temperature of the nanoparticle system,²⁷ and increases with the fluence, i.e., the size of nanoparticles (Table I). Indeed, it is rather difficult to calculate T_B for a practical magnetic nanoparticle system. Due to size effects, K_{eff} is different from bulk crystals and depends on the size of nanoparticles.²⁶ An inevitable size distribution of nanoparticles consequently gives rise to a distribution of K_{eff} and T_B .^{27,29} The dipolar interaction between nanoparticles can enhance the blocking temperature and even induce hysteretic behavior up to room temperature.³⁰

IV. CONCLUSION

To summarize, ferromagnetism was observed in Ni implanted ZnO crystals. However, the magnetic behavior is well explained in the frame of a magnetic nanoparticle system. Crystalline fcc-Ni nanoparticles were detected by XRD. Although the formation of Ni:ZnO based DMS by ion implantation at 623 K cannot be completely ruled out, the main contribution to the ferromagnetic properties arises from these small Ni nanoparticles. This is, however, in a sharp contrast with other ZnO based DMS reports.^{5–7} We have demonstrated that combining structural analysis and ZFCM/FCM measurement is a reliable approach to clarify the origin of ferromagnetism in transition metal doped ZnO.

- ¹H. Ohno, *Science* **281**, 951 (1998).
- ²I. Žutić, J. Fabian, and S. Das Sarma, *Rev. Mod. Phys.* **76**, 323 (2004).
- ³T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).
- ⁴K. Sato and H. K. Yoshida, *Jpn. J. Appl. Phys., Part 2* **40**, L334 (2001).
- ⁵M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, *Phys. Rev. Lett.* **93**, 177206 (2004).
- ⁶M. H. F. Sluiter, Y. Kawazoe, P. Sharma, A. Inoue, A. R. Raju, C. Rout, and U. V. Waghmare, *Phys. Rev. Lett.* **94**, 187204 (2005).
- ⁷P. Sati *et al.*, *Phys. Rev. Lett.* **96**, 017203 (2006).
- ⁸K. Ueda, H. Tabata, and T. Kawai, *Appl. Phys. Lett.* **79**, 988 (2001).
- ⁹H. J. Lee, S. Y. Jeong, C. R. Cho, and C. H. Park, *Appl. Phys. Lett.* **81**, 4020 (2002).
- ¹⁰J. H. Shim, T. Hwang, S. Lee, J. H. Park, S.-J. Han, and Y. H. Jeong, *Appl. Phys. Lett.* **86**, 082503 (2005).
- ¹¹K. Potzger *et al.*, *Appl. Phys. Lett.* **88**, 052508 (2006).
- ¹²S.-J. Han, T.-H. Jang, Y. B. Kim, B.-G. Park, J.-H. Park, and Y. H. Jeong, *Appl. Phys. Lett.* **83**, 920 (2003).
- ¹³D. P. Norton *et al.*, *Appl. Phys. Lett.* **83**, 5488 (2003).
- ¹⁴J. H. Park, M. G. Kim, H. M. Jang, S. Ryu, and Y. M. Kim, *Appl. Phys. Lett.* **84**, 1338 (2004).
- ¹⁵J. C. A. Huang, H. S. Hsu, Y. M. Hu, C. H. Lee, Y. H. Huang, and M. Z. Lin, *Appl. Phys. Lett.* **85**, 3815 (2004).
- ¹⁶S. R. Shinde *et al.*, *Phys. Rev. Lett.* **92**, 166601 (2004).
- ¹⁷T. Wakano, N. Fujimura, Y. Morinaga, N. Abe, A. Ashida, and T. Ito, *Physica E (Amsterdam)* **10**, 260 (2001).
- ¹⁸X. Liu, F. Lin, L. Sun, W. Cheng, X. Ma, and W. Shi, *Appl. Phys. Lett.* **88**, 062508 (2006).
- ¹⁹J. B. Cui and U. J. Gibson, *Appl. Phys. Lett.* **87**, 133108 (2005).
- ²⁰N. H. Hong *et al.*, W. Prellier, J. Sakai, and A. Hassini, *Appl. Phys. Lett.* **84**, 2850 (2004).
- ²¹J. H. Cho *et al.*, *Appl. Phys. Lett.* **88**, 092505 (2006).
- ²²S. Zhu, L. M. Wang, X. T. Zu, and X. Xiang, *Appl. Phys. Lett.* **88**, 043107

- (2006).
- ²³J. Ziegler, J. Biersack, and U. Littmark, *The Stopping and Range of Ions in Matter* (Pergamon, New York, 1985); SRIM 2000 code (www.srim.org).
- ²⁴W. K. Chu, J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).
- ²⁵B. D. Cullity, *Elements of X-Ray Diffractions* (Addison-Wesley, Reading, MA, 1978), p. 102.
- ²⁶M. Respaud *et al.*, Phys. Rev. B **57**, 2925 (1998).
- ²⁷M. Farle, Magnetism goes Nano, Proceedings of the 36th IFF Spring School—Juelich, Germany, 2005, Paper No. C4.2.
- ²⁸Y. Sun, M. B. Salamon, K. Garnier, and R. S. Averback, Phys. Rev. Lett. **91**, 167206 (2003).
- ²⁹L. G. Jacobsohn, M. F. Hundley, J. D. Thompson, R. M. Dickerson, and M. Nastasi, J. Vac. Sci. Technol. B **24**, 321 (2006).
- ³⁰Y. Xin, J. Lu, P. A. Stampe, and R. J. Kennedy, Appl. Phys. Lett. **88**, 112512 (2006).