Crystallographically oriented magnetic ZnFe$_2$O$_4$ nanoparticles synthesized by Fe implantation into ZnO

Shengqiang Zhou, K Potzger, H Reuther, G Talut, F Eichhorn, J von Borany, W Skorupa, M Helm and J Fassbender

Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, PO Box 510119, 01314 Dresden, Germany

Received 10 November 2006, in final form 11 December 2006
Published 2 February 2007

Abstract

In this paper, a correlation between structural and magnetic properties of Fe-implanted ZnO is presented. High fluence Fe$^+$ implantation into ZnO leads to the formation of superparamagnetic $\alpha$-Fe nanoparticles. High vacuum annealing at 823 K results in the growth of $\alpha$-Fe particles, but the annealing at 1073 K oxidizes the majority of the Fe nanoparticles. After a long term annealing at 1073 K, crystallographically oriented ZnFe$_2$O$_4$ nanoparticles are formed inside ZnO with the orientation relationship of ZnFe$_2$O$_4$(1 1 1)[1 1 0]//ZnO(0 0 0 1)[1 1 2]. These ZnFe$_2$O$_4$ nanoparticles show a hysteretic behaviour upon magnetization reversal at 5 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diluted magnetic semiconductors (DMS) have recently attracted huge research attention because of their potential application for spintronics devices [1, 2]. In DMS materials, transition or rare earth metal ions are substituted onto host cation sites and are coupled with free carriers to yield ferromagnetism via indirect interaction [3, 4]. ZnO doped with Fe was found to be ferromagnetic at room temperature [5–8]. However, the origin of the observed ferromagnetism in transition metal doped ZnO is still controversial, e.g. ferromagnetic clusters [9–12], or extrinsic reasons [13, 14] are discussed. Moreover superparamagnetic Co and Ni nanoclusters are formed by ion implantation into ZnO [15, 16] and TiO$_2$ [17, 18], respectively. To clarify the origin of the observed ferromagnetism, a careful correlation between structure and magnetism should be established by sophisticated characterization methods. Synchrotron radiation based x-ray diffraction (SR-XRD) is a powerful tool to detect small precipitates, while element selective measurement of the magnetic properties is desired, e.g. using conversion electron Mössbauer spectroscopy (CEMS). In this paper, employing the above-mentioned methods together with superconducting quantum interference device (SQUID) magnetometry, we report investigations on the evolution of structural and magnetic properties of Fe-implanted ZnO upon high vacuum annealing. Moreover the possibility to form crystallographically oriented Zn-ferrite embedded in ZnO is demonstrated. With respect to the crystal symmetry and lattice mismatch, our results suggest that other ferrites, which have been epitaxially grown onto MgO, SrTiO$_3$ and Y$_{0.15}$Zr$_{0.85}$O$_2$, and exhibit rich magnetic properties [19], could also be embedded inside single crystalline ZnO.

2. Experiments

Hydrothermally grown, commercially available ZnO single crystals were implanted with a $^{57}$Fe fluence of $4 \times 10^{16}$ cm$^{-2}$ at 623 K. The implantation energy of 180 keV yielded a projected range of $R_p = 83 \pm 35$ nm (TRIM code). The post-implantation thermal annealing was performed in a high vacuum ($p < 10^{-7}$ mbar) furnace from 823 to 1073 K for either 15 min or 3.5 h. Virgin and implanted samples were investigated using Rutherford backscattering/channeelling spectrometry (RBS/C), SR-XRD with an x-ray wavelength of 0.154 nm at Rossendorf beamline (ROBL) at the ESRF, SQUID (Quantum Design MPMS) magnetometry, room temperature CEMS and scanning electron microscopy (SEM).
3. Results and discussion

3.1. Secondary phase evolution

Figure 1(a) shows the SR-XRD patterns for the as-implanted and annealed samples. For the as-implanted sample, crystalline α-Fe nanoparticles were observed, and no other crystalline Fe-oxide (Fe₂O₃, Fe₃O₄ and ZnFe₂O₄) particles were detected. The crystallite size is calculated using the Scherrer formula [20]. The peak amplitude and crystallite size are compared in table 1. After 823 K and 15 min annealing, larger and more Fe nanoparticles are formed reflected by an increase and the sharpening of the corresponding peak at 44.4° in the 2θ-θ scan (figure 1(a)). After 1073 K and 15 min annealing, the Fe(1 1 0) peak almost disappeared and the sample already shows an indication of the presence of crystalline ZnFe₂O₄. After 3.5 h annealing at 1073 K, crystalline and oriented ZnFe₂O₄ particles are clearly identified. The inset shows a zoom of the Fe(1 1 0) peak to show the development of Fe nanoparticles more clearly.

3.2. Magnetism evolution

Figure 1(b) shows the magnetization versus field reversal (M–H) at 5 K. Magnetic hysteretic loops are observed for the as-implanted sample, which contains α-Fe nanoparticles. After annealing at 823 K for 15 min, the ferromagnetism is enhanced, i.e. Fe nanoparticles grow in size and amount. However, after annealing at 1073 K for 15 min, no hysteresis loop is observed. Probably the majority of Fe particles were oxidized to some amorphous nonmagnetic compound. The magnetism evolution is in good agreement with the XRD measurement. After annealing at 1073 K for 3.5 h, the hysteretic behaviour is observed again, which—according to the SR-XRD—cannot originate from metallic Fe but from ZnFe₂O₄ nanoparticles. Bulk ZnFe₂O₄ exhibiting normal spinel structure is a weak antiferromagnet with a Neél-temperature of 10.5 K [21], while epitaxial ZnFe₂O₄ thin films exhibit a higher Neél-temperature of 43 K [22]. However, recent experiments reveal that nanocrystalline ZnFe₂O₄ shows ferrimagnetic behaviour [23–31]. The explanation for such behaviour is the partial inversion of the spinel structure, i.e. the additional occupation of tetrahedral A sites by Fe and octahedral B sites by Zn leading to a strong superexchange coupling of the intra-sublattice Fe ions. Therefore, the ZnFe₂O₄ nanoparticles (see figure 1(a)) are responsible for the hysteretic behaviour upon magnetization reversal observed for the long term annealed sample.

In order to confirm the superparamagnetic properties of the embedded nanoparticles, zero-field cooled (ZFC) and field cooled (FC) magnetization versus temperature measurements were performed using SQUID. Figure 1(c) shows the ZFC/FC magnetization curves in a 5 mT field. For all samples, although there is a difference in magnetic moment, ZFC curves show a gradual increase (debloking) at low temperatures, and reach a plateau at a particular temperature of Tₘₐₓ, while all FC curves continue to increase with decreasing temperature. The shape of the ZFC/FC curves are general characteristics of magnetic nanoparticle systems [32], i.e. magnetic nanoparticles are the origin of the ferromagnetism in all the samples. The increase of Tₘₐₓ after annealing at 823 K for 15 min confirms the growth of α-Fe nanoparticles. After annealing at 1073 K for 3.5 h, ZnFe₂O₄ crystallites with an average grain size of 20 nm were formed. However the degree of inversion (transition from Fe³⁺ to Fe²⁺) is decreased with increasing crystallites [30], therefore comparing with the grain size of 6.6 nm and 14.8 nm in [30], the rather bigger grain size of ZnFe₂O₄ crystallites (20 nm) results in a small magnetic moment and a low Tₘₐₓ. Also the effective anisotropy constant of ZnFe₂O₄ is lower than that of α-Fe [29], which could explain the lower Tₘₐₓ than that of Fe nanoparticles [32]. The magnetic and structural properties were compared in table 1.

Figure 1. (a) SR-XRD patterns (2θ-θ scans) of Fe-implanted ZnO reveal the second phase development (from α-Fe to ZnFe₂O₄) upon annealing. (b) Magnetization versus field reversal revealing the magnetism evolution upon annealing and (c) ZFC/FC magnetization curves at 5 mT, which exhibit a typical characteristic of a magnetic nanoparticle system.
Table 1. Structure and magnetism evolution of Fe-implanted ZnO upon annealing.

| Annealing | Peak area of Fe(1 1 0) and crystallite size (nm) | Peak area of ZnFe₂O₄(3 3 3) and crystallite size (nm) | Saturation moment at 5 K (μB/Fe) | T₉₀₀ (ZFC at 5 mT) | X₉₀₀ (RBS/C) (%) |
|-----------|------------------------------------------------|-------------------------------------------------|-------------------------------|-------------------|-----------------|
| As-implanted | 487/7.1 | — | 0.24 | 146 (Fe) | 63 |
| 823 K, 15 min | 837/9.4 | — | 0.34 | 200 (Fe) | 57 |
| 1073 K, 15 min | — | — | — | — | 43 |
| 1073 K, 3.5 h | — | 462/20 | 0.14 | 23 (ZnFe₂O₄) | 29 |

3.3. Crystallographically oriented ZnFe₂O₄

In figure 1(a), the XRD pattern for the sample after 3.5 h annealing at 1073 K shows only three peaks of ZnFe₂O₄ (2 2 2) (3 3 3) and (4 4 4), which means that the crystallites of ZnFe₂O₄ are highly oriented with respect to the host matrix. The surface orientation is ZnFe₂O₄(1 1 1)/ZnO(0 0 0 1). The crystallographical orientation of ZnFe₂O₄ was revealed by the XRD pole figure. Figure 3 shows the pole figure for ZnFe₂O₄(3 1 1). The radial coordinate is the angle (χ) by which the surface is tilted out of the diffraction plane from 20° to 70°. The azimuthal coordinate (Φ) is the angle of rotation about the surface normal. The pole figure shows poles of ZnFe₂O₄(3 1 1) at χ ~ 29.5° and 58.5°, respectively, with sixfold symmetry. Since ZnO(0 0 1) (2θ = 36.25°) has a close Bragg angle with ZnFe₂O₄(3 1 1) (2θ = 35.27°), the poles of ZnO(1 0 1) also show up at χ ~ 61.6° with much more intensities. The result is consistent with the theoretical ZnFe₂O₄(3 1 1) pole figure viewed along [1 1 1] with rotation twins. The in-plane orientation relationship is ZnFe₂O₄[1 1 0]/ZnO[1 1 0]. Moreover, a 2θ–θ scan was carried out for ZnFe₂O₄(3 1 1)(6 2 2) and (2 2 0)(4 4 4), respectively, by tilting the sample with an angle of χ at an azimuthal position found by pole figure. The results are shown in figure 4, and confirm the crystallographical orientation of ZnFe₂O₄. The coherence length of crystallites is around 20 nm in the out-of-plane direction (table 1). The in-plane coherence length is evaluated to be also as large as 20 nm by measuring the diffraction of (3 1 1) at χ ~ 80°, nearly parallel with the surface [33]. Due to the fcc structure of ZnFe₂O₄ (α = 0.844 nm), it is not difficult to understand its crystallographical orientation onto hcp-ZnO (α = 0.325 nm) with twin crystallites of ZnFe₂O₄ of an in-plane rotation by 60° (figure 5). The lattice mismatch between ZnFe₂O₄ and ZnO is ~6%.

The orientation of ZnFe₂O₄ is also indirectly evidenced by RBS/channelling. The channelling spectra were collected by aligning the sample to make the impinged He⁺ beam parallel with the ZnO(0 0 0 1) axis. X₉₀₀ is the channelling minimum yield in RBS/C, which is the ratio of the backscattering yield at channelling condition to that for a random beam incidence [34]. Therefore, the X₉₀₀ labels the lattice disordering degree, and an amorphous sample shows a X₉₀₀ of 100%, while a perfect single crystal corresponds to a X₉₀₀ of 1–2%. Figure 6 shows the representative RBS/C spectra for different annealing
ZnFe$_2$O$_4$ nanoparticles synthesized by Fe implantation into ZnO

Table 2. Hyperfine parameters measured using CEMS for samples after different annealing treatment.

| Annealing temperature and time | Fe$^{3+}$ | Fe$^{2+}$ | Fe$^0$ |
|-------------------------------|----------|----------|--------|
|                              | FR (%)   | IS (mm s$^{-1}$) | QS (mm s$^{-1}$) | FR (%) | IS (mm s$^{-1}$) | QS (mm s$^{-1}$) | FR (%) | IS (mm s$^{-1}$) | QS (mm s$^{-1}$) |
| As impl. at 623 K             | 32.8     | 0.96     | 0.58   | 23.2   | 0.96   | 0.58   | 12.5   | 0.06  | 30.5   |
| 823 K/15 min                  | 42.6     | 0.53     | 0      | 31.5   | 0.78   | 1.29   | 18.2   | 0.07  | 31.7   |
| 1023 K/15 min                 | 26.3     | 0.56     | 0      | 16.7   | 0.68   | 1.52   | 11.2   | 0.07  | 20.5   |
| 1023 K/3.5 h                  | 62.4     | 0.37     | 0.95   | 22.5   | 0.94   | 0.54   | 12.5   | 0.06  | 30.5   |

a Fraction.
b Isomer shift.
c Quadrupole splitting.
d Magnetic hyperfine field.

Figure 3. Pole figure of ZnFe$_2$O$_4$(5 1 1) reveals the crystallographical orientation of ZnFe$_2$O$_4$ and its twin crystallites.

Figure 4. 2θ–θ scans of ZnFe$_2$O$_4$(3 1 1)(6 2 2) and (2 2 0)(4 4 0).

procedures. The humps in the channelling spectra mainly come from the randomly located Fe and the lattice disordering due to implantation. $\chi_{\text{min}}$ is drastically decreased after annealing at 1073 K for 3.5 h (table 1), which suggests the partial recovering of lattice damage, and the formation of an oriented secondary phase by thermal annealing [35]. In our case, the (111) axis of ZnFe$_2$O$_4$ is parallel to the ZnO(000 1) axis, the direction of the impinging He$^+$ beam, which reduces the backscattering yield.

Additionally SEM was performed to check the sample morphology. Figures 7(a) and (b) show the SEM results for the as-implanted and the annealed samples. After the annealing, the morphology was pronouncedly changed. Some

![Figure 5. Schematics for the crystallographical orientation of ZnFe$_2$O$_4$ onto ZnO.](image)

![Figure 6. Representative RBS/channelling spectra with different annealing procedures.](image)
Generally, spinel ferrites \((MFe_2O_4, M = Ni, Co, Fe, Mn, Zn)\) have a large variety of magnetic properties and have significant potential application in millimetre wave integrated circuitry and magnetic recording [19]. They all have an fcc structure with the lattice constant \(a\) of around 0.84 nm and exhibit different magnetic properties depending on the chemical composition and cation site occupancy [36]. In view of lattice mismatch, our results could suggest the epitaxy of spinel ferrites onto ZnO, and even a multilayered \(MFe_2O_4/ZnO\) structure given the growth method compatibility by pulsed laser deposition or molecular beam epitaxy for both the materials [19,37]. The magneto-transport properties of inverted \(ZnFe_2O_4\) nanoparticles have recently been investigated. Ponpandian and Narayanasamy discussed a hopping mechanism between \(Fe^{3+}\) and \(Fe^{2+}\) pairs present at the octahedral sites [38]. In [23], Shinagawa et al reported ferromagnetic \(ZnO\)-spinel iron oxide composites prepared by wet chemical process with a negative magnetoresistance of \(-0.35\%\) at room temperature. Thus, a hybrid structure of spinel ferrites/semiconducting ZnO could be a potential candidate for spintronic devices. The crucial point about spin injection from the nanoparticles into the host material, however, is the quality of their interface. Although the high degree of crystalline orientation indirectly suggests a very sharp interface, local investigations have to be performed in order to clearly reveal the interface structure.

4. Conclusions

Magnetic and structural properties were correlated in Fe-implanted ZnO crystals and we demonstrated the possibility to form crystallographically oriented Zn-ferrite with respect to the ZnO host single crystal. In the as-implanted samples, \(\alpha\)-Fe nanoparticles were the origin of the ferromagnetism, 823 K annealing induced the growth of Fe particles, however 1023 K, 15 min annealing oxidized the main part of Fe particles. Zn-ferrite was formed after 3.5 h annealing at 1073 K with the crystalline orientation of \(ZnFe_2O_4(1\,1\,1)/(1\,1\,0)/ZnO(0\,0\,0\,1)\) [1120]. The Zn-ferrite nanoparticles were partially inverted, and a strong A–B superexchange interaction produced the ferrimagnetic coupling.

Acknowledgment

We thank Dr N Schell for technical support for SR-XRD measurements.

Reference

[1] Ohno H 1998 Science 281 951
[2] Žutić I, Fabian J and Das Sarma S 2004 Rev. Mod. Phys. 76 323
[3] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science 287 1019
[4] Sato K and Yoshida H K 2001 Japan. J. Appl. Phys. 40 L334
[5] Han S-J, Song J W, Yang C-H, Park S H, Park J-H, Jeong Y H and Rhie K W 2002 Appl. Phys. Lett. 81 4312
[6] Venkatesan M, Fitzgerald C B, Lunney J G and Coey J M D 2004 Phys. Rev. Lett. 93 177206
[7] Wu P et al 2006 Appl. Phys. Lett. 89 012508
[8] Shon Y et al 2006 Appl. Phys. Lett. 89 082505
ZnFe$_2$O$_4$ nanoparticles synthesized by Fe implantation into ZnO

[9] Shim J H, Hwang T, Lee S, Park J H, Han S-J and Jeong Y H 2005 Appl. Phys. Lett. 86 082503
[10] Huang J C A, Hsu H S, Hu Y M, Lee C H, Huang Y H and Lin M Z 2004 Appl. Phys. Lett. 85 3815
[11] Potzger K et al 2006 Appl. Phys. Lett. 88 052508
[12] Park J H, Kim M G, Jang H M, Ryu S and Kim Y M 2004 Appl. Phys. Lett. 84 1338
[13] Che Mofor A et al 2005 Appl. Phys. Lett. 87 062501
[14] Abraham D W, Frank M M and Guha S 2005 Appl. Phys. Lett. 87 252502
[15] Norton D P et al 2003 Appl. Phys. Lett. 83 5488
[16] Zhou S, Potzger K, Gufei Zhang, Eichhorn F, Skorupa W, Helm M and Fassbender J 2006 J. Appl. Phys. 100 114304
[17] Wang C M, Shuttahanandan V, Thevuthasan S, Droubay T and Chambers S A 2005 J. Appl. Phys. 97 073502
[18] Zhu S, Wang L M, Zu X T and Xiang X 2006 Appl. Phys. Lett. 88 043107
[19] Suzuki Y 2001 Annu. Rev. Mater. Res. 31 265 (Review)
[20] Cullity B D 1978 Elements of X-ray Diffractions (Reading, MA: Addison-Wesley) p 102
[21] Singh D J, Gupta M and Gupta R 2001 Phys. Rev. B 63 205102
[22] Yahiro H, Tanaka H, Yamamoto Y and Kawai T 2002 Solid State Commun. 123 535
[23] Shinagawa T, Izaki M, Inui H, Murase K and Awakura Y 2006 Chem. Mater. 18 763
[24] Burghart F J et al 2000 Physica B 289–290 286
[25] Oliver S A, Hamdeh H H and Ho J C 1999 Phys. Rev. B 60 3400
[26] Zhou Z H, Wang J, Xue J M and Chan H S O 2001 Appl. Phys. Lett. 79 3167
[27] Chinnasamy C N, Narayanasamy A, Ponpandian P, Chattopadhyay K, Cuérand H and Grenèche J-M 2000 J. Phys.: Condens. Matter 12 7795
[28] Goya G F and Leite E R 2003 J. Phys.: Condens. Matter 15 641
[29] Ammar S, Jouini N, Fiévet F, Beji Z, Smiri L, Moliné P, Danot M and Grenèche J-M 2006 J. Phys.: Condens. Matter 18 9055
[30] Bohra M, Prasad S, Kumar N, Misra D S, Sahoo S C, Venkataramani N and Krishnan R 2006 Appl. Phys. Lett. 88 262506
[31] Respaud M et al 1998 Phys. Rev. B 57 2925
[32] Heinke H, Kirchner V, Einfeldt S and Hommel D 2000 Appl. Phys. Lett. 77 2145
[33] Chu W K, Mayer J W and Nicolet M A 1978 Backscattering Spectrometry (New York: Academic)
[34] Wu M F, Vantomme A, Hogg S, Pattyn H and Langouche G 1998 Appl. Phys. Lett. 72 2412
[35] Shikazumi S 1997 Physics of Ferromagnetism (Oxford: Oxford University Press) chapter 9
[36] Özgür Ü, Alivov Ya I, Liu C, Tekke A, Reshchikov M A, Dogan S, Avrutin V, Cho S-J and Morkoç H 2005 J. Appl. Phys. 98 041301 (Review)
[37] Ponpandian N and Narayanasamy A 2002 J. Appl. Phys. 92 2770