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Nanocluster formation in Co/Fe implanted ZnO

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Abstract Conversion electron Mössbauer Spectroscopy (CEMS) measurements were made on a ZnO single crystal sample implanted at room temperature (RT) with of 145 and 345 keV ^{59}Co ions with respective fluences of 1.15×10^{16} ions/cm^2 and 4.17×10^{16} ions/cm^2, followed by implantation of 60 keV ^{57}Fe to a fluence of 0.50×10^{16}/cm^2 to yield a 'box-shaped' implantation profile with a Co + Fe concentration of about 3.2 at. %. CEM spectra were collected after annealing the sample up to 973 K. The spectra after annealing up to 973 K are similar to spectra observed in other CEMS studies on Fe implanted ZnO, but show a dramatic change after the 973 K annealing step; it is dominated by a doublet component with fit parameters typical of Fe^{3+}. Magnetization curves of the sample after the 973 K anneal show hysteresis, with a small residual magnetization at RT that increases at 4 K. The saturation magnetization at 4 K was approximately 0.33 μ_B/CoFe ion, in good agreement with observations for 5–8 nm sized Co nanoclusters in ZnO.

Keywords ZnO · Co/Fe implantation · Nanoclusters

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1 Introduction

The theoretical prediction of room temperature ferromagnetism (RTFM) in p-type ZnO doped with 5 at % Mn ions [1] has driven the quest for the experimental realisation of RTFM in wide band-gap semiconductors doped with transition metal (TM) ions. In the case of Co doped ZnO, much of this study has been conducted on ZnO thin films (see, for example ref [2] and references contained therein). However, as pointed out by Borges et al. [3], it is the study of single crystal samples that would lead to an understanding of the modification of magnetisation of ZnO due to doping.

ZnO single crystals Co-doped by ion implantation to a fluence of 1 x 10^{17} ions/cm^2 and annealed at 800 °C, were observed to display ferromagnetic behaviour above room temperature (RT) but showed zero magnetoresistance [3]. Ferromagnetic behaviour has also been observed in Co implanted, Sn doped ZnO (see, for example [4, 5]). Zhou et al. [6] and Potzger et al. [7] studied the magnetic behaviour of ZnO single crystals implanted with 180 keV Co ions to fluences ranging from 0.8 x 10^{16} to 8x10^{16}/cm^2 at a temperature of 623K. After annealing above 823K, the formation of magnetic nanoclusters, of crystallite sizes 5 – 8 nm, were observed in the higher fluence implanted samples

To contribute to this quest we have undertaken conversion electron Mössbauer spectroscopy (CEMS) and magnetization investigations on ZnO single crystals implanted with ^{59}Co ions together with a small fluence of the Mössbauer probe ^{57}Fe ions. The concept of this experiment is thus to probe the local environment and microstructure, which is driven by the chemistry of the much higher amount of Co within the ZnO single crystal.

2 Experimental

Commercially acquired ZnO single crystals (Crystec GmbH) were implanted with ^{59}Co and ^{57}Fe ions using a multipurpose ion implanter, with ion implantation energies and fluences listed in Table 1. The samples were tilted at an angle of 7^{o} with respect to the direction of the ion beam in order to prevent channeling effects. The implantation parameters were chosen, following TRIM [8] simulations, to achieve a 'box' shaped implantation profile (Fig. 1) and a Co + Fe ion concentration of approx. 3 at. %, which was aimed at keeping lattice damage relatively low while at the same time incorporating enough TM ions in the ZnO lattice to give measurable magnetization signals.

CEMS measurements were performed on the as-implanted sample and after annealing the sample for 30 minutes in vacuum at temperatures up to 973 K. Magnetization measurements were made on the as-implanted sample and after the 973 K annealing, with a vibrating sample magnetometer (VSM) with a sensitivity of 10^{-6} emu (incorporated in a Cryogenics PPMS system).

3 Results and discussion

The CEM spectra presented in Fig 2, are similar to the spectra observed in previous studies on ZnO implanted with Fe to fluences of 10^{16}-10^{17} ions/cm^2 [9, 10] but differs from that observed in emission Mößbauer spectroscopy (eMS) studies on extremely low fluence (10^{11}-10^{12} ions/cm^2) implanted ZnO of Gunnlaugsson et al. [11]. In the eMS study the

Table 1 Energy and fluence of ion species implanted in ZnO

Ion	Energy	Fluence ($\times$ 10^{16}/cm^2)
^{59}Co	345 keV	4.17
	145 keV	1.15
^{57}Fe	60 keV	0.50

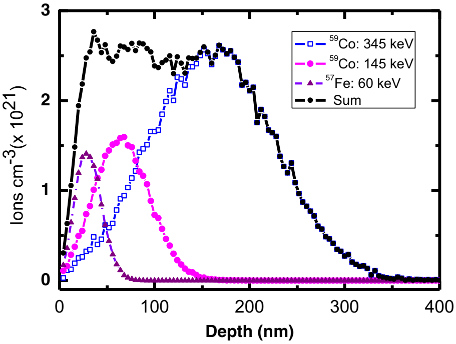

Fig. 1 TRIM simulation of implantation profiles of ^{59}Co and ^{57}Fe ions implanted in ZnO with energies and fluences listed in Table 1, and their sum

spectra were dominated by magnetic sextets due to paramagnetic Fe^{3+} complexes with relatively long spin-lattice relaxation times.

The analyses of the spectra in all these studies were conducted in terms of Fe being incorporated in the ZnO lattice in both Fe^{2+} and Fe^{3+} valence states which are distinguishable by their distinctly different isomer shift values. The same procedure has been followed in the present analysis in which Voigt line shapes with Gaussian broadening σ were used for the spectral components. Accordingly, the spectrum of the as-implanted sample was fitted with the following components:

i) a doublet D1, with isomer shift $\delta = 0.65$ mm/s, a quadrupole splitting $\Delta E_Q = 0.15$ mm/s This component is attributed to Fe in substitutional lattice sites (designated Fe_C);
ii) doublet D2, with $\delta = 0.96$ mm/s and $\Delta E_Q = 1.05$ mm/s, attributed to Fe^{2+} and
iii) doublet D3, with δ and ΔE_Q values of 0.60 and 1.56 mm/s, respectively, and a large line broadening ($\sigma = 0.7$ mm/s), due to Fe in implantation induced damage in the ZnO lattice (Fe_D)

These components show little change up to an annealing temperature of 773 K, as shown in Fig. 2, except for a reduction of the line broadening of component D2, which necessitated the inclusion of a second doublet component with parameters also indicative of Fe^{2+} (D4). A dramatic change in the spectrum is evident however, after the annealing step at 973 K, with components due to Fe^{2+} on Zn sites, and Fe in implantation induced damage regions, converting to a dominant doublet component (D5) with parameters typical of Fe^{3+}. The fit parameters of the spectral components (and their assignment) after the 773 K and 973 K annealing steps are listed in Table 2. Isomer shift values are given relative to α-Fe.

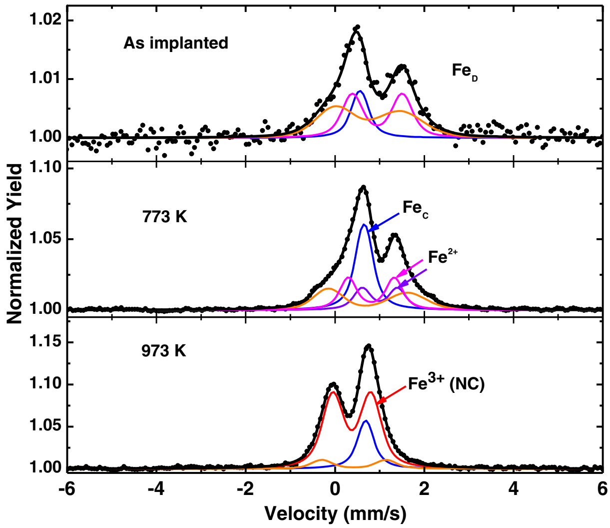

Fig. 2 CEM spectra of ZnO single crystal implanted with the profile of ^{59}Co and ^{57}Fe ions displayed in Fig. 1, after annealing at the temperatures indicated

Table 2 Isomer shifts (δ), electric quadrupole splittings (ΔE_Q) and fractions f of the components required to fit the spectra after annealing at 773K and 973 K, and their assignments

T_A	Component	Assignment	δ (mm/s)	ΔE_Q (mm/s)	σ (mm/s)	f (%)
773 K	D1	Fe_C	0.65 (2)	0.15(2)	0.15	34(2)
	D2	Fe^{2+}	1.02(3)	0.79(3)	0.20	16(3)
	D4	Fe^{2+}	0.81(3)	1.03(5)	0.20	25(3)
	D3	Fe_D	0.59(3)	1.76(7)	0.60	25(2)
973 K	D1	Fe_C	0.69(2)	0.15(2)	0.15	20(3)
	D3	Fe_D	0.42(5)	1.44(5)	0.60	9(2)
	D5	Fe^{3+}(NC)	0.38(2)	0.85(5)	0.30	71(3)

The magnetization curves obtained from the VSM measurements at RT and 4 K after the 973 K annealing step are presented in Fig. 3. The residual magnetization at room is negligibly small, but is clearly evident at 4 K, as expected for superparamagnetic clusters. A saturation magnetization of 0.33 μ_B per Co/Fe ion is observed at 4 K. This value is in good agreement with the values of 0.36 and 0.32 μ_B per Co ion previously observed for 5–8 nm sized Co nanoclusters implanted in ZnO [6].

The result of the magnetization measurements are consistent with superparamagnetic relaxation reflected in the CEM spectra by single domain particles. Above the blocking temperature T_B, clusters of size below 15 nm size behave as single domain particles. Thermal fluctuations of the magnetization axis occur at frequencies above the Larmor frequency of the ^{57}Fe nucleus ($\sim 10^8$ s^{-1}) [12] and the probe nuclei do not sense a preferred magnetization axis. This results in the absence of magnetic sextet(s) in the Mössbauer spectra collected in the RT measurements, as is evident in our results

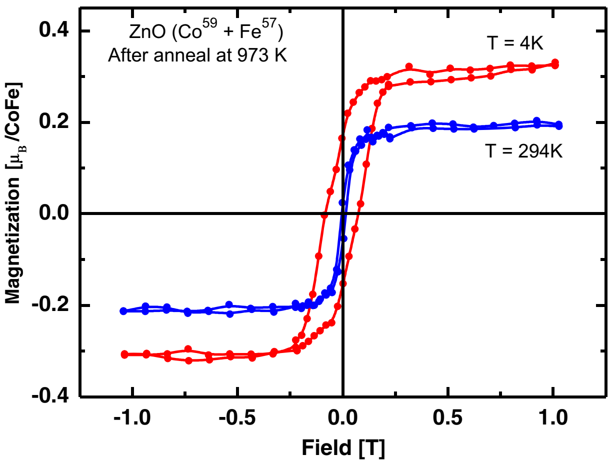

Fig. 3 Magnetization curves measured at 294 K and 4 K, of the ZnO single crystal implanted with ^{59}Co + ^{57}Fe ions, after annealing at 973 K

4 Conclusions

We have performed CEMS and magnetization measurements on a ZnO single crystal implanted with Co and Fe ions in a 'box' profile to a concentration of about 3.2 at. %. Our results show that after annealing at 973 K, the implanted ions form nanoclusters that display superparamagnetic relaxation. Comparison of the magnetization results with those of ref [6], indicate that the clusters are about 5-8 nm in size.

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