Search for the formation of magnetic complexes by ion implantation into suitable insulators

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Abstract: The search for the formation of magnetic complexes following ion implantation in substrates has progressed on two fronts. At one end are the investigations on magnetic clusters and complexes formed when the implantation fluences are ≥ $10^{17}/cm^2$, and at the other end are magnetic effects at extremely low fluence ($<10^{12}$ ions/cm^2) implantations due to implanted ion – vacany complexes. Here we report on our search for magnetic complex formation in the intermediate region, with the implantation of mass separated ^{57}Fe ions to fluences of 0.5 - 2.0 x 10^{16} cm^{-2} into ZnO and SiO_2 crystalline substrates. Characterization methods included Mössbauer spectroscopy on as-implanted and annealed samples, Rutherford Backscattering spectrometry and MOKE measurements.
The Mössbauer spectra of the Fe implanted ZnO and SiO_2 single crystals, annealed up to 1173 K and 1073 K, respectively, show that the Fe^{3+} ions remain fairly constant in the crystals, while the Fe^{2+} show some reordering. No clear evidence of magnetic clustering was obtained, but the CEMS data for ZnO implanted with 2 x$10^{16}/cm^2$ ^{57}Fe and annealed at 1173 K suggests a small (approx. 2 %) magnetic contribution. MOKE measurements on ZnO single crystals implanted with 1, 2 and 4 at. % ^{56}Fe in a box profile show ferromagnetic behaviour in the 4% implanted sample and weak paramagnetic or ferromagnetic behaviour at room temperature for the other samples. In a SiO_2 sample implanted with 1 x $10^{16}/cm^2$ ^{57}Fe, evidence of magnetic complex appears after annealing at 1073 K.

1. Introduction

The search for magnetic complex formation after ion implantation in substrates has progressed on two fronts. At one end are the investigations on magnetic clusters and complexes formed at when the fractional concentration of implanted ions is ≥ 4% (≥ $10^{17}/cm^2$), exemplified by the results of refs [1,2,3]. At the other end are the investigations of Gerd Weyer et al. [4] at CERN on Mössbauer studies on ZnO (as well as other oxides) following ion implantataion of extremely low fluences of ^{57}Mn. The ZnO spectra, in addition to the expected doublet structure due to Fe at substitutional and interstitial sites, displayed magnetic structures that have been anaylsed in terms a sharp sextet, two paramagnetic doublets, and two ferromagnetic magnetic distribution. The magnetic effects disappear above 600 K. The formation of the magnetic ordering is proposed to occur on an atomic scale upon the association of complexes of Mn/Fe probe atoms with the Zn vacancies that are created in the implantation process, and conversely, disappearance sets in above 600 K due to thermally activated annealing of the vacancies.

In this contribution we present some results of our search for the formation of magnetic clusters in substrates implanted with ferromagnetic ions in the fluence range 0.5 – 2.0 x $10^{16}/cm^2$. The main focus of the programme was to investigate the conditions required to achieve the production of such magnetic complexes in low fluence implanted Fe ions into bulk SiO_2, ZnO, and several other substrates. The program included investigations as functions of implantation fluence and annealing temperature of the substrates.

Nano-clusters of ferromagnetic ions of size below 5 nm have a high proportion of surface atoms which results in a narrowing of the d-band responsible for magnetism. This, coupled with quantum size effects, has been observed to lead to clusters with novel properties such as increase in the magnetic anisotropy and enhancements of the magnetic moment per atom. These results provided the stimulus for the current project.

2. Experimental details

Mössbauer spectroscopy (MS) which provides clear signatures of the onset of magnetic order was employed as our main characterization method, and accordingly the Mössbauer probe nuclide ^{57}Fe was used as the implanted Fe species. Mass separated ^{57}Fe ions were implanted at energies of 60 or 80 keV, and to fluences of 5 x 10^{15}, 1 x 10^{16} and 2 x 10^{16} cm^{-2}, using the Göttingen ion implanter into a range of substrates which included ZnO, 3C-SiC and SiO_2 single crystals. The ZnO and 3c-SiC samples were commercially obtained (from Crystec GmbH (Munich) and Maruben Corporation (Tokyo), respectively), while the SiO_2 sample was an epitaxial layer produced on a Si substrate by heat treatment in O_2 atmosphere. Conversion electron Mössbauer spectroscopy (CEMS) measurements were made on the as-implanted samples and after annealing for 30 mins in flowing N_2 at various temperartures in the range 573 K – 1173 K.

3. Results

Sample CEMS spectra of a ZnO single crystal samples implanted and annealed to the indicated fluences and temperatures, respectively, are displayed in Fig. 1, while Fig. 2 shows a CEMS spectrum after annealing at 1173 K. The components required to fit the spectra, and their assignments are listed in Table 1.

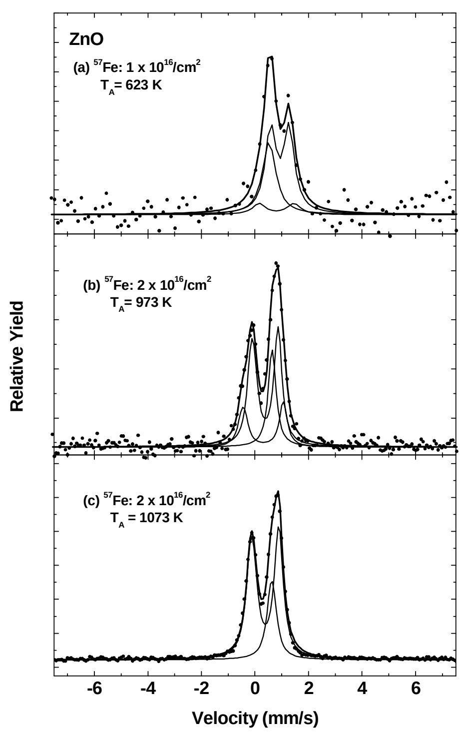
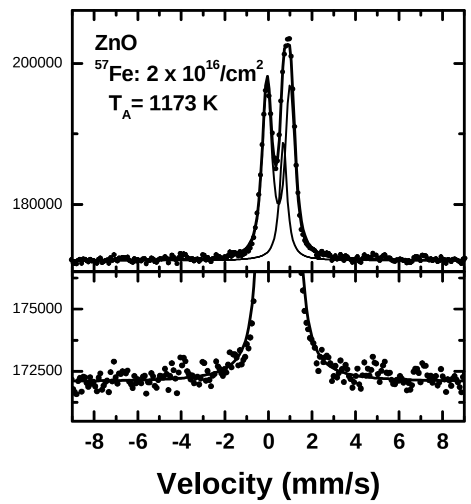


FIG 1: CEMS spectra of ZnO substrates implanted with ^{57}Fe to fluences of 1 x 10^{16}/cm^2 and 2 x 10^{16}/cm^2 and annealed at temperatures indicated.

TABLE I: Hyperfine parameters (isomer shift δ and quadrupole splitting ΔE) and fractions (*f*) of components required to fit the spectra of ^{57}Fe implanted ZnO (*d* is the implantation fluence).

Sample: ZnO	**Component**	**δ (mm/s)**	**ΔE (mm/s)**	***f* (%)**
1, $d = 1 \times 10^{16}/cm^2$	S1 (Fe^{3+})	0.53(5)	-	32(3)
T_A = 623 K	D1 (Fe^{2+})	0.93(5)	0.68(5)	59(4)
	D2 (Fe^{2+})	0.81(5)	1.3(1)	9(2)
2, $d = 2 \times 10^{16}/cm^2$	S1 (Fe^{3+})	0.64(5)	-	23(4)
T_A = 973 K	D1 (Fe^{2+})	0.37(5)	0.96(5)	57(5)
	D2 (Fe^{2+})	0.30(5)	1.50(6)	21(4)
2, $d = 2 \times 10^{16}/cm^2$	S1 (Fe^{3+})	0.63(5)	-	24(4)
T_A = 1073 K	D2 (Fe^{2+})	0.39(5)	1.01(5)	76(6)

FIG. 2: CEMS spectrum of ZnO implanted with 2 x $10^{16}/cm^2$ ^{57}Fe and annealed at 1173 K.



The annealing brings about changes in the population of the Fe in the different configurations, but there is no clear evidence of magnetic sextets in the spectra. However, Fig. 2 (expanded lower) suggests some structure on either side of the central resonance area which may be indicative of the onset of the formation of magnetic complexes. These account for a small fraction (approx. 2%) of the resonance effect.

Fig. 3 displays MOKE data collected from ZnO samples implanted with ^{56}Fe in a box-like profile at room temperature, at ion energies of 300, 190, 110 and 60 keV, and to fluences of 1.57 x 10^{16}, 3.14 x 10^{16} and 6.28 x 10^{16} cm^{-2}, i.e. Fe concentrations of 1, 2 and 4 at. %, and annealed in air at 700°C for 30 mins. Ferromagnetic behaviour is evident in the 4% implanted sample and weak paramagnetic or ferromagnetic behaviour at room temperature for the other samples.

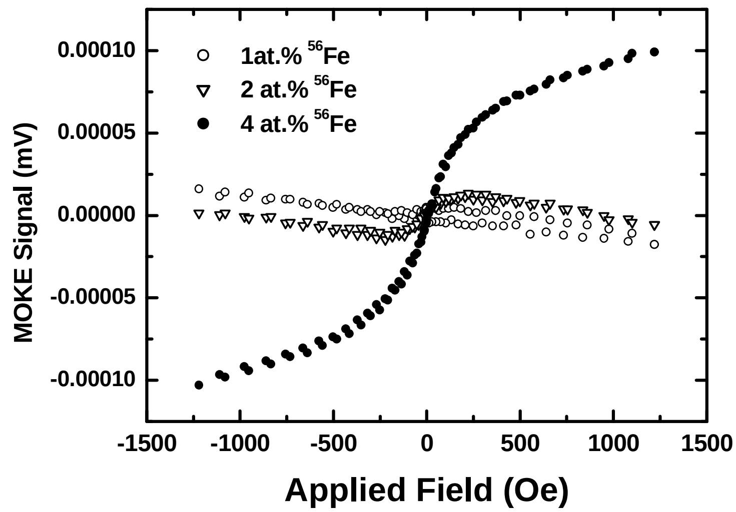


FIG. 3. MOKE signals from ZnO implanted with implanted ^{56}Fe in a box profile at the concentrations indicated.

ii) SiO_2

CEMS spectra from a SiO_2 sample implanted with 1 x 10^{16}/cm^{2} ^{57}Fe and annealed at 623 K and 1073 K are displayed in Fig.4.

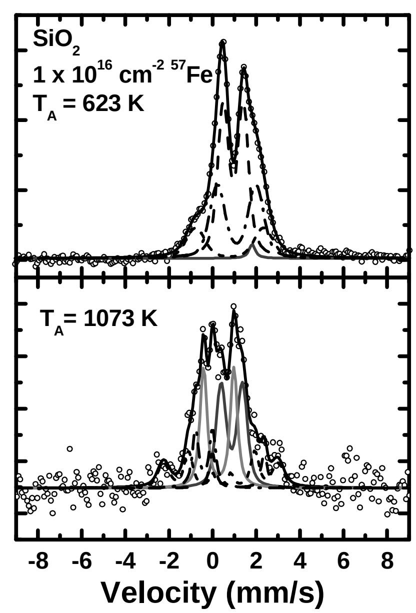


FIG. 4: CEMS spectra of SiO_2 implanted with 1 x 10^{16} ^{57}Fe/cm^{2}, and annealed at the temperatures indicated.

TABLE 2: Hyperfine parameters (isomer shift δ, hyperfine field (B_{hf}), quadrupole splitting ΔE) and fractions (*f*)) of components required to fit the spectra of ^{57}Fe implanted SiO_2. The isomer shifts are relative to α-Fe.

Sample: SiO_2	**Component**	**δ (mm/s)**	**ΔE/B_{hf} (mm/s)**	***f* (%)**
T_A = 623 K	S1 (Fe^{3+})	1.81(5)	-	2(2)
	D1 (Fe^{2+})	0.94(4)	0.91(4)	51(4)
	D2 (Fe^{2+})	0.78(4)	3.1(4)	15(2)
	D3 (Fe^{2+})	1.10(3)	1.77(4)	32(3)
T_A = 1073 K	D1	0.87(4)	0.97(4)	31(4)
	D2	0.28(3)	1.38(5)	28(5)
	D3	1.18(5)	2.37(5)	8(4)
	D4	-0.39(5)	0.78(8)	12(2)
	Sxt	0.40(4)	160(15)	21(4)

The quardupole splitting of the components observed after annealing at 623 K are in good agreement with those observed by Van der Heyden et al [3]; the isomer shifts are slightly different, which is not surprising given that these authors implanted ^{57}Co and the beta decay after effects are expected to have some effect on the elecron density in the vicinity of the probe nucleus. Structure is evident in the wings of the spectra which would require quadrupole splittings in excess of 5 mm/s to fit which is physicaly unrealistic. Fitting this with a magnetic sextet, yields a hyperfine field of 160(15) kOe.

ii) 3C-SiC

CEMS spectra of a 3C-SiC sample implanted with 1×10^{16} ^{57}Fe ions/cm^2 and annealed at 623 K and 973 K are displayed in Fig. 5(a). The spectrum, after annealing the sample at 623 K, required just one component, a quadrupole split doublet, with δ = -0.16(5) mm/s, and splitting ΔE = 1.20(4) mm/s, to give a fit. After annealing at 973 K, additional structure in the wings of the central component become evident. This has been fitted with a broad asymmetric doublet with δ = 0.12 (4) mm/s and ΔE = 1.7(2) mm/s.

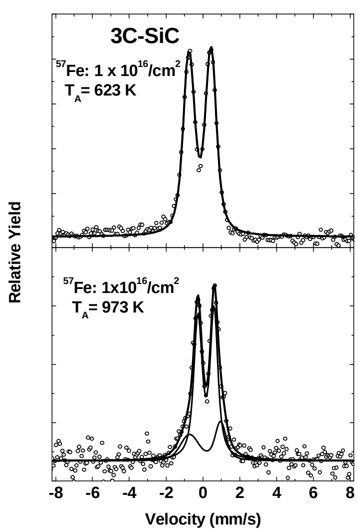


FIG. 5(a): CEMS spectra of 3C-SiC implanted with 1 x 10^{16} ^{57}Fe/cm^2, and annealed at 623 K and 973 K.

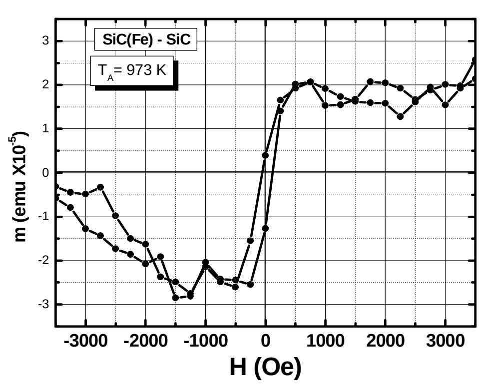


FIG. 5(b): Composite VSM magnetization plot of ^{57}Fe implanted 3C-SiC sample after annealing at 973 K.

Figure 5(b) displays a composite plot of magnetization signal obtained with a vibrating sample magnetometer from a 3C-SiC sample implanted with 1 x $10^{16}/cm^2$ ^{57}Fe and annealed at 973 K, subtracted from signals from a virgin sample. A small ferromagnetic effect is evident.

4. Discussion

Our MOKE measurements show clear evidence of formation of ferromagnetic complexes in the ZnO sample implanted with 4 at. % Fe, while the CEMS data suggests that this process may start setting in in samples implanted with 2 at. % Fe and annealed at 1173 K. In SiO_2 magnetic complexes may be forming after implantation of Fe of fluence 1 x $10^{16}/cm^2$ and annealed to 1073 K. Magnetization measurements to confirm these results are in progress.
Magnetization measurements have been made on a 3C-SiC sample implanted with 1 x $10^{16}/cm^2$ ^{57}Fe, which after annealing at 973 K displays a small ferromagnetic effect. Further measurements with more sensitive instrumentation are being undertaken. Future plans inlude Mössbauer and magnetization measurements on substrates implanted with ^{57}Fe at a range of energies to give a box profile, but keeping the total implantation dose below 5 x $10^{16}/cm^2$.

References

1. ZHOU, S., et al, „Fe implanted ZnO; Magnetic precipates versus dilution“, J. Applied Phys. 103 (2008) 023902, and refs contained therein.
2. HAYASHIA, N., et al., „Synthesis of iron and copper nano-clusters in SiO_2 by ion implantation“, J. Magn. & Magne. Mater. 290-291 (2005) 98-101
3. VAN DEN HEYDEN, M., et al., „Mossbauer Spectroscopy of ^{57}Co implanted SiO_2“, Hyp. Inter. 15/16 (1983)503-506
4. WEYER, G., et al., „Defect-related local magnetism at dilute Fe atoms in ion-implanted ZnO“, J. Appl. Phys. 102 (2007)113915.