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CONFERENCE PROCEEDING

Formation of magnetic nanoclusters in Fe implanted amorphous and crystalline SiO_2

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Abstract
Conversion electron Mössbauer Spectroscopy (CEMS) studies have been conducted on Fe implanted amorphous and crystalline SiO_2 which were annealed in air up to a temperature of 1000°C. For both samples, dramatic changes set in after the 1000°C anneal and the CEM spectra are dominated by strong ferromagnetic sextets. In the amorphous sample, the sextet is characterized by magnetic hyperfine fields of 33T, 31T and 29 T, consistent with the formation α-Fe nanoclusters. In the crystalline sample the ferromagnetic sextet has spectral parameters of $\delta = 0.38(3)$ mm/s and $B_{hf} = 52.3$T, consistent with formation of α-Fe_2O_3 clusters, reflecting the precipitation of the implanted Fe into such clusters. The line ratios of lines 1, 2 and 3 (and 6, 5 and 4) of the sextet are 3:4:1, reflecting alignment of the magnetic moment of the precipitates normal to the c-axis of the sample surface.

Keywords SiO_2 · Ion implantation · α-Fe_2O_3 · Magnetic nanoclusters

1 Introduction

Studies of the magnetic behavior of nano-sized clusters of transition metal atoms embedded in suitable host matrices are driven by the enhanced magnetic properties of these clusters compared to their bulk behaviour. The high proportion of surface atoms and a consequential reduction in the number of neighbours in nanoclusters lead to increased spin magnetic moment per atom. Additionally, quantum size effects and modified valence electron screening give such clusters quite novel properties. For Fe, Co and Ni nanoclusters, enhanced magnetic moments compared to their bulk values have been reported, while in Fe clusters below a critical size superparamagnetic behavior has been observed [1–3]. Magnetic par-

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ticles with diameter less than a critical value of 10–100 nm support only one domain, and such single domain magnetic particles have a range of technological applications [4]. These observations, as well as theoretical predictions of room temperature ferromagnetic behaviour in ZnO with low concentrations (5 at%) of Mn ions [5], have prompted wide international search for ferromagnetic behaviour in ion implanted oxides.

In ion implanted amorphous SiO_2, there exist several earlier studies. Low fluence implantation resulted in the formation of Fe oxides due to the initial substitution of the Si ion by the Fe ion. Higher Fe fluences and post-implantation annealing resulted in formation of Fe nanoclusters up to 10 nm in size [6]. Metallic Fe and isolated Fe^{2+} and Fe^{3+} in nanoparticles of Fe_3O_4 were observed in CEMS studies on Fe implanted into SiO_2 with fluence above 1 x $10^{16}/cm^2$ [7]. In glassy SiO_2, Fe doping has resulted in CEM spectra with magnetic relaxation peaks of dispersed Fe and paramagnetic doublets of Fe^{3+} and Fe^{2+} in the as-implanted sample. After oxidation at temperatures above 800°C, the formation of ferromagnetic structures set in, with spectral parameters attributed to precipitates of ε-Fe_2O_3 [8]. Higher fluence implantation (5 x $10^{16}/cm^2$) and post implantation annealing above 800°C resulted in the formation of ferromagnetic assemblies of ε-Fe_2O_3 and α-Fe_2O_3 [8].

In the present contribution we present results of our CEMS studies on the nucleation of magnetic nanoclusters in both amorphous and crystalline SiO_2 (α-quartz) samples implanted at room temperature with 60 keV ^{57}Fe and ^{56}F ions.

2 Experimental

The samples under study were a 460 nm thick amorphous SiO_2 layer, formed on a Si (100) surface heated to 1000°C in oxygen atmosphere, and a crystalline SiO_2 sample. The Fe ions were implanted into the samples at room temperature, with 60 keV energy through an aperture of 0.78 cm^2 with the sample at an angle of 7° to the beam axis in order to avoid channeling effects. The implantation into the amorphous sample was undertaken with the Göttingen implanter, with an ^{57}Fe fluence of $1.0\times10^{16}/cm^2$ (peak concentration = 3.1 at%), while the implantation into the crystalline sample was undertaken with the Jena implanter, with ^{57}Fe and ^{56}Fe ions to a total fluence of $1.5\times10^{16}/cm^2$ (peak concentration = 4.7 at%). SRIM/TRIM simulations give an estimate of the range of the 60 keV Fe ions in the crystalline SiO_2 substrate of 45 nm, with a straggle of 16 nm, and a vacancy yield of 1000 per implanted Fe ion, with overlapping Si and O vacancy profiles. The concurrent sputter losses are about 5–10 nm and preferential sputtering of O likely results into a SiO-like surface with a stoichiometry gradient towards the SiO_2 bulk.

CEM spectra were collected of the as-implanted samples and after annealing the samples for 30 min in air at temperatures up to 1000°C. The parallel plate CEMS detector was operated with acetone gas at a pressure of 35 mbar in constant pressure mode. The CEM measurements were performed at room temperature using a 25 mCi $^{57}CoRh$ source, with the velocity scale of the spectra calibrated with spectrum of an α-Fe foil at room temperature.

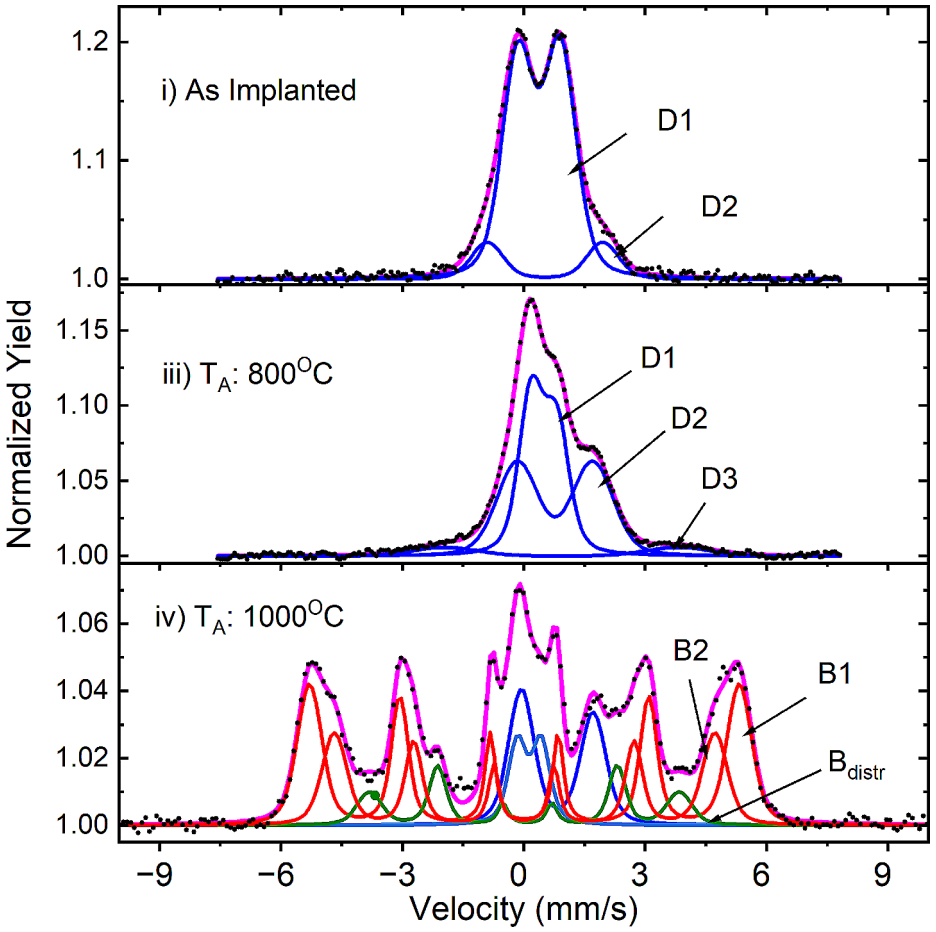

Fig. 1 Conversion electron Mössbauer spectra of an amorphous SiO_2 layer implanted with 60 keV ^{57}Fe ions to a fluence of 1×10^{16}/cm^2 and annealed at the temperatures indicated

3 Results and discussion

A preliminary report on our CEMS study of Fe implanted amorphous SiO_2 has been published earlier [9]. Re-analysis of the data is included herein. For consistency and direct comparison with other measurements [8], the data were analysed with spectral components with Lorentzian line shapes.

The CEM spectra of the Fe implanted amorphous SiO_2 sample, collected on the as-implanted sample and after annealing the sample at 800ºC and 1000ºC are presented in Fig. 1. The fit parameters are listed in Table 1.

Following the annealing of the sample at 1000ºC, the development of a broad sextet component sets in which accounts for approximately 75% of the spectral fraction. This component was analysed with four sextets of relatively large line widths and peak intensities kept in the ratio 3:2:1 1:2:3 for the amorphous SiO_2 host. The hyperfine fields of the sextet component, of B_{hf} = 33.5 T, 31.1T and 29.1 T, are consistent with the precipitation of

Table 1 Hyperfine parameters, isomer shift (δ), electric quadrupole splitting/shift (ΔE_Q/ ε), hyperfine magnetic field (B_{hf}), Lorentzian line width (Γ) and area fractions (A), extracted from the fits to the CEM spectra of the Fe implanted amorphous SiO2 sample, shown in Fig. 1

Annealing Temp, T_A	Component	δ (mm/s)	ΔE_Q (mm/s)	ε (mm/s)	B_{hf} (T)	Γ (mm/s)	A (%)	Assignment
As implanted	D1	0.29(4)	1.6(1)	-	-	0.68	24(4)	Fe3+
	D2	0.38(5)	0.88(8)	-	-	0.86	70(5)	Fe3+
	D3	0.94(10)	2.0(5)	-	-	0.68	6(3)	Fe2+
800°C	S1	0.28(8)	-	-	-	0.50	5(2)	Fe3+
	D1	0.49(4)	0.71(7)	-	-	1.00	67(3)	Fe3+
	D3	0.89(1)	1.8(1)	-	-	0.76	28(2)	Fe2+
1000°C	D1	0.17(8)	0.5(1)	-	-	0.60	12(2)	Fe3+
	D3	0.84(8)	2.0(2)	-	-	0.70	16(2)	Fe2+
	B1	0.02(3)	-	0.00(2)	33.5(2)	0.44	25(4)	α-Fe
	B2	-0.03(3)	-	-0.01(3)	31.1(3)	0.44	19(4)	α-Fe
	B3	0.01(4)	-	-0.01(4)	29.1(5)	0.50	15(4)	α-Fe
	Bdistr	-0.01(9)	-	-0.09(7)	25.3(7)	0.70	13(3)	X

the implanted Fe ions into metallic α-Fe nanoclusters distributed throughout the implanted SiO_2 layer. Appling the core+shell model of these clusters would then allow us to attribute the higher hyperfine field to Fe in the core of the clusters and the decreasing B_{hf} values to Fe ions in slightly reduced concentrations in the shell. The averaged B_{hf} value of the remaining magnetic components amounts to 25 T, which is close to that reported by Nomura et al. [8] for Fe^{3+} in ε-Fe_2O_3. However, we see no evidence of the two additional components with B_{hf} of 40 and 46 T required for such an assignment.

The CEM spectra of the Fe implanted crystalline SiO_2 sample observed after the different annealing stages are presented in Fig. 2. Paramagnetic components in the spectra, up to an annealing temperature of 800°C, reflect the presence of Fe^{2+} and Fe^{3+} ions due to Fe in implantation induced lattice damage. No broad magnetic relaxation component, as observed by Nomura et al. [8], is evident in our data. The fit parameters of the spectra, analysed in terms of spectral components with Lorentzian line shapes, are listed in Table 2.

Doublets D1 and D2 with respective isomer shifts of 0.20(4) mm/s and 0.41(5) mm/s, are attributed to Fe nanoparticles of size below the spin limit and hence of vanishing remanent magnetization. Annealing at 900 °C induces dramatic changes in the spectrum, with a marked decrease in the paramagnetic components and development of a strong ferromagnetic component with hyperfine parameters (δ = 0.40(3) mm/s, B_{hf} = 52.7(3) T) consistent with those of α-Fe_2O. Already after the 900° anneal, this component contributes more than 50% to the spectral area, which is increased further in intensity (75%) after annealing the sample at 1000°C. Our results display a strong coalescence of the majority of the implanted Fe ions into α-Fe_2O_3 precipitates, in sharp contrast to the observations of Nomura et al. [8]. Following annealing of their sample at 950°C, these authors observe very strong (77%) contribution to their CEM spectrum of sextets due to ε-Fe_2O_3, but only a small contribution (8%) from α-Fe_2O_3. Of note are the implantation parameters used in the work of ref. [8]. SRIM estimates give a range of 75 nm (with straggle of 25 nm) in crystalline SiO_2 for Fe ions of 100 keV energy and vacancy production rate in excess of 1500/ion. These parameters, together with the much higher fluence (5×10^{16}/cm^2), may account for the difference in the spectral components which characterise the CEM spectra presented in Fig. 2.

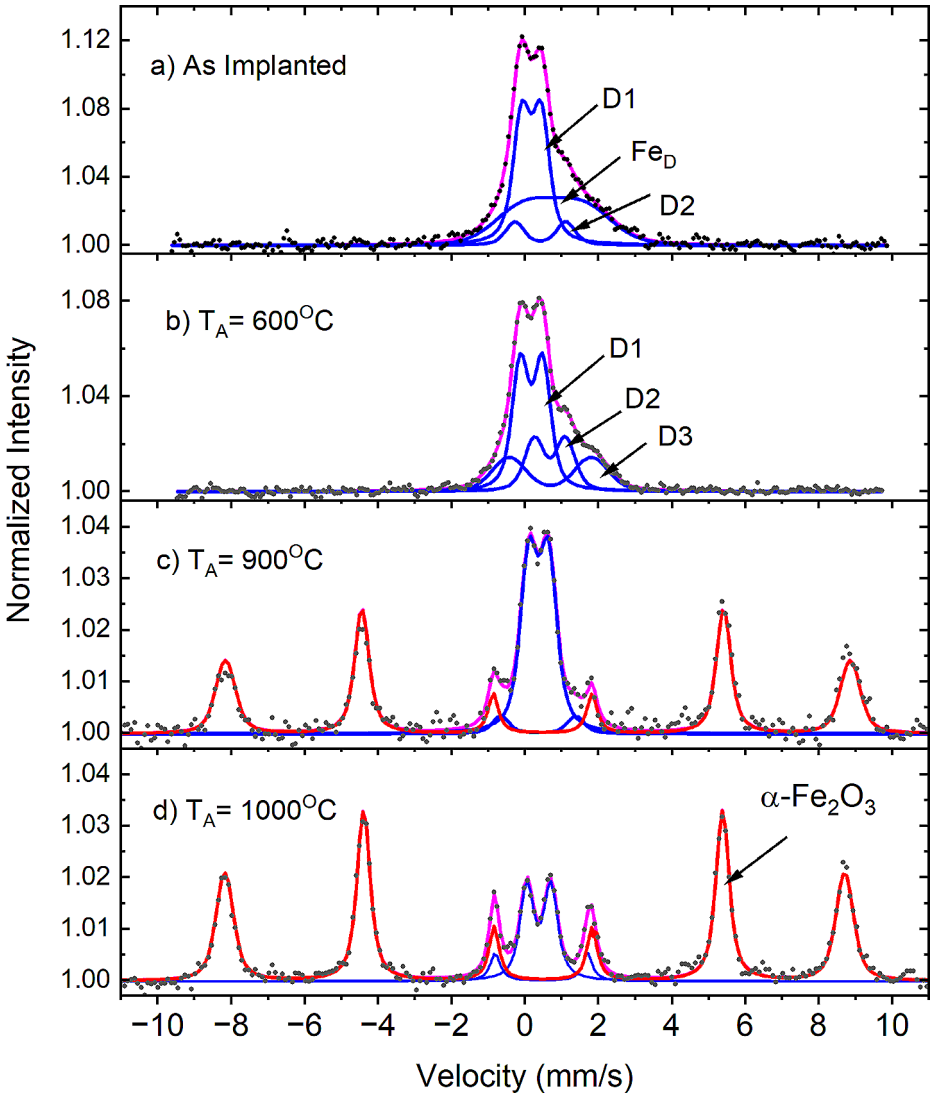

Fig. 2 CEM spectra of the crystalline SiO_2 sample implanted with 60 keV ^{57}Fe ions to a fluence of 1.5×10^{16}/cm^2 and annealed at the temperatures indicated

The relative intensities of the lines 2 and 5 of the Zeeman split sextet depend on the angle θ between the direction of hyperfine field direction and that of the 14.4 keV γ-ray beam from the Mössbauer source, and is given by the relation

$$cos^2 < \theta > \; = \; (4 - x) \, / \, (4 + x)$$

where the intensities of the six Zeeman split lines are in the ratio 3:*x*:1 1:*x*:3.

The relative line ratios of the Zeeman split ferromagnetic spectral component observed in our CEM spectra of the crystalline SiO_2 sample after the 900ºC and 1000ºC anneals are

Table 2 Hyperfine parameters of the spectral components extracted from the fits to the CEM spectra of the Fe implanted crystalline SiO_2 sample, shown in Fig. 2

Annealing Temp, T_A	Component	δ (mm/s)	ΔE_Q (mm/s)	ε (mm/s)	B_{hf} (T)	Γ (mm/s)	A (%)	Assignment
As implanted	D1	0.20(4)	0.54(5)	-	-	0.58	55(4)	Fe3+
	D2	0.41(5)	1.4(2)	-	-	0.46	12(3)	Fe3+
	D3	0.95(10)	1.6(3)	-	-	1.26	33(6)	Fe2+
600^0C	D1	0.19(2)	0.60(3)	-	-	0.50	56(3)	Fe3+
	D3	0.70(4)	0.92(3)	-	-	0.54	24(4)	Fe2+
	D3	0.74(7)	2.3(2)	-	-	0.70	19(4)	Fe2+
900°C	D1	0.38(3)	0.60(3)	-	-	0.50	4042)	Fe3+
	D3	0.33(3)	2.0(3)	-	-	1.00	3(1)	Fe3+
	B1	0.40(3)	-	-0.09(3)	52.7(3)	0.50	57(2)	Fe3+
1000°C	D1	0.38(3)	0.52(5)	-	-	0.44	20(4)	Fe3+
	D3	0.45(6)	2.5(2)	-	-	0.22	4(2)	Fe3+
	B1	0.38(3)	-	-0.11(2)	52.3(2)	0.40	76(4)	α-Fe_2O_3

3:4:1 1:4:3, which reflects the alignment of the hyperfine field parallel to the surface of the sample, i.e. the magnetization vector remains perpendicular to the c-axis of the substrate. Such an observation on spin pinning of α-Fe_2O_3 fine particles supported on high area silica has been reported in an early study of Kundig et al. [10], and there attributed to the pinning of the spins by the surface. In the present case, the spin pinning is most likely caused by the crystalline nature of the SiO_2-quartz sample and the strain induced by the implantation process, which cannot relax in the crystalline sample. For the amorphous case, as seen above, no preferred orientation can be expected and full relaxation of the ion implantation induced strain likely occurs at the given annealing temperatures.

4 Conclusions

We have performed CEMS studies of the magnetic behaviour of ^{57}Fe probe ions implanted in amorphous and crystalline SiO_2. Our results show that in amorphous SiO_2 the coalescence of the implanted Fe ions into α-Fe clusters can be achieved after annealing at 1000°C. In the crystalline sample, our CEM spectra show the development of a ferromagnetic spectral component setting in after annealing at 900°C, whose intensity increases after annealing at 1000°C, when it contributes 75% of the spectral intensity. The hyperfine parameters of this component are consistent with those of α-Fe_2O_3. The relative line intensity ratios of this component reflect pinning of the magnetic moment of the Fe probe nuclei perpendicular to the c-axis of the surface of the SiO_2 quartz sample, which may be caused by the interplay of crystalline nature of the sample and the ion implantation induced strain.

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Author contributions K.B.R., C.R. and H.H. planned the project.H.H. and C.R undertook the Fe implantation into the samples using the ion implanters at their home institutions.K.B.R. undertook the Conversion electron Moessbauer spectroscopy (CEMS) measurements in South Africa. All authors reviewed the results of the CEMS measurements.K.B.R. prepared the first manuscript text, which was reviewed by all authors and which then lead to the final manuscript.

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Data availability Provided in Supplemental Materials to this manuscript.

Declarations

Ethical approval Not required.

Competing interests The authors declare no competing interests.

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