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Article *in* Physics Procedia · December 2015
DOI: 10.1016/j.phpro.2015.12.072

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Physics Procedia

Volume 75, 2015, Pages 565–571

20th International Conference on Magnetism

Instability of ferromagnetic nanoclusters in Fe implanted amorphous SiO_2

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Abstract

A 460 nm thick amorphous SiO_2 layer, formed on a Si (100) surface by air-annealing the Si substrate at 1100°C for 24 h, was implanted with ^{57}Fe to a fluence of 1 x 10^{16}/cm^2 at room temperature and annealed at temperatures up to 1000°C. The implanted and annealed samples were studied by conversion electron Mössbauer spectroscopy (CEMS) and magnetization measurements.

The CEMS spectra up to an annealing temperature of 600°C showed the presence of a singlet due to dispersed Fe ions and paramagnetic doublets with hyperfine parameters characteristic of Fe^{2+} and Fe^{3+}. The spectrum after the 1000°C annealing was dominated (> 80%) by ferromagnetic sextets, the main components of which were sextets with a hyperfine field of 320(20) kOe and 264(20) kOe, showing the formation of Fe^0 clusters, in agreement with previous observations. Magnetization measurements (m(H)) on the sample after the 1000°C annealing showed a small hysteresis at 4 K and saturation magnetization with zero hysteresis at room temperature, reached with application of small external field.

The CEMS measurement on this sample was repeated after storing the sample under ambient conditions for a period of 6 months. The spectrum showed complete disappearance of the ferromagnetic sextets and the presence only of paramagnetic doublets due to Fe^{2+}. Evidently progressive oxidation of the Fe clusters had occurred. Magnetization results confirm the paramagnetic transformation of the Fe clusters.

Keywords: a-SiO_2, Fe implantation, ferromagnetic nanoclusters, paramagnetic transformation, stability

Selection and peer-review under responsibility of the Scientific Programme Committee of ICM 2015

doi:10.1016/j.phpro.2015.12.072

1 Introduction

There is considerable research interest in transition metal doped oxides, in particular on the formation, properties and stability of nano-sized clusters of transition metal atoms embedded in suitable metal oxide host matrices. These studies are motivated by the novel properties of such clusters, which are distinct from their bulk assemblies (see, for example, the topical review by Janisch et al. [1]). The high proportion of surface atoms leads to increased spin magnetic moment per atom towards the high spin limit, and to a quenching of orbital magnetism well below that due to crystal fields. These features coupled with quantum size effects and modified valence electron screening give such clusters quite novel properties. For example, magnetic moments enhanced by up to 35% compared to bulk values have been reported for free Fe, Co and Ni nanoclusters and superparamagnetic behaviour in Fe clusters below a critical size [2,3,4]. A particularly appealing feature is the enhanced magnetization coupled with an absence of magnetic hysteresis of such assemblies, which has potential applications in magnetic sensing and magnetoresistive devices and in high density magnetic data storage. The last, however, requires maintaining the stability of the nanoclusters.

There are several studies of nucleation and growth of transition metal (TM) clusters embedded in insulating oxide matrices. In the case of ion implanted Fe in SiO_2, low fluence implantation showed the presence of Fe oxides, attributed to the initial substitution of the cation by the Fe ion. Larger Fe fluences and post-implantation annealing resulted in a transformation of the cationic Fe species into metallic Fe nanoclusters up to 10 nm in size [5]. Sprouster *et al*. [6] report the formation of Co nanoparticles (NPs) varying in size from 3 to 17 nm in ion implanted SiO_2 layers grown on Si(100). The size of the NPs were found to be dependent on implantation fluence and annealing temperature. Studies by conversion electron Mössbauer spectroscopy (CEMS) on the size and nature of NPs formed in Fe implanted SiO_2 have been reported by several authors. Zhang *et al*. [7] studied the formation of Fe precipitates in a sample implanted with 5×10^{16} Fe/cm^2. The spectra of the sample annealed at 650^{o}C for 90 min. showed dominant magnetic sextet, reflecting the formation of Fe clusters in the SiO_2 matrix. Perez *et al*. [8] studied the clusters formed as a function of implantation fluence. For implantation fluences $\leq 6 \times 10^{16}$/cm^2, they observed the formation of $\approx$ 2nm sized particles similar to Fe_3O_4, but with increasing fluence they observed the formation α-Fe particles with size increasing to $\approx$ 30nm at a fluence of 2.5×10^{17}/cm^2. Nomura *et al*. [9], on the other hand, reported that implantation of 5×10^{16}/cm^2 Fe and post implantation annealing above 800^{o}C resulted in the formation of ferromagnetic assemblies of ε-Fe_2O_3 and α-Fe_2O_3.

The present work contributes to the earlier studies and presents results of our CEMS studies on the nucleation, growth and stability of magnetic nanoclusters formed in an amorphous SiO_2 epilayer implanted with 1×10^{16} ^{57}Fe/cm^2 and annealed up to 1000^{o}C.

2 Experimental

An amorphous SiO_2 layer was formed on a Si (100) surface by air-annealing the Si substrate at 1100^{o}C for 24 h. The SiO_2 epilayer was analysed with Rutherford Backscattering Spectroscopy (RBS) with a 900 keV He^{2+} beam, with the detector set at 165^o. The beam current was held at 15 nA and the total measurement charge was 9 μC. The RBS spectrum is shown in Fig. 1, together with a RUMP [10] fit to the data (solid line) which gave a uniform SiO_2 layer thickness of 460(1) nm.

The SiO_2 layer was implanted at room temperature with 60 keV ^{57}Fe ions to a fluence of 1 x $10^{16}/cm^2$ at the Göttingen ion implanter, with the beam raster scanned over the substrate surface. TRIM simulations [11] of the implantation profile yield an implantation range of 54 nm with a straggle of 18 nm.

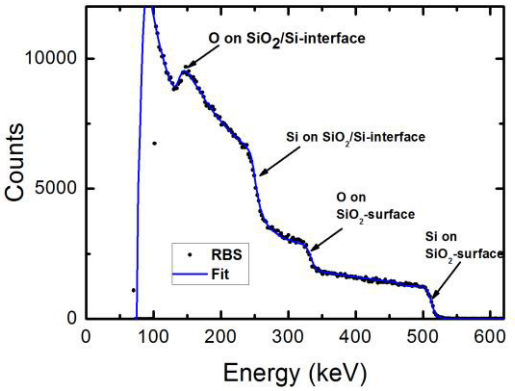

Figure 1 Rutherford backscattering spectrum of SiO_2 on Si(100) measured with 900 keV He^{2+} ions at 165°.

CEM spectra were collected of the as-implanted sample and after annealing the sample for 30 min. in air at various temperatures up to 1000°C. The parallel plate detector was operated with acetone gas at a pressure of 35 mBar in constant pressure mode. Measurements were performed at room temperature using a 25 mCi ^{57}CoRh source.

3 Results and discussion

The CEM spectra, collected after annealing the samples at the temperatures indicated are presented in Fig. 2. The spectra, up to an annealing temperature of 600°C, were decomposed into a single line component and three doublets (D1, D2 and D3), using Voigt line shapes for the spectral components. The spectra resemble those reported by Zhang *et al.* [7] and showed no evidence of a magnetic relaxation component as reported by Nomura *et al.* [9]. The fit parameters are listed in Table 1. The isomer shifts of doublets D1 and D2, 0.24(3) mm/s and 0.71(3) mm/s, respectively, are characteristic of Fe^{3+} and Fe^{2+}, most likely due to Fe nanoparticles of size below 5 nm as has been observed previously [8]. Doublet D3 (Fe_D) has a large linewidth, and its parameters are consistent with Fe located in damaged regions in the SiO_2 layer induced by the ion implantation.

On annealing at 800°C the Fe^{3+} doublet vanishes and a second doublet component with hyperfine parameters characteristic of Fe^{2+} appears. Also evident in the spectrum is a small contribution (13%) from a broad magnetic distribution with a mean hyperfine field of $\langle B_{hf} \rangle$ = 170 (40) kOe.

Further annealing of the Fe implanted SiO_2 sample at 1000°C for 30 min. results in the transformation of the major constituents in the spectrum into magnetic sextets, which account for > 80% of the spectral area. The magnetic components were approximated with two broad sextets and a magnetic distribution. The ratio of the peak intensities of the sextets was kept at 3:2:1:1:2:3 as angle dependent effects are not expected in the amorphous SiO_2 host. The sextet with the higher hyperfine

field, Sx1, (B_{hf} = 320(20) kOe) accounted for > 50% of the total spectral area. The average field of 320 kOe, which combined with the near zero isomer and electric quadrupole shifts, allow us to assign this component to metallic Fe clusters distributed throughout the implanted region of the SiO_2 epilayer, as has been observed by Perez *et al*. [8] and Zhang *et al*. [7].

The second sextet has an average hyperfine field of 263(20) kOe. A similar component has been observed by Zhang *et al*. [7], and attributed to Fe atoms located in the interface between α-Fe clusters and the SiO_2 matrix, where it may have Si or O atoms as nearest neighbour. The hyperfine field at Fe sites is reported to decrease by 27 kOe per Si nearest neighbour [12], suggesting (as has been observed by Zhang *et al*. [7], that the 263 kOe component may be attributable to a combination of distortions in the interface region and dilute concentrations of Si (and O) atoms in the Fe nearest neighbour.

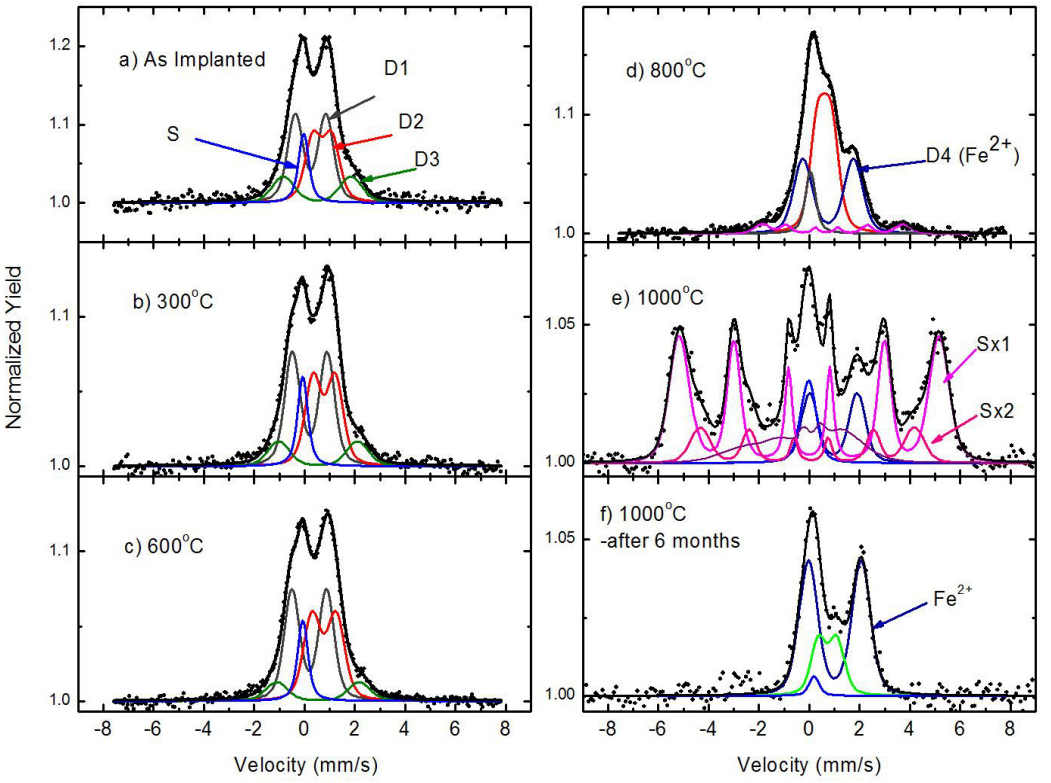

Figure 2 CEM spectra of the as-implanted Fe implanted SiO_2 sample and after annealing at the temperatures indicated

In addition to the sextet components, a broad single line component and a quadrupole split doublet were required to give acceptable fits to the data. The fit parameters of the spectral components and their assignments are collected in Table 1.

Table 1

Hyperfine parameters isomer shift (δ), quadrupole splitting (ΔE_Q), magnetic field (B_{hf}), quadrupole shift (ε), Gaussian broadening (σ) and areal fractions (A) extracted from the fits to the spectra shown in Fig. 2. The Lorentzian line width of the spectral components was kept at $\Gamma_{1/2}$ = 0.15 mm/s.

Annealing Temp, T_A	Component	δ (mm/s)	ΔE_Q (mm/s)	B_{hf} (kOe)	ε (mm/s)	σ (mm/s)	A (%)	Assign ment
As implanted	S	0.03(3)	-	-	-	0.25	12(2)	Fe^0
	D1	0.24(4)	1.22(9)	-	-	0.47	41(3)	Fe^{3+}
	D2	0.71(2)	0.74(2)	-	-	0.50	31(3)	Fe^{2+}
	D3	0.51(8)	2.7(4)	-	-	0.75	17(3)	Fe_D
300°C	S	0.07(3)	-	-	-	0.25	12(2)	Fe^0
	D1	0.21(3)	1.38(4)	-	-	0.47	42(3)	Fe^{3+}
	D2	0.78(3)	0.88(4)	-	-	0.50	34(4)	Fe^{2+}
	D3	0.55(7)	3.1(5)	-	-	0.75	13(4)	Fe_D
600°C	S	0.07(3)	-	-	-	0.25	11(2)	Fe^0
	D1	0.19(3)	1.38(4)	-	-	0.47	43(3)	Fe^{3+}
	D2	0.78(3)	0.96(4)	-	-	0.55	36(4)	Fe^{2+}
	D3	0.54(7)	3.3(5)	-	-	0.75	10(4)	Fe_D
800°C	S	0.04(3)	-	-	-	0.25	10(4)	Fe^0
	D2	0.60(5)	0.54(6)	-	-	0.45	45(4)	Fe2+
	D4	0.76(2)	2.01(4)	-	-	0.60	37(3)	Fe2+
	B_{dist}	0.8(2)	-	175(20)	-0.12	0.6	8(2)	
1000°C	S	0.03(3)	-	-	-	0.45	7(3)	Fe^0
	D4	0.96(3)	1.9(3)	-	-	0.50	12(3)	Fe2+
	Sx1	0.00(1)	-	320(20)	0.00(2)	0.6	52(3)	α-Fe
	Sx2	0.00(2)	-	263(20)	0.08(6)	0.6	14(3)	α-Fe
	B_{dist}	0.20(3)	-	123(30)	-0.3(2)	1.8	15(3)	
1000°C 6 months later	S	0.2(3)	-	-	-	0.25	3(2)	Fe^0
	D4	1.01(3)	2.10(7)	-	-	0.60	72(5)	Fe^{2+}
	D5	0.7(2)	0.75(5)	-	-	0.45	25(5)	Fe^{2+}

Magnetization measurements (m(H)) were conducted on the Fe implanted SiO_2 sample after the 1000°C annealing, using a vibrating sample magnetometer (VSM). The magnetization curves obtained at 293 K and 4 K are presented in Fig. 2. At 4 K, the sample shows a small hysteresis, with a coercivity of 0.05T. However it is the m(H) behaviour at RT, namely the attainment of saturation magnetization with zero hysteresis with application of small external field, that is of particular significance for the applications of embedded nanoparticles discussed above, provided, off course, that the magnetization is stable.

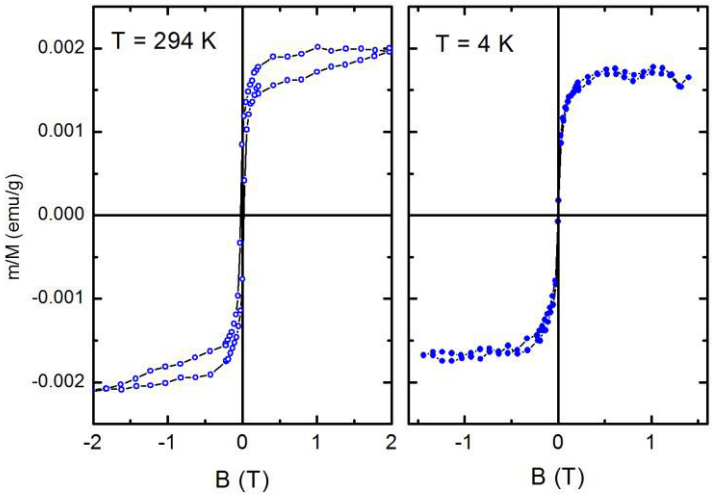

Figure 3 Magnetization curves of the Fe implanted SiO_2 sample after annealing at 1000°C, measured at RT and 4 K

The CEMS measurement on the annealed SiO_2 sample was repeated after storing the sample under ambient conditions for six months. The spectrum is shown in Fig 2(f). A surprising result is the disappearance of the magnetic sextets and the transformation of the spectrum to consist essentially of only two paramagnetic doublets. The dominant component (72%) is the doublet with an isomer shift of $\delta = 1.03(4)$ mm/s and a quadrupole splitting of 2.2(1) mm/s, clearly due to Fe^{2+}. The second doublet has $\delta = 0.7(2)$ and $\Delta E_Q = 0.75(5)$ mm/s; the isomer shift excludes assignment to Fe^{3+}. Magnetization measurements (Fig.4) show no evidence of hysteresis loops and confirm the paramagnetic transformation.

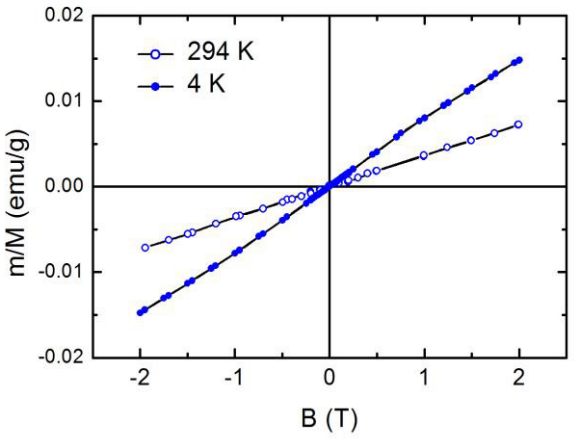

Figure 4 Magnetization curves measured at RT and 4 K.

A similar effect has been reported in Fe implanted ZnO by Zhou *et al*. [13], where annealing the implanted sample at 823 K resulted in enhanced ferromagnetic effects. However, on annealing above 1073 K no hysteresis loop was observed. The authors attributed this transformation to the majority of the Fe particles being oxidized to nonmagnetic compounds.

4 Conclusions

We have investigated the formation, characteristics and stability of Fe nanoparticles formed in an amorphous SiO_2 epilayer implanted with 1 x 10^{16}/cm^2 ^{57}Fe ions, applying both conversion electron Mössbauer spectroscopy and magnetization measurements. On annealing the sample up to 1000^{o}C magnetic sextets were observed in the CEM spectrum which could be attributed to Fe particles. Magnetization measurements at RT showed that the sample attained saturation magnetization in a low external field, without any evident hysteresis.

CEMS measurements on the sample after storage under ambient conditions for six months showed that, surprisingly, the magnetic sextets had disappeared, and a transformation of the Fe to Fe^{2+} had occurred. Magnetization measurements show no evidence of hysteresis loops and confirm the paramagnetic behaviour of the Fe inclusions. Our results indicate that oxidization of the Fe particles to some nonmagnetic compound had occurred over time, and suggests caution in the application of such clusters that are embedded in amorphous oxides.

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