

# Ion irradiation induced reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> and Fe<sup>0</sup> in triethoxysilane films

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Received 16 August 2005, in final form 9 September 2005

Published 14 October 2005

Online at [stacks.iop.org/JPhysCM/17/7023](http://stacks.iop.org/JPhysCM/17/7023)

## Abstract

Silica gel films prepared from mixtures of triethoxysilane (TH) and Fe nitrate Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were irradiated with various fluences of 3 MeV Au ions. Silicon 2p x-ray absorption (XAS) and L<sub>2,3</sub> x-ray emission spectra of irradiated TH:Fe films are found to be very similar to those of SiO<sub>2</sub>, providing direct evidence of the formation of a glassy matrix. Fe L<sub>2,3</sub> XAS shows the reduction of Fe<sup>3+</sup> ions at low fluence, initially attributed to the formation of Fe metallic nanoparticles. Mössbauer spectra of films irradiated with higher ion fluences are well fitted by a singlet associated with superparamagnetic Fe particles and a doublet associated with Fe<sup>2+</sup> ions in Fe–Si–O complexes.

## 1. Introduction

Nanoscale metallic particles have been the subject of recent studies, which attempted to understand their fundamental properties and to explore their possible use as catalysts, magnetic field sensors, high-density magnetic recording media, and drug delivery aids, among other things [1, 2]. This type of nanomaterial can be prepared using a variety of different methods, one of the most versatile being sol–gel chemistry. Ease of preparation is one of the factors that make silica gels attractive matrices for the growth of metallic nanoparticles. In addition, the glasses that are formed when the gels are thermochemically treated are chemically stable and have useful optical properties.

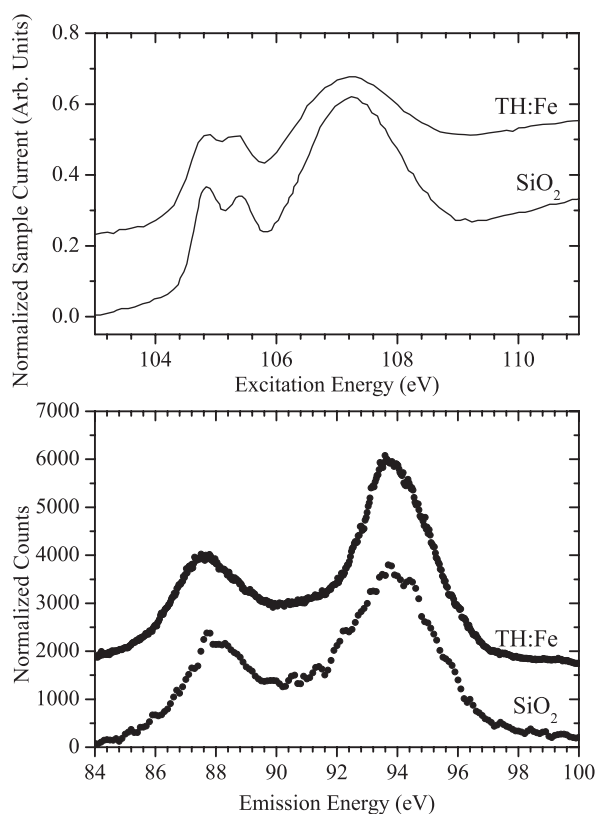
It has been shown that the irradiation of Si-based polymers and gels with very low ion fluences can induce a conversion into strong, high-density glasses [3–5]. In addition, the promotion of reactions between metal ions from salts and hydrido groups in gels prepared from triethoxysilane ( $\text{SiH}(\text{OC}_2\text{H}_5)_3$ , hereafter labelled TH) causes the formation of metal nanoparticles in these glasses [5, 6]. Due to the limited diffusion of atoms over short ranges during the ion irradiation process, the metal nanoparticles that are obtained have sizes that are determined by the dimension of the interaction volume of single ions with the gel matrix [7]. The practical consequence of this limited diffusion is a beneficial one, as the size distribution of the nanoparticles that are produced by ion irradiation is much narrower than that of particles obtained using a thermochemical treatment [6, 8].

The measured values of the magnetization indicate that not all of the Fe atoms are in metal clusters after the films have undergone high-fluence ion irradiation (the magnetization and cluster size were determined by means of magnetometry, electron-spin resonance (ESR) and transmission electron microscopy (TEM) [7–9]). In order to gain an understanding of the ion irradiation chemistry and to optimize the amount of metal nanoparticles that are obtained, the local changes in chemical structure must be characterized. The early stages of the conversion of the gel into a composite glass are especially interesting, because the reaction between Si–H groups and  $\text{Fe}^{3+}$  ions may produce either iron silicide or metal nuclei through successive steps of reduction. If the silicide is produced, the limited values of saturation magnetization that are measured on completion of the precipitation would be simply ascribable to the lower number of magnetons per Fe atom in clusters of Fe–Si alloy than in clusters of bcc Fe [10]. The two types of cluster cannot be distinguished by means of x-ray diffraction or TEM methods because of the extremely small size (2 nm) of the clusters. In this paper we use soft x-ray absorption spectroscopy (XAS) and soft x-ray emission spectroscopy (XES), along with Mössbauer analysis, to study a series of irradiated TH:Fe films; both techniques are sensitive to the local atomic and electronic structures of the excited atoms.

## 2. Experimental details

The TH films were synthesized from commercially available reagents, which were used without any further purification. The samples were obtained from Aldrich; the TH had a purity of 95% and the  $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$  had a purity of 98%. Equal volumes of TH and ethanol were combined and stirred for 1 h to allow hydrolysis of the ethoxide by the ambient moisture. Analysis of the TH gel matrix by means of observation of the nuclear reaction  $^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$  showed that the addition of water to the solution is not useful for hydrolysing the Si–O– $\text{C}_2\text{H}_5$  bond, as the formed hydroxide contains less than 2 at.% carbon.  $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$  was dissolved in the gelling solution, with a molar concentration of 10% nitrate per alkoxide. The gels were then deposited on Si substrates by spinning at 2000 rpm, yielding films with a thickness of 450 nm. The TH:Fe films were irradiated with a low current density ( $0.1 \mu\text{A cm}^{-2}$ ) of 3 MeV Au ions. The sample holder was cooled with flowing water to prevent significant heating of the specimen, which would otherwise have been brought on by absorption of the ions. The samples studied in the x-ray absorption and emission experiments were irradiated with low ion fluences ( $2 \times 10^{13}$ – $1 \times 10^{14} \text{ Au cm}^{-2}$ ) so that the early stages of the gel-to-ceramic conversion could be studied. The spectra were compared to those measured from a film irradiated with  $10^{15} \text{ Au cm}^{-2}$  (optimum for the magnetization) and a monolith that had been heat treated in vacuum. These latter samples were also studied using Mössbauer spectroscopy, in order to better characterize the structure that is obtained upon completion of the gel-to-ceramic conversion.

The conversion electron Mössbauer spectroscopy (CEMS) measurements on the irradiated TH:Fe film were performed at room temperature with a He/6% $\text{CH}_4$  flow proportional counter



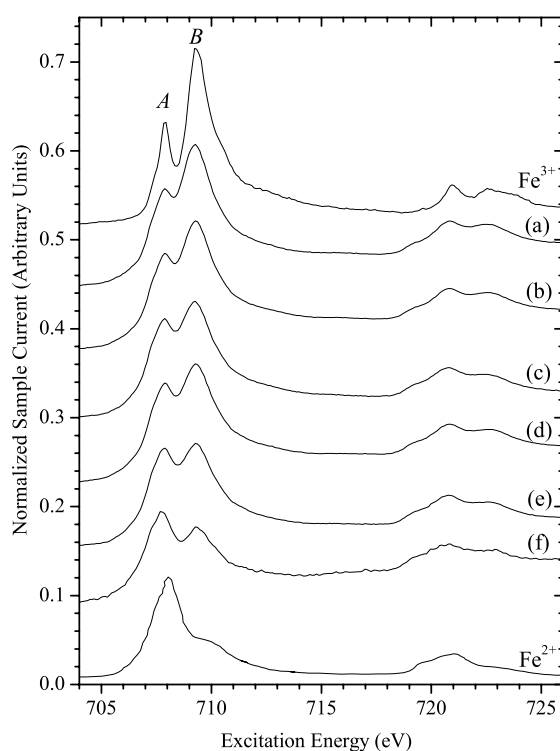
**Figure 1.** Si 2p XAS (top panel) and L<sub>2,3</sub> emission (bottom,  $h\nu_{\text{exc}} = 120$  eV) of a TH:Fe film irradiated with an Au ion fluence of  $2 \times 10^{13}$  Au cm<sup>-2</sup> as well as spectra of the reference sample SiO<sub>2</sub>.

and a <sup>57</sup>Co/Rh source. It should be mentioned that in this case the information depth is limited to about 100 nm (about 1/4 of the film thickness), because of the low escape depth of the conversion electrons. The TH:Fe film used for CEMS contained only the natural abundance of the <sup>57</sup>Fe isotope (2%), and therefore a long acquisition time was needed to obtain statistics that were adequate to allow for a first approximation of the hyperfine parameters. Mössbauer absorption measurements on a powder that was obtained by grinding a TH:Fe monolith yielded a stronger signal and confirmed the fitted values. Analyses of the Mössbauer spectra were performed by superimposing Lorentzian lines on the spectra using a least-squares fit program.

The soft x-ray absorption and emission spectra were measured using the soft x-ray fluorescence endstation at Beamline 8.0.1 at the Advanced Light Source synchrotron at Lawrence Berkeley National Laboratory. The details of this facility have previously been documented [11].

### 3. Results and discussion

The Si 2p XAS and L<sub>2,3</sub> XES spectra of a TH:Fe film are compared to those of a SiO<sub>2</sub> reference sample in figure 1. It is clear that both the absorption and emission spectra of the film resemble those of SiO<sub>2</sub> [12]. The shape of the emission spectrum is typical for the Si L<sub>2,3</sub> emission of SiO<sub>2</sub>, with the feature at 87.8 eV associated with transitions from s-symmetric valence band

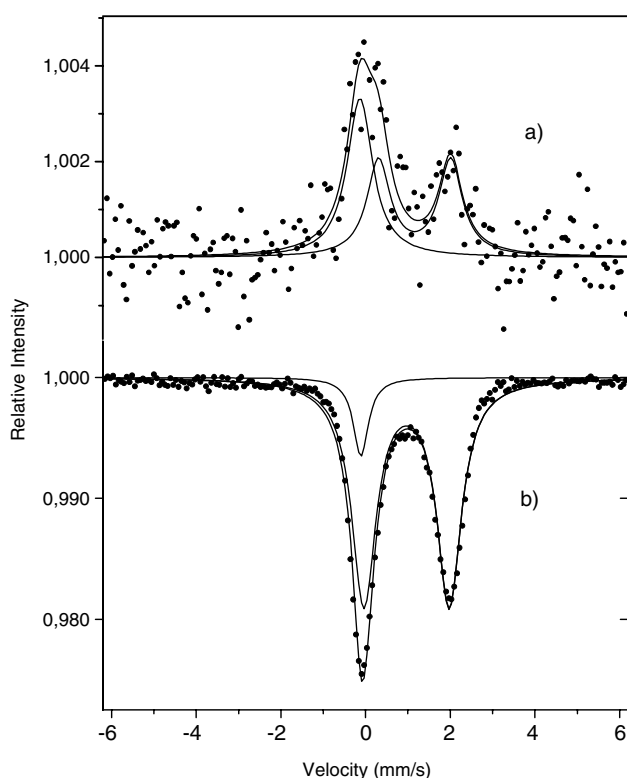


**Figure 2.** Fe 2p XAS of TH:Fe films irradiated with 3 MeV ion fluences of (a)  $2 \times 10^{13}$  Au cm $^{-2}$ , (b)  $4 \times 10^{13}$  Au cm $^{-2}$ , (c)  $8 \times 10^{13}$  Au cm $^{-2}$ , (d)  $1 \times 10^{14}$  Au cm $^{-2}$ , (e)  $1 \times 10^{15}$  Au cm $^{-2}$ , along with an annealed TH:Fe film and reference spectra of Fe $^{2+}$  and Fe $^{3+}$ .

(VB) states into the 2p core hole, and the peak at 93.7 eV stemming from transitions from d-symmetric VB states into the 2p core hole. The measured spectra also closely resemble previously published density of states calculations of the spectra of SiO $_2$  [13, 14]. Both XAS and XES spectra of all TH:Fe samples included in this study were measured. All of the Si-edge TH:Fe spectra were identical, and so only the spectra of the film irradiated with the lowest ion fluence ( $2 \times 10^{13}$  Au cm $^{-2}$ ) are included here. The agreement between the TH:Fe spectra and the SiO $_2$  spectra in figure 1 confirms that the gels are converted to glasses at even the lowest ion fluence.

The Si XES spectra of both pure Si and silicides have a characteristic peak at approximately 90 eV, as well as a shoulder on the feature that is centred at 93.8 eV [15]. These features are associated with Si 3s states, and are not evident in the TH:Fe spectra shown in figure 1. The absence of these features is significant, as it suggests that neither clusters of pure Si (observed in films without Fe that were irradiated with higher fluences [5]) nor clusters of silicides are found in the films.

The effects of varying ion fluence are seen clearly in the absorption spectra of the Fe sites in the films. Fe 2p XAS spectra reflect the different electron configurations of the different oxidation states of Fe [16]. Figure 2 shows the XAS spectra of the TH:Fe films, compared to the reference spectra of Fe $^{2+}$  and Fe $^{3+}$ . The intensities of the spectra have been normalized at the location of the low-energy peak 'A' (approximately 707.8 eV), and a vertical offset has been added. All of the spectra consist of two main features, associated with transitions from the 2p $_{3/2}$  (L $_3$ ,  $\sim 709$  eV) and 2p $_{1/2}$  (L $_2$ ,  $\sim 721$  eV) core levels.



**Figure 3.** (a) Conversion electron Mössbauer spectrum of a TH:Fe film irradiated with  $10^{15}$  Au cm<sup>-2</sup>; (b) for comparison, transmission Mössbauer spectrum of a powder obtained by grinding a TH:Fe annealed monolith.

Clear changes in the fine structure of the spectra as a function of ion fluence are seen in figure 2. The intensity of the prominent peak B on the L<sub>3</sub> feature decreases drastically with increasing Au ion fluence. The uppermost TH:Fe spectrum represents the sample irradiated with the lowest Au ion fluence, and its spectrum most closely resembles that of the Fe<sup>3+</sup> reference sample. As the ion fluence is increased, the spectra of the films begin to more closely resemble that of Fe<sup>2+</sup>. This trend indicates that the samples irradiated with low fluences contain mostly Fe<sup>3+</sup>, characteristic of the unreacted Fe(NO)<sub>3</sub>, with a portion of the Fe being reduced to either Fe<sup>2+</sup> or Fe<sup>0</sup> upon irradiation. The intensity of peak B is a minimum in the spectra of the heat-treated monolith and the sample irradiated at  $10^{15}$  Au cm<sup>-2</sup>, although the spectra suggest that, even under these conditions, a certain amount of Fe<sup>3+</sup> remains. XAS cannot be used to distinguish between Fe<sup>2+</sup> and Fe<sup>0</sup> oxidation states, because they have the same 3d<sup>6</sup> configuration.

The conversion electron Mössbauer spectrum of a TH:Fe 10% film irradiated with a  $10^{15}$  Au cm<sup>-2</sup> fluence is shown in figure 3. The singlet feature seen at zero velocity is attributed to the presence of superparamagnetic clusters of metallic iron (Fe<sup>0</sup>). There is also a doublet feature, having an isomer shift of 1.07 mm s<sup>-1</sup> and a quadrupole splitting of approximately 1.50 mm s<sup>-1</sup>, which is assigned to Fe<sup>2+</sup> ions in a Fe–Si–O complex [17]. Statistically better data were obtained in transmission mode from an annealed powder. The comparison of these two samples is based on the expectation that TH:Fe gels converted into SiO<sub>2</sub>:Fe glasses differ only in the size of the particles formed. The similarities between the Fe 2p XAS spectra (figure 2) of

the two similar samples studied using soft x-ray spectroscopy support this assertion. Like the conversion electron mode spectrum, the transmission mode Mössbauer spectrum also shows a singlet feature at zero velocity, as well as a doublet structure. This doublet has a higher value of the quadrupole splitting ( $2.02 \text{ mm s}^{-1}$ ) and a larger relative area than does the corresponding feature in the spectrum of the irradiated sample. These differences are attributed to the different sterical arrangement of Si–O–Fe groups in the matrix (close to that in pyroxenes). Residual  $\text{Fe}^{3+}$  ions are not detected by this technique.

#### 4. Conclusion

A combination of soft x-ray absorption/emission spectroscopy and Mössbauer spectroscopy was used to characterize the early stages of the ion induced reaction between Si–H and  $\text{Fe}^{3+}$  ions in triethoxysilane gel films. The reduction of  $\text{Fe}^{3+}$  in the films is shown to be a function of the Au ion fluence. The combination of the various spectroscopic techniques suggests the presence of both iron metal ( $\text{Fe}^0$ ) and  $\text{Fe}^{2+}$  in the irradiated samples. The  $\text{Fe}^{2+}$  ions are probably found in Fe–Si–O complexes. No evidence of the formation of silicide particles, which had been proposed as an explanation for the previously observed saturation of the magnetization of the films, was found in the spectra.

#### Acknowledgments

Funding by the Research Council of the President of the Russian Federation (Grants NSH-1026.2003.2), Russian Science Foundation for Basic Research (Projects 05-02-16438 and 05-02-16448), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program, and the Saskatchewan Synchrotron Institute is gratefully acknowledged.

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