
LOW-DIMENSIONAL SYSTEMS
AND SURFACE PHYSICS

Iron Nanoparticles in Amorphous SiO₂: X-ray Emission and Absorption Spectra

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Abstract—The local structure of the chemical bond of iron ions implanted into SiO₂ glasses (implantation energy, 100 keV; fluence, $1 \times 10^{16} \text{ cm}^{-2}$) is investigated using x-ray emission and absorption spectroscopy. The Fe *L* x-ray emission and absorption spectra are analyzed by comparing them with the corresponding spectra of reference samples. It is established that iron nanoparticles implanted into the SiO₂ vitreous matrix are in an oxidized state. The assumption is made that the most probable mechanism of transformation of iron nanoparticles into an oxidized state during implantation involves the breaking of Si–O–Si bonds with the formation of Si–Si and Fe–O bonds. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

Nanoclusters of 3*d* transition metals (iron, nickel, cobalt) dispersed into dielectric matrices are characterized by large values of the magnetic moment, coercive force, and shift in the hysteresis loop and exhibit a great variety of interesting magneto-optical properties [1]. This makes it possible to use these materials as optical switches, shutters or waveguides [2], enhanced magnetic refrigerants, and high-density magnetic recording media [3, 4]. Amorphous silicon dioxide SiO₂, which is the most important dielectric material in modern electronics, has been widely used as a matrix for dispersion of metal nanoparticles. At present, ion implantation is a powerful tool for introducing metal nanoparticles into dielectric matrices owing to the simplicity and accuracy of the control of the nanocomposite microstructure, the quantitative analysis of implanted ions and their distribution over the depth of the matrix and particle size, the distribution of implanted ions in a nanocluster, etc. Moreover, ion implantation is entirely compatible with modern technology for producing silicon semiconductors and can be accomplished with an almost arbitrary metallic dopant. In this work, the local configurations of the chemical bonds of iron ions implanted into SiO₂ glasses were investigated using soft x-ray emission and absorption spectroscopy.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Silicon dioxide SiO₂ was irradiated by iron ions at a dose of 16^{16} ions/cm² with the use of ⁵⁶Fe⁺ (which is close to the natural mixture of isotopes, sample *a*) and ⁵⁷Fe⁺ (isotope 57, sample *b*). Prior to ion implantation, glass samples 10 mm in diameter and 0.8 mm in thickness were subjected to wet chemical cleaning in a solution of H₂O₂ : H₂SO₄ = 1 : 1 at a temperature of 120°C, after which the samples were washed with deionized water and dried. The implantation of ⁵⁷Fe ions was accomplished on a DANFYSIK high-current implanter operating at a voltage of 200 kV at the Research Center Rossendorf, Institute of Ion Beam Physics and Materials Research, Germany. The samples were mounted on a target holder and affixed to it with an adhesive carbon tape. The implantation was performed with separated (according to mass) charged ⁵⁷Fe ions along the normal to the surface of the sample at room temperature. The residual pressure in the ion implantation chamber reached 10^{−6} Torr. The samples were irradiated at fluences ranging from 1×10^{14} to $1 \times 10^{16} \text{ cm}^{-2}$ and at a current density of 0.1–0.2 μA/cm². In each event of implantation, the energy *E* of iron ions was equal to 100 keV, which corresponded to their path in silicon dioxide *R_p* = 83 nm (the maximum in the Gaussian distribution) for doses up to $1 \times 10^{16} \text{ cm}^{-2}$. For the greatest

dose of ion implantation, which is equal to $1 \times 10^{17} \text{ cm}^{-2}$, the maximum in the ^{57}Fe distribution is located at a lesser depth (68 nm) due to an increase in the degree of sputtering (at approximately 15 nm for SiO₂). The maximum atomic fraction of ^{57}Fe in SiO₂ amounted to 20% for a dose of $1 \times 10^{16} \text{ cm}^{-2}$. The relative content of ^{57}Fe isotope in the implanted glass samples was approximately equal to 90% (the remaining 10% were accounted for by other iron isotopes). The implantation of $^{56}\text{Fe}^+$ ions was accomplished on a high-voltage implanter operating at a voltage of 500 kV at the Research Center Rossendorf, Institute of Ion Beam Physics and Materials Research, Germany. In this case, the conditions used for preparing the samples and for their implantation were similar to those described above. Since the ionic current provided by the second implanter was weaker, the mass separation used was smaller. As a result, the isotope composition of the implanted samples involved isotopes 55, 56, and 57 with the maximum concentration of ^{56}Fe .

The x-ray emission and absorption spectra were measured on a BL27SU Spring-8 beam line (Japan) with a soft x-ray fluorescence spectrometer. The well-focused ion beam (less than 10 μm in the transverse direction) made it possible to use a slitless spectrometer, which improved the throughput of the instrument and the detection efficiency. The slitless spectrometer with a spherical varied-line-spacing (VLS) grating and a back-illuminated (BI) charged-coupled device (CCD) detector [5] provided an energy resolution $E/\Delta E = 1000$.

3. RESULTS AND DISCUSSION

Our analysis of the Fe 2*p* x-ray absorption spectra is based on the data obtained by van der Laan and Kirkman [6] and de Groot [7], who carried out systematic investigations and interpreted the calculated 2*p* absorption spectra of 3*d* transition metal compounds. The 2*p* x-ray absorption spectra are allowed by the dipolar selection rules and correspond to electronic transitions from the 2*p* core level to the 3*d* vacant states, i.e., to the transition from the ground state with electronic configuration $2p^63d^n$ to the excited state with electronic configuration $2p^53d^{n+1}$. Since the Coulomb interaction between a hole at the 2*p* core level and 3*d* electrons is significant, the 2*p* x-ray absorption spectra are determined by the local electronic structure and provide information on the oxidation state and the symmetry of 3*d* transition metal ions in a particular compound. The $2p_{3/2}$ and $2p_{1/2}$ spectral components are well resolved by virtue of the core-hole spin-orbit interaction and have a multiplet structure because the broadening due to the core-hole lifetime is very small. As was shown in [6, 7], there is a clearly pronounced difference between the calculated 2*p* spectra for the ground states of different iron ions (Fe^{2+} and Fe^{3+}), which can be used to identify

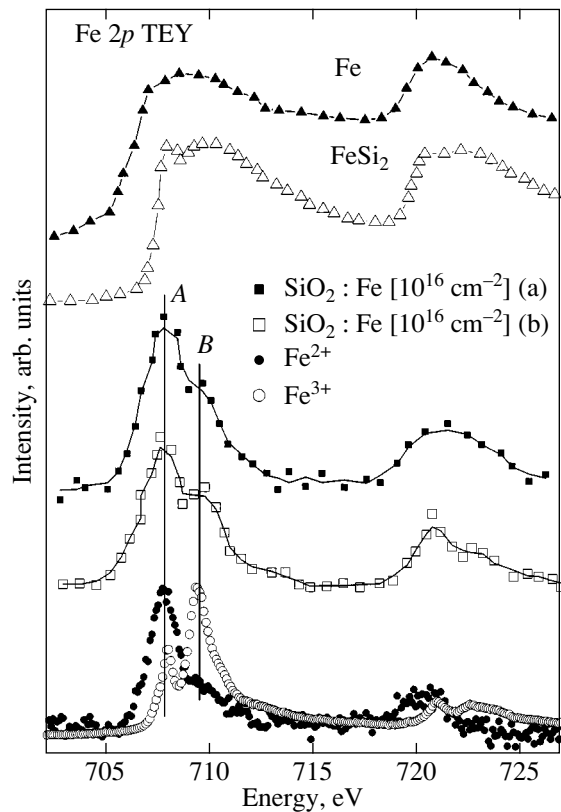


Fig. 1. Fe 2*p* x-ray absorption (TFY) spectra of iron-implanted SiO₂ glasses. The spectra of the reference samples are shown for comparison.

the chemical state of iron ions implanted into SiO₂ glasses. Figure 1 presents the experimental Fe 2*p* x-ray absorption spectra of iron-implanted SiO₂. The intensity of these spectra is normalized to the low-energy peak A, which is located at an energy of ~ 707.8 eV. We could measure the Fe 2*p* x-ray absorption spectra only for the samples irradiated at a maximum dose ($D = 1 \times 10^{16} \text{ cm}^{-2}$). The 2*p* x-ray absorption spectra consist of low-energy $2p_{3/2}$ (L_3) and high-energy $2p_{1/2}$ (L_2) components separated by approximately 13 eV. The relative intensity of the peak B located at an energy of ~ 709.3 eV in the x-ray absorption spectra for all samples of iron-implanted SiO₂ is very close to that of divalent iron (the spectrum is characterized by a higher intensity of the peak A); however, it differs substantially from the relative intensity of the peak B attributed to trivalent iron. It should be noted that the 2*p* x-ray absorption spectra cannot be described in terms of the one-particle density of states, because the electronic correlations in atoms with a partially filled 3*d* shell are very significant [6]. As a rule, the solid-state effects are introduced into atomic-like calculations of the 2*p* absorption spectra through the inclusion of a crystal field that accounts for the local symmetry of the metal atom and the matrix elements of different hybridizations of the 3*d* orbitals

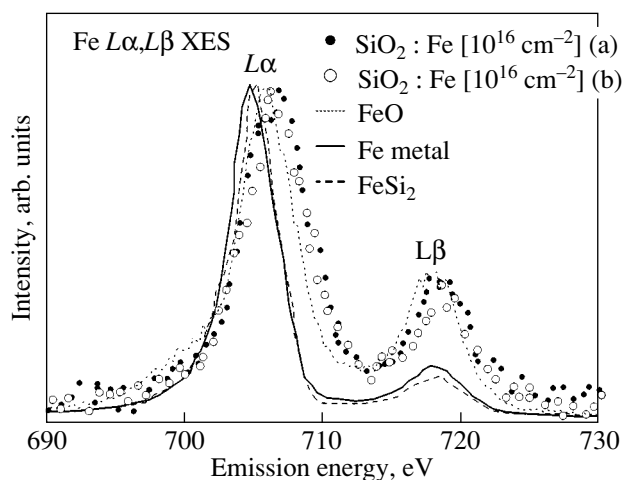


Fig. 2. Comparison of Fe $L\alpha$ and Fe $L\beta$ x-ray emission (Fe $L\alpha$, $L\beta$ XES) spectra of iron-implanted SiO_2 glasses with the spectra of the pure iron metal and FeO oxide.

with the surrounding ligands [6]. It is found that, within the single-configuration approach, the experimental L x-ray absorption spectra of $3d$ metals in different compounds can be reproduced fairly well. According to the experimental x-ray absorption spectra of trivalent and divalent iron atoms (Fig. 1), the double-peak structure of the Fe $2p$ absorption spectra is assigned to the final state with electronic configuration d^5 (Fe^{3+}) and the single-peak structure of these spectra is attributed to the final state with electronic configuration d^6 (Fe^{2+}), which roughly reflects the multiplet structure. Therefore, the above results allow the conclusion that dispersed iron nanoparticles interact with SiO_2 and can oxidize to the Fe^{2+} state. It was also established that the chemical state of iron atoms in iron-implanted silicon dioxide is not sensitive to the substitution for an iron isotope.

The Fe $L\alpha$ and Fe $L\beta$ nonresonant x-ray emission spectra of $\text{SiO}_2 : \text{Fe}$ (Fig. 2) can be analyzed in a similar manner. As in the case with the Fe $2p$ x-ray absorption spectra, we could measure only the samples irradiated at the dose $D = 1 \times 10^{16} \text{ cm}^{-2}$. The Fe $L\alpha$ and Fe $L\beta$ x-ray emission spectra are associated with the electronic transitions $\text{Fe } 3d4s \rightarrow 2p_{3/2, 1/2}$ and provide probing the Fe $3d4s$ occupied states. It can be seen from Fig. 2 that the intensity ratio $L\beta/L\alpha$ is very small for the pure metal and differs from the value of 0.5 expected for the statistical mean occupancy of the inner levels with $j = 3/2$ and $1/2$ due to the Coster–Kronig nonradiative transition $L_2L_3M_{4,5}$ [8]. It is known that the intensity ratio $L\beta/L\alpha$ increases upon changing over from pure $3d$ metals to their oxides, because the probability of the Coster–Kronig nonradiative transition $L_2L_3M_{4,5}$ occurring in $3d$ metal oxides is considerably lower than that in pure metals [9]. The intensity ratio $L\beta/L\alpha$ in the

spectra of the $\text{SiO}_2 : \text{Fe}$ samples under investigation is larger than that in the spectra of metallic iron and FeSi_2 and is almost identical to that in the spectrum of FeO. From the aforesaid, we can make the inference that, after the implantation, iron atoms in $\text{SiO}_2 : \text{Fe}$ are in a valence state of $2+$. This inference is in complete agreement with the results of measuring the Fe $2p$ x-ray absorption spectra (Fig. 1).

The results obtained can be interpreted as follows. It is known that nanocrystalline metal particles are thermodynamically metastable and chemically active. Iron nanoparticles are pyrophoric and can be readily oxidized [10]. According to our investigations, iron ions transform into an oxidized state with the subsequent formation of clusters during implantation of the SiO_2 glass. It is assumed that the ion implantation brings about the breaking of Si–O–Si bonds, the formation of Si–Si bonds, and the subsequent capture of oxygen atoms by iron atoms with the formation of FeO oxide in the form of small-sized clusters. A similar behavior is observed in the case of SiO_2 implanted by cobalt atoms [11].

4. CONCLUSION

The local structure of the chemical bond in amorphous silicon dioxide after iron ion implantation was studied using x-ray emission and absorption spectroscopy. It was revealed that the ion implantation is accompanied by the formation of iron nanoparticles in an oxidized state due to the breaking of Si–O–Si bonds and the formation of Si–Si and Fe–O bonds. In this case, the iron atoms have a valence of $2+$. It was demonstrated that the valence state of iron atoms in implanted amorphous silicon dioxide is not sensitive to substitution for an iron isotope.

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