

Ion-beam mixing at the Fe/SiO₂ interface: A conversion-electron Mössbauer spectroscopy and x-ray-diffraction study

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(Received 27 September 1988; revised manuscript received 6 December 1988)

The effect of ion-beam-induced atomic mixing and subsequent thermal transformations at the Fe:SiO₂ (single crystal) interface have been investigated by means of conversion-electron Mössbauer spectroscopy and small-angle x-ray-diffraction measurements. The ion-beam-mixed sample in the as-mixed state shows the presence of the Fe₇SiO₁₀ phase along with magnetic Fe-Si-O complexes. The mixed state undergoes structural modifications upon annealing at 450 °C for several hours leading to an increase in Fe³⁺-to-Fe²⁺ ratio. The as-deposited sandwich structure upon annealing at 450 °C leads to the formation of metal island structures.

Ion-beam-induced atomic-mixing effects in metal-insulator systems have attracted significant attention from researchers recently,¹⁻³ in view of the implications of such studies for our understanding of radiation-induced defect creation and diffusion mechanisms in insulating materials, and also for the development of insulator-based device technologies based on dry processing concepts. In the present paper we report the results of our studies on ion-beam mixing at the Fe:SiO₂ (single crystal) interface. This is an important material system for different reasons. First, Fe and SiO₂ are thought to be insoluble,⁴ and therefore the system is an interesting one for examination of beam-induced metastability. Second, this system has a potential for magneto-optic applications when produced in the form of compositionally modulated films.⁴ Third, silica has been extensively used as a support medium for both metallic iron as well as iron oxides in catalytic applications,⁵ and therefore the interface of Fe and SiO₂, and its modifications, are also of interest to the discipline of catalysis.

Single-crystal *c*-axis-oriented silicon oxide (SiO₂) substrates were used in the present investigations. The samples for ion-beam-mixing studies were prepared by depositing a 300-Å-thick iron overlayer, enriched to 30% in the concentration of the ⁵⁷Fe Mössbauer isotope in the Varian ultrahigh vacuum (UHV) system at a background pressure of 10⁻⁸ Torr. A number of freshly prepared Fe:SiO₂ composites were subjected to Ar⁺-ion bombardment at an energy of 100 keV up to a dose of 5×10¹⁶ ions/cm². The ion-beam-mixed and as-deposited samples were subjected to vacuum-annealing treatments (pressure approximately equal to 10⁻⁶ Torr) at a temperature of 450 °C for 1 and 6 h. Room-temperature conversion-electron Mössbauer (CEM) spectra were recorded with ⁵⁷Co:Rh as the source. To obtain the best-fit values of the hyperfine (hf) interaction parameters, computer fitting of the spectra was carried out by using the standard MOSFIT code.⁶ Wherever necessary, the composite Mössbauer spectra were deconvoluted following the procedure suggested by Le Caer and Dubois.⁷ The isomer-shift values reported in this work are with respect to α -Fe. X-ray-diffraction studies of the as-deposited and ion-beam-

mixed samples were performed by using a small-angle x-ray-diffraction technique employing the Seeman-Bohlin arrangement.⁸

The CEM spectrum of the as-deposited sample [Fig. 1(a)] can be resolved into magnetic as well as nonmagnetic components. The magnetic one corresponds to α -Fe. The nonmagnetic contribution is quadrupole doublet having an isomer shift (IS) of 0.16 mm/sec and a quadrupole splitting (QS) of 0.55 mm/sec. Such a doublet represents the Fe³⁺ state and it can be attributed to iron atoms (⁵⁷Fe) incorporated into the SiO₂ matrix due to deposition-induced reaction. The CEM spectrum of the sample, implanted at a dose of 1×10¹⁶ ions/cm² [see Fig. 1(b)], clearly shows mixing effects. The linewidth (Γ) for the case of the implanted sample (0.54 mm/sec) is considerably larger than that for the as-deposited sample (0.23 mm/sec), and this indicates that lattice disorder is created in the implanted sample.

The CEM spectrum of the sample implanted at a dose of 5×10¹⁶ ions/cm² [see Fig. 1(c)] shows significant change. It can be fitted with two doublets and two sextets ($H = 303$ kOe, 342 kOe). The hyperfine interaction parameters of one doublet are IS, 1.2 mm/sec and QS, 1.99 mm/sec, while those of the second doublet are IS, 0.15 mm/sec and QS, 1.25 mm/sec. It is well known that the hyperfine field at the Fe site reduces by 27 kOe per silicon near neighbor,⁹ while strongly bonded oxygen-rich iron compounds have a higher field value than that for α -Fe.¹⁰ The appearance of the 303 kOe magnetic component may thus be due to dilute concentration of silicon atoms in the iron overlayer in which ⁵⁷Fe atoms have one silicon near neighbor. The presence of the latter magnetic component (342 kOe) may be attributed to the combined effect of silicon and oxygen near-neighbor atoms in the ion-beam-mixed region. The two nonmagnetic components (doublets) can be identified as iron in Fe²⁺ and Fe³⁺ states.¹⁰ The appearance of these type of components in the CEM spectrum of the implanted sample can be explained on the basis of the disordered network of SiO₂ structures formed due to Ar⁺-ion implantation. In general, SiO₂ consists of an interconnecting ring system of SiO₄ tetrahedral units which are joined together via bridging oxygen. During

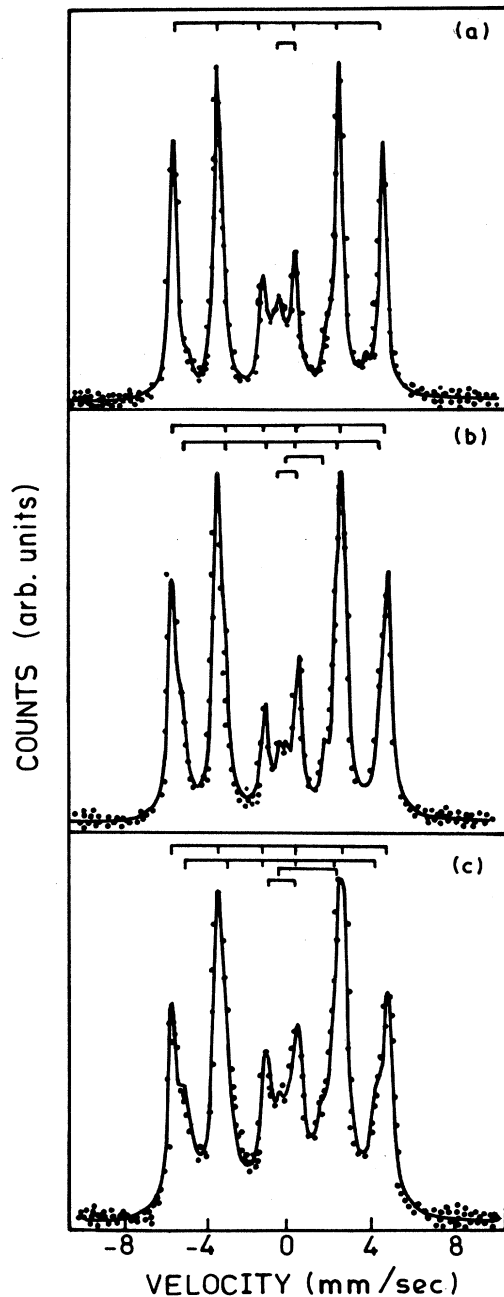


FIG. 1. Room-temperature CEM spectra of (a) as-deposited and (b), (c) ion-beam-mixed Fe:SiO₂ composites. The ion-beam fluences are for (b) 1×10^{16} ions/cm² and for (c) 5×10^{16} ions/cm².

Ar⁺-ion bombardment the Si-O bonds break¹¹ and Si and O atoms are displaced leaving charge inequality in the whole structure. In this distorted structure atoms from the iron overlayer could get incorporated, leading to iron in various states as observed in our case.

The x-ray-diffraction pattern obtained for the as-deposited sample [Fig. 2(a)] at a grazing angle of 1.0° clearly shows the contributions of α -Fe as well as SiO₂

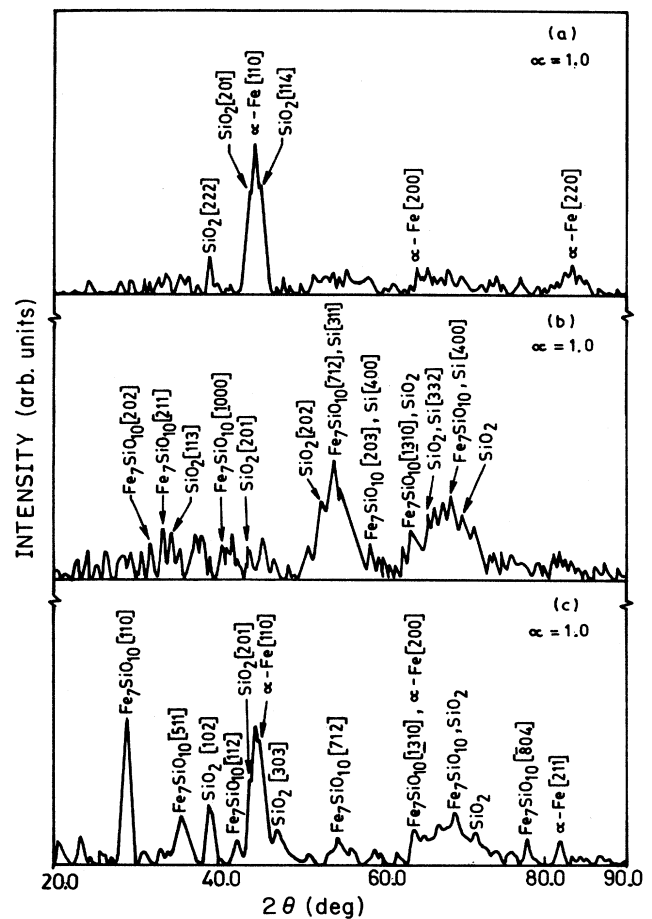


FIG. 2. Small-angle x-ray-diffraction pattern of (a) as-deposited and, (b) ion-beam-mixed Fe:SiO₂ sandwich structure, and (c) ion-beam-mixed Fe:SiO₂ composite annealed at 450°C for 6 h.

(substrate). The x-ray-diffraction pattern taken at the same grazing angle of the sample implanted at 5×10^{16} ions/cm² [Fig. 2(b)] shows absence of α -Fe which indicates that mixing has taken place. The diffraction lines are broad as compared to those for the as-deposited sample [Fig. 2(a)], which brings out the degree of the structural disorder induced by Ar⁺-ion bombardment. The x-ray-diffraction pattern exhibits the presence of an Fe₇Si₁₀ phase; a type of iron silicate which is known to contain iron in both 3+ and 2+ states,¹² as well as a possible presence of pure silicon when analyzed in terms of the line positions and their relative intensities. These observations are in agreement with the conversion electron Mössbauer spectroscopy (CEMS) results. Our CEMS and x-ray data suggest that both collisional and diffusional transport processes are active in the ion mixing at the Fe:SiO₂ interface. Collisional process leads to the formation of Fe-Si-O-type complex as well as silicon deficient iron silicate (Fe₇Si₁₀) while the presence of a dilute concentration of silicon in the iron matrix is possibly an outcome of the diffusional process. This is consistent with the results reported by Banwell *et al.*¹³ for

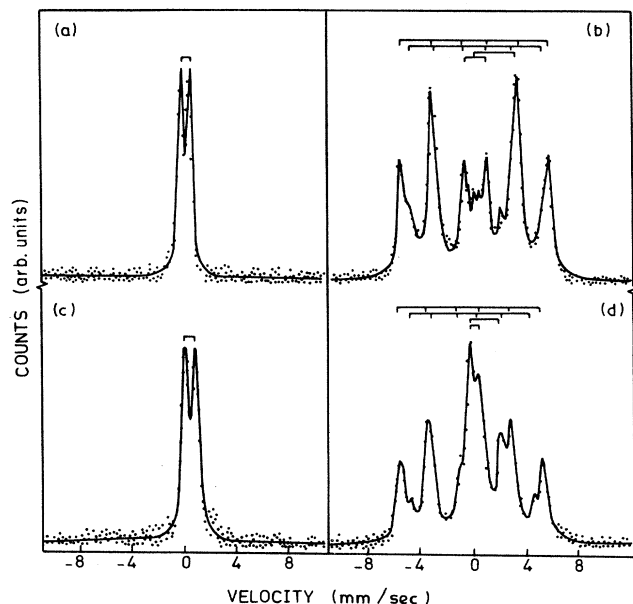


FIG. 3. Room-temperature CEM Spectrum of Fe:SiO₂ composite (a) as-deposited annealed at 450°C for 1 h, (b) ion-beam-mixed annealed at 450°C for 1 h, (c) as-deposited annealed at 450°C for 6 h, and (d) ion-beam-mixed annealed at 450°C for 6 h.

transition-metal (Ti, Cr, or Ni)/SiO₂ couples bombarded with energetic Xe⁺ ions.

In order to study the nature of recovery of the structural state of the interface, we carried out isothermal annealing (450°C) of the as-deposited and ion-mixed samples. The annealing time was varied from 1 to 6 h. The CEM spectra corresponding to the as-deposited samples annealed at 450°C for 1 and 6 h are shown in Figs. 3(a) and 3(c), respectively, while the spectra corresponding to the identically treated ion-beam-mixed samples are shown in Figs. 3(b) and 3(d), respectively. The ion-beam-mixed sample shows small changes upon annealing at 450°C for 1 h while significant transformation is seen to occur in the as-deposited sample for the same annealing treatment. It may be seen that the spectrum of the as-deposited and annealed sample [Fig. 3(a)] is completely different from that of the as-deposited sample [Fig. 1(a)]. This spectrum is seen to be made up of only one doublet with an IS, of 0.09 mm/sec and QS, of 0.69 mm/sec. It is important to note that these hf interaction parameters do not match with the parameters for any known Fe-Si-O complexes.¹⁴ Also, it is surprising that the α -Fe component is completely absent in this case. SiO₂ is a tetrahedrally bonded close-packed structure, and no significant diffusion of iron in SiO₂ can be expected to occur at such a low temperature (450°C).¹⁰ Hence, the presence of the doublet may possibly be attributed to growth of a metal island structure. Such island structures can lead to an effectively nonmagnetic spectral contribution, due to superparamagnetic relaxation. Metal islands actually grow in low adhesion couples such as Cu/SiO₂ or Au/SiO₂ but not in very adherent films.³ If the islands are indeed formed in our case, it should mean that the adhesion of Fe film with

SiO₂ is poor. A useful way to test poor adhesion is the etching method suggested by Battaglin *et al.*³ In our case, the as-deposited sample upon etching did not show any Mössbauer signal at all, indicating poor adhesion of the film. On the other hand, the ion-mixed sample showed the presence of a significant quantity of iron even after etching, showing that ion mixing forms chemical complexes at the interface that enhance adhesion. When the samples are further annealed at 450°C for 6 h, the CEM spectrum corresponding to the as-deposited sample does not show any further change, while the spectrum for the ion-mixed sample exhibits drastic changes. The spectrum for the ion-mixed sample can now be fitted with two sextets ($H=337$ and 287 kOe) and two doublets. The hf parameters of two doublets are as follows.

Doublet 1: IS, 1.22 mm/sec; QS, 2.14 mm/sec.
Doublet 2: IS, 0.43 mm/sec; QS, 0.78 mm/sec.

These two doublets are again attributed to the Fe²⁺ and Fe³⁺ states, respectively, as observed in Fe₇SiO₁₀. The significant changes in the hf interaction parameters can be attributed to the transformation of the defective state of Fe₇SiO₁₀ phase in the as-mixed sample into a structurally well-defined configuration subsequent to annealing. When this spectrum is compared with that of the as-mixed state [Fig. 1(c)], it is observed that the ratio of the contribution of Fe³⁺-to-Fe²⁺ state is increased from 0.21 to 3.33. This increase can be attributed to the role played by oxygen which is available in the ion-beam-mixed region. The sextet having a hf field of 337 kOe corresponds to α -Fe, while the other sextet (287 kOe, ~contribution 11%) can be attributable to ⁵⁷Fe atoms having silicon near neighbors. The precipitation of α -Fe as seen from the CEM spectrum is also reflected in the x-ray-diffraction pattern [Fig. 2(c)]. The x-ray-diffraction patterns taken at 1.0° [Fig. 2(c)] show presence of diffraction lines corresponding to α -Fe along with Fe₇SiO₁₀.

It is important to see that x-ray-diffraction patterns shown in Fig. 2(c) consist of broad lines similar to those observed in the as-mixed sample [Fig. 2(b)]. This means that the disorder created in the SiO₂ substrate at such a high dose value (5×10^{16} ions/cm²) cannot be completely annealed out at 450°C. This observation is consistent with the results reported by Fischer, Gotz, and Karge,¹⁵ who have shown that the temperature at which complete recrystallization of SiO₂ is obtained increases with the damage level. At very small defect concentrations a temperature of 425°C is sufficient. For heavily damaged layers the temperature needed is of the order of 1000°C. The CEMS as well as x-ray results clearly indicate that the degree of lattice disorder is high in our case.

In conclusion, the effects of ion-beam mixing and subsequent vacuum-annealing treatments on Fe:SiO₂ sandwich structure are investigated by using the techniques of conversion electron Mössbauer spectroscopy and small-angle x-ray diffraction. Ion mixing of the Fe:SiO₂ structure leads to the Fe₇SiO₁₀ phase along with Fe-Si-O-type complexes. Upon annealing at 450°C for 6 h, outmigration of α -Fe occurs with increase of Fe³⁺/Fe²⁺ ratio. The as-deposited sample when annealed at 450°C leads to formation of a metal island structure.

The financial support for this work by the Department of Science and Technology and the Department of Atomic Energy, India is gratefully acknowledged. Two of us (S.B. and S.N.Y.) are grateful to the Council of Scientific and Industrial Research, India for financial assistance.

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