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ION BEAM MIXING AT Fe:Al_2O_3 INTERFACE: A CONVERSION ELECTRON MÖSSBAUER SPECTROSCOPY STUDY

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The effect of ion beam induced atomic mixing and subsequent thermal transformations at the Fe:Al_2O_3 interface have been investigated by means of conversion electron Mössbauer spectroscopy [CEMS]. It is shown that the as-deposited and ion beam mixed samples exhibit distinctly different features. In particular, the ion beam mixed sample in as-mixed state shows the presence of $FeAl_2O_4$ along with non-stoichiometric FeO. Upon annealing at 600°C it shows precipitation of α-Fe with reduced contribution of $FeAl_2O_4$. The study of dose dependence of ion beam mixing has also revealed interesting features regarding the ion beam induced interface reactions.

1. INTRODUCTION :

Ion beam mixing is a novel radiation processing technique which can lead to concentrated surface alloys having newer and exotic physical properties /1/. Considerable work has already been done on ion beam mixing and the general features regarding the mixing process seem to have been understood reasonably well /2/. However, in order to develop an understanding regarding the atomistic aspects it is essential to use characterization techniques which can reveal such an information in great details. In our recent publications /2,3/ we have demonstrated that the technique of Mössbauer spectroscopy can be of great value in such studies. In the present paper we report the results of ion mixing studies in the Fe:Al_2O_3 system; which is a metal-insulator combination capable of offering interesting responses to radiation treatment.

2. EXPERIMENTAL :

Polycrystalline Alumina [α-Al_2O_3] substrates obtained from Materials Research Corporation [U.S.A.] were used in these studies. Subsequent to the use of recommended cleaning procedure the substrates were deposited with 230 A° thick iron overlayer containing 30% of ^{57}Fe isotope, at a clean background vacuum of 10^{-6} torr. A number of such freshly prepared composites were subjected to 100 keV Kr^+ ion bombardment to induce ion beam mixing. The ion beam mixed as well as the as-deposited samples were subjected to vacuum [10^{-6} torr] annealing treatments at 300°C,450°C and 600°C for one hour in each case. Room temperature CEMS spectra were recorded with ^{57}Co:Rh as the source. In the case of the studies of dose dependence, ion doses in the range between 1×10^{15} ions/cm^2 and 5×10^{16} ions/cm^2 were employed.

3. RESULTS AND DISCUSSION :

The CEMS spectrum corresponding to the as-deposited sample Fig.1(a) can be resolved into magnetic as well as non-magnetic components. The former one has an internal field of ~327 kOe and it clearly corresponds to the Fe atoms in the overlayer having the environment as in α-Fe. The small non-magnetic contribution is a quadrupole split doublet having an isomer shift [I.S.] of 0.36 mm/sec and a quadrupole splitting [Q.S.] of 0.85 mm/sec. Such a doublet represents Fe^{3+}

state, with ^{57}Fe atoms substituting the Al sites in the near interface region possibly at the intergrain surfaces in Al_2O_3.

Upon ion bombardment at a dose of 5×10^{16} ions/cm^2 the CEMS spectrum appears as shown in Fig.1(e). This has two non-magnetic contributions, both being quadrupole doublets. The h.f.parameters are (i) I.S.=1.00 mm/sec and Q.S.=1.65 mm/sec and (ii) I.S.=0.64 mm/sec and Q.S.=0.48 mm/sec. The doublet having I.S. of 1.00 mm/sec closely resembles the $FeAl_2O_4$ phase /4/ whereas the other doublet corresponds to FeO like order. The h.f. parameters in the latter case are different than those reported for stoichiometric FeO /5/; however such differences can occur in the radiation processed materials which have high concentration of defects (vacancies) and associated compressive stresses /6/. The CEMS spectrum of Fig. 1(e) clearly brings out that atomic mixing has occurred across the interface;and it also shows the varying environment experienced by the ^{57}Fe atoms in the interface layers.

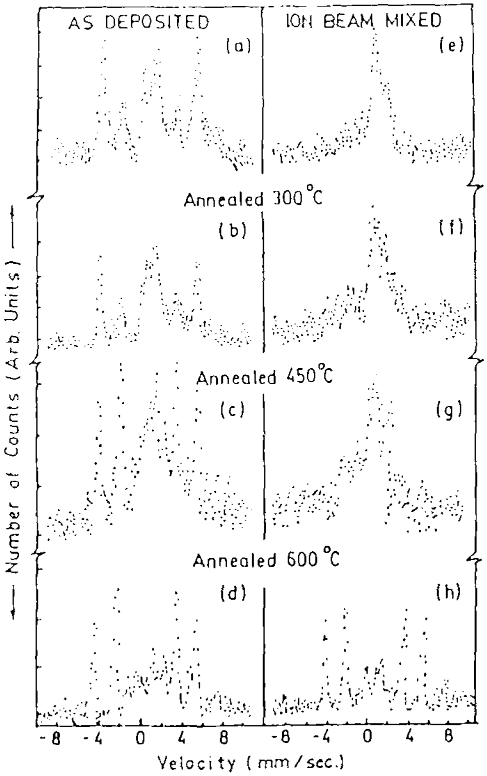

Fig.1. CEMS spectra of as-deposited and ion beam mixed Fe-Al_2O_3 composites.

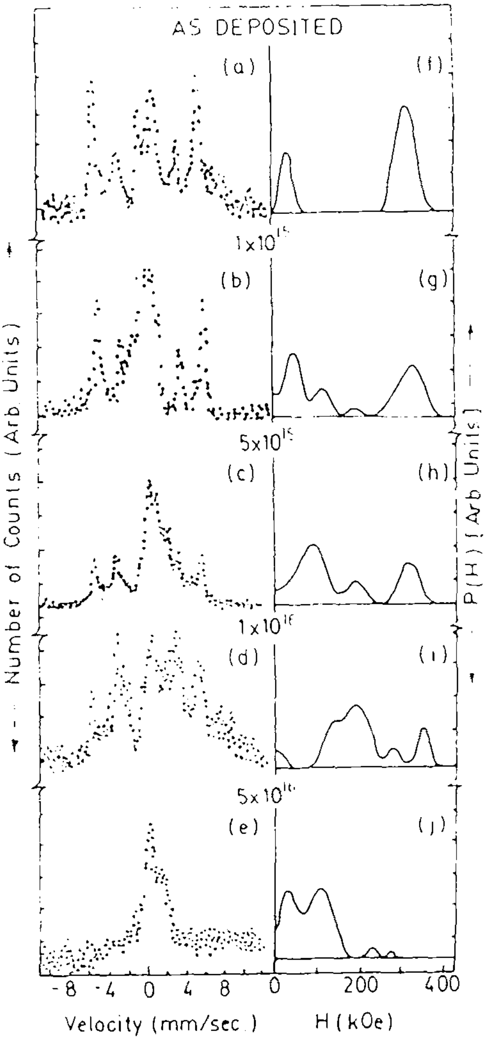

Fig.2. Variation of CEMS spectrum and P(H) distribution with ion dose (ions/cm^2)

When the as-deposited Fe:Al_2O_3 composite is annealed at 300°C for one hour [Fig.1(b)], the magnetic contribution [characteristic of α-Fe] is reduced in favour of the non-magnetic component. The non-magnetic component now has two contributions representative of the presence of Fe^{3+} state along with that of the Fe^{2+} state; which is in agreement with the results reported by Bhide et al./7/. The observation of change in the CEMS spectrum at a rather low temperature of 300°C can be attributed to the polycrystalline nature of the sample; since it is known that diffusion is extremely slow in crystalline Al_2O_3 below ~800°C at which sublattice relaxations begin to occur. The CEMS spectrum of the ion beam mixed sample annealed at 300°C for one hour is shown in Fig.1(f). This CEMS spectrum can be resolved into two quadrupole split doublets, one attributed to the $FeAl_2O_4$ phase /4/ while the other to the Fe^{3+} ions in Al_2O_3 matrix. The non-observance of the quadrupole split doublet corresponding to FeO like order present in the as-mixed state can be attributed to the decomposition of that phase leading to Fe^{3+} state in Al_2O_3 matrix. Stoichiometric FeO phase is known to decompose into Fe_3O_4 and Fe over a temperature range between 200°C and 570°C /8/. We did neither observe Fe_3O_4 nor Fe in our case, which should mean that the FeO like order observed in the as-mixed state is not stoichiometric and has a high concentration of defects which can lead to a change in the nature of the solid state reaction.

On further annealing at 450°C for one hour neither the as-deposited nor the ion beam mixed sample shows any significant change. The spectrum for the as-deposited sample [Fig.1(c)] shows an increase in the contribution of the Fe^{2+} state, with a minor change in the contribution of α-Fe while the spectrum of the ion beam mixed sample [Fig.1(g)] shows decrease in the contribution of $FeAl_2O_4$ phase at the cost of the Fe^{3+} state in Al_2O_3 matrix.

The CEMS spectrum of the as-deposited sample annealed at 600°C [Fig.1(d)] can be fitted with a sextet having h.f. field of 344 kOe [modified α-Fe] and a quadrupole doublet corresponding to Fe^{2+} ions in Al_2O_3 matrix. The spectrum shows change in the line intensity ratios from the values for the as-deposited case [Fig.1(a)] indicating release of deposition induced stresses. When annealed at 600°C the ion beam mixed sample shows drastic change in the CEMS spectrum [Fig.1(h)]. This spectrum now shows a magnetic contribution in addition to the non-magnetic one. This spectrum can be fitted with a sextet with h.f. field of 330 kOe [α-Fe] and a quadrupole doublet with I.S.=0.90 mm/sec and Q.S.=1.09 mm/sec which can be attributed to $FeAl_2O_4$ phase. Thus in the case of the ion beam mixed sample, annealing at 600°C leads to a reduction of the non-magnetic component of the spectrum corresponding to $FeAl_2O_4$ phase in favour of the magnetic one and one obtains precipitation of α-Fe. This shows that Fe tends to outmigrate from the defective state produced due to ion bombardment upon high temperature thermal treatment.

4. DOSE DEPENDENCE OF ION BEAM MIXING :

The results of the studies of dose dependence are shown in Fig.2. The P(H) distribution of the as-deposited sample [Fig.2(f)] exhibits only one major peak at ~330 kOe [α-Fe], as expected. With increase in the value of the implantation dose the peak at ~330 kOe shows a systematic decrease in intensity with emergence of peaks corresponding to lower values of h.f. fields. Also, the line-widths of the Mossbauer spectra show a systematic increase with implantation dose, which indicates increase in the degree of disorder.

In addition to the use of deconvolution procedure/9/ we also used the conventional Mossbauer fitting method to obtain h.f.interaction parameters. In the sample bombarded with 100 keV Kr^+ ions at a dose of 10^{15} ions/cm^2 we could identify the increase in the contribution of non-magnetic components. This component comprises of two quadrupole split doublets, one of which is due to Fe^{3+} ions in Al_2O_3 matrix while the other [I.S.=0.82 mm/sec and Q.S. 1.40 mm/sec] due to the presence of FeO like order. It may be noted that the parameters of the second doublet are in agreement with those reported by D. J. Elias et al./5/. The possibility of formation of an oxygen coordinated iron phase subsequent to bombardment at a dose of 10^{15} ions/cm^2 at room tempreature is not surprising, since Naguib et al. /10/ have shown that the disorder in Al_2O_3 increases slowly up to a fluence of 1 x 10^{15} ions/cm^2 and the estimated ratio of the number of O and Al atoms displaced from their respective sites is found to be 3:1 per Kr^+ ion. Thus there are more oxygen atoms available for chemical interaction with iron atoms as compared to the Al atoms.

As the dose is increased from 10^{15} ions/cm^2 to 5 x 10^{15} ions/cm^2 gradual changes are seen to occur in the nature of the CEMS spectrum. The low field components (non-magnetic) exhibit increase in intensity without any drastic change in their distribution. On the other hand, if the sample is bombarded at a dose of 1 x 10^{16} ions/cm^2, the spectral features indicate a significant increase in disorder and associated changes. The corresponding CEMS spectrum can be fitted with one sextet [α-Fe] and two quadrupole-split doublets. One of these doublets corresponds to non-stoichiometric FeO like order (I.S.=0.78 mm/sec, Q.S.=1.30 mm/sec) and the other to the formation of $FeAl_2O_4$ phase. The non-observance of $FeAl_2O_4$ phase at low and intermediate doses can be attributed to the fact that some Al atoms displaced by bombardment move into the vacant sites normally present in the Al_2O_3 structure, leading only to reduction of the density of disorder. Naguib et al. /10/ have studied the dose dependence of structural disorder and have shown that at low doses the disorder is less than expected due to bombardment induced annealing. They have also reported that at a dose of ~10^{16} ions/cm^2 the damage saturates, leading to the possibility of change in the nature of solid state reaction as observed in our case. Further increase in the dose to a value of 5x10^{16} ions/cm^2 once again leads to a change in the CEMS spectrum. This spectrum can be fitted with two quadrupole-split doublets; one due to the $FeAl_2O_4$ phase while the other due to the FeO like order [I.S.=0.64 mm/sec, Q.S.=0.40 mm/sec]. The contribution of α-Fe is seen to be negligibly small. It may further be pointed out that the isomer shift corresponding to the FeO like order shows a gradual decrease from the value of 0.83 mm/sec at a dose of 10^{15} ions/cm^2 to 0.64 mm/sec at a dose of 5x10^{16} ions/cm^2. Such a decrease in the isomer shift with increase of the ion dose can be attributed to the bombardment-enhanced lattice strain which is invariably developed in the host lattice.

5. CONCLUSION :

Ion beam induced atomic mixing and subsequent thermally induced transformations are studied for the case of the single interface Fe:Al_2O_3 system. The ion dose dependence of the mixing process has also been investigated. A number of interesting features concerning the microscopic aspects of the mixing reactions have been brought out. In particular, it has been shown that ion beam mixing at >10^{16} ions/cm^2 leads to formation of $FeAl_2O_4$ and non-stoichiometric FeO. Upon high temperature [600°C] annealing precipitation of α-Fe is seen to occur.

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