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Abstract. – The mixing mechanism of thin layers of Au, Pt or W embedded in silica when irradiated with 4.5 MeV Au ions was studied as a function of the ion fluence ϕ, temperature T and layer thickness d. Analysis of the diffusion process by means of Rutherford backscattering spectrometry showed that the spreading of metal peaks was anisotropic and that their variance varied as ϕ at room temperature or ϕ^2 at 100 K. This behavior is attributed to an association of metal atoms with diffusing defects.

Ion implantation offers a means of inserting high concentrations of metals or semiconductors in silica, providing to the doped film interesting optical properties when they precipitate as nanometer-sized clusters [1], [2]. Nevertheless, ion beam mixing of silica-metal multilayers would be a more suitable route to obtain homogeneous films, because of the intrinsic concentration gradient of implanted films and the resulting heterogeneity of cluster size. In the course of preliminary experiments [3], [4] it appeared that the mixing process was more complicated in silica-metal mutilayers than in other systems [5]-[8]. Particularly, electronegative metals (Au, Pt, Ag, Cu) tended to segregate laterally to form balls, as they do during heat treatments [9], and their anisotropic diffusion into silica could not be explained in terms of ballistic effects. Therefore, it was necessary to investigate in greater detail the mixing mechanism of single metal layers embedded in silica.

This letter reports the dependence of the mixing rate of Au, Pt and W films under irradiation with 4.5 MeV Au ions on the ion dose ϕ (0.1 to 20×10^{15} cm^{-2}), temperature T (100 or 300 K) and thickness d of metal films. The metals were selected for their similar mass but different reactivities with Si and O, and the irradiation beam because it was easily provided by our accelerator.

The targets were prepared by electron-gun evaporation of 4 to 17 nm of metal then 100 nm of silica, on thermally grown silica films with a thickness of 500 nm. The beam power was kept below 0.5 W cm^{-2} and the sample holder was cooled with water to prevent its heating during irradiation at 300 K. The ion range was about 1 µm and the energy density deposited per ion in atomic collisions (2 keV nm^{-1} according to TRIM simulations [10]) exhibited no
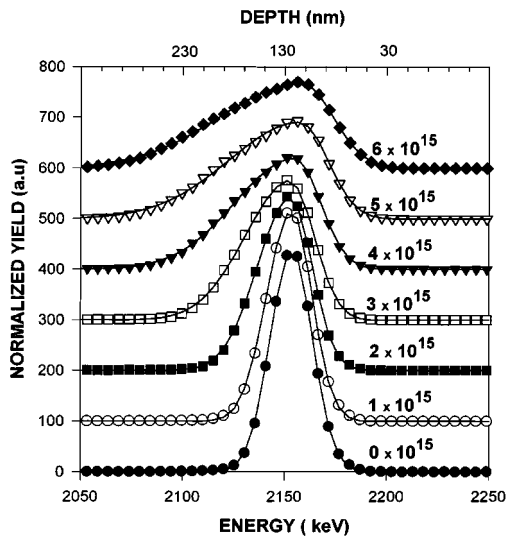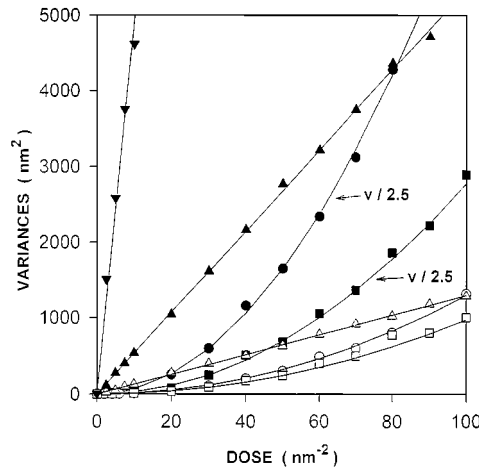
DEPTH (nm)

Fig. 1

Fig. 2

Fig. 1. – Backscattering spectra of Au atoms (Si and O signals are in the energy range of 0 to 1365 keV) recorded at normal incidence, from a Au film 14 nm thick irradiated at 100 K with Au ions. Fluences in cm^{-2} are indicated on the right part of the figure. The energy was converted to depth (top scale) by assuming that the atomic density of the target was equal to that of bulk silica ($6.6 \times 10^{22}\ cm^{-2}$). Symbols show experimental spectra and solid lines show fits with two Gaussian functions centered at 2150 keV.

Fig. 2. – Variances of the depth distributions of metal atoms, v_{in} (full symbols) and v_{out} (open symbols), plotted as a function of the Au fluence, given in nm^{-2} to ease the calculation of rates v/ϕ. Squares: 14 nm Pt at 100 K, circles: 14 nm Au at 100 K, triangles: 17 nm Pt at 300 K, inverted triangles: 17 nm Au at 300 K. The data corresponding to v_{out} of Au at 300 K were omitted for the sake of clarity, because they were very close to those of Pt at 300 K. Solid lines are fits with factors reported in table I.

depth gradient in the whole film thickness.

Rutherford backscattering (RBS) spectra of 2.4 MeV He ions were recorded at a scattering angle of $165°$ and at normal incidence (*in situ* analysis in alternation with irradiations), or with the normal to the target tilted by $65°$ with respect to the incident beam in order to increase the depth resolution. Typical changes of the shape of metal peaks with the ion fluence are displayed in fig. 1. Since their widening was asymmetrical, they were fitted with two Gaussian functions centered at the same energy and with respective variances v_{in} (inward *i.e.* on the low-energy side) and v_{out} (outward). These variances were corrected for the in energy straggling of the detector (FWHM of 12 keV) by subtracting the variances measured before irradiation.

The agglomeration of metal layers was studied by means of X-ray diffraction at a glancing incidence of $0.5°$. These analyses showed that the size of Au and Pt crystals in films irradiated at 300 K increased from 6 ± 2 nm to 16 ± 2 nm, independently of d, while all films irradiated at 100 K and W films at 300 K did not coalesce. The coarsening of Au and Pt grains was not due to beam heating because it progressed within a given fluence range. But, its suppression at low T means that it was controlled by the radiation enhanced diffusion of defects following collision cascades. Note that the lateral segregation of heavy marker atoms in a light matrix

TABLE I. – *Values of mixing efficiencies* v/ϕ (*in* nm^4). *In the case of films irradiated at* 100 K *they are given for an arbitrary dose of* 5×10^{15} *ions* cm^{-2} (*middle point of curves*) *since variances vary as* $C\phi^2$, *and the proportionality factor* C *is given in parentheses.*

Metal	Au	Pt	W	Au	Au	Pt	W	Pt	Au
d(nm)	17	17	10	10	5	4	5	14	14
T(K)	300	300	300	300	300	300	300	100	100
v_{in}/ϕ	510	54.0	29.8	27.3	16.6	2.5	2.2	17 (0.695)	41 (1.65)
v_{out}/ϕ	15.6	12.8	13.1	9.1	4.7	1.5	1.5	2.4 (0.097)	3.2 (0.13)

induces an alteration of RBS spectra, due to the difference in the energy lost by He ions depending on their path in the composite [11]. In the present case it was insignificant with respect to that due to the mixing since, using the formula proposed in ref. [11], it corresponded to an apparent motion of the metal layer of at most 4 nm outward and to a thickness increase up to 16 nm.

Recoil implantation is undoubtedly a cause of preferential forward transport of heavy impurities in light targets, but this anisotropy vanishes when the thickness of a heavy marker layer becomes of the same order of magnitude as the mean range of matrix atoms displaced during primary collisions with ions [6] (10 nm in the present case [10]). Moreover, the shift and broadening of metal peaks would be very similar for Au, Pt, W atoms on account of their comparable masses. The observed anisotropy in diffusion fluxes also cannot be ascribed to a depth gradient in the density of defects. However, the flux of defects coming from inside the target was larger, simply because the inner silica film was thicker. The relevance of this parameter was confirmed by the result of additional experiments of two types: *a*) the irradiation of similar 100 nm silica / metal / 500 nm silica targets with 200 keV Ar ions, *b*) that of 100 nm silica / metal / 100 nm silica with 4.5 MeV Au ions. In both cases the spreading of the metallic layer was found to be perfectly symmetrical because the fluxes of defects in the silica network were comparable on both sides of the metallic layer (the range of defects created by 200 keV Ar ions is of 200 nm [10]).

The strong dependence of the mixing rate v/ϕ on the mobility of both interstitials and vacancies in the silica matrix was evidenced by the change of the kinetics as a function of T (see fig. 2). Indeed, at 300 K both v_{in} and v_{out} varied in proportion to ϕ, as it is generally observed for any random walk process within a diffusion layer [7], [8], while they varied proportionally to ϕ^2 at 100 K. The latter power law can be attributed to two other rate limiting processes: *a*) the diffusion of defects outside the mixed region [7], or *b*) a chemical reaction at the interface [8]. The formation of oxides or silicides must be ruled out in the case of Au and Pt, because their enthalpies are very low or positive. But the combination of metal atoms with matrix defects at the periphery of the mixed region, for forming more mobile complexes, is probable for two reasons. First, one can reasonably suppose that the solute atoms lie on interstitial rather than on substitutional sites, since their radiation-enhanced diffusion was noticeable even at 100 K, while vacancies are known to be mobile at higher temperatures in silica [5]. The occurrence of this type of diffusion at low T is evidenced by the anisotropy of the metal flux (see fig. 1) and by the fact that the measured mixing rates are much higher than rates of ballistic mixing within regimes of linear cascades or spikes (estimated to 0.35 and 6 to 10 nm^4 using the formula of ref. [8]). Secondly, it is very likely that the interstitial metal atoms tend to form complexes with vacancies because of their large size and that the

complexes are more mobile than the simple defects. Such a coupling would account for a correlation between the anisotropy of the metal atoms and matrix defects fluxes, and for a control of the mixing kinetics by that of combination when vacancies are not mobile [12]. The hypothesis of an higher mobility of the complexes would also help to explain the magnitude of the mixing rates (see table I) with respect to those of silicon-metal systems irradiated under comparable conditions [8]. Note finally that the variation of the mixing rate with a higher power of d than 2 is not correlated to the increase of the amount of energy transferred to recoils in the vicinity of the metallic layer (in this latter case the mixing rate would vary as d or d^2). At the present stage of investigations, this result can only be explained by an increasing efficiency of the metal barrier to trap vacancies when the formed spheroids with a constant diameter of 16 nm, whatever the initial thickness of the film, are more contiguous because the metallic layer is initially thicker.

In summary, the mixing efficiency of Au, Pt or W with silica is not at all correlated to quantities such as the heat of mixing or the heat of formation of compounds as in other systems [5], [7], [8]. The high mixing rates measured are likely due to the formation of vacancy-impurity complexes which are mobile at low T in the silica network. The less soluble metal (Au) exhibits the strongest tendency to combine with matrix defects for migrating faster than more soluble ones.

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