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Alkali Depletion and Ion-Beam Mixing in Glasses

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Abstract

Ion-implantation-induced alkali depletion in simple alkali-silicate glasses ($12\text{M}_2\text{O} \cdot 88\text{SiO}_2$) has been studied for implantations at room temperature and near 77K. The results are consistent with a mechanism for alkali removal, by heavy-ion bombardment, based on radiation-enhanced migration and preferential removal of alkali from the outermost layers. Similar results were obtained for mixed-alkali glasses ($((12-x)\text{Cs}_2\text{O} \cdot x\text{M}_2\text{O} \cdot 88\text{SiO}_2)$ where, in addition, a mixed-alkali effect may also be operative. Some preliminary experiments with ion implantation through thin Al films on SiO_2 glass and on a phosphate glass show that inter-diffusion takes place and suggest that this ion-mixing technique may be a useful method for altering the physical properties of glass surfaces.

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1. Introduction

In the SiO_2 glass structure each Si is tetrahedrally bonded to four O and each O to two Si atoms to form a continuous network. The addition of alkali to the melt in the form of an oxide (M_2O ; M = alkali) breaks up this network. In order to accommodate the additional O, two dangling oxygens are formed for each M_2O molecule added and two alkali ions are loosely bound to the oxygen of the Si-O O-Si structure. The addition of the alkali thus opens up the network and increases the void volume. This more open structure and the weak bonding of the alkali ions make this type of glass an ionic conductor when an electric field is applied and also makes it possible for ion exchange to occur when in contact with liquids. This latter process can be detrimental when H_2O is the liquid (weathering) or it can result in strengthening of the glass when a larger alkali ion from the liquid is exchanged for that in the glass.

Alkali depletion in alkali-containing glasses is also a radiation effect which has been noted in many instances (see, e.g., [1-3]) where glasses have been subjected to electron or ion bombardment. This early work has been reviewed by Carter and Grant[4]. These experiments showed that charged particle irradiation resulted in movement of the alkali ions toward the surface and into the vacuum from a depth roughly corresponding to the depth of penetration of the particle. The determination of elemental concentrations by Auger electron spectroscopy (AES) is difficult in alkali-containing glasses because of the disappearance of the alkali signal with time due to the electron (0.3 - 3 keV) analysis beam[5-8]. Also, techniques such as secondary-ion-mass-spectroscopy (SIMS), which use ion-beam milling in order to depth profile elemental concentrations, have similar difficulties because of the alkali mobility[9]. However, Rutherford backscattering spectroscopy (RBS) does allow an accurate measurement of the depth-profiles of near-surface alkali because of the higher

beam energy (typically, 1-3 Mev) and the ability to simultaneously probe in depth without high beam fluence.

Ion implantation is an interesting means for altering the near-surface properties of glasses either through the chemical activity of the implanted species or by the implantation damage. In experiments on crystallization of lithium-alumina-silicate glasses by Arnold and Borders[10,11] and Borders and Arnold[12], RBS was used to demonstrate that heavy ion implantation first removed alkali ions from the region of the implanted-ion distribution and that continued implantation to higher fluence levels removed alkali from the entire near-surface region to a depth well beyond the Ion projected range. This means of altering the near-surface composition was used by Arnold and Peercy[13] to bring about low-temperature crystallization of a Li_2O glass after inert gas implantation. Low-temperature crystallization occurred because the loss of Li from the implanted region caused this region to be readily phase separable.

Recent work[14-18] by Italian scientists, principally at Padova, Trento, and Catania, has been directed toward an understanding of these processes. They have been able to describe the alkali loss curves by two different models; a) an electric field enhanced movement for electrons and light ions (H)[14-16], and b) a model of radiation-enhanced diffusion in the implanted region in the case of heavy-ion implantation[17,18]. Radiation-enhanced migration has also been used in the interpretation of the observed interpenetration of ion-implanted semiconductor/metal film composites to form stable compounds[19].

In the present paper, RBS techniques are used to study the alkali depletion in a series of alkali-silicate glasses and in some mixed-alkali glasses. The results can be interpreted in terms of a radiation-enhanced diffusion mechanism. Some results are also presented on preliminary work on radiation-enhanced mixing of glass and metal composites. These latter experiments could lead to useful changes in the surface properties of glass.

2. Experimental

The alkali-silicate glasses studied had the composition $12M_2O \cdot 88SiO_2$ ($M = Li, Na, K, Rb, Cs$). The mixed alkali glasses were Cs-based and had the composition $(12-x)Cs_2O \cdot xM_2O \cdot 88SiO_2$ ($x = 3, 6, 9, 12$ and $M = Li, Na, K, Rb$). Not all of the mixed-alkali glasses were used in the work reported in this paper. All glasses were finished either with diamond paste or alumina in non-aqueous media or on dry paper. Sample dimensions were 1.27 cm x 0.635 cm x 0.1 cm.

Implantations of Xe or N_2^+ were made using an Accelerators, Inc. ion implanter (10 - 250 keV) with samples at room temperature or near 77K. Rutherford backscattering depth profile analyses were made using the Sandia National Laboratories' tandem Van de Graaff accelerator. The probe particle was 2.8 MeV $^4He^+$ and the detector angle was 164°.

Standard evaporation techniques (10^{-8} Torr base vacuum system) were used to produce the thin Al films on the samples used for studies of interpenetration of metal and glass constituents as a result of ion implant damage.

3. Results and Discussion

The depletion of K from a $12K_2O \cdot 88SiO_2$ glass is shown in Fig. 1 as a function of ion fluence for 250 keV Xe implants. These RBS spectra show only the K edge region and have been vertically separated for clarity. The energy losses of the 2.8 MeV He beam have been converted to a depth scale as shown at the top of the figure. The projected range of 250 keV Xe in this glass is $R_p \cong 1060 \text{ \AA}$ using the empirical range relation, $R_p = (530 \times E(\text{keV}) / \rho Z_1)$, where $\rho = 2.31 \text{ g/cm}^3$ and $Z_1 = 54$, established by Wu et al [20]. Figure 1 shows that K is removed, at the lower fluences, from a depth corresponding rather closely to the projected range and that the depletion profile in this region mirrors the expected ion distribution. The subtraction of the $5 \times 10^{16} \text{ Xe/cm}^2$ profile from that of the reference gives the distribution of lost K as shown

in Fig. 2. The integral of this distribution yields a deficit of 1.2×10^{17} K/cm².

Table I summarizes the K depletion results for the series of alkali-silicate glasses which have been implanted with 5×10^{16} 250 keV Xe/cm² at room temperature. The losses are compared with the ionic radii and with the relative mobilities of the ions. These loss data show no correlation with the ionic mobility (measured at 380°C). The slight tendency shown to associate increasing alkali loss with decreasing radii values is discounted in view of the fact that calculated single M-O bond strengths[21] and percent ionicity[22] would predict greater losses with increasing ionic radius (or Z). It should also be noted that the lower depletion values for the Rb- and Cs-glasses probably are due to the correspondingly large concentrations of H in these hygroscopic glasses. It is concluded that the data show no preferential loss due to chemical species.

The above conclusion tends to favor a model of radiation-enhanced migration. In further support of this model, a reduction of alkali loss is observed when implantation is carried out at 77K. Figure 3 shows a typical RBS result for the $12\text{K}_2\text{O} \cdot 88\text{SiO}_2$ glass implanted near 77K with 5×10^{16} 250 keV Xe, compared to the RT result and with the reference spectrum. The loss at low temperature is only about one-half that at RT. Similar results were obtained for the other glasses and, again, the losses were approximately equivalent.

Figure 3 also shows a reduced RBS yield from O and Si in the implanted region. This decrease in yield per unit energy/channel is not due to a loss of O and Si but to the decreased fractional concentrations of these scatterers resulting from the large local concentrations of Xe (≤ 13 at.%) and to the larger stopping power of Xe. Thus, when the relative concentration profiles are calculated and the Xe is included, the Si and O remain constant, and the K is reduced.

The near-77K and the room-temperature results both suggest that radiation-enhanced diffusion takes place within the implanted region. This conclusion is based on the argument, given by Liau et al[23], that (a) the local diffusion coefficient should be proportional to the energy deposition and, thus, to the number of defects formed, and (b) the transport to the surface should be proportional to the product of this local diffusion coefficient and the concentration gradient. The data of Figs. 1 and 3 show the inverse relation of concentration gradient and energy deposition/diffusion coefficient; i.e., the gradient is least at the minimum of the depletion profile (which corresponds to the maximum of the energy deposition profile). In the Liau et al studies[23] the rate-limiting factor in the loss process depends upon the sputtering rates of atoms in the outermost few layers. Although we have indicated that sputtering rates are low, some loss does occur through near-surface collisions. The rates of sputtering are expected[23] to be proportional to the partition of energy among the atomic constituents. Although K is the heaviest element, it is also the most loosely bound and will be preferentially ejected. This surface deficit will drive the movement of alkali toward the surface as observed.

Further insight into the processes at work can be gained by examining the results for the mixed-alkali glass system $(12-x)\text{Cs}_2\text{O} \cdot x\text{M}_2\text{O} \cdot 88\text{SiO}_2$ ($x = 3, 6, 9, 12$; $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$). For these glasses, implants of N_2^+ were used in order not to complicate the RBS profiles. Figure 4 shows the results for a room-temperature implantation of 5×10^{16} 100 keV N_2^+/cm^2 on $6\text{Cs}_2\text{O} \cdot 6\text{K}_2\text{O} \cdot 88\text{SiO}_2$ glass. The insets show the loss profiles of Cs and K. Table II shows the integrated losses for glasses in this K series and incomplete data on glasses from the Rb- and Na-series. There are two points to be made concerning these data: (1) the lighter alkali is, within experimental error, preferentially removed and, (2) the addition of the M alkali lowers the amount of Cs removed. This

latter result is in keeping with the general phenomenon observed for many physical properties in mixed-alkali glasses and is known as the mixed-alkali effect[24]. Briefly stated, the mixed-alkali effect is operative when the addition of a second alkali to the glass causes large non-linear changes in certain physical properties (alkali diffusivity, electrical conductivity, viscosity, chemical durability, etc.). The effect is not completely understood, but the consensus favors the addition of an electrodynamic interaction term generated due to the difference in mass of the alkali ions[25]. In the present case, however, it may be simply due to the greater sputter loss rate of the lighter ion from the surface, which we have suggested is probably the rate determining factor in the alkali-silicate glasses. A clearer picture may emerge when all these glasses are examined.

The average total alkali loss from the samples in Table II is about $5 \times 10^{16}/\text{cm}^2$. This represents about 0.5 alkali lost per incident N ion (the 100 keV N_2 breaks up into two 50 keV N particles on entering the sample). The ratio of the number of alkali lost per incident ion to that for the alkali-silicate glasses is $2/0.5 = 4$. On the other hand, the ratio of the energies deposited into nuclear processes for the 250 keV Xe ion and the 50 keV N ion is about 5. This fair agreement is reasonably good evidence that the overall effect -- that of a locally increased diffusion coefficient -- is due to the damage produced in the collision cascade.

These interesting results on compositional changes in glass have encouraged the investigation of inducing the interchange of glass constituents with thin metal films such as has been demonstrated in semiconductor metal structures[19]. Some preliminary results are shown in Fig. 6 for 5×10^{16} 200 keV Xe incident on SiO_2 glass with a 700 Å Al film. The range of the Xe ion in Al is about 730 Å. The movement of O into the Al film, accompanied by Al

migration into the bulk of the glass can be seen to occur at this fluence. Caution must be used, however, in analyzing this type of experiment because Clark and Baglin[26] have shown that many metal films, including Al, tend to ball up under ion bombardment. The RBS spectra for such a situation would show a decrease in intensity of the Al concentration at the surface and scattering from the exposed interface O atoms will appear at higher energies. SEM micrographs of the surface after implantation showed that agglomeration of the film indeed had occurred. However, the data of Fig. 6 show RBS spectra for a silver-activated phosphate dosimeter glass (66.2%O, 4.2%Al, 22.1%P, 4.7%K, 0.9%A, 1.9%Ba) also coated with a 700Å Al film and implanted with 6×10^{16} 200 keV Xe ions/cm². SEM measurements showed no agglomeration or separation of the Al film. The RBS spectra show that the film has become thinner due to sputtering. Note that the final film thickness is also reflected by the shape of the Xe distribution. Assuming uniform sputter removal of the matrix, the change in slope in the Al distribution on the low-energy side shows the beginning of the diffusion profile of Al into the glass. It is also seen that the altered layer, consisting of interpenetrating Al and O, extends from the SiO₂/Al interface finally obtained after implantation to a depth in the glass corresponding to the thickness of the Al film sputtered away.

These results, although incomplete, do indicate that it is possible to intermix glass and metal at the surface and should allow favorable physical property changes to be made.

4. Conclusions

Alkali depletion in heavy-ion bombarded alkali-silicate glasses can be interpreted as resulting from radiation-enhanced migration in the implanted region with movement toward the surface due to preferential sputtering of alkali.

There is some evidence for a mixed-alkali effect in $(12-x)\text{Cs}_2\text{O} \cdot x\text{M}_2\text{O} \cdot 88\text{SiO}_2$ glasses; however, the results might also be due to partition of deposited energy between light and heavy alkali ions. Experiments with ion-induced interdiffusion of glass constituents and metal film atoms suggest that the modification of the physical properties of glass surfaces can be brought about by this method.

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Table I

Alkali-Ion Loss for 5×10^{16} 250 keV Xe/cm² Incident on $12\text{M}_2\text{O} \cdot 88\text{SiO}_2$ Glass at Room Temperature

<u>M</u>	<u>Loss</u> ($\times 10^{17}$ /cm ²)	<u>Ionic</u> <u>Radius</u> (Å)	<u>Mobility</u> <u>Relative to Na</u> (at 380°C)*
Li	1.3	0.68	0.3
Na	1.1	0.97	1
K	1.2	1.33	.0007
Rb	1.0	1.47	-
Cs	0.6	1.67	-

*G. H. Frischat, Ionic Diffusion in Oxide Glasses (Trans-Tech Publications, 1975) p. 130.

Table II

Alkali-Ion Loss for 5×10^{16} 100 keV N_2/cm^2 Incident on $(12-x)Cs_2O \cdot xM_2O \cdot 88SiO_2$ Glass at Room Temperature

<u>M</u>	<u>x</u>	<u>Depleted Cs ($\times 10^{16}$)</u>	<u>Depleted M ($\times 10^{16}$)</u>	<u>Depleted Total ($\times 10^{16}$)</u>
K	3	1.9	1.6	3.5
	6	1.6	3.4	5.0
	9	0.9	2.6	3.5
	12	-	6.8	6.8
Rb	6	0.7	2.1	2.8
	9	0.7	5.0	5.7
Na	3	2.5	5.4	7.9

FIGURE CAPTIONS

- Fig. 1 RBS K depth profiles for 250 keV Xe implanted into $12\text{K}_2\text{O} \cdot 88\text{SiO}_2$ glass at various fluence levels. The traces are offset for clarity.
- Fig. 2 K loss profile obtained by subtracting the 5×10^{16} 250 keV Xe induced K profile from the reference spectrum. The integrated K loss is 1.2×10^{17} K/cm².
- Fig. 3 RBS histogram spectra for $12\text{K}_2\text{O} \cdot 88\text{SiO}_2$ glass showing the O, Si, and K edges for: — reference sample, after implant at room temperatures, + + + after implant at temperatures near 77K. All spectra were taken at room temperature.
- Fig. 4 RBS histogram spectra for a $6\text{Cs}_2\text{O} \cdot 6\text{K}_2\text{O} \cdot 88\text{SiO}_2$ glass after implantation at room temperatures with 5×10^{16} 100 keV N_2 /cm². The insets show the Cs and K loss profiles obtained by subtracting the implanted spectrum from the reference spectrum. The integrated loss values are given in Table II.
- Fig. 5 RBS spectra for fused silica glass with a CVD 700Å Al film before (—) and after (....) implantation with 5×10^{16} 200 keV Xe/cm² at room temperature.
- Fig. 6 RBS spectra for phosphate glass (composition given in text) with a CVD 700Å Al film before and after 6×10^{16} 200 keV Xe/cm² at room temperature. These spectra were obtained with the target normal at -55° with respect to the incident beam (high-resolution RBS).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig.5