

ALKALI MIGRATION IN GLASSES ON ELECTRON, PROTON AND HEAVIER ION IRRADIATIONS

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Résumé. - On présente une étude systématique des modifications du profil de Na dans un verre silico-sodo-calcique produites par des irradiations par des électrons, protons ou ions lourds. Les résultats sont discutés sur la base d'une diffusion assistée par le champ électrique et d'éjection préférentielle de Na.

Abstract. - We present a systematic study of the Na profile modifications in soda-lime silica glasses after electron, proton and heavier ion irradiations. The results are discussed in terms of field assisted diffusion and Na preferential sputtering.

Introduction. - It is well known that when glasses are irradiated with electrons (as in Auger Electron Spectroscopy) or ion beams (as in Secondary Ion Mass Spectroscopy) their surface composition undergoes marked modifications (see for example refs. 1-5).

Soda-lime-silica glasses have been irradiated by 2-5 keV electrons, 600 keV protons and 50 keV Ar⁺ and N⁺ ions. In the case of electron or proton irradiations, the detected Na profile modifications have been explained on the basis of the ordinary and field assisted migration processes, whereas in the case of heavy ion bombardment, a preferential sputtering mechanism has been inferred. We determined the Na depth concentration profiles, before and after irradiations, by using the ²³Na(p, α)²⁰Ne nuclear reaction. Such a technique has the advantage that very low proton fluences and doses are required, causing no detectable changes in the actual Na profiles (6).

a) **Electron irradiation.** - Commercial soda-lime-silica glasses have been irradiated in a "KRATOS-ES 300" XPS-Auger apparatus with electron beams having energies between 2.5 and 4.5 keV and current densities, I , between 1 and 4 $\mu\text{A}/\text{cm}^2$ (7,8). A decay of the Na surface concentration was observed during irradiations, in agreement with data reported in the current literature. Measurements of Na depth concentration profiles after electron bombardments indicate that Na tends to accumulate towards the inside of the sample, at a depth comparable to the maximum electron range (9). In figure 1a,b we report the Na depth concentration profiles after 2.5 keV ($I=1.2$ and 4.0 $\mu\text{A}/\text{cm}^2$) and 4.5 keV ($I=4.0 \mu\text{A}/\text{cm}^2$) irradiations.

The comparison between the Na profiles obtained after irradiations at the same energy but different currents clearly indicates the effect of the beam power deposition in the sample. In connection with the Na surface depletion, a Ca surface accumulation

has been detected by analyzing the same samples with the Rutherford backscattering technique (10) (see inset in fig. 1b).

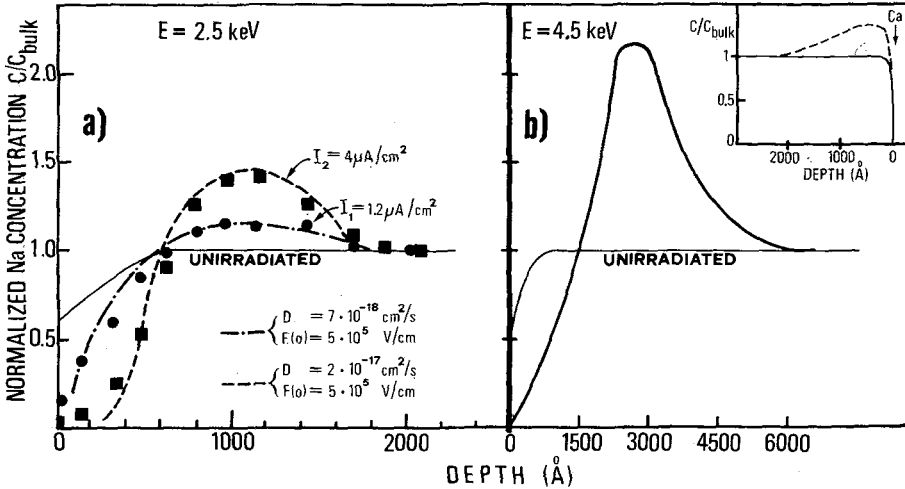


Fig. 1 : (a) Experimental (●, ■) and calculated (---, -.-) Na depth concentration profiles, normalized to the unirradiated bulk value, for 2.5 keV electron irradiation at two current densities. The Na profile of an unirradiated specimen is also reported; (b) experimental Na depth concentration profile after 4.5 keV-electron irradiation. In the inset we report the Ca profiles, before (-) and after (--) irradiation.

Modifications in the Na depth concentration profiles have been quantitatively described on the basis of the continuity equation for the ordinary and field assisted diffusion(11):

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} - \mu \frac{\partial}{\partial x} (F(x,t)n(x,t)),$$

where $n(x,t)$ is the Na concentration at depth x and time t , D is the constant diffusion coefficient, μ the Na mobility, connected to D by the Einstein relation, and F the electric field. The boundary conditions are discussed in ref. 11. Considering F and D as free parameters in the numerical integration of the continuity equation, we have obtained, by a fitting procedure, the profiles reported as dashed and dashed-dotted lines in figure 1a. The obtained F and D values are also indicated. The Na surface concentration decay during irradiation is very well fitted by using the same numerical approach(11).

b) Proton irradiation. - In order to clarify the results obtained for the electron irradiation and to confirm the field assisted Na migration model, we studied the Na profile modifications in proton irradiated glasses(7,12). To avoid surface charging and desorption phenomena, which may occur during proton bombardment, a thin Al layer, about 15 nm thick,

was evaporated on the sample surface. In figure 2a we report the Na depth concentration profiles (full points), for unirradiated and proton irradiated soda-lime-silica glasses.

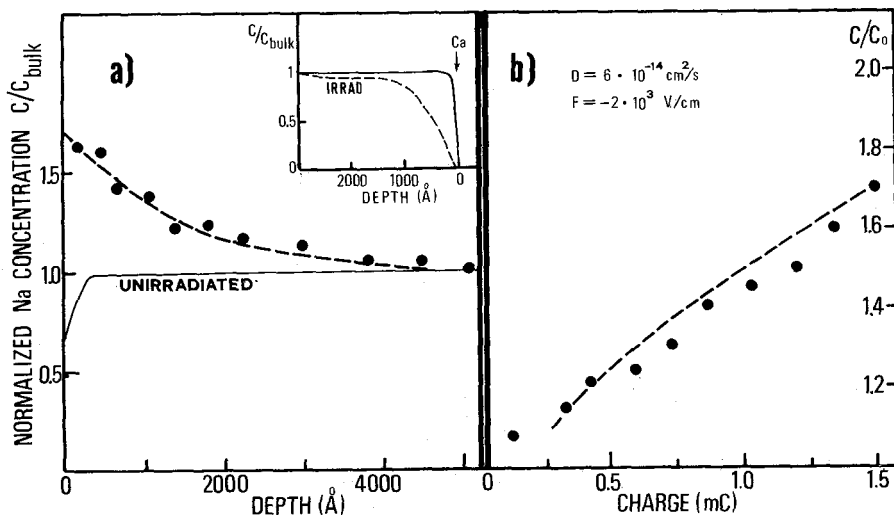


Fig. 2 : (a) Normalized Sodium profile concentration Vs depth for unirradiated (-) and 600 keV proton irradiated (●) soda-lime silica glasses. (b) The evolution during proton irradiation of the Na surface concentration normalized to the unirradiated value. Calculated curves (---) are also reported with the indication of D and F values used in the calculations. The proton current density was $7.5 \mu\text{A cm}^{-2}$.

The evident Na migration towards the surface is accompanied by a Ca surface depletion (see the inset). In fig. 2b the time dependence of the surface Na accumulation is also reported. Using the fitting procedure utilized in the numerical analysis of electron irradiation processes, we have obtained the profiles reported as dashed lines in fig. 2 and the corresponding D and F values. In this case the calculated electric field is opposite in sign with respect to that evaluated for the electron irradiated glasses. This result suggests that the incident particle charge deposition mainly determines the electric field formation.

c) Heavy ion irradiation. - Implants on soda-lime-silica glasses with 50 keV Ar^+ and N^+ ions have been performed at a current of $2 \mu\text{A/cm}^2$, varying the dose between 10^{15} and $5 \cdot 10^{16}$ ions/ cm^2 . As a result, a Na depleted surface region has been observed. In figure 3 we report the Na profiles after 50 keV Ar^+ (doses 2 and $4 \cdot 10^{16}$ ions/ cm^2) and 50 keV N^+ (at a dose of $2 \cdot 10^{16}$ ions/ cm^2) implantation.

We can explain these results in terms of a phenomenological model which accounts for the preferential ejection of Na atoms from the surface and for a radiation enhanced diffusion coefficient of Na in the Ar^+ or N^+ ions path⁽¹³⁾. Such a local radiation enhanced diffusion is related to the local deposition of energy in the nuclear collision processes⁽¹⁴⁾. In

the ion range region we assumed a diffusion coefficient D^* , larger than the Na self diffusion coefficient quoted in literature for glasses of same composition. The calculated Na profiles, compared to the experimental results, are also reported in fig. 3.

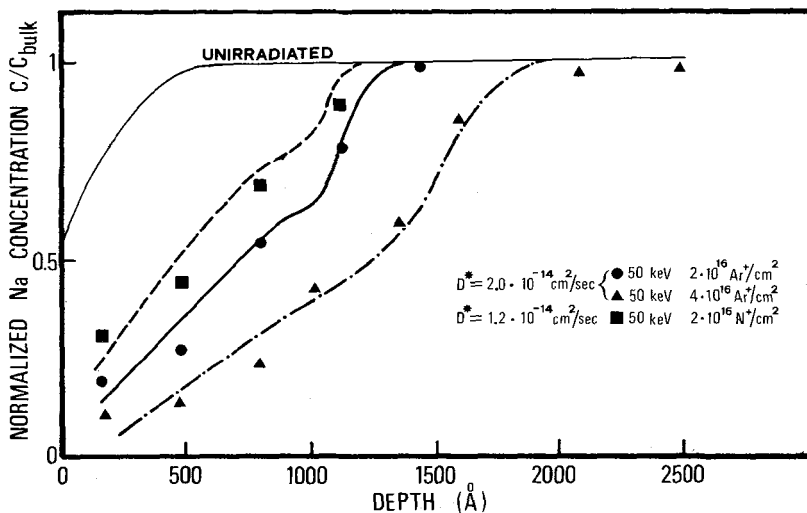


Fig. 3 : Sodium depth concentration profiles after 50 keV Ar^+ and N^+ irradiations at different doses. Calculated profiles are also reported.

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