

Cooperative Transport Effects in Electron-Irradiated Glasses

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Cooperative effects during both alkali-Ca and Na-K migration under electron irradiation of glasses have been pointed out for the first time by analysis of experimental data in the framework of the thermodynamics of irreversible processes.

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It is well known that the alkali Auger signal during Auger-electron spectroscopy (AES) of alkali silica glasses decreases.¹⁻⁴ The concentration-versus-depth profiles of alkali, Na in particular, determined by nuclear reaction analysis (NRA) after electron bombardment, showed that the alkali depletion in the first few surface layers is accompanied by an accumulation at a depth roughly corresponding to electron range.^{5,6}

The alkali concentration profile as detected by NRA and the decrease of alkali surface concentration as observed during AES have been satisfactorily described by integration of the continuity equation for the ordinary and electric-field-assisted diffusion process.⁷

The mechanism of alkali desorption, observed for high electron current density, has been extensively discussed by Wang, Ohuchi, and Holloway.⁸ However, the quoted model⁷ cannot explain the "anomalous" behavior of the Ca ions in soda-lime glasses during electron irradiations.² Indeed, during AES the Ca signal shows a strong increase which cannot be explained by the electric-field-assisted diffusion process (Ca⁺⁺ migrates, in this case, against the electric field direction) nor by an electron-stimulated desorption of carbon contamination.² Moreover, a Ca accumulation in the first hundred angstroms beneath the surface has been detected by analysis of the electron-irradiated glasses with the Rutherford backscattering technique,⁵ while Na accumulates in depth.

In this Letter we attempt to show that the Ca⁺⁺ migration, as opposed to alkali migration, may be explained by consideration of the correlation effects in the transport processes of the different elements diffusing during electron irradiation of glasses.

Here we analyze theoretically the experimental results reported by Gossink, Van Doveren, and Verhoeven² during AES of 20% K₂O, 10% CaO, 70% SiO₂ and 20% Na₂O, 10% CaO, 70% SiO₂ glasses. Figure 7 of the paper by Gossink, Van Doveren, and Verhoeven² shows the surface concentration evolution, as a function of irradiation time, of all the atomic constituents of the K-Ca glass. The K Auger signal

drops rapidly while the Ca signal increases. In contrast the Si and O signals show a much slower increase. Similar results are observed during the irradiation of Na-Ca glass. However, the decrease of the Na signal was so rapid, considering the irradiation conditions used, that it could not be recorded. These experimental results suggest that only alkali and calcium are the mobile atomic elements. Nevertheless, two other components must be considered in the global transport process: the primary incident electrons and the holes created by bond breaking during irradiation.

Recently⁹ Miotello showed that the primary electrons in a dielectric solid are mobile during AES while a recombination process with the positive surface charges, due to secondary electron emission, must be operative, since breakdown phenomena are not observed during AES. It has been shown,⁹ through integration of Poisson's equation, that the electric field strength E induced in a dielectric solid during AES attains a steady value very quickly (10^{-4} – 10^{-3} sec) and that the alkali ions do not play a relevant role in the electric field formation. Such a field is almost a linear function of the depth,⁷ assuming maximum value at the glass surface and going to zero at a depth roughly corresponding to the electron penetration range. On the basis of these results, here we simply assume an interaction between the alkali (and Ca) ions and the electrostatic field created by the primary electrons as well as by the surface positive charges due to secondary electron emission.⁹ Excellent agreement between theoretical and experimental results (see Fig. 1 below) confirms that other interaction processes between primary electron and alkali (and Ca) ions are not relevant. Finally, since no data are available for the lifetime, mobility, or density of holes created in insulators by bond breaking during electron irradiation, we consider a constant value for their density along the incident electron path. Such an assumption is likely, since the atomic elements Si and O are not mobile.¹⁰

We now elaborate on the continuity equations for the alkali and calcium ionic transport processes in the

framework of the thermodynamics of irreversible processes. The molar composition of the irradiated glasses suggests that we can consider the alkali and calcium atoms as "dilute" constituents in the SiO_2 solvent. As a consequence the Kirkendall effect may be neglected in the alkali and Ca diffusion processes. Since the electron beam size is much larger than the other lengths involved in the problem (i.e., electron penetration range and atomic species migration depth), the atomic fluxes may be written in a one-dimensional form. The alkali (Na or K) and Ca atomic fluxes may be written, according to the notation of Adda and Philibert¹¹ as follows:

$$J_i = -\frac{L_{ii}}{T} \frac{d(\tilde{\mu}_i - \tilde{\mu}_R)}{dx} - \frac{L_{i2}}{T} \frac{d(\tilde{\mu}_2 - \tilde{\mu}_R)}{dx}, \quad (1)$$

$$J_2 = -\frac{L_{2i}}{T} \frac{d(\tilde{\mu}_i - \tilde{\mu}_R)}{dx} - \frac{L_{22}}{T} \frac{d(\tilde{\mu}_2 - \tilde{\mu}_R)}{dx},$$

where $i = \text{Na}$ or K and $2 = \text{Ca}$. L are the phenomenological coefficients relating fluxes and forces; $\tilde{\mu}_R$ is the electrochemical potential of the "solvent" which is an average combination of Si and O atoms; T is the glass temperature, constant throughout the depth involved in atomic migration, which roughly corresponds to the primary electron penetration depth. Indeed, according to the simple model calculation of Pittaway,¹² a steady-state regime for the surface temperature is attained in a very short time and a flat temperature distribution is expected in the first thousand angstroms beneath the surface.

By use of the Gibbs-Duhem¹¹ relation, the quantity $\tilde{\mu}_R$ may be eliminated in Eqs. (1). Moreover, since in our approach the analyzed system depends only on two independent variables n_i and n_2 , the alkali and Ca atomic concentrations, the chemical potential may be written as $\mu_i = \mu_i(n_i, n_2)$ and

$$\frac{d\mu_i}{dx} = \frac{\partial \mu_i}{\partial n_i} \frac{dn_i}{dx} + \frac{\partial \mu_i}{\partial n_2} \frac{dn_2}{dx}.$$

A similar expression holds for $d\mu_2/dx$. By use of this relation in Eqs. (1), after a trivial derivation and an appropriate arrangement of the terms, we can write the fluxes J in a form analogous to Fick's first law. Finally, the continuity equations for the alkali and Ca atomic concentrations are

$$\frac{\partial n_i}{\partial t} = D_{ii} \frac{\partial^2 n_i}{\partial x^2} + D_{i2} \frac{\partial^2 n_2}{\partial x^2} - u_i \frac{\partial}{\partial x} (n_i E), \quad (2)$$

$$\frac{\partial n_2}{\partial t} = D_{22} \frac{\partial^2 n_2}{\partial x^2} + D_{2i} \frac{\partial^2 n_i}{\partial x^2} - u_2 \frac{\partial}{\partial x} (n_2 E),$$

where $n(x, t)$ is the alkali and Ca concentration at time t and depth x below the surface ($x=0$), D are the "diffusion coefficients" which are considered in-

dependent of concentration (dilute impurity limit), and u are the mobilities. In this "three-component" system, mobility and diffusion coefficients are not connected by the simple Einstein relation.

Since in the Auger experiments Gossink, Van Doveren, and Verhoeven² used glass surfaces as obtained by fractured homogenized samples, we may safely assume a constant initial concentration of alkali and Ca along the depth. Some other boundary conditions have been discussed, in a different context, in Ref. 6 and by Miotello and Mazzoldi.¹³

General analytical solutions of Eqs. (2) are not available and there is not a straightforward method for fitting Eqs. (2) to the experimental data. The procedure we have adopted is to obtain a numerical solution for the given experimental conditions with a particular set of diffusion, mobility, and electric field parameters. We repeated the calculations systematically, varying the input parameters until the results fitted the experimental data satisfactorily. This fitting procedure is an empirical trial-and-error procedure. As we discussed in a previous paper, the Auger signal for the change of the surface atomic concentration of elements migrating according to Eqs. (2) (when $D_{i2} = 0$) can generally be obtained by integration of Eqs. (2) with different pairs of diffusion and mobility constants.¹³ However, here the term of Eqs. (2) which describes the correlation process by the D_{2i} coefficient removes this kind of ambiguity. Indeed, the trend of the Auger signal now depends on the in-depth alkali profiles.

In Fig. 1(a) we show the experimental *LMM* Auger signals of K and Ca during the AES of K-Ca glass as taken from Fig. 7 of Ref. 2. The full lines are the calculated Auger signals (the mean free path of the Auger electrons has been included in the calculation).¹³ In Fig. 1(b) we report the experimental (see

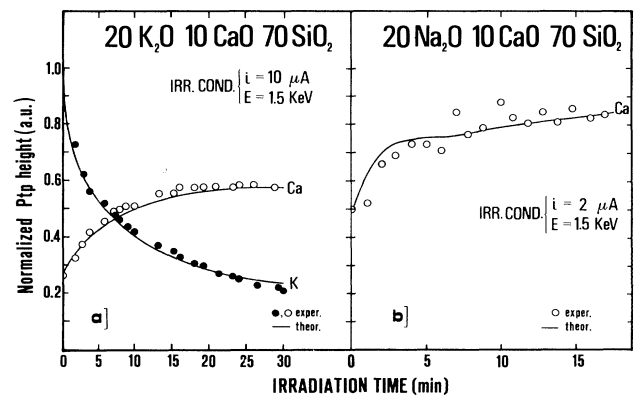


FIG. 1. Experimental (Ref. 2) and calculated alkali and calcium Auger peak heights as functions of electron bombardment time. The theoretical functions are obtained with the parameters reported in Table I.

TABLE I. Parameter values used for the calculated curves reported in Figs. 1 and 2. Thermal diffusion coefficient value available in literature D_{th} is also included. For alkali glasses the index 2 refers to elemental Na.

	D_{ii} (cm ² /sec)	D_{i2} (cm ² /sec)	u_i (cm ² /V·sec)	D_{22} (cm ² /sec)	D_{2i} (cm ² /sec)	u_2 (cm ² /V·sec)	$E(0)$ (V/cm)	T (K)	D_{th} (cm ² /sec)
K-Ca glass	5×10^{-15}	0	1.5×10^{-13}	5×10^{-15}	5×10^{-15}	0	2×10^4	380	...
Na-Ca glass	10^{-14}	0	3.6×10^{-13}	3×10^{-15}	3×10^{-15}	0	5×10^4	315	4×10^{-17}
K-Na glass	10^{-16}	0	2.0×10^{-15}	10^{-14}	10^{-14}	5.5×10^{-14}	4×10^4	350	...
Na glass	10^{-14}	...	2.5×10^{-13}	4×10^4	350	...
K glass	10^{-16}	...	2.5×10^{-15}	4×10^4	350	...

Fig. 9 of Ref. 2) and calculated *LMM* Auger signal for the element Ca during AES of Na-Ca glass. The experimental *LMM* Auger signal of Na has not been reported, while in the calculations the constant parameters of Eqs. (2) were chosen in such a way as to determine a disappearance of the Na signal in a time interval of less than 1 min.

The calculated parameters, for both glasses, are reported in Table I. To our knowledge, the present investigation is the first of its kind in a dielectric amorphous phase and consequently no comparisons are possible.

However, we note that the D_{ii} and D_{22} diffusion constants are some orders of magnitude greater than the ones which are expected for ordinary processes in glasses of similar composition¹⁴ (considering also the heating effects of the electron beam). The result is related to the breaking of the electronic bonds during irradiation.¹⁰ In addition, for some useful comments on the high values of the correlation coefficients D_{2i} , see the paper by Cooper¹⁵ and references therein.

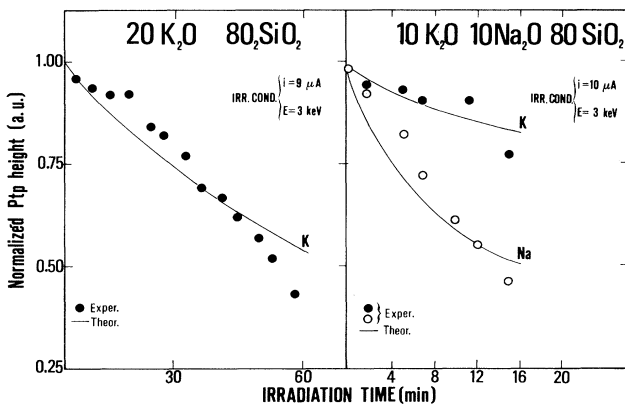


FIG. 2. Experimental (Ref. 2) [after the residence time (Ref. 8)] and calculated Auger peak heights as a function of electron bombardment time. The theoretical profiles are obtained with parameters listed in Table I. Experimental Na profile is not reported since it disappears very quickly as observed in the case of Na-Ca glass.

Moreover, we should like to note that the calculated values of the alkali mobility and the diffusion constants D_{ii} can be connected by the simple Einstein relation. This fact is consistent with the values $D_{i2}=0$ provided that Ca^{++} ionic migration does not influence the alkali diffusion.

Finally values $u_2=0$ suggest both that the chemical potential of Ca strongly depends on alkali concentration and/or that some screening effects for the Ca ionic charge are operating. This last fact is clearly supported by the results of Fig. 2. Here the experimental data for K and Na in mixed-alkali glasses of Ref. 2 (Figs. 4 and 6) are reported with the theoretical profiles obtained as in Fig. 1. From the calculated diffusion and mobility coefficients, reported in Table I, the following conclusions may be drawn: Both in mixed-alkali glass and in K glass the diffusion coefficient and mobility of K atoms are the same and connected by the simple Einstein relation (i.e., K migration is not influenced by the Na atoms). As opposed to these results, the Na diffusion coefficient is the same both in Na glass and in Na-K glass while its mobility is strongly reduced from Na glass to Na-K glass. On the basis of this result we may infer that K alkali ions induce some screening effects both on Na and Ca charges in glasses.

Before concluding, we remark that our analysis of transport processes in glasses under irradiation, introducing correlation coefficients, i.e., a more general treatment of diffusion process,¹⁴ provides new elements (screening effects) for a more general theory on the ionic mobility in mixed-alkali glasses. We note that up to now at least eight models have been proposed in this field, but no single theory is universally accepted nor fully accounts for all features of the mixed-alkali effect.¹⁶

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