Na⁺ Transport Through Sodium Containing Insulators Under Proton Irradiation

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The transport of sodium ions through soda-lime glass and $Na\beta^{n}$ -alumina crystals submitted to 600 keV-proton bombardment was studied. For soda-lime glass, the results can be interpreted as being due to the enhanced electric field assisted diffusion of Na^{+} . The order of magnitude of the electric field generated inside the glass as a result of the proton bombardment could be experimentally determined and agrees well with theoretical predictions. For $Na \beta^{n}$ -alumina, however, the proton results do not agree with those predicted by the electric field assisted diffusion model.

I. Introduction

The irradiation technique based on high energy ions is commonly employed in order to modify the surface properties of materials and is widely used in semiconductor and metal surface engineering. Nevertheless, its application to introduce surface modifications in insulating materials is far from being routine. One of the reasons for the difficulty in the application of this technique to insulators is the lack of knowledge, on a microscopic scale, of the physical processes occurring in dielectric materials during ion bombardment, where both electronic excitations and nuclear collisions are important for a complete description of the phenomena. Among the different effects induced by the ion irradiation at the near-surface layers of a dielectric, the enhancement of the ionic mobility is one of the most iniportant features. Thus, ionic conductors, as alkalicontaining glasses or the β "-aluminas, are natural candidates to investigate this point.

In the past years, the Padova Group has showed that, for alkali-silicate glasses irradiated with energetic charged particles (electron, protons and heavy ions), the alkali-ions mobilities have been enhanced by several orders of magnitude^[1]. They have also showed that the modifications of sodium profiles in irradiated soda-lime glass can be described in terms of three main processes: radiation-enhanced transport, electric fieldassisted migration and preferential sputtering of the sodium atoms. For irradiated β "-alumina crystals, the situation is different and this empirical model has obtained only partial success in describing the sodium depth profile inodifications. In fact, for Na β "-alumina crystals implanted with noble gas ions, the modifications on the sodium depth profiles are well reproduced by this model^[2-5], the only difference being the strong dependence on the nuclear stopping power for the preferential sputtering mechanism, contrary to those observed for glasses, where this mechanism depends on the electronic stopping power^[1]. On the other hand, the results obtained for β "-alumina irradiated with electrori beams are somehow contradictory and cannot be described within the same model^[6,7].

The aim of the present study is to obtain more information on the processes which govern the surface modifications of quite different sodium-containing insulators, soda-lime glass and β "-alumina, when irradiated by energetic charged particles. Thus, we irradiated samples of these materials with 600 keV protons and followed the sodium surface concentration by using the (p, α) resonant reaction on sodium. The time evolution of the sodium concentration at the outermost layers of the samples gives new insights about the masstransport mechanisms in both materials. In particular, we determined experimentally the order of magnitude of the electric field generated inside the soda-lime glass due to proton irradiation.

II. Experimental Procedure

11.1. Soda-lime Glass Samples

It has been more than half a century since Zachari-

asen suggested that alkali silicate glasses consist of a continuous random networlr of Si - O - Si bridging bonds with singly valent ions (such as Na^+ ions) and doubly valent ions (such as Ca^{2+} ions) ionically bonded to $Si - O^-$ non-bridging oxygen atoms. Figure 1 shows a scliematic two-dimensional representation of this model^[8]. Since the Na^t and Ca^{2+} ions are held to sites only by the Coulomb attraction, it is to be expected that these ions can migrate from site to site as a random diffusion or as electric migration if an electric field is applied. For soda-lime glass submitted to a DC potential, Na^+ ions are the most mobile charge carriers, followed by hydrogen species, most probably H^+ , unless the electrodes block the in-diffusion of hydrogen from the atmosphere^[9]. In this case, Ca^{2+} ions are also mobile and electrons are the charge carriers in the alkali-depleted layer near the $cathode^{[10,11]}$.



Figure 1: Two-dimensional representation of the Zachariasen's glass model.

The soda-lime glass samples, 1.2 mm thick, were obtained from the same set of commercial microscope slides. The glass composition was given by: 72% of SiO_2 , 7.9% of CaO, 12.6% of Na_2O , 2.4% of MgO, 2.2% of Al_2O_3 and 2% of other oxides (in w.t %). Rutherford Back Scattering (RBS) analysis confirms this composition at the surface layers. To apply an external electric field on the samples during the irradiations, we deposited thin metallic films as electrodes on both sides of the slide. On the beam entrance side of the sample, we deposited an aluminum film, 30nm thick, as electrode and, on the other side of the slide, we deposited a chromiun-gold bilayer, 200nm each film. Before the film depositions, the samples were etched 10 min in 4% HF solution in order to remove the hydrated

surface layers. As we used a beam chopper to determine the beam current, we could apply an electric field through the sample without the special cares needed with the electronic systems used for beam current measurements directly on the irradiated samples.

11.2. Na β "-alumina Samples

Sodium β "-alumina is the prototype of the twodimensional superionic conductor: it is characterized by a remarkcable value of the room-temperature ionic conductivity ($\sigma \simeq 10^{-1} \Omega^{-1} cm^{-1}$) and by a quite small ionic activation energy (tenths of eVv), with sodium cations being the charge carriers ^[12]. The crystal structure of sodium β "-alumina is schematically represented in figure 2. As is evident from this figure, it is made up of compact spinel blocks of essentially Al_2O_3 , which are stacked and held together by A1-O-A1 groups (see fig. 2a). The oxygens in the bonds that link successive spinel blocks are usually referred to as bridging or column oxygens: they define the so-called conduction plane region, where alkali cations are also located. Two adjacent spinel blocks are rotated by 120° with respect to each other, so that it is necessary to consider three spinel blocks and three conduction planes in order to obtain the unit cell of β "-alumina in the R3m space group (fig. 2b). The conduction planes are relatively open regions within which the mobile Na^+ ions can easily diffuse by means of a vacancy mechanism. The ion migration takes place along the different available sites (i.e., Beevers - Ross and mid-oxygen sites) of the two-dimensional honeycomb-like lattice generated by the hexagonal arrangement of bridging oxygens (fig. 2c). No measurable ionic diffusion occurs through the close-packed spinel structure at room temperature.

Single crystals of sodium β^{n} -alumina were obtained by melting $NaCO_3$, MgO and Al_2O_3 with standard procedure^[12]. Their composition was $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ and typical dimensions were 10 x S x 3mm³. The crystals used in this work were cleaved along the sodium-rich conduction planes. Rutherford backscattering measurements were used to check the stoichiometry at the surface layers of the crystals. All crystals had quite a good appearence, without any macroscopic crackings or extended cleavages. Before the irradiations, the samples were annealed at 200°C for 24 hours to ensure a nearly thorough dehydration and were then stored in silica gel to prevent surface contaminations^[13].



Figure 2: Schematic representation of the structure of sodium β^{n} -alumina: (a) sketch of the atomic arrangement in the spinel blocks; (b) over-simplified unit cell in the R3 \overline{m} space group; (c) ionic arrangement in the conduction plane: the O(5) sites are drawn (shaded circles) with respect to a bottom layer of close-packed oxygens. The top layer of close-packed sxygens bounding the plane has been lifted away. Finally, the honeycomb network connecting the different sites available to mobile cations during their diffusion is also depicted.

11.3. Proton Irradiation and Nuclear Reaction Analysis

Sodium depth profiles were obtained by means of the ${}^{23}Na(p,\alpha){}^{20}Ne$ nuclear reaction which has a resonance at 591.6 keV, with a width of 0.6 keV. The indepth sodium concentration profile was determined by increasing the proton energy in steps of 2 keV. The alpha particles were detected by a large-area surface barrier detector at 150° with the beam direction (solid angle = 0.1 sr) covered by a 6μ m-thick aluminized my-lar foil to avoid pile-up effects due to proton backscattering.

Proton irradiations were made at room temperature. The samples were mounted on a 0.1° precision goniometer. H_2^+ beams were used in order to obtain higher current beams. The use of molecular projectiles deteriorates the energy resolution of the beam, but with no dramatic effects at the near-surface layers, as can be seen in figure 3. In this figure we present the sodium depth profile of Na β "-alumina crystals, measured along the c-axis, using both H^+ and H_2^+ beams. So, if we use a 594 keV/nucleon proton or H_2^+ beams, the resonance occurs at a depth close to the surface of the irradiated crystal. The depth resolution thus attained is about 20nm. In this way, we could follow the time evolution of the sodium surface concentration during the irradiation by measuring the alpha counts for fixed proton doses. When glass samples covered with thin-film electrodes were irradiated, the incident energy is slightly greater (596 keV/nucleon) than those used for Na β "-alumina samples in order to produce the nuclear resonance at nearly the same depths. The incident dose was measured using a beam chopper which intercept the beam just in front of the sample. A second surface barrier detector measured the particles backscattered by the chopper. This backscattering yield is carefully calibrated and gives the absolute incident dose measurement with an accuracy of 3%.



Figure 3: Sodium depth profiles of Na β "-alumina crystals measured with H^+ and H_2^+ beams. The lines are only eyeguides.

Proton and H_2^+ bearns were provided by the 4MV

Van de Graaff accelerator at tlie Physics Department – PUC-Rio. The beam spot on tlie sample was $2mm^2$.

III. Results and Discussions

111.1. Soda-lime Glass

In figure 4, the ratio between the sodium surface concentration and the initial concentration of soda-lime glass is shown as a function of the irradiation time. The teclinique measures the sodium concentration over the outer 20 nm. The results clearly show that after a delay time interval, called residence time τ_{R} ^[1], during which the sodium concentration remains constant, there is a sodium migration to the outermost layers of tlie glass sample. The residence time depends on the beam current density: τ_R decreases with the beam current. In our case, it is approximately equal to 100 s for a beam current of $5\mu A/cm^2$ and 10 s for $15\mu A/cm^2$. It can be understood as tlie time needed to attain a miniinum concentration of defects, forming a network of available sites for the jonic motion. If this concentration is less than a critical value, sodium ions are restricted in their motion and cannot migrate towards the surface of tlie sample^[14].</sup>



Figure 4: Sodium surface concentration normalized to the initial concentration as a function of 600 keV – H^+ irradiation time obtained for glass samples without (–•–) and with (–•–) an external applied electric field (10kV/cm) for a beam current of $5\mu A/cm^2$. Results for $15\mu A/cm^2$ without external field are also shown.

Previous studies on Na^+ rnigration in protonirradiated soda-silicate glasses^[1,15] showed that the time evolution of the sodium concentration profile during proton bombardment can be described by the mass transport equation:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} (D \frac{\partial n}{\partial x}) + \frac{\partial}{\partial x} (\mu E n), \qquad (1)$$

where n = n(x, t) is the sodium concentration at depth x (the surface is at x=0) and time t, D is the sodium diffusion coefficient and μ is the sodium mobility connected to D through the Nernst-Einstein relation. E is the electric field generated in the neutralization process of the incident ions and includes the secondary-electron emission process. The sodium preferential sputtering can be taken into account through the boundary condition

$$D\frac{\partial n}{\partial x} + \mu E n = \sigma \phi x_{\circ} n , x = 0, \qquad (2)$$

where a is the sodium sputtering cross-section, ϕ is the inciclent ion flux and x_{o} the depth, beneath the surface, from which sputtering processes may occur $(x_{\circ} \lesssim \ln m)$. Because of these many different contributions, the electric field must be treated as a free paraineter. As a time interval less than $10^{-5}s$ is needed to attain a steady-state regime for the electric field^[16], it can be assumed that E is independent of the time t. The neutralization process of the protons, which is responsible for the electric charge distribution inside the glass, lias a very complicated velocity dependence, and so the depth dependence, E, is usually assumed to be x independent for the first few microns of depth. In a previous publication^[15], making E = 0 for depths greater than 5pm (proton projected range = $6.5\mu m$), tlie electric field strength used to describe the experimental sodium profiles with the numerical solution of equation (1) was $E = -2 \times 10^3 V cm^{-1}$. The minus sign iridicates that the electric field is oriented from the center of the positive charge distribution (roughly the R_p position) to the surface, which was grounded.

In order to test this point of the model, we irradiated the glass samples with proton beams and, at the same time, applied an electric field with opposite polarity than that of the field generated by the protons neutralization. The results are represented by the open circles in figure 4. The sodium surface concentration remains constant for time intervals greater than τ_R . For electric fields with strengths lower than $10^4 V cm^{-1}$, the results were quite similar to those obtained without an applied electric field. The τ_R is the same and

the sodium increasing ratio is nearly independent of the external fielc. For electric fields with intensities higher than $10^4 V cm^{-1}$ the situation is completely different. A sodium depletion appears at the outermost layers, just bencath the cathode. These results can be qualitatively understood in the following way: when an external field is applied to unirradiated soda-silicate glasses, all sodium ions move along the field direction, leaving a thin layer where there is only SiO_2 . The field in this sodium-depleted region can be very intense, reaching the order of the dielectric breakdown. In our case, both fields - the one due to the neutralization process of the incident propons and the external one - are "switched on" at the same time. The fact that the concentration of sodium at the surface remains constant - and even decreases - for electric fields above $10^4 V cm^{-1}$ shows that these fields compensate each other. Thus, the thickness of the depleted layer is negligible and the field can be calculated ir first order as the applied voltage divided by the thickness of the glass sample. Thus, these results show the combination of the enhancement of the mobility of sodium ions due to proton irradiation and the Na^+ migration guided by the resultant electric field.

The obt ined value for the critical electric field strength, $10^{4}Vcm^{-1}$, differs by a factor of five from the predicted one ^[15], which is more than reasonable, considering the crude theoretical model used to describe the previous experimental results.

III.2. Na β "-alumina

We irradiated Na $\beta^{"}$ -alumina crystals in a way that the incident beam direction could be either perpendicular or parallel to the crystallographic c-axis. In figure 5 we present the results for the sodium surface concentration as a function of the irradiation time for proton (or H_2^+) beams inciding perpendicularly to the c-axis (i.e., parallel to the conduction planes). Within the experimental dispersion, the sodium concentration at the outermost layers of $\beta^{"}$ -alumina remains constant for long irradiation times and different beam current densities. When the direction of incidence was parallel to the c-axis (i.e., perpendicular to the conduction planes) the results were similar: the sodium surface concentration was uniffected by proton irradiation.



Figure 5: Sodium surface concentration normalized to the initial concentration as a function of 600 keV – H^+ irradiation time obtained for $Na \beta^{"}$ -alumina crystals. The conduction planes were aligned with the beam direction. Squares: $5\mu A/cm^2$, triangles: $10\mu A/cm^2$ and circles: $15\mu A/cm^2$.

As the transport of Na^{t} through the spinel-blocks is virtually forbidden in an undamaged sample^[12], this</sup> last result can be understood as due to the fact that the point defects generated by proton beams did not damage the crystalline structure of β "-alumina to provide short-circuits for the motion of sodium ions along a direction perpendicular to the conduction planes. The transport of Nat through the spinel blocks was observed only for electron currents a thousand times more intense^[6] than those used in this work for proton (or H_2^+) beams, or when the crystals were bornbarded with heavier ions^[3,4,5]. For these situations, the Na^+ transport along the c-axis direction is well described by equation (1). On the other hand, when the crystalline structure of β "-alumina is preserved, the electric field is certainly not the driving force for sodiuin transport along the conduction planes as is clear from the results presented in figure 5. When the β "-aluminas were bombarded perpendicularly to the c-axis by light projectiles, electrons or protons, the high mobility of Na^+ in this planes probably acts in such a way that it compensates the injection of an excess of electric charge during the irradiation. The formation of sodium clusters at the surface of $\beta^{"}$ -alumina when irradiated by electron bearns aligned with the conduction $planes^{[6,7]}$, for example, was attributed to local heating effects. As the proton beams used in this work dissipated at least 20 times less power than the above-mentioned electron

beams, the sodium surface concentration should remain constant, as expected if beam heating is now the predominant mechanism.

IV. Summary and Conclusions

In this work we have measured the time evolution of the surface concentration of sodium in soda-lime glass and Na β "-alumina crystal irradiated with 600 keV proton beams. The results obtained for soda-lime glass can be discussed in terms of a model for the transport of sodium ions in irradiated glasses which includes three main processes: radiation-enhanced transport, electric field-assisted migration and preferential surface sputtering of the alkali element. Previous results for heavily damaged Na β "-alumina crystals^[2-6] can also be described within the same model. When the layered crystalline structure of β "-alumina remains undisturbed, this model fails in describing the Na^+ motion along the conduction planes. We believe that the high mobility of sodium ions in these planes compensates the injection of electric charge when the crystals are irradiated in a geometry in which the conduction planes are aligned with the beam direction. Local beam heating effects cannot be discarded if one wants to find an explanation for these results, and it is clear that more work is needed to clarify this point.

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