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INFLUENCE OF ION IMPLANTATION AND GAS EXPOSURE ON THE CHARGE IN SILICON OXIDE CREATED BY ELECTRONIC EXCITATION

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Abstract

Low energy electron bombardment of amorphous SiO_2 induces point defects such as oxygen vacancy by electronic excitation. The defects build a macroscopic negative charge by trapping of electrons on the localized levels in the band gap; this phenomenon was previously described as the "mirror" effect. In the present paper, we investigate, by mirror effect, the behavior of the charge after an argon, nitrogen and oxygen implantation at 1 and 4 keV, and after exposure to the same gases at various low pressures. We observe a difference of behavior between Ar (or N_2) and O_2. The results reinforce the outstanding role of oxygen in the defect production in SiO_2 by electronic excitation.

Key words: Electronic excitation, oxygen vacancy, electron spectroscopy, silicon oxide, charge, localized levels, ion implantation, pressure.

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Introduction

Radiation effects in insulators have a great role in a wide range of industrial and technological domains such as energetics, space and electronics. Alumina in nuclear reactors, insulators in spacecrafts, metallic layers on insulating substrates in MOS* for instance, can be heavily damaged by beams of ionizing particles and are submitted to aging. Radiation effects have been extensively studied for years but the exact nature of all phenomena involved is still poorly understood. Among them the phenomenon of charging up has been left apart mainly because of the great difficulties it leads to in spectroscopic studies. However, an approach to this problem in terms of solid state physics allowed us to link charging effect, secondary emission and point defects creation under irradiation (LeGressus et al., 1982, 1984; Vigouroux et al., 1983). For example, such an approach in terms of defects created under electron bombardment led us to a better understanding of damage in SiO_2 under electronic excitation (Vigouroux et al., 1985). The purpose of the present paper is to progress into the physico-chemical study of the defects created under electronic excitation by investigating the charge behavior in function of pressure and nature of gas exposure. The outstanding role of oxygen in the mechanism of defects creation led us to consider the behavior of the charge in the presence of supplementary oxygen atoms due to O^+ ions implantation or to O_2 gas exposure. We compare these results with those obtained with argon and nitrogen and we propose an interpretation in terms of electronic structure of the insulator.

Radiation effects in SiO_2 have been much studied (Griscom 1979, 1985; O'Reilly and Robertson, 1983) but under low energy bombardment, the mechanism of defect production is not yet quite well established. Vigouroux et al., (1985) have

*metal oxide semiconductor

completed experiments on amorphous and crystalline SiO_2 which exhibited an analogous behavior under electron bombardment (20 keV). This experiment showed that the charge had been created by impinging electrons since the intrinsic defects in both samples are quite different. The low energy value of the electrons does not allow any displacement of oxygen atoms by direct transfer of momentum: at 20 keV, the maximum energy which can be transferred is 2.8 eV. Another process for creation of defects would be electronic excitation following the work by Tanimura et al. (1983). These authors interpreted the volume increase of quartz under dense pulsed electron beam in terms of creation of an unstable Frenkel pair. Vigouroux et al.(1985) then proposed a similar mechanism through creation of an oxygen vacancy after relaxation of an exciton induced by the primary electron beam.

Experimental

As in our previous studies, we use a JEOL JAMP-3 electron microscopy and spectroscopy equipment under Ultra High Vacuum which has been described elsewhere (Vigouroux et al., 1984, 1985). The ion gun on line for classical etching was used for implantation of ions at 1 and 4 keV with current of around 2 microamps. On the other hand microleaks allow gas exposure at given pressure in the analysis chamber.

Under electron beam of 20 keV energy for instance negative charges are trapped in the bombarded sample. They create a macroscopic potential, even after the irradiation is stopped, which is stable in UHV. This is the "mirror" effect which has been extensively described elsewhere (Vigouroux et al., 1983, 1984, 1985).

Use of the mirror effect

The 1 keV equipotential sphere observed by electron microscopy is large enough for considering that the classical relation:

$$V = Q/4\pi\varepsilon_o d \qquad (1)$$

is applicable. Q is the stored charge in the insulator and d is the radius of the equipotential. The mirror size is therefore directly correlated to the trapped charge in SiO_2. On the other hand, the shape of the mirror gives some information on the implantation of the charge. Its deformation is linked with the charge drift.

At room temperature and in UHV, the mirror is stable (Figure 1). Under any kind of electrical, mechanical or thermal perturbation, one can observe an increase

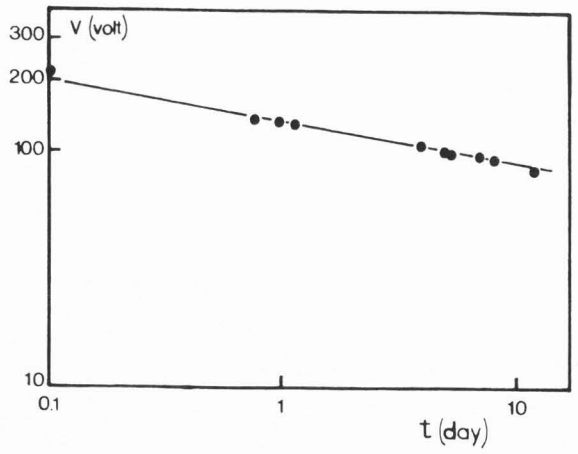

Figure 1: Kinetics of the mirror disappearance at room temperature, the charge decrease corresponds roughly to a few electrons per day. The vacuum is 10^{-9} Torr. V_d corresponds to V_d value in Figure 2.

of the kinetics of the mirror disappearance: an ion bombardment induces enhanced electron secondary emission which leads to re-arrangement in the solid. Under electron bombardment ions and electrons are re-emitted by stimulated desorption. Positive ions are accelerated by the created electric field and contribute to the increase of the kinetics of disappearance. Pressure and temperature also influence the kinetics as we will see below.

Care is needed in this type of experiment: some devices present in the analysis chamber might hide the phenomenon. For instance, all devices with a heated filament must be turned off because they are sources of ions and electrons which can interact with the mirror. On the other hand the photomultiplier and the cylindrical analyzer induce an electric field which can perturbate the mirror in the same way.

Experimental techniques

The use of the JAMP 3 Auger Microprobe allows 2 types of measurements:

A method, electron spectroscopy: after creation of the mirror (20 keV), the sample is drifted 2 mm (distance d) from the incident beam (Figure 2) in order that the electrons reach the surface of the insulator without being reflected by the 1 keV equipotential. At that place, an electron spectrum can be recorded. One observes a lack of low energy secondary electrons up to a V_d value. This value corresponds to the maximum energy of the

electrons which cannot cross the energetic barrier induced by the charge. The V_d shift represents the surface potential at the analyzing point.

B method, scanning electron microscopy: we use the mirror strictly speaking, the size of which is proportional to the implanted charge. If we assimilate the 1 keV equipotential to a half-sphere, one has:

$$d = Q/4\pi\varepsilon_o V \qquad (2)$$

where V =1kV and d is the radius of the mirror. The average radius of the equipotential is determined by measuring the surface area A and calculating:

$$d = \sqrt{A/\pi} \qquad (3)$$

The reported kinetics are therefore d=f(t).

Both methods presented here above induce a perturbation of the measure: the analysing beam (A method) can create other defects and implant negative charges. The B method requires taking pictures, therefore scanning the surface. It is possible to take a picture in less than 40 seconds, which represents a time of 40.10^{-6} seconds on every point of the scanned area. This latter method appeared to us as less damaging.

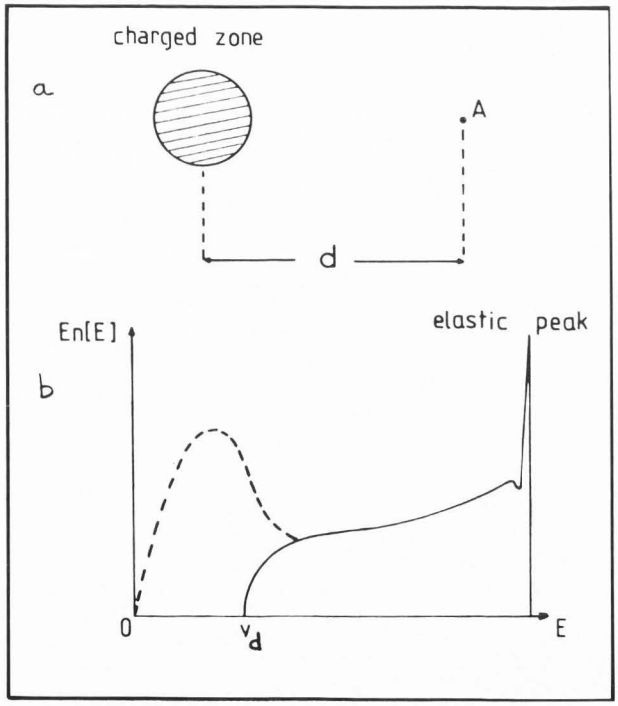

Figure 2: (a) schematic view of the bombarded area inducing the mirror effect and of the impact of the analyzing beam (A). (b) electron spectrum recorded at A; the V_d value corresponds to a shift of the emitted electrons due to the implanted charge.

Sample preparation

The glass samples used in the present study have impurity concentrations less than 1 ppm. However, the proportion of OH groups is very difficult to evaluate and to anneal out. All the experiments described here were achieved on Tetrasil SE containing less than 10 ppm OH. Their size was 10x10x1 mm . Their faces were polished.

Ion implantation

The gas is directly sent into the ionization chamber of the ion gun, therefore the ionic vacuum in the analysis chamber is preserved. The sample is bombarded during 30 minutes with an absorbed current of 2 microamps. The pressure goes up to 2.10^{-6} torr in the chamber. We used 2 accelerating voltages (1 and 4 kV) in order to change the implantation depth of the ions. After the bombardment, the mirror experiment is achieved in UHV again after pumping the chamber.

Gas exposure

We study the kinetics of the mirror disappearance in presence of a controlled gas atmosphere in front of the sample. The gases are oxygen, nitrogen and argon and the partial pressure goes from 10^{-8} to 10^{-4} torr.

Experimental conditions

Before every experiment, the sample is etched with argon during 15 mn at 3 keV and 3 microamps. The mirror is created with electrons of 20 keV primary energy electrons during 45 seconds. The mirror image (by SEM) is achieved with electrons of 1 keV primary energy and a primary current of 5.10^{-10} amps. The picture is taken in 40 seconds.

Results

Ion implantation

The kinetics of the disappearance of the charge with time are plotted on Figure 3. The main features are the following: (i) the charge is very stable (room temperature); no difference in the kinetics between the 3 gases is noticeable. (ii) the charge under 4 keV ion energy is always higher than under 1 keV implantation. (iii) argon and nitrogen have similar behavior but the implantation with oxygen induces mirrors whose sizes are smaller than for the other gases.

Controlled atmosphere

The kinetics are plotted on Figure 4. Previous experiments showed that the disappearance kinetics was fitted by a power law. If we represent all our results on log-log plots, the slope of

the straight lines at t>150 minutes is shown on Figure 5. This corresponds to a time scale of an aging phenomenon. Argon and nitrogen have a similar behavior but oxygen seems to exhibit a singularity at $P \simeq 10^{-5}$ torr.

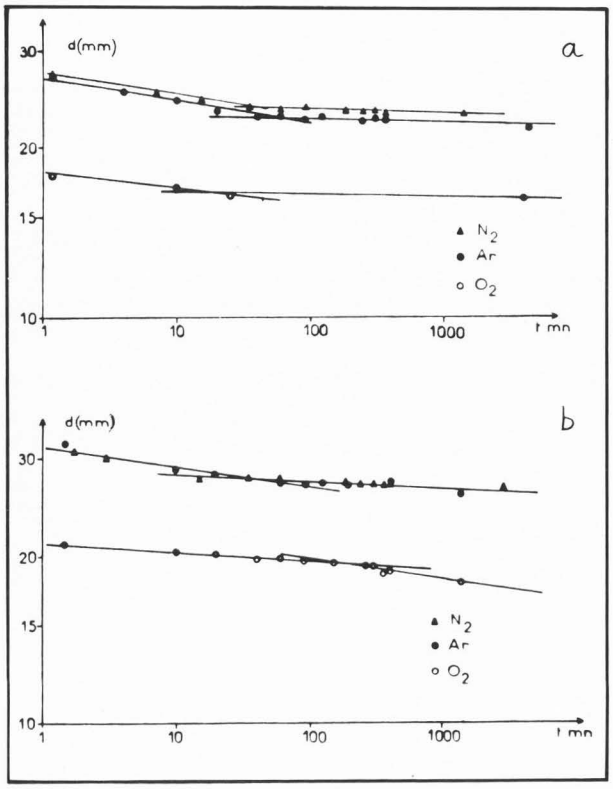

Figure 3: Kinetics of mirror disappearance after ion implantation for primary energy of 1 keV (a) and 4 keV (b). The curves are representative of argon, oxygen and nitrogen implantation. d is the mirror size.

Discussion

Effect of ion implantation

Under ion bombardment, atoms of oxygen, argon or nitrogen can be trapped as interstitials in the lattice. Two effects of the bombardment can be considered: (i) defect production depending on the atom mass; (ii) chemical effect depending on the nature of the atom. Experimental data show that the difference between Ar and N_2 is not noticeable. Moreover the difference between O_2 on one hand and Ar and N_2 on the other hand imply a chemical effect. The implanted oxygen atoms can recombine with E'-centers in order to build peroxy radicals. The number of E'-centers in the insulator then diminishes compared to Ar and N_2 implantation and the oxide stoichiometry is therefore altered. As the probability of trapping an electron is higher on E'-center than on peroxy radical (Vigouroux et al., 1985), a decrease of the number of E'-centers induces a decrease of the charge.

Effect of the controlled atmosphere

Figure 5 shows an increase of the disappearance speed of the mirror with pressure. The collisions of the atoms on the solid are responsible for the decrease of the charge in the insulator: as the incident atoms are thermal (a few meV kinetic energy), a possible mechanism is that proposed by Hagstrum (1954) and Boiziau (1982) for the interaction solid -excited helium. Figure 6 shows the energy diagram of surface-helium atom separated by an infinite distance. In the vicinity of the surface, the excited helium atom forms a quasi-molecule with the solid, which has a hole on the 1S state of helium. The 2S state is either empty (ionized helium) or occupied (metastable helium). One can observe that after the interaction, the He atom is de-excited and an electron is emitted into the vacuum. This mechanism is explained by the overlapping of wave functions of the helium 2S level and the electronic states of the surface (Figure 7):
- if there is overlap of the 2S level and the band gap, an electron is ejected from the solid while another electron from the valence band fills the 1S level.
- if there is overlap of the wave-functions of the 2S level and the valence band of the solid, one electron from the valence band fills the 1S level while the ejected electron comes from the 2S level, occupied in the case of a metastable atom (or filled through Tunnel effect from the valence band when the atom is ionized).

When we consider the molecular orbitals of oxygen,argon and nitrogen (Figure 8) one realizes that the mechanism described above is difficult to apply with the couple SiO_2-N_2 or SiO_2-O_2. The energy levels of the three species are much too deep for the electrons from the valence band to reach the free levels of the gas. On the other hand, the charged solid can be modeled as an electric field which is intense enough to perturb the levels of the gas and may in some cases excite the molecules. These molecules were chosen because of their non-polar character and their similar polarizability (Table 1).

Experiments of chemisorption of CO on nickel have shown that the least bound occupied levels of the species in the vicinity of the surface can be shifted several eV under electric field (Mucchielli et al., 1980). Therefore they can be located at the same binding

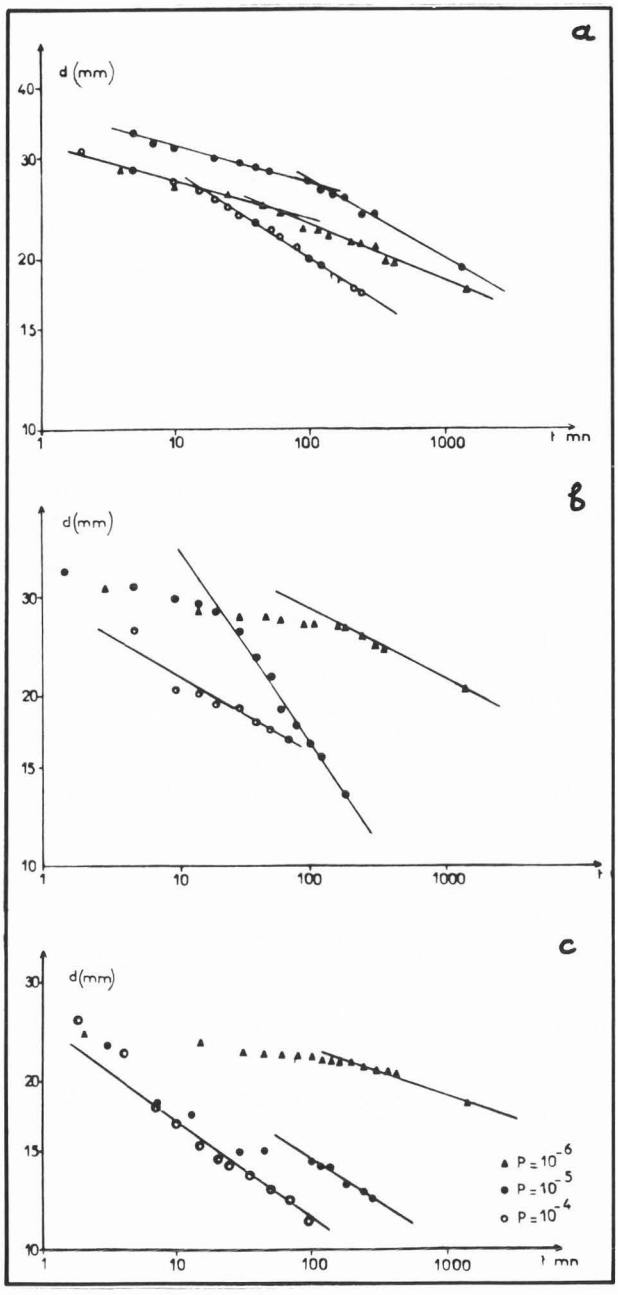

Figure 4: Influence of gas pressure on the kinetics of mirror disappearance for argon (a), oxygen (b), nitrogen (c). d is the mirror size.

molecule	Ar	02	N2
polarizability (A^3)	1.77	1.60	1.64

Table 1: Polarizability of argon, oxygen and nitrogen molecules.

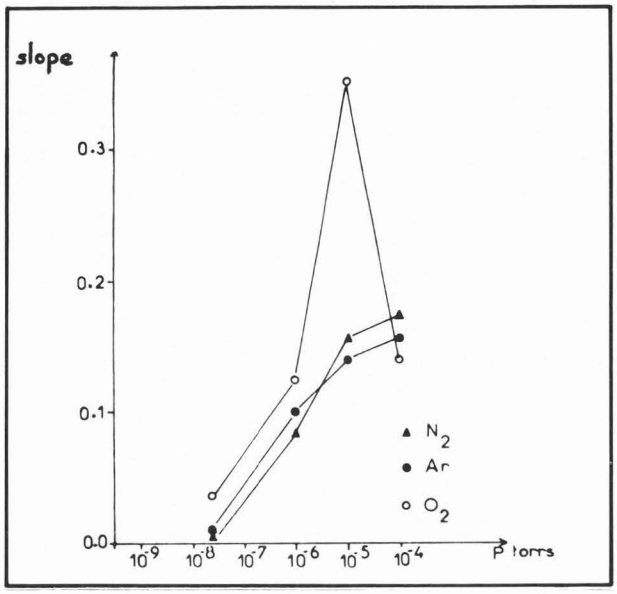

Figure 5: Slopes of the curves representing the different kinetics from Figure 4 in function of pressure.

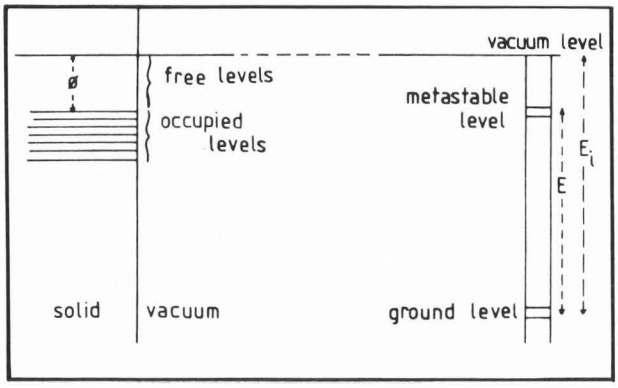

Figure 6: Energy diagram of the couple solid-He atom separated by an infinite distance.

energies as localized levels in the band gap of SiO_2. We can hence apply the mechanism described above to the case of the decrease of charges in an insulator under residual atmosphere: the electric field induced by the charges implanted by irradiation excites the molecules of the gas; during de-excitation on the walls of the solid, an electron is ejected which comes from the occupied levels in the band gap (Figure 9).

The charge diminishes more rapidly when the number of interactions gas-solid increases, i.e., when the pressure increases. This phenomenon is observed for Ar and N_2 and also for oxygen but in this latter case, it appears that a supplementary effect is superimposed at 10^{-5} torr. This effect is still not well known and further experiments must be

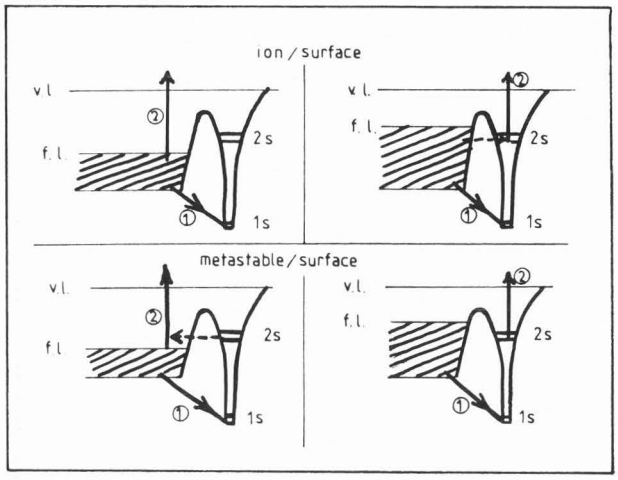

Figure 7: Energy diagram of interaction between a surface and a helium excited atom or helium ion (from ref. Boiziau 1982).

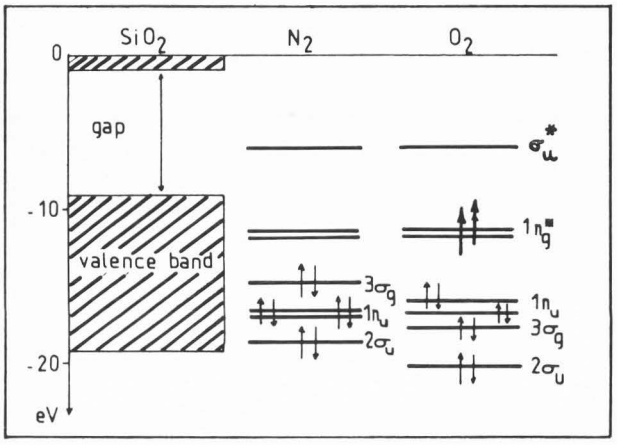

Figure 8: Electronic configurations of molecular levels of oxygen and nitrogen compared to the electronic structure of SiO_2 in the fundamental state.

carried out further in order to explain it.

Conclusion

From the description of the electronic structure of SiO_2, we showed that point defects induce energy levels in the band gap. Under irradiation, a mechanism of creation of these defects had been proposed (Vigouroux et al., 1985) and had put into evidence the great role of the oxygen atoms in this process. In order to confirm these approaches, we achieved experiments on the influence of pressure and ion implantation and showed that there is no drastic difference in the behavior of the charge with time between Ar and N_2. On the contrary, the role of oxygen seems reinforced by the change in the amount of charge created after ion

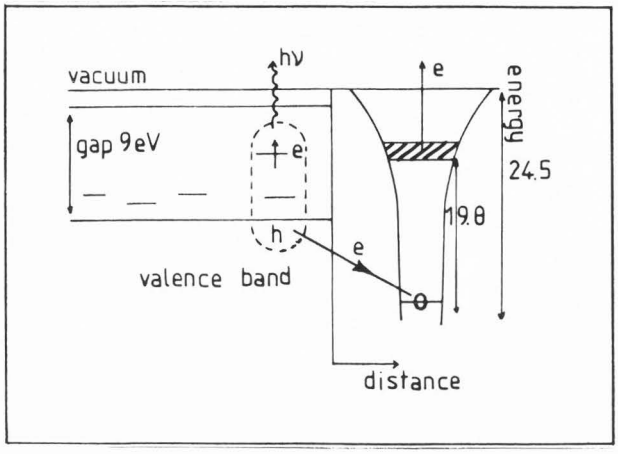

Figure 9: Interaction energy diagram of an incident molecule impinging on a SiO_2 surface. A photon or electron emission is induced by the de-excitation of the molecule in the vicinity of the surface. This process can give rise to a positive charge on the insulator (from ref. Vigouroux et al., 1984).

bombardment and by the singular behavior of charge decrease under oxygen atmosphere. We can propose an explanation for the latter point in terms of the change of energy levels of the gas under the high electric field created by the charge on the surface of the glass. The former point may be understood in terms of modification of the number of E'-centers in function of the impinging atom type.

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Discussion with Reviewers

TJ Shaffner: How thick is the oxide on your samples and how was it prepared? Does the electron beam of the SEM penetrate through the oxide?

Authors: The sample was an amorphous silica sample of 1 mm thickness; the beam therefore was unable to penetrate through the sample. The oxide was a commercial Tetrasil.

TJ Shaffner: How reproducible are the curves in Figure 4? Why is there a consistent change in slope near 20 min for the argon and oxygen curves? What is the significance of these transition points, and are they reproducible?

Authors: The question of reproducibility is a difficult one concerning experiments on glass and more generally on insulators. However we can say that the experiment was correct enough to consider the initial points (t=0) as very reproducible. The slopes are also very reproducible and so are the "transition" points. But the time at which they appear is less sure. The first part of the curve could be due to some surface desorption effect. The second part of the curves could be the manifestation of some depolarization effects in the insulator which are known to follow a power law decrease. But this explanation needs to be confirmed.

TJ Shaffner: A 4 keV ion implant resulting in a surface potential of 2 keV implies a field strength near 10^8 V/cm. If these are realistic numbers for your experiments, would not one expect dielectric breakdown in the oxide? Could not charge bursts be responsible for the anomalous behavior in the oxygen curve (Figure 4) at 10^{-5} Torr?

Authors: The local fields present in the oxide in these experiments are actually of this order of magnitude, that means in the range of dielectric breakdown. We agree that some breakdown could occur inducing light emission for example. But we cannot detect it in our apparatus. However the effects we described in a previous paper (Vigouroux et al., 1985) might be a manifestation of these bursts you mention.

TJ Shaffner: Would not one expect some field enhanced emission below V in figure 2?

Authors: We think so and we described such an effect in Vigouroux et al. (1985).

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