Ion Neutralization Processes at Insulator Surfaces and Consequent Impurity Migration Effects in SiO_2 Films

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We have developed a model for the interaction of ions with insulator surfaces. This model describes in detail the processes whereby ions of different ionization potentials are neutralized at the surface and predicts that ion bombardment can cause impurity-ion migration in such films, depending on ionization potential. Such migration is demonstrated to occur, in agreement with the model, by use of radiotracer techniques employing ^{22}Na deposited on SiO_2 films.

Insulator charging effects lead to severe problems in a number of fields, including semiconductor device processing,[1] and analysis of thin films.[2] In addition, charging effects are important in such techniques as xerography.[3] This paper gives, for the first time, the detailed theory of the ion-insulator interaction in ion impact on insulator surfaces, which predicts that in some cases these processes can lead to impurity migration in insulators at room temperature. Such mobilization of monovalent impurities such as sodium is caused by capture of the electron binding them Coulombically, and is a function of the ionization potential of the bombarding ion and its velocity. Confirmatory data from experiments using ^{22}Na as a radiotracer are given.

Consider an insulator such as SiO_2. We shall discuss the processes of ion neutralization at the surface in the following series of steps: (i) What happens to the ion as it approaches the surface as a result of the dielectric polarization of the surface and subsequent force on the ion, (ii) what are the neutralization processes possible at the surface, and (iii) what are the subsequent charge-transfer processes? We shall first consider the case of an ion traveling at very low velocity and follow this by discussing the dependence of this behavior on ion velocity.

To explain the neutralization of an ion at an insulator surface it is first necessary to discuss the insulator properties. The band structure shown for SiO_2 in Fig. 1 is basically that discussed by DiStefano and Eastman.[4,5] In their model of the SiO_2 structure the valence band has considerable detailed structure, including two narrow, high mass bands near the valence-band edge, with slight band tailing into the band gap, as shown here. The exact details of the valence-band structure are not, however, basic to our model. The electron affinity and the band gap are those given by DiStefano and Eastman and also by Powell and Derbenwick.[6]

As an ion approaches the surface of an insulator film it induces polarization of the material, thus giving an image charge effect (similar to that occurring in the case of processes at metal surfaces[7]) which is modified by the dielectric constant of the insulator.[8] The resultant force on the ion causes a shift in its ionization potential which may be written (to first order) as

$$\Delta E = 3.6 Q^2(\epsilon - 1)/D(\epsilon + 1) \qquad (1)$$

(neglecting the repulsive term which arises from interpenetration of the electron clouds and the Pauli principle, since the ion velocity is small[8]), where ϵ is the dielectric constant of the insulator, ΔE is the shift in ionization potential in units

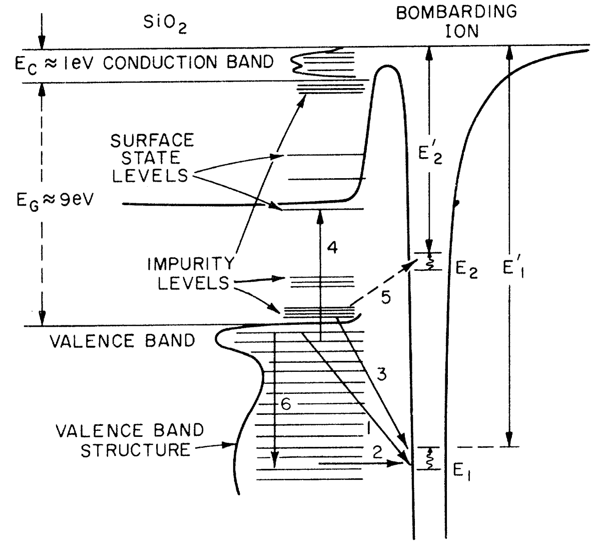

FIG. 1. Neutralization processes which an approaching ion may undergo at an insulator surface (SiO_2 is used as an example). Ions of type E_1 are, e.g., Ar^+, He^+, $N_2{}^+$; ions of type E_2 are B^+ and Ca^+.

of eV, D is the ion's distance from the surface in angstrom units, and Q is the ion charge in units of electronic charge. This shift in ionization potential may drastically affect the processes undergone by the ion at the surface during neutralization. It is typically of the order of 0.4 eV at 5 Å from the surface, rising to 1 eV at 2 Å, for a singly charged ion.

Impurity levels are also shown in the band gap of the SiO_2. Their position close to the conduction- and valence-band edges is suggested by the work of Segal[9] in which it was shown that addition of alkalis to fused quartz caused some narrowing of the band gap of the glass, as measured by uv transmission. The work of Bennett and Roth[10] suggests that hydrogen in SiO_2 may give other impurity levels deeper in the gap, as are also shown in Fig. 1.

As the ion approaches within 3 Å of the surface, the probability of its neutralization at the surface increases, as shown by Hagstrum[7] for the case of ion neutralization at metal surfaces. The exact neutralization process undergone by the ion is a strong function of its ionization potential. As illustrated in Fig. 1, however, a basic distinction must first be made between ions such as argon or nitrogen whose ionization potentials are greater than $E_G + E_C$, illustrated in Fig. 1 as E_1, and ions whose ionization potentials are much less, such as boron or calcium, illustrated as E_2. Ions of the former type will undergo neutralization at the surface in processes whereby electrons from the valence band of the insulator are transferred to the ion in Auger or resonance processes (with very high probability), similar to those discussed by Hagstrum for processes at metal surfaces.[7] They then physically impact the surface as neutral atoms. Ions of the latter class, however, cannot undergo such transitions and, therefore, do not exchange charge with the insulator at its surface, but travel on into the insulator as ions. Ions whose ionization potential (in the region of maximum transition probability, 2–3 Å from the surface[8]) falls close to the valence-band edge may cause impurity transition effects but not bulk effects.

An ion of class E_1, such as Ar^+ or N_2^+ will take part in Auger or resonance processes with bulk or impurity levels as illustrated in Fig. 1. Transitions 1 and 3 represent electronic Auger processes in which the "down" electron[7] comes from a bulk or impurity level, respectively, requiring the excitation of a second electron into a "surface state" or trap level as in transition 4.[3] Here the pairs of transitions corresponding to the Auger process would be (1, 4) or (3, 4). The "up" electron could be excited out of the insulator entirely if the ionization potential E_1', at impact, is large enough. Transition 2 is a resonance process which does not require excitation of a second electron. The resultant hole may subsequently radiatively de-excite. The consequence of these neutralization processes is that the ion is neutralized by an electron from the surface monolayers and travels into the insulator as a neutral atom. In the neutralization processes at the first monolayer, either positive holes or positive impurity ions are produced as a result of the neutralization. For example, sodium in SiO_2 may be bound[1] as $\equiv Si-O^-Na^+$. Neutralization from an impurity level is equivalent to the process

$$\equiv Si-O^-Na^+ + Ar^+ \rightarrow Ar^0 + \equiv Si-O + Na^+, \qquad (2)$$

where the Na^+ is now free to move in the insulator film, away from the surface, since there are no free electrons in the SiO_2 to provide another binding electron.

An ion of class E_2 cannot take part in any such processes, transitions such as 5 being, of course, forbidden. Two consequences follow: (a) No impurity mobilization can occur by the neutralization processes described above, and (b) the ion will not be neutralized at the surface but will travel into the insulator film as an ion.

Transitions undergone by ions of type E_1, such as Ar^+, give rise to positive holes and positive ions at the surface. DiStefano and Eastman[4,5] suggest that the holes are strongly trapped at the surface. The ions (such as Na^+ and K^+) produced in these processes may migrate through the insulator film and be trapped at the SiO_2/Si interface (as occurs, e.g., during voltage and temperature stressing of these films[11]). The positive holes trapped at the surface provide the driving field for this ion migration. On the other hand ions of class E_2 such as B^+ should not undergo such neutralization and thus not produce such impurity mobilization. For ions intermediate between these extreme cases, such as P^+, transitions from impurity levels but not bulk levels may occur.

The effect of increasing ion velocity are (i) to decrease the effective ionization potential of the ion still further due to the repulsive term[8] neglected in Eq. (1), and (ii) when the ion energy is high enough, to reduce the time spent by the ion in the region of maximum neutralization probability to the point where Auger and/or resonance processes can no longer take place.[12] For Ar^+ ions this energy would be expected to be of the order of 20 keV. For B^+ the corresponding energy is about 10 keV. As the ion energy increases, the transitions occur closer to the surface.[8] In other words, differences in behavior between, say, B^+ and Ar^+ ions in their effects on bombardment, at energies less than 10 keV, cannot be ascribed to (ii) alone. (Alkali ions may be a special case for impact on insulating films containing alkali impurities, in that resonance processes may take place at the surface during bombardment, or alkali-alkali exchange processes occur on the surface after bombardment, leading to impurity transport by mechanisms other than those discussed above.)

To test the predictions of the model described above, the following experiments were performed. Films of SiO_2 on Si 5000 Å thick were prepared under conditions known to lead to a minimum amount of sodium contamination. NaCl containing 1% ^{22}Na as a tracer was then evaporated onto the sample surface at a surface concentration of $2\times10^{13}/cm^2$ Na. Samples were bombarded to doses of $1\times10^{14}/cm^2$ by ions of Ar^+, B^+, and P^+, as being representative of ions of classes E_1 and E_2 and intermediate between these, at energies of 2 keV. The samples were then etched in steps of 200 Å in a planar etch of 15:1 H_2O:HF solution. The amount of Na in the etch solutions was determined by counting the coincident γ rays from ^{22}Na. (In unbombarded control samples processed in parallel, all the ^{22}Na was found to be removed by the first etch.)

The predictions of the proposed model for these ions and energies are that (i) the Ar^+ ions will definitely cause sodium mobilization, (ii) the B^+ ions will definitely not cause such mobilization, and (iii) the P^+ ions may not produce mobilization (the band-edge and gap positions are not well enough known). The results are shown in Fig. 2. It may be immediately observed that $8\times10^{11}/cm^2$ Na was transferred across the SiO_2 film by the bombardment by Ar^+ ions. No ^{22}Na was transferred across the oxide film by bombardment by either B^+ or P^+ ions, in agreement with the predictions of the model as described above, to within the sensitivity of the measurement ($\pm 4\times10^9$ total Na/cm^2). In parallel experiments, in which the charge in the oxide film was measured by etch-off experiments followed by formation and testing of metal-oxide-semiconductor capacitors, the charge distribution in the oxide was also in agreement with the model's predictions, e.g., the boron ions carried their charge to their range in the oxide film.

Recent work by Hughes and Baxter,[2] in which profiles of Na in SiO_2 films were measured in a Cameca ion microprobe using O^+ and O^- ions, is also in agreement with the model described, in that O^+ gave a pile up of Na at the SiO_2/Si interface and O^- did not. The ionization potential of O^+ puts it in class E_1, and thus O^+ is capable of producing impurity mobilization. O^- ions, however, cannot undergo neutralization processes such as those described above, and therefore would not be expected to cause impurity mobilization effects.

In other experiments we have also found that N_2^+ ions mobilize sodium in SiO_2, in the same

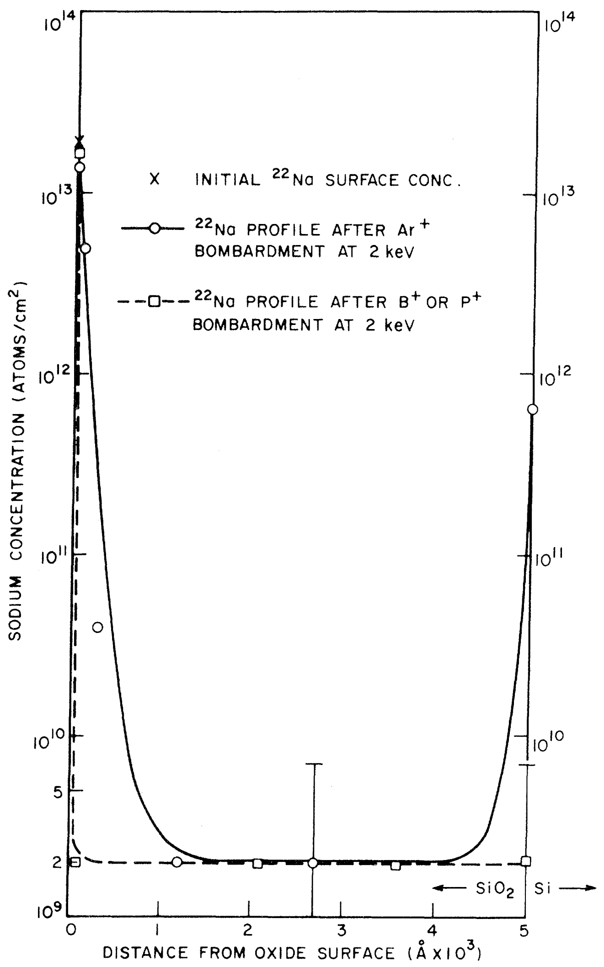

FIG. 2. Sodium transferred across an SiO_2 film by bombardment with 1×10^{14} Ar^+ at 2000 eV; no sodium is transferred by bombardment with B^+ and P^+ ions to the same dose at 2000 eV (lower curve), within detection limits.

way as do Ar^+ ions, with slightly higher efficiency. Details of experiments performed with these and other ions will be reported elsewhere.

In conclusion, we have shown that ion neutralization processes at insulator surfaces can cause impurity mobilization in the bombarded films which is a function of the bombarding ion's ionization potential and velocity. In particular, Ar^+ bombardment at 2 keV or less has been shown to cause migration of alkali-metal ions in bombarded SiO_2 films. The consequences for plasma processing, ion implantation, and analysis of insulating films we believe to be far-reaching, in that in all these operations positive ions are impacted on insulating film substrates, and, therefore, impurity migration processes resulting from this bombardment can occur.

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Attenuation of High-Frequency Acoustic Waves on the Low-Temperature Side of the MnF_2 Néel Point

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We present acoustic-attenuation experiments at frequencies up to 1000 MHz in the vicinity of the Néel point of MnF_2. They show that the attenuation is maximum in the low-temperature phase near the transition, and the temperature at which that maximum appears decreases as the frequency increases. A brief scanning of the theory is given which explains this new effect in terms of relaxation of staggered magnetization.

One of us has recently presented[1] preliminary experiments showing a completely asymmetric behavior of the attenuation of ultrasonic waves around the Néel point of the antiferromagnetic crystal MnF_2. In the low-temperature phase, the attenuation has a maximum which shifts to lower temperature when the frequency is increased from 100 to 1000 MHz. The temperature shift is as large as 10°K at the highest frequency. In this Letter we would like to summarize new experimental results and present an explanation of this phonemenon in terms of the relaxation of the order parameter, namely, a Landau-Khalatnikov effect. This has very often been invoked to explain anomalous behavior of the acoustic attenuation around a critical temperature[2]; but the only circumstances where it has been firmly proved is the case of the λ transition of helium.[3] We hope to prove here its effectiveness in the case of the antiferromagnetic transition of MnF_2.

Theoretical arguments supporting this idea may be given along the following lines. A longitudinally polarized acoustic wave modulates the distance between magnetic ions coupled by exchange forces leading to a Hamiltonian of the form

$$\mathcal{H}_{\text{coupling}} = \sum\nolimits_{q'} G(qq')\mathcal{E}(-q)S_z^{(1)}(q')S_z^{(2)}(q-q'),$$

where $G(qq')$ is proportional to a derivative of the exchange constant J with respect to the distance between the ions, $\mathcal{E}(q)$ is the strain associated with the acoustic wave, and $S_z^{(1)}$ and $S_z^{(2)}$ are the Fourier components of the magnetization of each sublattice. $\mathcal{H}_{\text{coupling}}$, of course, must include terms involving transverse components of spin operators, but these terms do not enter into the discussion, which is concerned only with the fluctuations of the order parameter. There is a