Effect of Bombardment by Glass-Forming Ions on Thermally Stimulated Ionic Conductivity of Sodium in SiO_2

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Thermally stimulated ionic conductivity measurements have been made of sodium motion through SiO_2 grown thermally on silicon, and through thermal SiO_2 after bombardment by Ar^+, B^+, and P^+ ions of 5 keV energy. Ion implantation of SiO_2 by glass-forming ions such as B^+ or P^+ creates traps at the SiO_2-Al interface that can markedly reduce Na^+ motion in SiO_2.

Instability of silicon semiconductor devices due to sodium motion in thermal SiO_2 has been a central problem in semiconductor technology.[1-3] Two primary methods have been used to eliminate sodium-induced instabilities: stringent cleanliness during processing or the high-temperature formation of thin passivating layers of a second insulator such as phosphosilicate glass (PSG)[4-6] or silicon nitride[7] on the completed device. Thermally stimulated ionic-conductivity (TSIC) curves provide a sensitive method of measuring the kinetics and amount of ion motion in an insulator.[8] In this note I present TSIC curves due to sodium motion in thermal SiO_2, both before and after ion bombardment by 5-keV B^+, P^+, and Ar^+ ions. They show that ion bombardment of SiO_2 by "glass-forming" ions may provide a new low-temperature method of passivating thermal SiO_2. The results also suggest an alternative interpretation of experimental observations of sodium motion in SiO_2, which have been cited by McCaughan, Kushner, and Murphy (MKM)[9] in support of their theory of ion-insulator interactions.

The theory of MKM predicts that ion-neutralization processes as ions approach an insulator surface can lead to impurity migration in insulators at room temperature. They assumed that sodium occurs at the surface of SiO_2 as an ionic species, Coulombically bound, after evaporation as NaCl, e.g., as $Si\text{-}O^-Na^+$. Neutralization of bombarding ions at an insulator surface occurs by Auger or resonance processes as the ion approaches the surface.[10] If the ionization potential of an incoming ion is greater than E_G+E_C, where E_G is the band gap of the insulator and E_C is the electron affinity, resonance transitions of electrons from the insulator can neutralize the incoming ion; either positive holes or positive ions are produced as a result of the neutralization. If positive ions such as Na^+ are produced, they may move away from the surface and diffuse to the Si-SiO_2 interface. When the ionization potential of the incoming ion is less than E_G+E_C, such neutralization processes cannot occur; no Na^+ ions are released to move through the SiO_2. Examples of the first class of ions, designated as E_1 ions, are Ar^+ or N_2^+; examples of the second class, designated as E_2 ions, are B^+ and P^+.

To confirm their theory, MKM grew 5000 Å of SiO_2 on silicon wafers and evaporated NaCl containing 1% radioactive Na^{22} at a surface concentration of Na^+ of 2×10^{13} cm^{-2} onto the SiO_2 surface. Samples were then bombarded with 1×10^{14} ions/cm² of 2-keV Ar^+, B^+, and P^+ ions. Sodium motion occurred after Ar^+ bombardment, as determined by radioactive tracer measurements; no Na^+ motion occurred after B^+ or P^+ bombardment. They took these observations as confirmation of their theory.

MKM selected B^+ and P^+ for ion bombardment experiments because their ionization potentials are less than E_G+E_C for SiO_2. However, B^+ and P^+ also readily form glasses with SiO_2. Phosphosilicate glass inhibits Na^+ motion in SiO_2.[4-6] It is effective in concentrations as low as 4% and probably in lower concentrations. Passivating properties of borosilicate glasses (BSG) have been investigated much less extensively though there is some effect on sodium motion.[11,12] The passivating properties of dilute BSG layers have not been reported. Passivating glasses should not be formed by Ar^+ or N_2^+ ions. The failure of MKM to observe Na^+ motion after bombardment by B^+ and P^+ could be due to formation of BSG or PSG films which trap Na^+ ions rather than to differences in ion-neutralization processes.

To test this hypothesis, TSIC curves of Na^+ motion in thermal SiO_2 were measured before and after ion bombardment by 5-keV Ar^+, B^+, and P^+ ions. Ion motion in unbombarded sam-

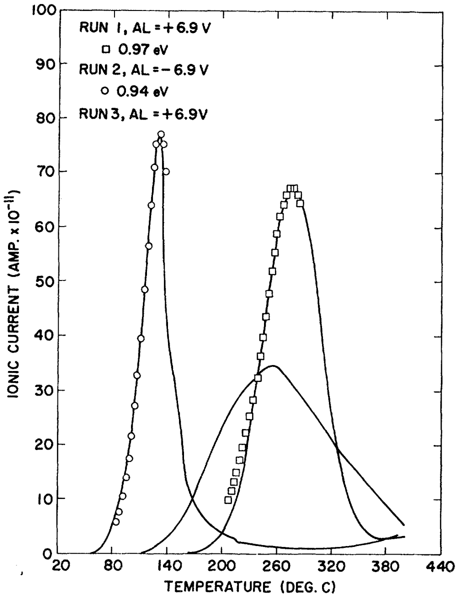

FIG. 1. First three TSIC curves due to Na^+ motion in 5000-Å thermal SiO_2 films. Mobile Na^+ concentration, 1.4×10^{13} ions/cm^2.

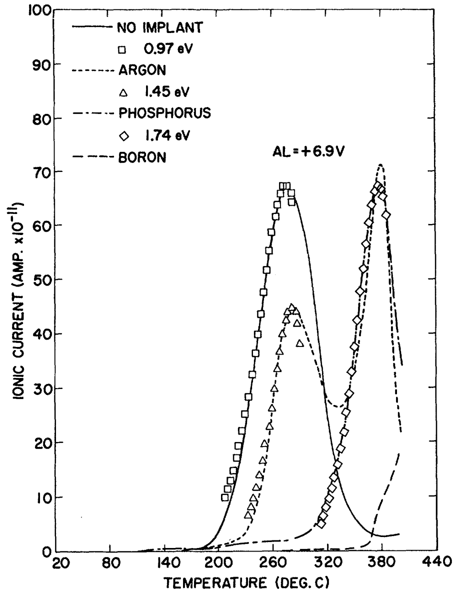

FIG. 2. Initial TSIC curves due to Na^+ motion in ion-implanted SiO_2 films. Oxide thickness, 5000 Å.

ples was measured on thermal SiO_2 films, 5000 Å thick, which were grown on 2-Ω-cm p-silicon of ⟨100⟩ orientation. Metal-oxide-silicon (MOS) capacitors were formed by evaporating Al dots on the SiO_2 surface after $\sim10^{13}$ ions/cm^2 of Na^+ were evaporated as NaCl. Procedures to measure and analyze TSIC curves have been described.[8,13] A hyperbolic heating rate, $1/T=1/T_0-at$, was used throughout to simplify data analysis, where T is the temperature in degrees Kelvin and T_0 is the initial temperature. Figure 1 shows TSIC curves for the first three polarizations of an MOS sample. Curve 1 is the initial polarization, with Al at +6.9 V. Na^+ moves from the SiO_2-Al interface to the Si-SiO_2 interface. On reversing polarity Na^+ moves from the Si-SiO_2 interface to the SiO_2-Al interface. The third curve at the same bias voltage is much broader than the initial TSIC curve for Al at +6.9 V. The total integrated intensity for each of the curves of Fig. 1 is proportional to the total amount of Na^+ moved; it is constant within 10%. Points for curves 1 and 2 are calculated for the given activation energies, using procedures given in Ref. 8. Curve 3 was not fitted well by a single activation energy. The well-known asymmetry in Na^+ motion with bias of MOS structures is clearly shown in Fig. 1; Na^+ moves at much lower temperatures from the Si-SiO_2 to the SiO_2-Al interface, although the activation energies are only slightly different.[14,15] The average field across the SiO_2 in Fig. 1 was about 1.2×10^5 V/cm. Similar Na^+ motion through thermal SiO_2 occurs at lower or higher fields. At fields of 10^6 V/cm, Na^+ motion in thermal SiO_2 can be detected at about 80°C for the initial polarization.

To examine the effect of ion bombardment on Na^+ motion, 5000-Å thermal SiO_2 films were bombarded with 3×10^{14} ions/cm^2 of 5-keV B^+, P^+, and Ar^+ ions. After bombardment, MOS structures were formed in the same way as for unbombarded thermal SiO_2. Initial TSIC curves for ion bombarded samples are shown in Fig. 2, as well as the initial curve for an unbombarded sample. For the unbombarded sample, the peak TSIC current was at 270°C. The Ar^+-bombarded sample had one peak, reduced in magnitude, at 270°C and a second peak at 380°C. The P^+-bombarded sample had a single peak at 380°C; the B^+ bombarded sample had almost no charge motion below 380°C during initial polarization. Calculated points for different energies are also shown for the rising edge for three curves. No activation energy was calculated for the boron-bombarded sample since there was no peak in the TSIC curve. Assuming a range of ~100 Å for 5-keV P^+ ions and ~200 Å for 5-keV B^+ ions,[16] the surface concentrations of P^+ and B^+ are about 10^{20} cm^{-2} or 1%. In spite of the low concentration, the BSG and PSG films are very effective in suppressing Na^+ mobility.

Thus, the difference between Na^+ motion after Ar^+, B^+, or P^+ bombardment lies in a difference in trap structure which develops at the outer SiO_2 interface after bombardment by glass-forming ions. Ion bombardment by non-glass-forming ions such as Ar^+ or Na^+[17] reduces sodium ion mobility somewhat; bombardment by glass-forming ions, however, is most effective in introducing new traps for Na^+.

It is implicit in the theory of MKM that neutralization of an incoming ion is necessary before Na^+ is produced that can move in SiO_2. Figure 1 shows that a large fraction of sodium evaporated as NaCl is already ionized and can move in SiO_2 without any further ionization processes. It is only necessary that the Na^+ be released from traps at the surface, and that there be a driving field. Although the average surface temperature rise during bombardment by 10^{14} ions/cm^2 of 2-keV ions is small, thermal spikes with temperatures rising several hundred degrees can occur for short time intervals, in regions containing a small number of atoms, due to "knock-on" processes.[18] The temperature rise in localized regions of SiO_2 would be sufficient to release Na^+ from traps during ion bombardment. Sputtering of SiO_2 and other insulators by keV ions provides further evidence for localized energy transfer processes during ion bombardment.

The driving field for Na^+ motion can be provided by a metal electrode in TSIC experiments, or by positive surface charge induced by ion bombardment. Bombardment of SiO_2 surfaces by charged particles, either electrons or ions, develops a positive charge on the surface. There has been little quantitative work on the magnitude of charging of SiO_2 and its dependence on ion energies; however, fields sufficient to cause dielectric breakdown can occur.[19,20] The polarity of the field will drive Na^+ to the Si-SiO_2 surface. A polarizing voltage of 6.9 V was used in Figs. 1 and 2 because it would correspond to a modest field to develop during ion bombardment.

Thus, it has been shown by TSIC measurements on MOS structures that initial motion of Na^+ from the SiO_2-Al interface to the Si-SiO_2 interface, through thermal SiO_2, is controlled by traps of about 1.0 eV energy at the Al-SiO_2 interface. At the Si-SiO_2 interface, the trap energy for Na^+ motion is about 0.9 eV. Ion bombardment by keV ions introduces traps at the outer interface of thermal SiO_2 films which can profoundly influence Na^+ motion in SiO_2. Bombardment by glass-forming ions such as B^+ or P^+ is particularly effective in creating new and deeper trap levels. While the ion-insulator interactions proposed in Ref. 9 may occur, the Na^+ mobility experiments presented do not provide unequivocal support for them.

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