Mobilization of sodium in SiO_2 films by ion bombardment

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As part of an investigation of the mobilization and movement of ions in SiO_2 films resulting from bombardment by ions in the 5–2000 eV energy range, we have used radioactive ^{22}Na to follow the movement of sodium. The sodium (1-at.% ^{22}Na) was initially on the surface of the SiO_2 at a concentration of $\sim 2 \times 10^{13}$ sodium atoms/cm^2. We have shown (a) that ion bombardment of SiO_2 films on Si by many ions of interest in device processing or testing (Ar^+, N^+, N_2^+, Ne^+, He^+) causes sodium drift away from the oxide surface to the SiO_2/Si interface, with a small percentage remaining in the bulk, (b) that nearly all the impurity sodium on the outside surface of an oxide film can be drifted into the oxide as a result of ion bombardment, given high enough dose [$\sim 10^{16}$ cm^{-2} for the ion in (a)], (c) that the transfer of sodium away from the oxide surface at a given ion dose is energy dependent, peaking for Ar^+ ions around 500 eV, but still remaining measurable down to 5 eV and up to 2 keV, (d) that ion implantation of B^+ and P^+ or Si^+ ions at 2 keV does not cause sodium movement in SiO_2, (e) that the amount of sodium moved through an oxide film by bombardment increases linearly with ion dose over the dose range 1×10^{12} to 1×10^{16} cm^{-2} for Ar^+ ions, (f) that the drift of sodium away from the oxide surface to the SiO_2/Si interface is independent of dose rate, (g) that the flatband shifts in bias-temperature stressing of metal-oxide-semiconductor samples subjected to ion bombardment correlate well with the amount of sodium transferred to the SiO_2/Si interface seen in the tracer experiments, (h) that the sodium movement results observed corroborate the hypothesis that the dominant charge-transfer and drift process is related to the ion-neutralization processes at the oxide surface and, (i) therefore, all experiments or processes in which ions are impacted on insulator films should be carefully examined for harmful effects due to the sodium-mobilization effects described here. These include backsputtering, ion microprobe analysis, and ion scattering spectrometry.

I. INTRODUCTION

It has been shown in a previous paper[1] that ion bombardment of SiO_2 films on Si leads to interface charge in the oxide films, located at the SiO_2 interface and on the outside surface. It has also been shown that this charged species is mobile under bias-temperature (BT) stress conditions (275 °C, $\pm 10^6$ V/cm). In further papers[2,3] the hypothesis was presented that this charged species consists of ions of impurities present in the outer layers of the SiO_2 film, mobilized at room temperature by the interaction of the ion beam with the oxide surface.

In this paper we describe experiments using radiotracer ^{22}Na to demonstrate directly that impurity-ion mobilization does take place under bombardment by certain ions, and not by others, in a manner consistent with the hypothesis mentioned above. Sodium, initially bound on the oxide surface, is shown to move readily across the oxide films at room temperature after ion bombardment by specific ions.

II. EXPERIMENTAL

A. Ion bombardment system and procedures

The ion-bombardment system used for these experiments has been fully described in an earlier publication.[1] It consists of an ion source of either the plasma arc discharge or electron bombardment type, either of which gives an ion beam energy spread of a few eV at most, coupled to an Einzel lens and deflection plate system together with a mass analyzer magnet, and multiple slice holder in the target chamber. Figure 1 shows the apparatus diagramatically. Target current, typically

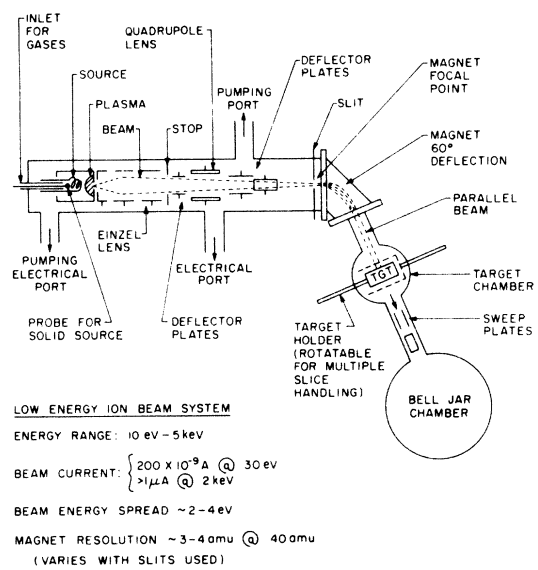

FIG. 1. Apparatus for ion bombardment of SiO_2 films on silicon. Beam energies up to 5 keV and down to 5 eV may be obtained, beam currents up to 2.5 μA have been recorded.

in the range 0.1–5.0 μA, was measured using Ortec nuclear counting equipment.

B. Sample preparation and post-ion-bombardment analysis

The oxides used in these studies were either 5000 or 10 000 Å of steam-grown oxide, grown using cleaning and annealing procedures known to result in oxides with $(1-5)\times10^{10}$ cm^{-2} mobile ion content.[4]

Sodium, containing either 1- or 0.1-at.% radioactive ^{22}Na, was evaporated from a heated filament in vacuum into the sample surface. Immediately prior to this step, the oxides were cleaned by stripping off 200 Å of the oxide using dilute hydrofluoric acid. (Profiles taken prior to bombardment show that all the sodium is initially on the outside surface.) Samples were counted before and after bombardment as a check of sputtering loss. (<1% was lost.)

Profiles of the distribution of sodium through the oxide after bombardment were carried out using 15 : 1 :: H_2O : HF as a planar etch for the oxide (with an etch rate of 200 Å/min).[5] The procedure described removes all sodium from the surface, as shown in experiments using nonbombarded oxides having sodium on their surfaces. Because of changes in etch rate due to the ion bombardment, the thickness of the layer etched was checked by comparison of the oxide color with an ellipsometrically measured set of oxide samples. Both sample and etch solution were counted to determine the ^{22}Na content and thus, through the known ^{22}Na/^{23}Na ratio, the total sodium content.

The counting of ^{22}Na can be done in a number of ways. There is (i) β counting of the positron decay particle, (ii) γ counting of the 0.51-MeV γ rays from the positron decay, and (iii) γ-γ coincidence counting of the two 0.51-MeV γ rays, given off coincident in time and at 180° to each other when the positron decays. We chose to use (iii) due to its inherently low background without shielding (~5 counts per minute) and its relatively simple electronics and detectors. Figure 2 schematically shows the setup used. Only γ rays of 0.40–0.60 MeV passing through both detectors in a 2×10^{-8} sec window are detected.

III. RESULTS

A. Introduction

We have studied the profiles of sodium in SiO_2 (initially all on the outside surface) after bombardment by a number of ions of different ionization potentials and at different energies. We have obtained the dependence on kinetic energy and dose of the movement of sodium for one of these ions (Ar^+) in detail, and for some others in lesser detail. We have profiled the oxides to determine the location of sodium after bombardment for all ions used, and related these profiles to the metal-oxide-semiconductor (MOS) effects observed in uncontaminated oxide sample.

B. Dose-rate dependence and field-only drift of sodium

It has been observed that under certain conditions (*viz.*, high electric field, high contaminant levels), room-temperature drift of sodium can take place in SiO_2.[6] In order to determine whether this effect could complicate the results of our ion-bombardment experiments, the following experiments were performed. An SiO_2 sample 4000 Å thick, having 2×10^{13} Na/cm^2 containing 1-at.% ^{22}Na, was split in two; each piece was bombarded by Ar^+ ions to a dose of 10^{14} ions/cm^2, one at a beam current of 2 μA, the other at a current of 10 nA. Thus, the final electric field across the samples, caused by the bombardment, was the same, but the 2-μA sample took only a few seconds to reach this dose while the 10-nA sample took ≈30 min. Immediately after bombardment each slice was washed in NaCl solution and had 3000 Å etched off. Thus, the times and field-time product during bombardment were considerably different for each sample. It was found that identical quantities of ^{22}Na moved across the oxide in each case. In addition, no dose-rate dependence was observed for any other ion or energy. Thus, the amount of ^{22}Na moved across by bombardment by ions of one species at a given dose and energy is independent of dose rate. If drift of sodium across the oxide by field alone were occurring here, then some dose-rate dependence would be expected. The fact that this dependence does not occur reduces the possibility that field-only sodium drift is a complicating factor in these experiments.

C. Effects of different ions on mobilizing sodium in SiO_2

The mobilization of sodium in SiO_2 by bombarding ions is expected to be governed by both the ionization potential and the kinetic energy of the ions. Table I below illustrates cross correlations between energy, velocity, time to travel 2 Å near the surface,[7] and ionization potential (uncorrected for image force effects; this will be discussed in Sec. V) for each ion used in the study. The most important points to be gleaned from this table are: (i) Argon and nitrogen ions move sodium in SiO_2 at all the energies used in the study; (ii) hydrogen ions can move sodium in SiO_2 at low velocity (less than 1×10^7 cm/sec), but not at higher velocity; and (iii) boron, phosphorus, and silicon ions at 2 keV do not move sodium through SiO_2 from the surface.[9]

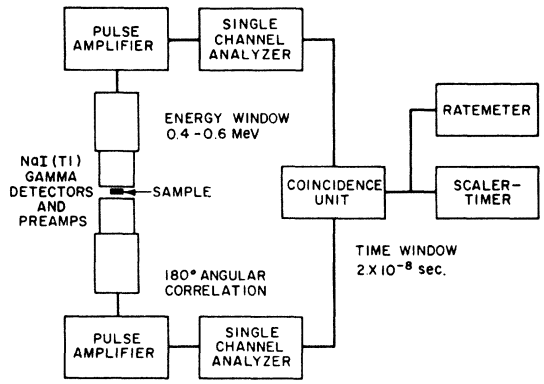

FIG. 2. Counting equipment for ^{22}Na. The coincident γ rays from positron annihilation are detected by the NaI scintillator crystals, preamplifiers, and single-channel analyzers followed by coincidence counting in a narrow window.

These results imply some common characteristic or characteristics for the ions in the top half of the table, differentiating their behavior from the ions in the lower half of the table. These factors will be discussed in Sec. V.

D. Profiles of sodium in ion-bombarded SiO_2

Of the many profiles we have obtained, Figs. 3 and 4 represent typical profiles for the movement of sodium in SiO_2 after bombarding by ions which cause sodium drift.

Figure 3 illustrates the profile of sodium obtained by successive etching of the SiO_2 film in HF solution, after a dose of 1.1×10^{14} Ar^+/cm^2 at 500 eV (on an oxide 5000-Å thick). Both the etch solutions and the sample were counted to give the profile. We may note that (i) of the sodium that moved, nearly all drifted to the SiO_2/Si interface, and (ii) approximately 10^{12} Na/cm^2 moved to the SiO_2/Si interface, i.e., an efficiency of $\approx 1\%$ (or 1 sodium atom per 100 incident ions). Note that the total initial sodium concentration on the surface was $\approx 3\times10^{13}/cm^2$. Figure 4 gives the profile for a similar sample bombarded at the same energy with a dose of 1.1×10^{15} Ar^+/cm^2. Here the efficiency for the movement of sodium is just less than 1%. Note, however, that a large fraction of the sodium initially on the outside surface moved to the SiO_2/Si interface during bombardment, and therefore, we must be entering a saturation regime, in that less sodium is left on the SiO_2 outside surface to be moved by a further ion dose. It is also noteworthy that some of the sodium that drifted away from the outside surface of the SiO_2 has been trapped throughout the bulk of the SiO_2, mostly in the region near the outside surface. The amount trapped in the bulk of the oxide is, however, only a small fraction of the total which traveled through the oxide to the SiO_2/Si interface. All bombarding ions causing sodium drift in the oxide to the interface gave similar profiles. At high doses, small amounts of sodium were detected throughout the oxide, but always much less than that trapped at the SiO_2/Si interface, i.e., there was an indication that there are a small number of traps in the oxide, in particular near the bombarded surface. This was true for Ar^+, Ne^+, N_2^+, N^+, He^+, and the lowest-energy H_2^+ bombardment.

In summary, it is apparent that sodium, initially on the surface of the oxide, is mobilized by the ion bombardment with an efficiency of ~1 sodium atom per 100 incident ions, moves through the film and piles up at the SiO_2/Si interface.

E. Energy dependence of the movement of Na by Ar^+ ions

A dose of Ar^+ ions of $1\times10^{14}/cm^2$, i.e., a dose less than that at which saturation occurs under the conditions of the experiment (see Sec. III F), was chosen for a study of the energy dependence of the amount of sodium moved across the oxide film by the action of the beam. For the 5-eV experiments, a 200-eV beam was decelerated to the target by a six-element decelerating lens assembly.

TABLE I. Energetics of ion-neutralization processes.

Ion	Ionization potential (eV)	Ion energy (eV)	Ion velocity (cm/sec)	Na moved?	Time to travel 2 Å (10^{-15} sec)
Ar^+	15.76	5–2000	4.9×10^5–9.8×10^6	Yes	41–2.0
N_2^+	15.58	500–2000	5.9×10^6–1.2×10^7	Yes	3.4–1.7
N^+	14.53	500	8.3×10^5	Yes	2.4
Ne^+	21.56	500	7.0×10^6	Yes	2.9
He^+	24.48	500	1.5×10^7	Yes	1.3
H_2^+	15.43	40–50	6.2×10^6–6.9×10^6	Yes	3.2–2.9
H_2^+	15.43	100–1000	9.8×10^6–3.1×10^7	No	2.0–0.6
H^+	13.56	500	3.1×10^7	No	0.6
P^+	10.48	2000	1.1×10^7	No	1.8
B^+	8.30	2000	1.9×10^7	No	1.1
Si^+	8.15	2000	1.2×10^7	No	1.7

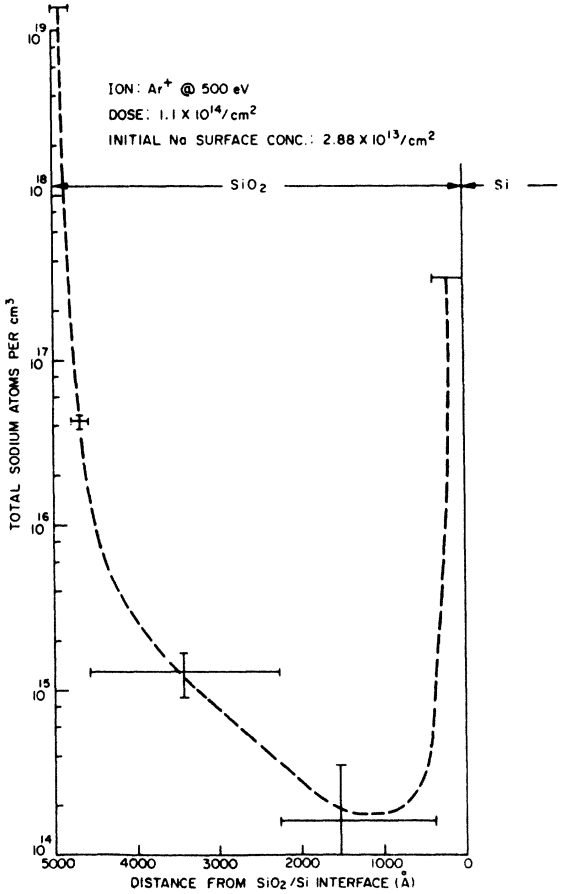

FIG. 3. Sodium profile in SiO_2 caused by A^+ ion bombardment at $10^{14}/cm^2$. Note some sodium in oxide but most at the SiO_2/Si interface.

The results of this series of experiments are plotted in Fig. 5 as a function of both energy and velocity. The important features to be noted from the figure are, (i) the amount of sodium moved across the oxide rises quite sharply from the lowest energies to 500 eV, and falls off more gently on the higher-energy side, at 2 keV being only a factor of 4 less than at 500 eV (an Ar^+ energy of 500 eV corresponds to a velocity of approximately 4.9×10^6 cm/sec); and (ii) the amount of sodium moved across at 5 eV bombarding energy ($v=4.9\times10^5$ cm/sec) is not negligible. Thus, while the kinetic energy of the ion does play an important role in the amount of sodium moved across the oxide film, the fact that at the low energies of 100 eV, and more particularly 5 eV, measurable amounts of sodium do move, indicates that processes in addition to kinetic processes are taking place. Since the maximum potential reached by the surface is determined by the beam energy as well as the oxide thickness, there will be a lower driving field for the moving Na^+ ions in the oxide at the lower-energy end of Fig. 5. The maximum surface potential[10] reachable by a 5000-Å SiO_2 film, assuming a breakdown strength of $\approx 8\times10^6$ V/cm is approximately 400 V, reached at a dose of $\simeq 2\times10^{13}/cm^2$. This may account for the maximum in the curve which occurs at a beam energy of 500 eV in our data, which was taken at points several hundred eV apart in energy. The falloff above 500 eV must be for some alternate reason, however, since the oxide film should reach maximum surface potential before the falloff and remain there. This type of experiment should lead to a better understanding of the process, but at this point any more detailed interpretation would be premature. The effect, however, of the increasing drift field due to the increasing ion kinetic energy, i.e., the maximum potential that the oxide surface can reach as a function of energy, may be the reason for the decrease in the amount of sodium moved with energy below 500 eV.

F. Dose dependence of the amount of sodium moved by 500-eV Ar^+ ions in SiO_2

An energy of 500 eV for Ar^+ ions was chosen for these experiments as that giving the most sensi-

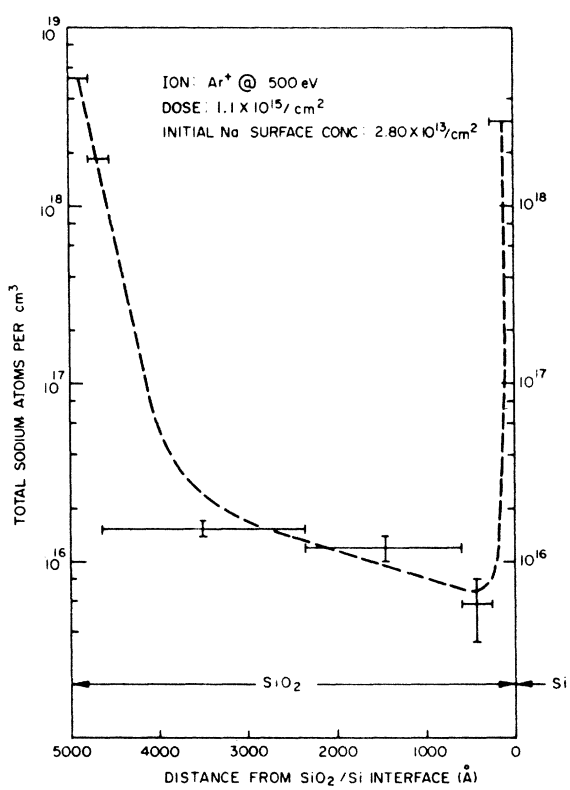

FIG. 4. Effects of $10^{15}/cm^2$ Ar^+ ion bombardment on sodium transport. Note increased sodium at SiO_2 film itself, far from the range of the bombarding ions.

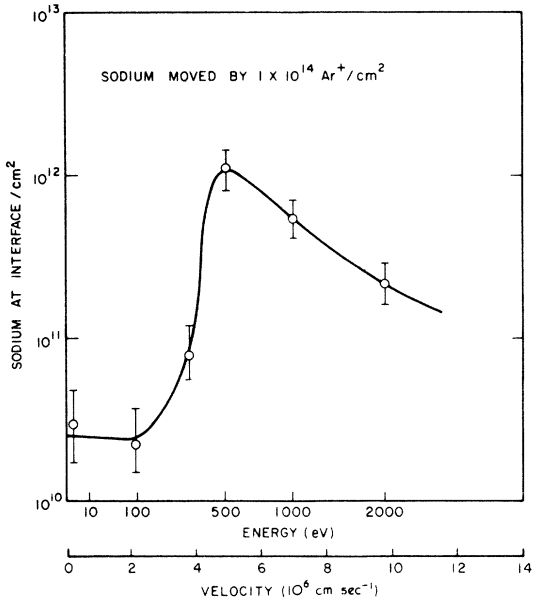

FIG. 5. Effects of ion energy (velocity) at constant dose and oxide thickness on sodium transferred to SiO_2/Si interface. The falloff at lower energies may be due to the reduced field across the oxide at lower ion energies.

tivity according to the values of Fig. 5 Sec. III D. The results of these experiments are shown in Fig. 6. It is apparent that there is a linear increase in the amount of sodium moved across the oxide film as the dose is increased. The amount of sodium moved seems to increase by slightly more than a factor of 10 when the dose is increased by a factor of 10; this may be due to a small field-only drift as mentioned in Sec. III B. It may be noted that above a dose of $5\times10^{14}/cm^2$ saturation begins to occur. We should note, however, that at this point most of the sodium originally on the surface [$\approx(2-3)\times10^{13}$ Na/cm^2] has already been moved across the film away from the outside surface, so the saturation is due to the depletion of available sodium at the surface. A few samples with $\approx 1\times10^{14}$ Na/cm^2 were bombarded in this series; they showed saturation effects at a higher dose, confirming this result. The efficiency, i.e., sodium moved/ion, is about 1 per 100; this is approximately the order of the coverage of the top monolayer of the oxide by the evaporated sodium.

The implications of these results are important, viz., (i) almost all the contaminating sodium ($3\times10^{13}/cm^2$) can be moved from the surface by an ion dose of just over 10^{16} ions/cm^2, i.e., 1 mA for less than 2 sec; (ii) while the dose needed to move all the sodium will vary with energy, between 100 and 2000 eV the dose variation is less than an order of magnitude. The implications of these results will be discussed in more detail in Sec. V.

G. Variation of quantity of sodium moved by different ions at the same energy

The amount of sodium moved by ions of Ar^+, He^+, Ne^+, N^+, and N_2^+ was compared at an energy of 500 eV and a dose of 1.5×10^{15} cm^{-2}. The results are shown in Table II.

The variation in amount of sodium moved in the SiO_2 is just under one order of magnitude. Several points are apparent: (i) Since the Ar^+ is near the peak of its energy-versus-sodium-moved curve at 500 eV, the changes with the ion noted above cannot be just an ion velocity effect (e.g., one would then expect the Ar^+ to be the most efficient ion, since any other ion would be at a greater or lesser velocity; in fact, the N_2^+ ion is the most efficient for sodium transfer across the oxide); (ii) despite the fact that the velocities of Ne^+ and He^+ are quite different and the ionization potentials of Ne^+ (21.6 eV) and He^+ (24.5 eV) are relatively close, there is less than a factor of 2 between them in the amount of sodium they move at the same dose, yet there is a factor of 10 between Ne^+ and N^+ whose velocities are close, but whose ionization potentials are quite different. This simply points out the complex relationship between the ionization potential of the ion, its velocity (or energy), and the sodium movement produced by it. We should note, however, that the velocity of a He^+ ion at 500 eV is the same as that of an Ar^+ ion at 5 keV, i.e., we may infer that since a He^+ ion moves sodium in SiO_2 at 500 eV, then an Ar^+ ion may move sodium at energies up to at least 5 keV.[11,12]

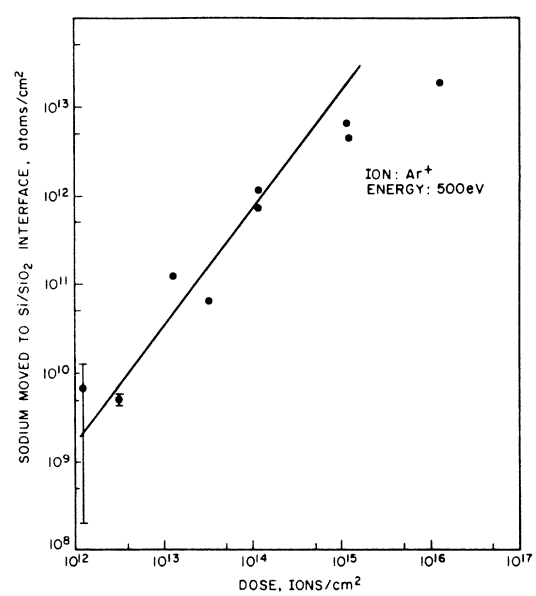

FIG. 6. Effect of increasing ion dose at constant 500-eV Ar^+ ion energy. Note linear relationship until saturation effects set in at high doses.

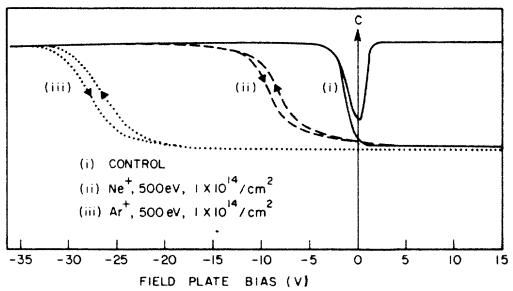

FIG. 7. Comparison of MOS high-frequency *C-V* curves on samples bombarded by Ne^+ and Ar^+ ions at 500-eV energy. Note the ratio of the flatband voltage shifts ($\approx 3:1$).

H. Dependence on oxide thickness

Samples using 5000 and 10 000 Å of SiO_2 were used in experiments at the same dose and energy for the same ion. Identical amounts of sodium were transferred to the SiO_2/Si interface in each case. Thus, the amount of sodium moved across the oxide is independent of oxide thickness in this range.

IV. COMPARISON WITH MOS RESULTS

It has been shown in a previous paper[1] that ion bombardment leads to interface charge in bombarded SiO_2 films on Si. The work presented here shows that if sodium is present in the outside layer of a film of SiO_2, ion bombardment can transfer it across the oxide film to the SiO_2/Si interface. We may note some similarities between the behavior of the interface charge produced in MOS systems and the movement of the sodium in the experiments reported here.

(i) At doses less than $10^{15}/cm^2$, the sodium in these experiments is located at the two interfaces after bombardment. This behavior was also found for the charge in the earlier MOS work.

(ii) There is sodium movement found for ion energies down to 5 eV in the present work. In the earlier MOS work, 10-eV Ar^+ ions were found to cause some interface charge buildup.

(iii) Within the error of the MOS measurements and the radiotracer measurements, similar behavior is found for N_2^+, N^+ and Ar^+ ions, (i.e., while a factor of 2 variation is found in the radiotracer experiments, the scatter in the MOS experiments is greater than this).

(iv) In the MOS work, it was found that there was about a factor of 7 difference between the SiO_2/Si interface charge produced by 10-eV Ar^+ ions and that produced by 600-eV ions; Fig. 5 shows a slightly larger factor for sodium movement, but again, within the errors of both measurements, these results are the same.

(v) The results here indicate that the saturation effects observed in the earlier work may be due to depletion of the surface layer of mobile charge carriers.

(vi) In neither work is any dose-rate dependence seen.

(vii) It is observed in this work (Table II) that the ratio of sodium moved by Ar^+ and Ne^+ at 500 eV is about 3.4. Two MOS samples, otherwise identical, were bombarded by 1×10^{14} Ne^+ and Ar^+, respectively. The results are shown in Fig. 7. It will be observed that the general behavior of the Ar^+ (iii) and Ne^+ (ii) bombarded samples is similar, i.e., hysteresis is in the trapping direction, high interface state density is seen, and the ratio of flat-band voltage (V_{FB}) shifts in the two samples is approximately 3.5. This very close agreement with the sodium result is probably fortuitous; the V_{FB} ratio should be stated as 3.5 ± 1. In any case, the MOS results parallel the sodium-drift results.

(viii) It should be noted that the charge introduced into SiO_2 by ion bombardment is mobile in the same way as sodium has been found to be mobile in SiO_2, i.e., it gives BT stress shifts at elevated temperature, which can have values up to the total induced interface charge.[23]

(ix) In the MOS experiments[1,2] it was found that bombardment by 500-eV H_2^+ ions cause considerable interface charge buildup in SiO_2 samples. The results here show that 500-eV H_2^+ ions do not cause sodium ions to move in SiO_2. Thus, we infer that the observed mobile charge carriers in the H_2^+ bombardment experiments are not sodium ions.

(x) We have observed that bombardment of SiO_2 films by B^+, Si^+, and P^+ ions at 2 keV caused no sodium migration in SiO_2 (Ref. 3) at a dose of $2\times10^{14}/cm^2$. We therefore performed the following experiments. Four Si slices, two with MOS quality SiO_2, two with ^{22}Na contaminated SiO_2, were implanted with B^+ and P^+ ions at 2 keV to a dose of $1\times10^{14}/cm^2$. As already described,[3] neither B^+ nor P^+ at 2 keV moved sodium through the SiO_2. The MOS results were rather startling, however, as illustrated in Fig. 8. The V_{FB} (flat-band volt-

TABLE II. Amount of sodium mobilized by various ions studied.

Ion energy 500 eV Ion	Ion dose $1.5\times10^{15}/cm^2$ Na at SiO_2/Si interface/cm^{-2}	Ion velocity, (cm/sec)
N_2^+	1.5×10^{13}	5.8×10^6
N^+	1×10^{13}	8.3×10^6
Ar^+	5.5×10^{12}	4.9×10^6
He^+	2.1×10^{12}	1.5×10^7
Ne^+	1.6×10^{12}	6.6×10^6
Si^+	$<2\times10^9$	1.2×10^7

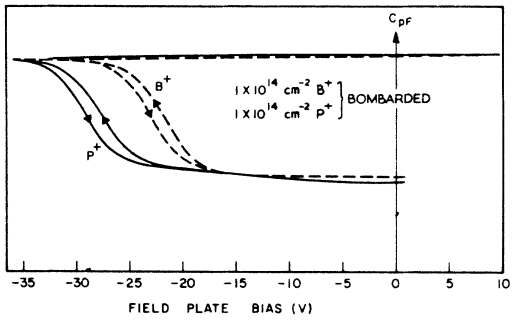

FIG. 8. Comparison of the effects of B^+ and P^+ ion bombardment on the MOS properties of previously identical SiO_2 films on silicon. The meaning of the curves is discussed in detail in the text of Sec. IV(x).

age) shift observed in the case of the boron implantation is slightly greater than would be expected on the basis of the location of the boron in the oxide if, as expected, it retained its charge on entering the oxide. The V_{FB} shift for the phosphorus implant is, however, much greater than would be expected on this basis alone. (The B^+ range is less than 100 Å, the P^+ range is less than 50 Å.) The implication is that some charge carrier other than Na^+ is mobilized by the P^+ implant and to a much lesser extent by the B^+ (perhaps holes or H^+ for example), or that interface charge is produced by some other mechanism. These results agree with earlier (unreported) experiments performed by the authors in which it was shown that 5-keV B^+ ions at a dose of $10^{14}/cm^2$ caused charge up in bombarded oxides, the charge being located in two regions, one near the boron ions's range, the other (small) at the SiO_2/Si interface.

A recent paper by Hickmott[25] showed that in samples ion implanted with P^+ or B^+ prior to sodium-compound deposition, the subsequent movement of sodium (after metallization) under elevated temperature conditions, was retarded. He suggested that our results previously reported[3] and discussed above (x) were due to formation of a phosphosilicate or borosilicate gloss film during B^+ or P^+ ion bombardment. These results do not take cognizance of the fact that ion bombardment of a sample *prior* to $^{22}NaCl$ deposition (I) is by no means identical to ion bombardment of a sample *after* $^{22}NaCl$ deposition (II). In the first case (I), subsequent bias-temperature stress experiments measure only the effect of the *total* B^+ or P^+ dose on subsequent Na transport at elevated temperature, whereas, in the second case (II), cumulative effects during the bombardment are measured. Thus, if some critical dose of B^+ or P^+ ions were required to eliminate sodium movement an experiment of type I would not detect it, while an experiment of type II would. Hickmott did show, however, that at total doses similar to ours the B^+ and P^+ bombardments reduced considerably the subsequent sodium transport at elevated temperature. Thus, our P^+ and B^+ results as described above do not provide unequivocal support for the theory of Sec. V. For further confirmation of the effect of ionization potential we have used Si^+ ions as bombarding ions. The mass of Si^+ is between that of Ne^+ and Ar^+, both of which move sodium in SiO_2. The ionization potential, is however, close to that of B^+, i.e., 8.3 eV. No boron or phosphorus glass will be formed in this case so any difference between the effects of Si^+ bombardment and those of Ar, or Ne^+ bombardment should be due to ionization potential alone. Two halves of one ^{22}Na sample with initially $2\times10^{13}/cm^2$ Na were bombarded by $1\times10^{15}/cm^2$ of Ar^+ and Si^+ (at 2 keV), respectively. The sample bombarded by Ar^+ showed massive sodium transport similar to that shown in Fig. 4; the sample bombardment by Si^+ showed a factor of 350 less sodium at the SiO_2/Si interface after bombardment, confirming the overriding importance of the ionization potential in the sodium mobilization process.

In addition, in experiments to be reported elsewhere (performed in conjunction with C. W. White) it has been demonstrated that the formation of small amounts of phosphosilicate glass (similar to those in Hickmott's paper) prior to Ar^+ bombardment does not reduce the ^{22}Na transport caused by Ar^+ by a significant factor, but that small amounts of borosilicate glass are of significance in this regard. Thus, both the Si^+ and P^+ results presented

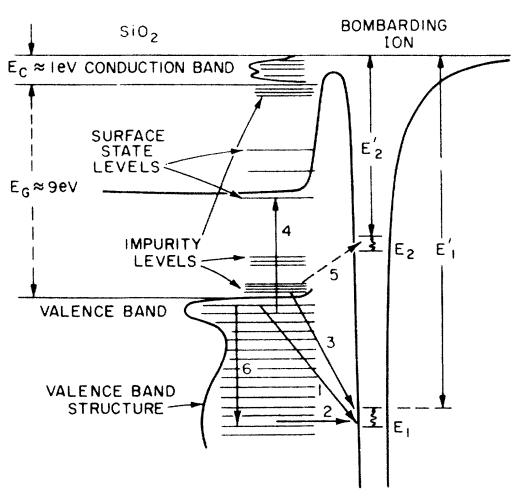

FIG. 9. Ion bombardment of an SiO_2 surface. The insulator band gap is shown, as is the relative position of the ionization potential of the bombarding ion. Transition 2 is a resonance transition; transitions (3, 4) (1, 4) are Auger transitions, and 5 is forbidden. The shift of ionization potential near the surface due to image force effects is also shown. (See text, Sec. V.)

above are evidence for the validity of the ion-neutralization processes discussed in Sec. VI.

In conclusion, the MOS results obtained earlier are paralleled by the sodium-drift results obtained in this work. It is not thereby implied that the only charge carrier causing the observed charge buildup in the MOS experiments is sodium. Rather it is implied that sodium not necessarily observable in BT stress measurements may certainly contribute to the charge buildup effects observed in the MOS experiments, and that other charge carriers, perhaps protons, also have a role. We will discuss the implications of our results in ion-probe microanalysis of SiO_2 films in Sec. VI.

V. CORRELATIONS WITH THEORY

It was previously hypothesized,[2,3] that the dominant mechanism of ion-bombardment charge degradation in MOS structures is the ion-neutralization process at the surface, whereby ions neutralized at the surface of the insulator in either Auger or resonance processes could cause removal of the binding electrons of monovalent impurities. In the field resulting from the neutralization at the surface, these impurities could drift to the SiO_2/Si interface and, trapped there, cause the MOS charge degradation. In this model, the kinetic energy enters the picture mainly as it affects the "potential" neutralization process, but of course, is dependent on the existence of the potential neutralization, not a kinetic process as such.

Figure 9 (modified from Ref. 3) illustrates the various atomic processes which may occur when an ion bombards the surface of SiO_2. The values of the bandgap and electron affinity are those currently accepted.[13] There is some question as to where a "Fermi level" should be drawn for a wide band-gap insulator, particularly where surface trap levels or surface impurity levels may exist. In this case, we have drawn the Fermi level at the surface close to the valence band. A relatively small amount of charging and discharging of surface trap levels would be sufficient to cause drastic shifts in this effective Fermi level, and, in any case, the position of the "effective" Fermi level is unimportant to the model. Consider firstly a bombarding ion of ionization potential greater than $E_C + E_G$ (such as Ar^+) with ionization potential E_1. As the ion approaches the surface the ionization potential changes as a function of distance to some value E_1' where $E_1' = E_1'(x)$. Near the surface Auger processes such as those illustrated as (1, 4), (3, 4) may occur; so also may resonance processes, (2). Processes (1, 4) or (2) lead to holes in the valence band. Processes (3, 4) or (6) (deexitation of a hot hole) may result in the freeing of bound impurity ions so that they may move, in the SiO_2, away from the surface. Ions such as Si^+, P^+, or B^+ whose ionization potential is less than $(E_G + E_C)$, e.g., E_2, cannot undergo transitions such as those described above, transitions such as (5) being forbidden, so that sodium migration will not be caused by these ions, by this mechanism. The possibility exists, of course, that buildup of charge on the surface of the oxide by ions of type E_2 may cause some field-only drift of impurities in the oxide film away from the surface[14] though our results with B^+ and P^+ as bombarding ions would suggest that this occurs to a much lesser extent than for type E_1 ions.

The results reported in this paper lend good support to the proposed model. The dominant result predicted by the model, and borne out by these experiments, is that sodium may move at room temperature in the SiO_2 as a result of the ion bombardment for bombarding ions whose ionization potential is large enough. Thus, the model predicts that Ar^+, N_2^+, He^+, and N^+ ions will all cause mobilization of sodium. It also predicts that B^+ or Si^+ ions cause significantly less mobilization and that P^+ ions may or may not. (The exact value of the bandgap and position of the conduction band relative to the vacuum level are not well-enough known in this borderline case.) These predictions are borne out by experiment. Theory also predicts that there will be an ion velocity above which no Auger or resonance processes will take place. That this may be the case is indicated by the H_2^+ and H^+ results which illustrate that for high velocity the type of transitions causing ion movement may not be taking place.

A recent paper by Osburn and Raider[14] suggests that sodium may be caused to move in SiO_2 by bias alone. The experimental arrangement in our experiments and those of Ref. 14 are dissimilar. In particular, Osburn and Raider used NaCl contaminated SiO_2 films all of which had metal electrodes evaporated into their surfaces prior to any bias experiments, whereas no metal film was used in our experiments. The effect of this metal film is to provide additional mechanisms for dissociation of NaCl molecules between the metal and the oxide film. The results of this experiment may not, therefore, be carried over directly to the case of our experiments.

The detailed theoretical implications of the mechanism will be discussed in a later paper in relation to this work, and to the work on MOS and radiotracer effects in neutral bombardment being published separately.[15]

The prediction may be made, however, that in SiO_2 all monovalent ions will probably move away from the bombarded surface under ion bombardment, and they may also move in a similar manner in other insulators.

VI. PRACTICAL IMPLICATIONS

A. Backsputtering

It should firstly be pointed out that any backsputtering in a plasma is a two-way process biased (perhaps strongly) towards one side, i.e., deposition always occurs along with removal, just as the reverse occurs in deposition. Indeed, it has been shown[16a] that metal atoms may be transferred from one sample to another during metal deposition by rf sputtering. Thus, any sodium or other impurity on a sample holder or an adjacent sample may be transferred to any sample on the holder, or onto the holder itself, during backsputtering. This implies that, during backsputtering, any inherent impurities or any redeposited impurities may be driven through the backsputtered oxide film to the SiO_2/Si interface. Indeed, the effects are worst in the voltage regime most favored for backsputtering, i.e., with an Ar plasma, at 300–2000 eV. Thus, any backsputtering followed by metal deposition over an oxide film will inevitably result in mobile charge contamination of the oxide film. Any plasma exposure of an oxide film in the presence of sodium impurities will result in these impurities being incorporated into the oxide film, and some may appear at the SiO_2/Si interface, depending on the field across the oxide during deposition. That such processes do occur has recently been shown in detail.[16b]

B. Ion implantation

All that may currently be said with certainty from our results is that implantation with B^+ or P^+ at 2 keV will not result in mobilization of sodium in an oxide film. Further work will be reported later.

C. Ion microprobe analysis, ion scattering spectrometry and auger electron spectroscopy in the analysis of oxide films

In these analysis methods, an energetic ion beam of Ar^+, O^+, O_2^+, or He^+ in the range 500 eV–10 keV is impacted onto the oxide film under investigation.

A recent study[17] utilizing an ion microanalyzer purported to give profiles of sodium in SiO_2 grown under various conditions. The profiles given bear considerable resemblance to those described in Sec. III of this paper. While the energies used are a little higher than we report here (5 keV as opposed to our maximum of 2 keV), considerations of ion velocity and ionization potential lead us to state that under their conditions, ion movement as we have described will inevitably occur, aided by the sample heating which occurs during their intense ion bombardment. A typical surface sodium concentration as given in the report is $1\times10^{12}/cm^2$. Ion current densities used in the ion microprobe analyzer are of the order of 1–5 mA/cm^2, i.e., $\approx 6.2\times10^{15}-3\times10^{16}$ ions/sec cm^2. As a typical sputtering rate was 120 Å/min, this implies that most of the surface sodium can be driven into the oxide by the mechanisms described in Sec. V, and in the manner illustrated in Sec. III of this paper. Thus, profiles of sodium in SiO_2 (and probably of potassium also) obtained by the use of this instrument do not represent the distribution before interactions with the ion beam. More recent work by the same author[18,19] shows comparison of profiles of sodium implantations taken on an ion microprobe with O^+ and O^- primary ions. The profiles obtained using O^+ ions showed all the sodium piled up at the SiO_2/Si interface in the manner we have described and predicted. The profile obtained using O^- did not show this pileup in exact agreement with our predictions attributing the ion drift to positive ion neutralization at the surface.

Ion scattering spectrometry[20] uses a technique whereby He^+ or Ar^+ ions of energy <3 keV are scattered in binary scattering from surfaces of films to be measured. Our results imply that this method also will be very restricted in its application to analysis of impurities in insulating films.

In Auger-electron spectroscopy films are often characterized in profile by sputtering while examining the Auger spectra. The sputtering is usually performed by ≤ 1 keV Ar^+ ions. Our results imply that this technique may also give erroneous impurity profile values in insulating films.

The erroneous values of sodium or potassium concentration profiles obtained by the above methods will, of course, also be wrong at the outside surface, since this concentration will change during measurement long before even one monolayer is removed.[21a,21b]

Profiles of oxide films obtained using Rutherford scattering at high energies will, of course, not be affected by the mechanisms discussed in this paper, since the high velocities of the bombarding ions preclude the processes discussed from taking place. If any field does build up across the oxide film of course, some field-only drift effects might be expected.

VII. SUMMARY

We have shown (i) that radiotracer techniques are a powerful tool for studying the distribution and concentration of ions in SiO_2 with specificity and sensitivity, better than found using, e.g., MOS methods, (ii) that ion bombardment of SiO_2 films on Si by many ions of interest in device processing or testing causes impurity drift away from the oxide surface to the SiO_2/Si interface, (iii) that most of the drifted ions travel to the SiO_2/Si interface, but a small percentage stays in the bulk, (iv)

that all the impurity sodium on the outside surface of an oxide film can be drifted into the oxide as a result of ion bombardment, given high-enough dose, (v) that the transfer of sodium away from the oxide surface at a given ion dose is energy dependent, peaking for Ar^+ ions around 500 eV, but still remaining measurable down to 5 eV and up to 2 keV, (vi) that B^+, Si^+, and P^+ ions at 2 keV do not cause sodium movement in SiO_2, (vii) that the amount of sodium moved through an oxide film by bombardment increases linearly with ion dose, (viii) that the drift of ions away from the oxide surface to the SiO_2/Si interface is independent of dose rate and oxide thickness, (ix) that the results of the ion-bombardment experiments on MOS samples correlate well with these results using radiotracer impurities, (x) that the sodium movement results obtained are additional corroboration of the hypothesis that the dominant charge transfer and drift process is related to the ion neutralization processes at the oxide surface,[1] and, (xi) therefore, all experiments or processes in which ions are impacted on insulator films should be carefully examined for erroneous results or harmful effects due to the sodium mobilization effects described here.

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[4]Oxide sample preparation procedure: (a) Standard silicon cleaning procedure. (b) Steam oxidation in furnace with SiC liner (1050 °C). (c) N_2 anneal, 1100 °C, 20 min. (d) Forming gas anneal, 600 °C, 30 min.

[5]Etch procedure: Immerse sample in ≈ 15 ml of etch solution for appropriate time (with continuous agitation), remove, rinse in NaCl solution three times, rinse in deionized water twice, saving all solutions for subsequent counting.

[6]D. R. Kerr, Reliability Symposium, Las Vegas, 1970 (unpublished); and (private communication); D. J. Silversmith (private communication).

[7]Hagstrum has shown (see Ref. 8) that the region of maximum neutralization probability is a few Å wide, close to the surface. This time gives an indication of whether Auger or Resonance processes are probable or not (e.g., if $T \approx 10^{-17}$ sec neutralization processes have low probability).

[8]H. D. Hagstrum. Phys. Rev. 96, 336 (1954).

[9]If the ion energy is 300 eV, say, then the maximum oxide surface potential that can be reached is 300 eV (Ref. 10). This will be reached for SiO_2 at a dose determined by the oxide thickness. This may, of course, be the reason for the fall on the low-energy side in Fig. 5.

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[11]Note that if it were solely the electric field moving the sodium in the oxide, the amount of sodium moved by different ions would be expected to be the same in each case (since the range of each ion in the oxide at these energies is very small).

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