THE NEUTRALIZATION OF Na^+ IONS IN HCl GROWN SiO_2

J. P. STAGG and M. R. BOUDRY

Philips Research Laboratories, Redhill, Surrey, England

Résumé. — Le courant ionique résultant d'une excitation thermique (la méthode « TSIC ») est utilisé pour étudier les propriétés dynamiques des ions Na^+ dans un capaciteur MOS, oxydé avec un mélange O_2/HCl . On trouve qu'un ion peut être pris au piège à l'interface Si-SiO_2 , soit dans un état chargé, soit dans un état neutre. Le processus de neutralisation est examiné selon la concentration de Cl dans l'oxyde, ainsi que la durée et la température sous une tension positive sur le métal.

Abstract. — The kinetic behaviour of Na^+ ions in (HCl) MOS capacitors has been studied by the method of thermally stimulated ionic currents (TSIC). Both charged and neutral trap states at the Si-SiO_2 interface were identified. The dependence of the ion neutralization process on oxide chlorine content, and on the time and temperature of positive bias stress was investigated.

1. Introduction. — HCl oxides in which chlorine is incorporated in the oxide during growth are sometimes used in MOS structures as a means of suppressing flatband voltage instabilities due to Na^+ ion drift. Previous reports [1, 2] have shown that partial or complete neutralization of the Na^+ at the Si-SiO_2 interface can occur in these oxides. It is known [1, 3] that the neutralized ions are trapped much more strongly at this interface than are charged ions in normal dry oxides. One objective of this paper is to quantify the trap energies in HCl oxides and to describe the dependence on the oxide chlorine level so that subsequent Na detrapping at any temperature may be calculated. This is done by the method of Thermally Stimulated Ionic Currents (TSIC) [4, 5, 6]. The kinetics of ion neutralization also are important because of the possibility of transient flatband voltage shifts when ions are drifted to the Si-SiO_2 interface. These ions could be ions initially present at the metal interface in a virgin device or neutralized ions which have been detrapped and moved to the metal interface. One factor determining the magnitude of this effect at a given temperature is the neutralization rate. We therefore describe experiments which measure the amount of neutralization after positive (+ve) bias stress for approximately 0.5 minute for a wide range of temperatures and for different chlorine levels. Some isothermal measurements of the amount of neutralization as a function of time were also made on oxides considered [3] to provide relatively good passivation.

2. Sample description. — The samples were n type silicon oxidized in dry oxygen for 2 minutes, a mixture of dry oxygen and HCl gas in argon for 30 min., then annealed for 10 min. in dry Nitrogen gas at the same temperature. HCl concentrations in the range 1 to 10 % were used and the oxidations performed at temperatures of 1 100 °C, 1 150 °C, and 1 200 °C. The oxides (of thickness $\sim 1\,000$ Å) were deliberately

contaminated with Na^+ in the range 3×10^{11} to 9×10^{12} ions cm^{-2} by immersion in solutions of NaCl of known concentration. Aluminium dots of diameters 0.01 to 0.08 cm were deposited using a W-filament evaporator. The oxide chlorine content was determined on other samples oxidized in the same batch by X-ray spectrometric methods calibrated by nephelometry.

3. Experimental. — A sample was mounted in an evacuated chamber [5], voltage bias applied to the substrate, and the charge or current measured by a Keithley 616 electrometer connected *via* a probe to a selected aluminium dot. The sample was heated to a temperature of at least 600 K and a bias corresponding to a field of -1 MV/cm applied. After cooling at this bias, a 10 kHz $C-V$ curve was measured at 220 K. The bias polarity was then reversed and a TSIC plot recorded as the sample was heated at 0.8 K/s.

A typical +ve bias TSIC curve is shown in figure 1.

FIG. 1. — TSIC curves for HCl oxide (6 % HCl for 33 min. at 1 150 °C on $\langle 100 \rangle$ Si substrate. $\text{Na}^+ = 9 \times 10^{12}$ ions cm^{-2} , $\text{Cl} = 4.9 \times 10^{15}$ atoms cm^{-2}). The +ve bias curve was recorded after -ve bias stress at 640 K; -ve bias curves recorded after +ve bias stress at 120 °C for times of approx. 0.5 min. (—), 20 min. (- - -), and 228 min. (- . - .).

This shows the characteristic peak due to Na^+ ion detrapping from the Al-SiO_2 interface. This TSIC curve is found to be the same shape as that observed in dry grown oxides after the same bias temperature treatment.

The sample was then cooled to 220 K and a $C-V$ curve measured. The voltage shift of the curve from its former position was measured and the corresponding amount of charge at the Si-SiO_2 interface calculated. This charge was compared with that total integrated over the + ve bias TSIC curve to determine the fraction of the total charge which had been neutralized. Negative bias was then applied and a negative (– ve) bias TSIC curve recorded as the sample was heated again. Figure 1 shows three such curves, each recorded after different periods of + ve bias stress. The striking feature in this diagram is the second Na^+ ion peak at high temperatures in addition to the one at lower temperatures also observed in dry oxides. Experiments on samples with Na densities in the range 3×10^{11} to 3×10^{12} ions cm^{-2} established that only charge detrapped in the – ve bias TSIC curves below about 400 K had contributed to the $C-V$ shift. The high temperature peaks therefore correspond to Na^+ ions which are neutral when at the Si-SiO_2 interface. For samples oxidized in the same batch both charged and neutral peak positions are, at most, only weakly dependent on Na^+ density.

In references [4, 5] it is shown that the charged peak in dry oxides is due to 1st order detrapping of Na^+ ions from sites with a range of trap energies. The same methods may be used to investigate the neutral peak. That a single energy is insufficient to characterize the neutral peak is shown by performing the experiment of figure 2. The TSIC curve was interrupted halfway through the peak maximum, cooled and then reheated still at – ve bias. The form of the curve shows that the detrapping process cannot be characterized by a single energy and strongly suggests a range of energies. Analysing the data according to a distributed energy model in the way described in references [4, 5] leads to a plot of the density of initially occupied traps, $n_0(E)$, versus energy, E , together with an associated pre-

FIG. 2. — TSIC full curve (—) with interrupted ramp experiment (---) and calculated $n_0(E)$ plot for HCl oxide. (6 % HCl for 30 min. at 1 100 °C on $\langle 111 \rangle$ Si substrate. $\text{Na}^+ = 4.3 \times 10^{12} \text{ cm}^{-2}$, $\text{Cl} = (1.8 \pm 0.3) \times 10^{15} \text{ cm}^{-2}$).

exponential frequency factor, β , derived from the interrupted ramp data. We find

$$\beta = 4 \times 10^{11} \cdot \text{s}^{-1} \text{ eV}^{-1/2},$$

within an order of magnitude, the same as for the normal charged peaks in dry oxides. Using the $n_0(E)$ plot derived from the full TSIC curve in figure 2, the interrupted ramp curves may be accurately predicted given the temperature-time profiles.

In the $n_0(E)$ plot (Fig. 2) the neutral peak is seen to overlap the charged peak. The effect of increasing the chlorine content is to shift the neutral peak to larger energies as shown in figure 3. Measurements on a variety of samples with chlorine levels in the range 0.7 to $8 \times 10^{15} \text{ cm}^{-2}$ showed that the energy range of the neutral peak was determined by the chlorine content, approximately independent of oxidation temperature and whether the Si substrate is $\langle 100 \rangle$ or $\langle 111 \rangle$. The charged and neutral peaks overlap substantially for Cl levels $< 10^{15} \text{ cm}^{-2}$. A minimum level of $3 \times 10^{15} \text{ cm}^{-2}$ is necessary to provide good separation. The neutral peaks in oxides with $> 5 \times 10^{15} \text{ Cl cm}^{-2}$ all exhibited low energy tails, similar to that shown in figure 3 but sometimes with structure, extending down to about 1.0-1.15 eV. The stability of a device with respect to detrapping of neutralized ions at a field of -1 MV/cm may be calculated from $n_0(E)$, using the kinetic equations of the model [4, 5].

FIG. 3. — $n_0(E)$ profiles of the neutral Na traps in oxides with different chlorine levels.

Figure 1 illustrated that the degree of neutralization depends on the length of time during + ve bias stress. A similar set of experiments was performed in which the maximum temperature of the + ve bias TSIC experiment was varied, the sample remaining within a few degrees of this temperature for about 0.5 min

before cooling. The degree of neutralization is plotted as a function of reciprocal maximum temperature in figure 4. Results on oxides with chlorine densities between 2.4 and $8 \times 10^{15} \text{ cm}^{-2}$ are spaced between the two lines shown, but have been omitted for clarity. The amount of neutralization is shown to increase with higher temperatures or larger chlorine levels. In this range of chlorine level the results suggest that complete neutralization can eventually be achieved after a sufficiently high temperature + ve bias treatment.

FIG. 4. — Neutralization *versus* reciprocal temperature after + ve bias stress for approx. 0.5 min. at that temperature.

A further set of experiments to measure the amount of neutralization as a function of time was performed on samples prepared in the way described by Kriegler and Devenyi [3]. The results are shown in figure 5. The data was obtained from two types of experiment.

For times greater than 7 min the charged Na^+ density was found after cooling to 220 K and measuring the C - V curve shift and also from a subsequent - ve bias TSIC curve. For shorter times the Keithley electrometer was used in the Coulomb mode: starting with all the ions at the Al interface and with - ve bias applied to the sample, the total charge transported following + ve bias for a time t was measured; the bias was then reversed and after a delay of about 1 min, during which the charged ions alone were returned to the Al interface, the amount of neutralized charge was

FIG. 5. — Time dependence of the neutralization process. (Sample details: $\langle 100 \rangle$, 6% HCl at 1 150 °C for 33 min., annealed at 1 150 °C and also 475 °C after metallization, $\text{Na}^+ = 9 \times 10^{12} \text{ cm}^{-2}$. $\text{Cl} = 4.9 \times 10^{15} \text{ cm}^{-2}$; $\langle 111 \rangle$, 5.4% HCl at 1 150 °C for 30 min., 1 150 °C anneal only, $\text{Na}^+ = 9 \times 10^{11} \text{ cm}^{-2}$, $\text{Cl} = 5.6 \times 10^{15} \text{ cm}^{-2}$).

given by the final reading of the electrometer. This figure was verified by measuring a subsequent - ve bias TSIC curve. Figure 5 shows that the isothermal neutralization process cannot be described by a single time constant. The time required for, say, 50 % neutralization at 120 °C is much greater than the time constant of 4 s given by Kriegler and Devenyi [3]. The discrepancy may be because their measurements were confined to short times and the results were interpreted assuming a single time constant. The tangent slope near the origin in figure 5 corresponds to a time constant of less than 90 s. Some results at 150 °C are shown also. The data of figure 5 indicates that a range of activation energies is involved but there is not sufficient data, however, for reliable estimation of the energies and pre-exponential factors.

4. Conclusion. — The measurements of the $n_0(E)$ profile for the neutral Na^+ traps enable quantitative assessments to be made of the stability of HCl oxides with respect to detrapping of the Na^+ from the Si-SiO₂ interface. Neutralization in samples regarded as providing relatively good passivation is shown to occur much more slowly than previously suggested and with a range of time constants at a given temperature.

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