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SPECIAL TOPICS

Investigation of mobile ions in MOS structures using the TSIC method

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Mobile ions in SiO_2 layers of MOS structures have been investigated with the thermally stimulated ionic current (TSIC) method. Two distinct peaks were observed in the temperature range 30–350°C, the first at about 150°C and the second at about 300°C. Measurements on samples intentionally contaminated with either sodium or potassium show that the first peak is due to the motion of sodium ions, whereas the second peak results from the motion of potassium ions. The surface-trapping model describes the curves well when a Gaussian spread in activation energy is assumed. When a physically plausible value for the emission time constant is assumed (10^{-12} s), an activation energy is found that is consistent with an emission-limited process.

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I. INTRODUCTION

As a result of the work of many investigators, it is a well-known fact that alkali contamination can cause serious MOS-device instabilities (for an extensive list of references on this subject see Hickmott¹). Sodium, in particular, has been shown to be the major cause, but also potassium can possibly have a similar effect.²

These electrical instabilities arise from charged alkali ions which drift across the oxide layer when an appropriate gate voltage is applied. This leads to a charge redistribution in the oxide and therefore to a change in flatband voltage. At room temperature, such a charge redistribution is generally established only after a very long time, but at elevated temperatures this redistribution takes place at a much higher rate.

Despite the great amount of research done on this subject, the physical background of the observed instabilities is not yet completely understood. One possible way to investigate the ion drift is the application of the thermally stimulated ionic current (TSIC) technique to a MOS capacitor.^{1,3,4} In this technique, the temperature is raised while the electrode charging current is measured at a constant gate voltage.

II. EXPERIMENTS

The experimental setup for measuring TSIC curves is shown in Fig. 1. The time-temperature relationship is given by

$$T(t) = T_f - (T_f - T_i) \exp(-t/t_0), \quad (1)$$

$T_f \approx 500^\circ\text{C}$, $t_0 \approx 15$ min; T_i is the initial temperature.

FIG. 1. Experimental setup to record thermally stimulated ionic currents (TSIC) through SiO_2 .

Note that the heating rate decreases at higher temperatures.

The thermally stimulated currents were always measured after an appropriate BTS treatment (15 min at 350°C and a gate voltage of ± 5 V). Before measurements at a positive gate voltage the stress voltage was negative (all ions are then driven to the oxide-metal interface), and for measurements at a negative gate voltage the stress voltage was positive.

All samples used in this investigation were prepared by oxidation of 10- Ω cm *n*-type (100) silicon wafers at 1200°C in pure O_2 to give an oxide thickness of 1500 Å. Aluminum electrodes were deposited either by the electron-gun technique or by evaporation from a tungsten filament. Only the samples with evaporated electrodes were subjected to an anneal treatment (30 min at 450°C in wet N_2). All measurements were done immediately after fabrication on virgin samples. Two typical TSIC curves are shown in Fig. 2; one at a positive gate voltage, the other at a negative gate voltage. We observe

FIG. 2. Typical TSIC curves as obtained from a sample with aluminum electrodes evaporated from a tungsten filament for negative and positive gate voltage.

two distinct peaks, which suggests that we deal with two mobile ionic species. The total number of ions that crossed the oxide can be obtained by integration of the electrode charging current as a function of time. This results in 1.9×10^{12} ions/cm² for the low-temperature peak and 2.5×10^{12} ions/cm² for the high-temperature peak for both curves.

The curves of Fig. 2 were obtained from a sample with aluminum electrodes evaporated from a tungsten filament, which is often mentioned as a major source of ionic contamination. To check this, another sample was provided with e-gun-deposited aluminum electrodes. The number of ions is now 1.6×10^{11} cm⁻² and 4×10^{11} cm⁻² for the low- and high-temperature peaks, respectively. So, we see that the e-gun technique produces a much lower contamination level. The number of ions is the same for positive and negative gate voltages. This proves that to at least 350 °C, the electrodes are blocking, which is a basic assumption in the emission theory treated in Sec. III. Nearly always the second peak has been neglected in the treatment of TSIC curves, and it was unknown what kind of ionic species was involved. Therefore, some contamination experiments were carried out. The SiO₂ surfaces of some samples were contaminated by immersing the wafer in a $10^{-4}N$ aqueous solution of either NaCl or KCl. In accordance with the experiments of Raider *et al.*,⁵ this process was carried out at room temperature (22 °C) for 5 min without agitation of the solution. After contamination, the wafers were blown dry and provided with aluminum electrodes. These were made by the e-gun technique to minimize the background contamination.

The resulting TSIC curves are shown in Fig. 3(a) for a negative and in Fig. 3(b) for a positive gate voltage. We see that a large low-temperature peak (1.2×10^{12} ions/cm²) is caused by the sodium contamination. On the potassium-contaminated sample, however, a small low-temperature peak, possibly due to a background sodium contamination and a large high-temperature peak (1.1×10^{12} ions/cm²), are observed. This contamination experiment indicates clearly that potassium ions are mobile in SiO₂ layers and responsible for the high-temperature peak. It is remarkable that in the not intentionally contaminated samples even more potassium than sodium ions have drifted across the oxide. Nevertheless, in literature, only recently,² attention has been paid to potassium ions, which is probably due to the very high activation energy for the emission, making their motion only easily detectable at temperatures above 250 °C, as will be shown in Sec. III.

III. THE SURFACE TRAPPING MODEL

Recently, Hickmott⁴ presented the surface trapping model to analyze TSIC curves. The basic assumption is the following: After the BTS treatment, the ions are trapped near one interface in traps with a certain activation energy. Once emitted from a trap, the ions are driven by an appropriate electrical field to the opposite side where they are trapped again. Retrapping at the interface and trapping in the bulk of the oxide are neglected in this theory.

When the temperature is raised, emission takes place at an increasing rate, resulting in an increasing current. After some time, most of the ions have been emitted and the current decreases. Mathematically, this process can be described by the following differential equation:

$$F(t) = -\frac{dN(t)}{dt} = \frac{N(t)}{\tau_0} \exp\left(-\frac{E_0}{kT(t)}\right), \quad (2)$$

where $F(t)$ is the flux of ions emitted at time t , $N(t)$ is the concentration of ions still trapped at time t , τ_0 is the emission time constant, and the emission probability is given by the Boltzmann factor with a single activation energy E_0 . In the absence of transport limitation, the ions move at once to the opposite side, so the electrode charging current density is given by

$$J_m(t) = qF(t). \quad (3)$$

FIG. 3. TSIC curves of intentionally contaminated samples for negative (a) and positive (b) gate voltage. Electrodes deposited by the e-gun technique.

FIG. 4. Comparison of experimental and theoretical TSIC curves, according to the surface trapping model for negative (a) and positive (b) gate voltage. (---): single level; (—): Gaussian spread; □: experimental values from Fig. 2.

From integration of Eq. (2), we obtain

$$F(t) = \frac{N(0)}{\tau_0} \exp \left[-\frac{E_0}{kT(t)} - \frac{1}{\tau_0} \int_0^t \exp \left(-\frac{E_0}{kT(t)} \right) dt \right], \quad (4)$$

where Eq. (1) gives the relation between time and temperature. Knowing the temperature at which the current reaches its maximum and the temperature at which the current reaches one-half of its maximum

value, we can compute τ_0 and E_0 and subsequently the complete TSIC curve.

Applying this theory to the TSIC curve of Fig. 2 at a negative gate voltage, we see [Fig. 4(a), dotted line] that the falling side of the current peak, in particular, is fitted unsatisfactorily (the lower value of the half-maximum temperature is used as is usual).

Therefore, a refinement to the single-level theory is introduced. It is assumed that the activation energy has a Gaussian spread around a mean value at the start of the measurement. Consequently, the charge concentration $N(t)$ in Eq. (2) is now replaced by a charge density $n(t, E)$ of charge trapped with an activation energy E at time t ,

$$\frac{dn(t, E)}{dt} = -\frac{n(t, E)}{\tau_0} \exp \left(-\frac{E}{kT(t)} \right). \quad (5)$$

The total charge still trapped at time t is obtained after integration,

$$N(t) = \int_{-\infty}^{\infty} n(t, E) dE. \quad (6)$$

The boundary condition of a Gaussian spread in the activation energy is expressed as

$$n(0, E) = \frac{N(0)}{\sigma(2\pi)^{1/2}} \exp \left[-\frac{1}{2} \left(\frac{E - E_0}{\sigma} \right)^2 \right], \quad (7)$$

where σ is the spread in activation energy. After integration of Eqs. (5) and substitution into Eq. (6), we obtain with boundary condition (7)

$$F(t) = \int_{-\infty}^{\infty} \frac{N(0)}{\sigma(2\pi)^{1/2}} \exp \left[-\frac{E}{kT(t)} - \frac{1}{2} \left(\frac{E - E_0}{\sigma} \right)^2 \right] - \frac{1}{\tau_0} \int_0^t \exp \left(-\frac{E}{kT(t)} \right) dt dE. \quad (8)$$

The results of computer calculations on this theory are also shown in Fig. 4(a) (solid curve). We see a much better agreement with experiment on the falling side of the current peak. The TSIC curve for a positive gate voltage [Fig. 4(b)] shows a much better agreement for the falling side of the sodium peak, whereas the rising side has a worse fit. This can be easily explained by an asymmetrical distribution in which activation energies above E_0 are more strongly represented than those below E_0 .

The trapping constants calculated at a gate voltage of ∓ 2.5 V are summarized in Table I. The single-level interpretation ($\sigma = 0$) gives nearly the same results. Two remarks have to be made with respect to the physical interpretation of these constants.

TABLE I. Constants in the surface trapping model with Gaussian spread, computed at $V_G = \mp 2.5$ V. The curves are shown in Fig. 4.

	Na ⁺ ions		K ⁺ ions	
	Al → Si	Si → Al	Al → Si	Si → Al
E_0 (eV)	0.46	0.46	0.97	1.31
σ (eV)	0.054	0.031	0.042	0.030
τ_0 (s)	3.0×10^{-4}	5.8×10^{-5}	8.7×10^{-7}	9.7×10^{-10}

FIG. 5. Comparison of experimental and theoretical TSIC curves, according to the surface trapping model with the assumption of $\tau_0 = 10^{-12}$ s for negative (a) and positive (b) gate voltage. (---): single level; (—): Gaussian spread; $\square$: experimental values from Fig. 2.

(1) One should expect the emission time constant (τ_0) to be of order 10^{-12} s, related to the atomic frequency factor. The many orders of magnitude deviation of computed values is therefore hard to understand physically. Hickmott¹ ascribes this deviation to a fast retrapping of just emitted ions, resulting effectively in a larger value

TABLE II. Constants in the surface trapping model with Gaussian spread and with a physically plausible emission time constant ($\tau_0 = 10^{-12}$ s), $V_G = \mp 2.5$ V. The curves are shown in Fig. 5.

	Na ⁺ ions		K ⁺ ions	
	Al $\rightarrow$ Si	Si $\rightarrow$ Al	Al $\rightarrow$ Si	Si $\rightarrow$ Al
E_0 (eV)	1.10	1.01	1.65	1.65
σ (eV)	0.158	0.086	0.091	0.061

of τ_0 . It is obvious that in this case the interpretation given above is no longer valid.

(2) The calculated activation energies for emission of Na⁺ ions may be compared with the activation energy for sodium mobility in SiO₂ layers (0.63 eV), as found by Kriegler and Devenyi.⁶ In order to have a purely emission-limited process, the activation energies for emission should be greater than 0.63 eV. A curve fitting, based on Eq. (8) with the assumption $\tau_0 = 10^{-12}$ s is shown in Figs. 5(a) and 5(b). The single-level theory can no longer explain the experimental results, but the introduction of a Gaussian spread gives a satisfactory fitting. The trapping constants in this case are summarized in Table II. As can be seen, a value of the activation energy is now found which is consistent with the requirements of an emission-limited process.

IV. CONCLUSIONS

Summarizing, we can draw the following conclusions:

(1) The TSIC technique is extremely suitable to investigate ionic contamination in insulators.

(2) Mobile ions are either sodium or potassium ions. However, the trapping of potassium ions is much stronger than the trapping of sodium ions, making detection in, for example, a BTS quality control test more difficult (making use of the constants of Table II, the time constant for potassium motion would be 100 h at 200°C and 320 s at 300°C).

(3) A Gaussian spread in the activation energy of the traps describes the experimental TSIC curves to a much better extent than the single-level theory, but the actual activation energy distribution is probably slightly asymmetric.

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