Sensitivity of MOS structures for contamination with H\(^+\), Na\(^+\), and K\(^+\) ions

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Results of contamination experiments on MOS structures with aqueous solutions of NaCl, KCl, acetic acid, and purified water are presented. A special grid-shaped electrode (Al or polycrystalline Si) was developed for these experiments. Various after-treatments were applied. At temperatures of 250 and 350°C, the \(I-V\) curve shows two distinct peaks caused by ion transport in the oxide. Contamination with H\(^+\) and Na\(^+\) ions had a pronounced influence on the area of both peaks. The results showed that it is impossible to attribute the first peak to transport of Na\(^+\) ions only and the second to that of K\(^+\) ions. It is concluded that the first peak results from ion transport under conditions of thermodynamic equilibrium and that the second peak is controlled by the rate with which ions are released from traps at the interfaces. Models for both transport mechanisms are presented.

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I. INTRODUCTION

Investigation of the transport of ions in the oxide of MOS structures is very important because these ions influence the stability of MOS transistors. Alkali ions and the hydrogen ion have been shown to be the most important contaminations in the oxide (for an extensive list of references see Deal\(^1\) and also Hickmott\(^2\)). In the ISFET device a special use is made of this sensitivity for hydrogen and alkali ions.\(^1\)

Few facts about the transport behavior of the different ionic species in SiO\(_2\) have been published.\(^4\) A method for studying the behavior of ions is the TSIC method.\(^2\) In this method the temperature is changing with time in a programmed way, while the voltage bias is kept constant. Another method to investigate the behavior of ions in the oxide is the quasistatic \(I-V\) method of Kuhn and Silversmith.\(^7\) In this method the temperature is constant and the bias is varied. We prefer the \(I-V\) method for the sake of the experiment and the interpretation of the results. At elevated temperatures (150-400°C) \(I-V\) curves show two distinct peaks caused by ion transport in the oxide. Recently, Derbenwick\(^3\) and also Stagg\(^4\) concluded that the first peak was due to Na\(^+\) transport, whereas the second was caused by K\(^+\) transport.

In this paper, the results of several contamination experiments are presented. The amount of ions related to each peak was measured as a function of the type and duration of the contamination. A special type of electrode was used and various after-treatments were applied. In particular Derbenwick's conclusion was checked.

II. EXPERIMENTAL METHOD

Contamination experiments are usually carried out as indicated in Fig. 1(a).\(^1\) The oxide is contaminated first and the electrode is made afterwards. In that case the vacuum present during Al evaporation, the eventual substrate heating, the photolithography, the annealing of the radiation damage, and other after-treatments all interfere with the intentional contamination. Applying the contamination in that way it is also necessary to use a large number of separately prepared samples and as a consequence of that, uncertainty arises about the references. To avoid these problems a new type of MOS structure was developed [Fig. 1(b)]. This MOS structure consists of a grid-shaped electrode, as shown in Fig. 2. The windows are 5×5 μ. First, the after-treatments are applied and then the shape of the grid is etched using standard photoresist techniques. Thus, the oxide surface in the openings of the electrode has also received all after-treatments. Wafers were prepared for each type of electrode material. Every wafer contained 64 MOS structures and was subdivided by scribing and breaking into smaller pieces. Contamination of the MOS structures was carried out by

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![FIG. 1. Methods for the contamination of the oxide. (a) Method as described in the literature. (b) Method as used in our experiments. (c) Situation at the window in the electrode.](image)
immersing these pieces during different periods of time in the following aqueous solutions:

(1) NaCl: p.a., contamination: K—0.00005%; Ca and Mg—0.001%; metals—0.003%; Br and I—0.003%.

(2) KCl: p.a., contamination: Na—0.005%; Ca and Mg—0.001%; metals—0.001%; Br and I—0.0005%.

(3) HAc: (acetic acid) p.a., contamination: metals—0.00001%; Na and K—smaller than 0.00001%.

The concentration of the contaminants was 0.1 g molecular weight in 1 liter of water. It should be noted that the acetic acid is not as completely dissociated as NaCl and KCl. The proton concentration is about $1.3 \times 10^{-3}$ mol/liter. The solutions were prepared with water having a resistivity of 0.5 MΩ cm. This implies that this water contains a mobile ion concentration of about $1.5 \times 10^{-4}$ mol/liter.

(4) H₂O: two qualities: 0.5 and 2–5 MΩ cm.

The MOS structures were immersed in the solutions for various periods. After this the MOS structures were immediately rinsed in water of 2–5 MΩ cm, spin-dried, heated up to 250 °C, and measured. After the measurement the same piece with MOS structures was again immersed in the same solution for a further period of time.

We assume that only the surface layer of the oxide at the windows in the electrode is contaminated. Due to side diffusion, a small part of the absorbed contaminants comes under the influence of the fringing fields at the edges of the windows, Fig. 1(c). We believe that we can therefore only determine the behavior of the contaminated structure at the edges parallel to the unintentionally contaminated major part of the MOS structure.

The same measuring setup as described by Kuhn and
Silversmith was used. When I-V curves are recorded at elevated temperatures, two distinct peaks are found (Figs. 3 and 4). One peak is always found close to the voltage zero and it has a symmetrical shape. We shall refer to this peak as No. 1. The other peak appears after the first one and its position depends on the direction of the voltage sweep. The shape of this peak depends on the temperature and the sweep rate and it will be referred to as peak 2. The area of the peak divided by the sweep rate yields the amount of ions related to this peak. The area under the peaks was almost independent of the sweep direction. Those results obtained starting with a positive bias are shown in Figs. 3 and 4. For the experiments reported, we used 10-7 cm <100> Si substrates. The oxide was thermally grown in dry oxygen at 1150°C to a thickness of 1000 Å.

Measurements were carried out using a triangular voltage sweep. Before the actual measurement the MOS structure was heated to 250°C with a bias of +15 V in order to bring all mobile ions to the interface Si-SiO2. After the current at this bias ceased, measurements were started. In this way a comparable starting point was achieved for all MOS structures. In order to check the effect of relaxation, preliminary experiments were carried out at sweep rates of 30 and 300 mV/s. The shape of the peaks depended on the sweep rate, but the areas under the peak remained almost constant, provided the amplitude of the sweep was large enough. For practical purposes a sweep rate of 300 mV/s was chosen. The curve remained reproducible after several measuring cycles. From this we concluded that no further side diffusion took place after the MOS structure has been heated for some time at 250°C under positive bias. Some measurements we carried out at 350°C, because then the peaks are sharper and small amounts of ions related to the second peak can be determined. At 250°C the peaks are more widely separated and the resolution is better (see Fig. 5).

III. EXPERIMENTAL RESULTS

Because in our opinion the interpretation of the results of our research is complicated and should be open for discussion, the data in Figs. 6–9 are presented in close relation with the actual experiments as a function of the immersing time. The active area of our grid-shaped electrode is not known. We estimated that this area can be as small as 1% of the total electrode area. This means that the actual surface density may be a hundred times larger than the values presented in Table I and Figs. 6–9.

The electrode materials used in the experiments were the following:

(a) Aluminum electrode: Evaporated in vacuum from a tungsten filament without heating the substrate. No after-treatment was applied.

(b) Aluminum electrode as in the first case, but now an after-treatment was applied during a period of 30 min at 450°C in wet N2 before etching the electrode. During this after-treatment a chemical reaction takes place between the aluminum and the oxide by which an ion-sensitive zeolite-type surface layer is formed.

(c) Polycrystalline silicon electrode: Phosphorus doped, deposited at 650°C, activated at 1100°C for 15 min, and after-treated at 500°C in wet N2 for 30 min. A gettering phosphosilicate glass (PSG) layer g is automatically formed in this structure.

A. Aluminum electrode without after-treatment: measuring temperature is 250°C

The results of the contamination experiments are shown in Fig. 6 as a function of the immersing time. The I-V curves were recorded at 250°C. Without any intended contamination of the oxide, the amount of ions as derived from the area under the first peak was 2.0 × 10^{14} ± 10^{10} cm^2 (Table II). The amount related to the second peak is much larger, viz., 7.8 × 10^{13} ± 10^{12} cm^2.

**TABLE I. Increase in the amount of ions with respect to the initial values in different MOS structures.**

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>4 h NaCl</th>
<th>4 h KCl</th>
<th>4 h HAc</th>
<th>4 h NaCl</th>
<th>4 h KCl</th>
<th>4 h HAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, no after-treatment; 250°C</td>
<td>1 × 10^{14}</td>
<td>...</td>
<td>...</td>
<td>1 × 10^{14}</td>
<td>1 × 10^{14}</td>
<td>1 × 10^{14}</td>
</tr>
<tr>
<td>Al, after-treatment; 250°C</td>
<td>1 × 10^{11}</td>
<td>...</td>
<td>8 × 10^{11}</td>
<td>4 × 10^{11}</td>
<td>3 × 10^{11}</td>
<td>6 × 10^{11}</td>
</tr>
<tr>
<td>Al, after-treatment; 350°C</td>
<td>1.5 × 10^{11}</td>
<td>1 × 10^{11}</td>
<td>4.3 × 10^{11}</td>
<td>6 × 10^{11}</td>
<td>6 × 10^{11}</td>
<td>8 × 10^{11}</td>
</tr>
<tr>
<td>P-doped poly-Si; 350°C</td>
<td>4.9 × 10^{11}</td>
<td>2 × 10^{11}</td>
<td>3.9 × 10^{11}</td>
<td>3.7 × 10^{11}</td>
<td>2.3 × 10^{11}</td>
<td>1.9 × 10^{11}</td>
</tr>
</tbody>
</table>

FIG. 5. I-V curves measured at two different temperatures (sweep rate is 300 mV/s, annealed Al electrode; t_m = 1000 Å; 10-7 cm <100> Si substrate).
In the case of contamination with solutions containing sodium chloride and acetic acid, the area of the first peak increases as a function of the immersing time. Raider et al. on the contrary report that acids had no influence. We found that contamination with the potassium chloride solution or with water (2-5 MΩ cm) had no effect. The number of ions related to the second peak changes relatively slowly and only the influence of Na⁺ is pronounced. It is reported in the literature that the second peak is largely influenced by K⁺. Our results clearly contradict this conclusion and we believe that the difference is caused by the methods of sample preparation.

B. Aluminum electrode with after-treatment: measuring temperatures are 250 and 350 °C

The results of the I-V curves recorded at 250 °C are

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Peak 1 (cm²)</th>
<th>Peak 2 (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, no after-treatment; 250 °C</td>
<td>2.0 × 10¹⁹ (1 × 10¹⁹)</td>
<td>7.8 × 10¹⁹ (1 × 10¹⁹)</td>
</tr>
<tr>
<td>Al, after-treatment; 250 °C</td>
<td>1.8 × 10¹⁹ (1 × 10¹⁹)</td>
<td>2 × 10¹⁹ (1 × 10¹⁹)</td>
</tr>
<tr>
<td>Al, after-treatment; 350 °C</td>
<td>2.5 × 10¹⁹ (2 × 10¹⁹)</td>
<td>3.9 × 10¹⁹ (2 × 10¹⁹)</td>
</tr>
<tr>
<td>P-doped poly-Si; 350 °C</td>
<td>2 × 10¹⁵ (1 × 10¹⁵)</td>
<td>2 × 10¹⁵ (1 × 10¹⁵)</td>
</tr>
</tbody>
</table>
and Na'. The influence of H' was so strong that the amounts of ions related to the first and second peaks could not be properly separated at long immersion times. K' contamination has a greater influence on the second peak than Na' contamination. This is the only case in which we found the influence of K' ions to be greater than that of Na' ions. H2O (0.5 mΩ cm) did not show any influence.

C. Phosphorus-doped polycrystalline Si electrode: measuring temperature is 350 °C

For both peaks relatively small initial amounts of ions, viz., 2 × 10¹¹ cm⁻² were found at 350 °C (Table II). The sensitivity for ion contamination was, however, so large that only short contamination times could be applied (Fig. 9). Both peaks increase during contamination by Na' and H' ions. The increase of the second peak due to K' is noticeable. H2O (2–5 MΩ cm) caused a slight increase in the ions related to the first peak. In spite of the gettering action of a PSG layer at

![Figure 8](image1.png)

FIG. 8. Results of contamination experiments on the MOS structure with an Al electrode with after-treatment. Measuring temperature is 350 °C. — NaCl contamination; ——— HAc contamination; ——— KCl contamination; ——— H2O reference. The vertical bars give the standard deviation of the experimental results.

![Figure 9](image2.png)

FIG. 9. Results of the contamination experiments on the MOS structures with a phosphorous-doped poly-Si electrode. Measuring temperature is 350 °C. — NaCl contamination; ——— HAc contamination; ——— KCl contamination; ——— H2O reference. The vertical bars give the standard deviation of the experimental results.

The results are presented in Fig. 8. Note the logarithmic scale. At the measuring temperature of 350 °C, an increase in the amount of ions is observed compared to the measurements at 250 °C for comparable samples. This increase observed at 350 °C could be due to increased side diffusion or to the trapping mechanism at the surface. The number of ions related to the first peak is again strongly influenced by H' and Na'. The influence of K' was so strong that the amounts of ions related to the first and second peaks could not be properly separated at long immersion times. K' contamination has a greater influence on the second peak than Na' contamination. This is the only case in which we found the influence of K' ions to be greater than that of Na' ions. H2O (0.5 mΩ cm) did not show any influence.
high temperatures, the surface of the oxide showed a clear aptitude to absorb contaminations at low temperatures.

IV. INFLUENCE OF H₂O, H⁺, Na⁺, AND K⁺

A. H₂O

Contamination by water of a resistivity in the range 0.5–5 MΩ cm had hardly any effect. It is possible that our experimental method is not sensitive enough.

B. H⁺

The effect of H⁺ ions is large and at least as important as that of Na⁺ contamination, especially if we consider that acetic acid is not completely dissociated. Only in the case of an untreated aluminum electrode is the structure more sensitive for Na⁺ than for H⁺, as is also reported by Raider et al.⁴

C. Na⁺

Contamination with Na⁺ ions gave in every experiment we conducted an increase of the first peak area. The magnitude of the increase shows that Na⁺ ions are very rapidly taken up by the oxide. This fact is also reported in literature for untreated oxide.⁵

D. K⁺

The effect of K⁺ ions on the first peak is small compared to the influence of H⁺ and Na⁺ ions. The effect of K⁺ on the second peak is equal or smaller than that of Na⁺ and H⁺ ions. The conclusion of Derbenwick⁴ and Nauta⁶ that the second peak is mainly due to K⁺ ions is in our opinion a result of the different way of contaminating the oxide. We also conducted experiments in which we first contaminated the oxide and made the aluminum electrode afterwards. In this case, we can confirm Derbenwick's conclusion⁴ that the change in the first peak is due to Na⁺ contamination and the second to K⁺.

V. MAIN FEATURES OF THE FIRST AND THE SECOND PEAKS

A. First peak

The first peak is always found at a positive voltage of about +0.5 V. The voltage drop across the oxide is then small. This means that the ions involved immediately respond to changes in diffusion and electric forces. A model for this behavior of ions is presented in the theoretical part of this paper as the so-called equilibrium model.

B. Second peak

The following characteristics were found:

(1) The second peak did not show a specific sensitivity for a particular sort of ion.

(2) The shape and sometimes the magnitude depended on the interface from where the ions drift (Fig. 4). This points towards different trapping levels at the boundaries of the oxide. An asymmetric behavior is also reported in the literature.⁶

(3) Peak 1 increases at the cost of peak 2 during repeated measurements for MOS structures with an Al electrode without after-treatment. If the sweep rate was decreased considerably, then the final result was found immediately.

(4) There is a very clear difference between structures with an Al electrode with or without an after-treatment, as can be seen in Table II.

(5) Uncontaminated samples prepared with e-gun evaporation showed no second peak. The duration of the after-treatment had no influence on this fact. Derbenwick also reported that a second peak was absent in the case of e-gun evaporation.⁴

In principle two mechanisms can explain the above-mentioned facts:

(i) The existence of trapping levels at the interfaces of the oxide with the electrode material and the semiconductor.

(ii) The ions show relaxation effects when the electric forces change. Especially remarks (2)–(4) point towards trapping at the interfaces. A trapping model to explain the transport of ions at a constant temperature is described in Sec. IV C.

C. Theory

Figure 3 shows a typical result of an I-V measurement. Two different types of peaks can normally be distinguished.
D. Equilibrium model

In a previous paper we have derived a detailed model for the description of ion transport in the oxide. In this model it is assumed that during transport the ion distribution can be approximated by an equilibrium distribution, which implies that the electrochemical potential is constant in the oxide. Under these conditions the following analytical expressions are found for the charge density \( q N(x) \) and the electric field \( E(x) \) (where \( x \) is the distance from the electrode) (Fig. 10):

\[
E(x) = \frac{2aT}{q} \tan(ax+b), \quad (1)
\]

\[
N(x) = \frac{2kTe}{q} \frac{a^2}{\cos^2(ax+b)}. \quad (2)
\]

The integration constants \( a \) and \( b \) can be derived from the following two boundary conditions: (a) The integral of the electric field over the oxide thickness is equal to the negative applied voltage and (b) The total charge per unit area at the electrode, found from experimental results, is the integral of the charge density over the oxide thickness.

To elaborate \( I-V \) curves, numerical calculations of a succession of equilibrium states are required. It can then be shown that the shape of the first peak is correctly predicted and the maximum of the peak is found at an applied voltage equal to the negative work-function difference between the electrode and the Si substrate (Fig. 11).

E. Trapping model

This model describes the situation when ions are captured in traps near the interfaces. The most plausible explanation for these traps could be the potential drop brought about by image forces. The ions can be released from these traps in two ways. Hickmott and Nauta describe how this can happen by an increase of temperature. In the following model we will show that an electric field also can release these ions. The transport of ions through the oxide is considered to occur relatively fast compared to the release rate. This means that the rate with which ions are released from traps determines the transport properties in the oxide. It is assumed that ions are not trapped in the bulk of the oxide and that both silicon and metal electrodes have a blocking function. The ionic current is determined by the rate with which ions acquire the necessary energy to leave the traps.

Thus,

\[
I = -q \frac{dn(t)}{dt} = qvn(t) \exp \left(-\frac{E_0}{kT}\right), \quad (3)
\]

where \( n(t) \) is the number of trapped ions at time \( t \), \( v \) has the dimension of a frequency, and \( E_0 \) is the trap depth. Under the influence of a constant-sweep rate, the barrier height of the trap will decrease (Fig. 12). The barrier heigth of the trap will decrease (Fig. 12).

\[
E_0 = E_0 - q\omega t^\frac{1}{2}
\]

and

\[
I = -q \frac{dn(t)}{dt} = qvn(t) \exp \left(-\frac{-E_0 + q\omega t^\frac{1}{2}}{kT}\right). \quad (4)
\]

FIG. 12. The influence of an electric field on the trap depth. ---, image potential; ---, potential from constant electric field; ---, resulting potential.
where \( w \) is the proportionality constant. Then Eq. (4) leads to

\[
\int_{n(0)}^{n(t)} \frac{dn(t)}{n(t)} = \int_0^t v \exp\left(-\frac{E_0 + q\omega t^\frac{1}{2}}{kT}\right) dt. \tag{5}
\]

Integration of Eq. (5) gives

\[
\ln\left(\frac{n(t)}{n(0)}\right) = -2v \left(\frac{kT}{q}\right)^2 \exp\left(-\frac{E_0}{kT}\right) \times \left[\exp\left(\frac{q\omega t^\frac{1}{2}}{kT}\right)\left(\frac{q\omega t^\frac{1}{2}}{kT} - 1\right) + 1\right]. \tag{6}
\]

The amount of ions still in traps will then be

\[
n(t) = n(0) \exp\left[-2v \left(\frac{kT}{q}\right)^2 \exp\left(-\frac{E_0}{kT}\right) \times \left[\exp\left(\frac{q\omega t^\frac{1}{2}}{kT}\right)\left(\frac{q\omega t^\frac{1}{2}}{kT} - 1\right) + 1\right]\right]. \tag{7}
\]

With the aid of Eq. (4), we find the current \( I(t) \)

\[
I(t) = qv n(0) \exp\left[-\frac{E_0 + q\omega t^\frac{1}{2}}{kT} - 2v \left(\frac{kT}{q}\right)^2 \exp(-E_0/kT) \times \left[\exp\left(\frac{q\omega t^\frac{1}{2}}{kT}\right)\left(\frac{q\omega t^\frac{1}{2}}{kT} - 1\right) + 1\right]\right]. \tag{8}
\]

There is a maximum in the current at \( df(t)/dt = 0 \), which leads to

\[
t_{\text{max}}^{\frac{1}{2}} \exp\left(\frac{q\omega t_{\text{max}}^\frac{1}{2}}{kT}\right) = \frac{q\omega}{2v k T} \exp\left(-\frac{E_0}{kT}\right). \tag{9}
\]

According to the Schottky theory with image forces\(^\text{13}\) the proportionality constant \( w \) is equal to

\[
w = \left(\frac{q}{4\pi \varepsilon_0}\right)^\frac{1}{2} \alpha \frac{1}{L}. \tag{10}
\]

For a Poole-Frenkel type of trap,\(^\text{14}\) \( w \) is equal to

\[
w_{PF} = 2w_S, \tag{11}
\]

where \( \alpha \) is defined by

\[
V = \alpha t. \tag{12}
\]

\( L \) denotes the thickness of the oxide.

From the determination of the maximum of the second peak at two sweep rates, the value of \( v \) and \( E_0 \) can be calculated using Eq. (9). In Fig. 13 we show two kinds of calculations using Hickmott's\(^\text{2}\) and Nauta's\(^\text{1}\) parameter for the frequency factor. It is clear that for an optimal curve fitting the parameters must be varied. The results, however, show that in principle this trapping model can account for the second peak.

**VI. CONCLUSIONS**

**A. First peak**

The first peak is caused by the transport of ions under conditions of electrochemical equilibrium. The equilibrium model provides a sufficient description of the first peak. This first peak cannot be assigned to a special type of ion.

**B. Second Peak**

Trapping at the interfaces is responsible for the second peak. The experimental results show that the second peak is not caused by a specific type of ion. The trapping model gives a fair description of this second peak.

We consider the conclusion that oxides are very sensitive for contamination by acids as being very important because during the fabrication of MOS transistors the oxide layers are in intensive contact with acids for longer periods during the etching of contact windows and the metal. The contamination rate is much larger in the case of Al and poly-crystalline-Si structures with after-treatment than in the case of untreated Al.

**ACKNOWLEDGMENTS**

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\(^\text{13}\)J. Frenkel, Phys. Rev. 54, 647 (1938).