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Conduction and charge storage in Cr-thin SiO₂-pSi structures

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Résumé. — Il est montré que les structures Cr-SiO₂-pSi ayant une couche de silice obtenue par oxydation thermique dans un mélange HCl/O₂/N₂ ont des caractéristiques électriques uniformes et reproductibles à faible niveau d'injection. De plus, le phénomène de claquage observé à haut niveau d'injection est associé à un stockage de charges positives dans l'isolant.

Abstract. — It is shown that Cr-SiO₂-pSi devices with an SiO₂ layer obtained by thermal oxidation in HCl/O₂/N₂ mixture have uniform and reproducible electrical properties at low injection level. Furthermore the breakdown phenomenon observed at high injection level has been associated with a positive charge storage within the insulator.

1. Introduction.

The electrical properties of thin oxide layers have been extensively studied and are of great importance for MOS VLSI reliability. This subject has recently gained considerable importance because of new applications of ultra thin SiO₂ layers. Indeed EEPROMs and related devices derive advantage from the current flowing through the oxide layer under an electric field ranging between 9 and 13 MV cm⁻¹. The reliability of the device is a critical parameter related to the behaviour of the insulator under such fields.

In particular a breakdown mechanism has been observed for various thickness and oxide preparation parameters associated with negative [1-2] or positive [3-4] charge storage in the insulator and interpreted in terms of avalanche multiplication [5] or electron trapping during current injection [6].

From the results in the literature there is no evidence for a universal behaviour of the silicon dioxide and the growth conditions should certainly control the oxide properties under high electric field. In this paper we present results obtained on Cr-SiO₂-Si(p) devices with a SiO₂ layer 70-200 Å thick obtained under low partial pressure of oxygen in a HCl/O₂/N₂ mixture. These growth conditions are very well adapted to ultra thin insulating layers and insure a good uniformity of the oxide [7].

First the electrical properties of MIS capacitors at low field will be presented followed by the results about breakdown.

2. Experimental procedure.

Metal-oxide-semiconductor capacitors have been fabricated on 5 Ωcm p-type < 100 > oriented silicon wafers. After standard cleaning the wafers were oxidized at 1050 °C in dry O₂ during four hours. Windows have been opened by oxide etching prior to re-oxidation at 950 °C in a N₂/O₂ (10 %)/HCl (0.2 %) mixture respectively during 10, 15, 30, 60 min. Then 300 Å thick square chromium dots have been evaporated onto the oxide. No annealing has been performed in order to avoid contamination of the oxide layer by metallic impurities. The thickness of the oxide layer measured by the C-V technics has been found to be 185 Å, 130 Å, 90 Å and 72 Å.

Measurements have been made on fifteen samples of each batch using the experimental apparatus shown on figure 1. For each sample current-voltage (I-V) followed by high (1 MHz) and low (1 kHz) frequency capacitance measurements. Then the I-V curve has been again recorded up to breakdown. For some samples pulse stress has been applied followed by static I-V and C-V measurements.

3. Experimental results and discussion.

3.1 LOW LEVEL CURRENT INJECTION. — Typical J-V curves corresponding to electron injection from the metal are shown on figure 2 for some samples.

At low level the current follows a Fowler-Nordheim Law [8]. This can be shown first when the electric field \(E_{ox}\) corresponding to a given current is computed from the applied voltage by solving Poisson and Gauss
equations assuming a metal to semiconductor barrier height equal to $-0.06 \text{ eV}$ [9]. As shown on figure 3 this field is independent of the insulator thickness $d_{ox}$ in agreement with Fowler-Nordheim injection. Second if we plot the $J$-$V$ curve in a Fowler-Nordheim graph the curve is linear within the whole current range (Fig. 4). Assuming an electron effective mass in silica equal to 0.5 [10] the metal to insulator barrier height $\mathcal{\Omega}_m$ can be calculated from the slope of this curve. Results are presented in table I and show a satisfactory agreement with results obtained by photoelectric measurements [11].

### Table I.

<table>
<thead>
<tr>
<th>$d_{ox}$ (Å)</th>
<th>$k_2$ (V cm$^{-1}$)</th>
<th>$\mathcal{\Omega}_m$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>$2.40 \times 10^8$</td>
<td>2.90</td>
</tr>
<tr>
<td>90</td>
<td>$2.21 \times 10^8$</td>
<td>2.76</td>
</tr>
<tr>
<td>130</td>
<td>$2.44 \times 10^8$</td>
<td>2.94</td>
</tr>
<tr>
<td>185</td>
<td>$2.13 \times 10^8$</td>
<td>2.69</td>
</tr>
</tbody>
</table>

$$J = A k_1 \delta_{ox} \exp(-\frac{k_2}{\delta_{ox}})$$

$$\mathcal{\Omega}_m = \left(\frac{k_2}{4.83 \times 10^7}\right)^{2/3}.$$
3.2 THICKNESS OF THE OXIDE LAYER.

The thickness of the oxide layer has been evaluated from the maximum of the capacitance curve. A small spreading (lower than 7%) of the capacitance value has been observed from device to device. This has not to be correlated with a possible spreading of the thickness because of the good reproducibility of the current but rather to experimental difficulties associated with probing.

3.3 HIGH LEVEL CURRENT INJECTION.

As shown on figure 2 when the current is increased beyond a threshold value the device breaks definitely. No self-healing breakdown has been observed during pulse measurement. The electric field at breakdown has been found to depend upon the oxide thickness as shown on figure 8 and follows approximately a $d_{ox}^{-\gamma}$ law with $\gamma \approx 0.5$. Different values have been obtained in the literature ranging between 0.21 [16] to 0.66 [17] for SiO$_2$ layers. A value of 0.5 is predicted by the simplest breakdown theory based on avalanche ionization in the oxide layer [18]. In order to investigate more deeply the origin of the breakdown we have made pulse measurements with voltage pulse amplitude $V_p$ larger than the static breakdown voltage value and 200 $\mu$s long. After each single pulse low level $J$-$V$ and high frequency $C$-$V$ curves have been recorded.

Results are shown on figures 8 and 10 in the case of a 130 Å thick oxide layer.

Both figures show the creation of a positive charge in the oxide layer, the influence of this charge being greater on the $C$-$V$ curve than on the $J$-$V$ one.

This fact can be interpreted through a localization of the charge very near the SiO$_2$-Si interface in accordance with a significative increase of the interface state density as shown in figure 11.

Even if the breakdown appears to be related to the creation of a positive space charge possibly at the origin of an impact ionisation mechanism the last phenomenon is not at the origin of the positive charge.
Fig. 7. — Energetic distribution of interface states as a function of the oxide thickness $d_{ox}$ obtained from: — difference between low and high frequency capacitance — Terman’s Method.

Fig. 8. — Dependence of the electric field at breakdown $\varepsilon_{BD}$ upon the oxide layer thickness.

Fig. 9. — Low level current-voltage curve before and after single pulse stress. 1: initial and after $V_p = 15$ V; 2: after $V_p = 20$ V.

Indeed constant current stresses have been performed at a current level two decades lower than the current level at breakdown and also a positive charge appears with a very long time constant as shown on figure 12.

Fig. 10. — Capacitance-voltage curve before and after single pulse stress. 1: initial; 2: after $V_p = 15$ V; 3: after $V_p = 20$ V; 4: after $V_p = 25$ V.

Fig. 11. — Influence of a single voltage pulse on the surface state density. Experimental conditions are the same as for figure 10.

4. Summary.

We have shown that Metal-70-200 Å SiO$_2$-Si diodes with oxide obtained at high temperature in partial pressure of O$_2$ and HCl have good electrical properties with stable and reproducible J-V curves following the Fowler-Nordheim law.

A breakdown mechanism related to a positive charge build-up near the SiO$_2$-Si interface has been shown. The origin of this charging is not well understood and is not due to impact ionization even if this last mechanism can initiate the breakdown once the charge is sufficiently high.
Fig. 12. — Influence of a constant current stress on the capacitance-voltage curve. 1 : initial; 2 : after $J = 10^{-9}$ A-10 min; 3 : after $J = 10^{-7}$ A-5 min; $d_{ox} = 130$ Å.

References

[7] CAPILLA, J. et al., to be published.