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Charge generation in metal-oxide-semiconductor capacitors during Fowler-Nordheim stress

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Abstract. — Experimental observations are reported concerning the influence of some technological processes on the generation rate of positive oxide charge and interface states during high electric field stress. Our results on positive oxide charge generation are consistent with a model of impact ionization in silicon dioxide and we think that acoustic-phonon runaway is the controlling process for impact ionization in SiO₂ in films thicker than 20.0 nm at fields higher than 7 MV/cm. We have found that the positive charge is mainly due to trapped holes when the electrons are injected at the gate/SiO₂ interface.

1. Introduction.

In Metal-Oxide-Semiconductor (MOS) devices, positive charge appears in any such stress situations as the application of a high electric field, an ionizing radiation, an avalanche injection and so on.

Many studies have been performed on this subject, but the mechanisms for the generation of positive charge and interface states have been controversial issues because of the complexity of the phenomena taking place in the oxide under stress. Some correlations between interface states and positive charge has been even put forward by several authors [1-3] at least for a part of the interface state density. Previous works [3-6] have shown that interface states are not produced during a Fowler-Nordheim (F.N.) injection when performed at low temperature, but they are essentially generated during the warming up. Measurements performed by some of us on similar samples have confirmed this possibility when an electron injection is realized from the gate [6]. It has been proposed [7-9] that the generation of interface states proceeds by the reaction of the silicon bonds with hydrogen which is given by :

$$= Si^{0} + H \rightarrow \equiv Si - H$$

$$= Si^{0} + H_{2} \rightarrow \equiv Si - H + H .$$
(1)

Hydrogen is always present in the SiO_2 bulk and/or at the interfacial regions and its density depends on the gate material.

An important question is how the energy needed, for the positive charge, is transfered from the carrier to the oxide. Actually, there is many discussions on this subject in the literature [10-12]. The positive charge can be due in the oxide layer to two main degradation mechanisms which are the phenomena of « impact ionization » and « trap creation » produced by any electron with energy exceeding 8 eV and 2 eV respectively. In the impact ionization process, holes are produced in the oxide bulk closer to the anode interface and, under the applied field they can move to the cathode interface where some are trapped. Arnold *et al.* [11] have shown that acoustic phonon runaway proposed by Cartier and McFeely [12] is the controlling process for impact ionization in SiO₂ and their simulations reveal that this electron runaway phenomenon appears at electric field above approximately 7 MV/cm. In the trap creation process, mobile hydrogen-related species can be release by hot electrons in the oxide near the anode interface, then they can move to the cathode interface where they produce oxide electron traps and interface states. Furthermore, it has been shown that similar interfacial defect generation can also occur near the anode for both mechanisms [9].

Other authors [13, 14] discuss to know if the generated positive charge is due to trapped holes or anomalous positive charge (APC). They suggest that the relative amounts of the APC defects depend on the presence of hydrogen in the oxide and its interaction with trapped holes.

The aim of this paper is to try to understand if the defects generated at high electric field stresses are produced by impact ionization, to verify the influence of some technological parameters on the energy dispersion mechanism and if the generated positive charge can be interpreted as trapped holes.

2. Experimental details.

P-MOS capacitors used in this experiment were fabricated on Boron doped Si $\langle 100 \rangle$ substrate $(N_A = 1.5 \text{ to } 4.5 \times 10^{15} \text{ cm}^{-3})$. The gate has an area of $5.44 \times 10^{-4} \text{ cm}^2$ and the oxide thickness in the range 18-52 nm is deduced from the capacitance measurement. All the samples were supplied by the L.E.T.I. (¹). Main sample characteristics are listed table I.

F-N tunnel electron injection was performed in accumulation at room temperature. The density of injected charge N_{inj} is calculated by current integration over the stress time. Our experimental method is the following one : $C_{HF}(V_g)$ at 1 MHz and $C_{LF}(V_g)$ (quasi-static method) curves of non-stressed samples were measured first. Then, a constant electric stress was applied during a set up time and C-V curves were recorded thereafter. This procedure was repeated until the breakdown of the sample. The energetic spectrum of interface states was determined by comparison of both high and low frequency C-V curves and the variation of the surface state density, at midgrap, was plotted vs. injected charge. This method of determination of the density of interface states, through less precise than other ones (conductance, DLTS...), is used here as a quick mean of controlling the variation of interface state density.

3. Experimental results and discussion.

Figure 1 shows that to create an important positive charge and numerous interface states, an injected charge density superior to some 10^{15} cm⁻² and a high electric field superior to some 7 MV/cm are necessary. These results are in excellent agreement with those found in previous work [15].

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Sample	Oxidation	e _{ox}	Post	Gate
	Conditions	(nm)	anneal	
LIR4	900°C-O2	29 4	Ar 1050°C	Al post anneal
	+ 5 % HCl			450°C N2-30 mn
LIR19	900°C- wet O ₂	42 5	Ar 1050°C	Si - Poly
	+ 6 % HCl		·	
LIR17	900°C- wet O2	52.8	Ar 1050°C	Al post anneal
	+ 6 % HCl			450°C N ₂ -30 mn
HCL50	1000°C-O ₂	26.3	N ₂ 20 mn	Al post anneal
	+ 3 % HCl			450°C N ₂ -30 mn
HCL94	950°C-O ₂	29.2	N ₂ 1 Hour	Al post anneal
	+ 3 % HCl			450°C N2-30 mn
HCL71	975°C-O2	34,4	N ₂ 20 mn	Al post anneal
	+ 3 % HCl			_450°C N2-30 mn
LIR9	900°C-O2	18.4	Ar 1050°C	Si - Poly
	+ 5 % HCl			

Table I. — Sample characteristics.

According to the macroscopic approach of Solomon *et al.* [16], the impact ionization coefficient follows the law :

$$\alpha (E_{\rm ox}) = \alpha_0 \exp(-H/E_{\rm ox}) \tag{2}$$

where α is the positive charge generation rate, α_0 and H depend on oxide technological parameters, and E_{0x} is the oxide field.

Chen et al. [17] have shown that, at low fluences, the oxide charge Q_{ox} can be expressed as :

$$Q_{\rm ox} = q \eta \cdot \alpha \left(E_{\rm ox} \right) \left(e_{\rm ox} - e_{\rm t} \right) N_{\rm int} \tag{3}$$

where η is the trapping efficiency, i.e. the rate of generated charge that becomes trapped, e_{0x} is the oxide thickness and :

$$e_{t} = \frac{\phi_{B}}{qE_{ox}} \tag{4}$$

is the thickness of the tunneling region; ϕ_B is the energy barrier at the gate-SiO₂ interface. Equation (4) assumes that the cathode field is almost equal to the oxide field which is a good approximation for low charge fluence.

The change in flat band voltage due to an oxide charge Q_{ox} is :

$$\Delta V_{\rm FB} = -\frac{\tilde{x}}{\epsilon_{\rm ox}} Q_{\rm ox} \tag{5}$$

where \bar{x} is the positive charge centroid from the gate and ε_{ox} is the oxide dielectric permittivity.



Fig. 1. — Evolution of flat band voltage (a) and of interface states (b) vs. applied stress field for various injected charges.

As \bar{x} is unknown, we are going to introduce the concept of effective charge Q_{eff} , which corresponds to a charge localized at the interface Si-SiO₂ and producing the same effect than Q_{ox} . We can then write :

$$\Delta V_{\rm FB} = -\frac{Q_{\rm eff}}{C_{\rm ox}} \quad \text{with} \quad Q_{\rm eff} = -\frac{\bar{x}}{e_{\rm ox}} Q_{\rm ox} \,. \tag{6}$$

Equation (3) is valid only for small N_{inj} ($\approx 10^{15}$ cm⁻²), because ΔV_{FB} and Q_{ox} sature at large fluence. This saturation is due to the attainement of a steady state between impact ionization and recombination, then the equation (3) is therefore valid for small ΔV_{FB} when the effects of recombination can be neglected [17].

We have then :

$$\alpha (E_{\rm ox}) \eta = \frac{Q_{\rm eff}^0}{q N_{\rm inj} (e_{\rm ox} - e_{\rm t})}$$
(7)

where Q_{eff}^0 is the effective charge for low N_{inj} (we have taken Q_{eff} and not Q_{ox} because the ratio \bar{x}/e_{ox} is close to one : the positive charge is situated near the substrate-Si/SiO₂ interface).

The product $\alpha \eta$ has been calculated with $Q_{\text{eff}}^0 = 8 \times 10^{-8} \text{ C/cm}^2$ (with $\Delta N^+ = 5 \times 10^{11} \text{ charges/cm}^2$ and $Q_{\text{eff}} = q \Delta N^+$) for different technologies and E_{ox} values and ln ($\alpha \eta$) vs. $1/E_{\text{ox}}$ has been plotted in figure 2.



Fig. 2. — $\alpha \eta$ product variation vs. $1/E_{ox}$ for various technologies.

As it can be seen, the experimental values can be fitted by a straight line for $8 \le E_{ox} \le 11 \text{ MV/cm}$. Hence, in this field range where is the Fowler-Nordheim region, impact ionization is confirmed.

DiMaria *et al.* [18] have confirmed that positive charge and interface states can be due to impact band gap ionization in oxide because the energy of the hot electrons can exceed 8 eV. High energy tails have been observed in the electronic energy distributions for thicker oxides at high fields [11, 19] and that this phenomenon can be explained by the acoustic-phonon runaway. This process takes several hundred angstroms to develop. Then, band-gap ionization will begin to occur at 7.5 MV/cm only on films of oxide thickness \ge 20-40 nm, with this threshold field increasing rapidly on thinner oxides.

We can see in figure 1 that beyond an oxide electric field about 7 MV/cm, there is a formation of positive charge and interface states; this threshold field can be interpreted as the field crucial for electron-hole pair generation by impact ionization under high-field stress.

The conclusion of the above study is in excellent agreement with the data of figure 2. We can then write :

$$\alpha (E_{ox}) \eta = A \exp \left(-\frac{B}{E_{ox}}\right). \tag{8}$$

The technological conditions have a clear influence on the product $\alpha (E_{ox}) \eta$. DiMaria *et al.* [20, 21] have shown that no processing dependence is found in α , but the hole trap density (and therefore η) have a strong dependence upon the oxide post-processing.

The relation (8) have led us to believe that the trapped hole is the dominant positive charge in samples damaged by the negative bias stress.

However, the origin of the positive charge is still an open subject. Trombetta *et al.* [13] suggest that positive charge near Si-SiO₂ interface exists in at least two fundamentally

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different forms. These forms are the trapped hole and the anomalous positive charge (APC) center or « slow states ». Normally, the APC center exchanges charge reversibly with the silicon substrate and acts as a slow interface trap with a time constant for the exchange of charge on the order of minutes or longer whereas a trapped hole undergoes irreversible quantum mechanical tunneling to the silicon substrate. We use the same procedure described in reference [13] to verify if the positive charge can be interpreted as APC or trapped holes. In figure 3, we show C.V curves after degradation in accumulation at a field of – 9.5 MV/cm and a fluence of 5×10^{16} cm⁻² (curve 2); immediately following electron injection, a field of – 4.5 MV/cm was applied to the gate during 1 800 s (curve 3); next a 4.5 MV/cm field during 1 800 s (curve 4), then a field of – 4.5 MV/cm during the same time (curve 5) and next a 4.5 MV/cm field during the same time (curve 6) were applied to the gate. With a 4.5 MV/cm field (curve 4), a portion of the positive charge has disappeared, certainly by tunneling of holes to the Si-substrate. If we begin again the same procedure several times, no variation of the positive charge is observed. We show, in our case, that the positive charge cannot be reversibly charged and discharged by application of bias of alternating sign.

We think these results indicate that the positive charge cannot be interpreted as anomalous positive charge or slow states but rather results from impact ionization and the subsequent trapping of the generated holes.



Fig. 3. — C.V curves after degradation in accumulation at -9.5 MV/cm and a fluence of 5×10^{16} cm⁻² (curve 2); immediately following electron injection, a bias of -4.5 MV/cm was applied to the gate during 1 800 s. Then the sign of the bias was changed every 30 mn.

Some holes diffuse at 300 K to the $Si-SiO_2$ interface where interface states are produced. This suggestion is in agreement with the experimental results show in figure 1, where the formation of positive charge or interface states as a function of the stress field are similar.

Recently, Roh *et al.* [14] argued that trapped holes and APC are related defects : the formation of APC depends on the presence of hydrogen in the oxide; the interaction of hydrogen with a trapped hole produces H or H^+ species which interact with the SiO₂ lattice near the Si/SiO₂ interface to produce APC.

In our case, for the curves obtained in figure 3, we realize an electron injection from the Algate; therefore holes are generated near the Si/SiO_2 interface where the availability of the presence of hydrogen is low comparatively as the Al/SiO_2 interface. Then, at the Si/SiO_2 interface, there is weak APC formation and this agrees with the results obtained by Roh *et al.* [14] in thicker oxides (85 nm); they have shown that the relative amount of APC and trapped holes generated by high field tunnel injection of electrons in thermal oxides is dependent on the sign of the bias used to induced injection : positive bias results mainly in APC whereas negative bias results in trapped holes.

4. Conclusion.

We have shown in this paper that in our samples, one could interpreted the generation of positive charge and interface states in SiO₂ by impact ionization at fluences of 10^{15} to 10^{18} electrons per cm² and high fields superior to 7 MV/cm. We see that a field of 7 MV/cm is required to accelerate electrons to energies high enough to cause electron-hole pair generation by hot electron impact. This phenomenon has been theoretically explained by an acoustic-phonon runaway model, presented by DiMaria *et al.* We have shown, that the positive charge, in the case of Al-gate injection of electrons, is mainly due to trapped holes and does not result from the creation of anomalous positive charge. This is consistent with the model presented by Roh *et al.*

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