Electric bidirectional stress effects on metal–oxide–silicon capacitors

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Bidirectional electron injections were performed in thick and thin oxides of metal–oxide–silicon capacitors under a constant oxide electric field. Results show that dissymmetry, due to electron trapping near both oxide interfaces, is accentuated when the oxide is thin. However electron trapping is more marked when oxide is thick. Two kinds of thick oxide were used: wet and dry technologies. Wet oxide contains relatively more defects than dry. This is due to hydrogen incorporation in wet oxide during the oxidation process. But this difference is not well marked, because boron atoms injected after the oxidation process would deactivate hydrogen atoms. We describe the electron trapping by a well-known power law. The exponent of this law depends on oxide field polarity and also on oxide thickness but is technology independent. Results also show a nonexpecting behavior of tunneling current during bidirectional stress at a constant voltage. Here, we describe its causes and effects. © 2001 American Institute of Physics. [DOI: 10.1063/1.1334368]

I. INTRODUCTION

It is well known that electric field, during bidirectional electron injection, causes damage in memory and logic technologies.1–7 For instance, in some memory devices the electric field polarity reversal determines the write and erase cycles. Repetition of this procedure induces degradation in the oxide.6,7 In flash memories, oxide situated between the floating gate and substrate loses its insulating properties. This causes a loss of electronic charges from the floating gate across the oxide toward the substrate.

The aim of this work is the study of repeated electric stress effects when a field of alternated polarity is applied to two kinds of metal–oxide–semiconductor (MOS) capacitors. This approach will enable us to give complementary information about thickness effects on creation defects and on their electrical behavior when the high electric field polarity changes even if the polycrystalline gates are doped differently (n⁺ and p⁺). We will also discuss the difference in wet and dry oxide technologies.

Our results show some main striking points: First, the electron trapping phenomenon is slightly higher in oxide regions near the Si/SiO₂ interface than near the gate/SiO₂ interface for both oxide thicknesses and technologies. Second, under the same stress conditions, wet oxide contains relatively more trapped effective negative charges than dry oxide. This may be due to water incorporation during the oxidation process. However, this asymmetry intensity remains weak. In addition, electron trapping is reduced in thin oxide. This is consistent with data obtained during unidirectional stress. It is well known that the electron trapping increases with increasing oxide thickness. But for thin oxide, asymmetry of this phenomenon is accentuated at the beginning in bidirectional stress.

We fitted all curves by different simple laws such as logarithmic [Ln(Q_{inj}/Q_0)] and exponential [1−exp−(aQ_{inj}/Q_0)] laws, but all data are well fitted by a power law (Q_{inj}^n) especially of thick oxide, but data of thin oxide are relatively spread. The exponent α depends on field polarity. It seems to depend on oxide thickness, but it is technology independent. An amazing behavior was observed in the variation of tunneling current during bidirectional stress at a constant voltage; this will be discussed below.

In the following, we present sample description and experimental procedure in Sec. II, then results in Sec. III. We discuss these results in Sec. IV, and then in Sec. V, we conclude on the subject by suggesting some prospective studies in order to contribute to the understanding of generation and neutralization mechanisms occurring during bidirectional electron injections in these oxide thicknesses and technologies.

II. SAMPLE DESCRIPTION AND EXPERIMENTAL PROCEDURE

Description of thick oxides (labeled n⁺-poly.Si MOS capacitors) was given in Ref. 8. These samples were supplied by the CEA-LETI of Grenoble, France. For thin oxides (labeled p⁺-poly.Si gate MOS capacitors), we studied MOS structures fabricated on a (100) n-type silicon phosphorus doped to 1.5×10¹⁵ cm⁻³. Oxide thickness (11 nm) was grown at 1100 °C using rapid thermal oxidation (RTO) for 65 s. The p⁺-type polycrystalline (boron doped) gate area is 9×10⁻⁴ cm². The samples have been submitted to annealing at 450 °C in a H₂/N₂ environment. They were supplied by the LAAS of Toulouse, France.

In the present work, we periodically perform electron injection in MOS capacitors from both oxide interfaces.
under a constant high electric field. This field polarity is inverted several times (see Fig. 1). This induces a change on the travel direction of injected electrons through the oxide. We proceed as follows: First, electrons are injected in MOS capacitors under an average oxide field \( E_{\text{ox}} \) (of about 10 MV/cm) for a negative gate bias \( V_g^- \) until reaching a given injected charge density \( Q_{\text{inj}} \). Then electron injection is reversed under the same oxide field but for a positive gate bias \( V_g^+ \) until the same charge value \( Q_{\text{period}} \) is reached. This procedure is repeated several times until the sample breaks down. We notice that the procedure is repeated several times until the sample breaks down much more rapidly than the other sample. For this reason, we choose \( Q_{\text{period}} \approx 0.01 \text{C/cm}^2 \) for thin oxide. For thick oxide, we use a different \( Q_{\text{period}} \) (0.0016–0.32 C/cm\(^2\)). Obtained data show the same behavior.

Figure 2 shows typical curves of tunneling current variations during bidirectional stress of thick oxide. Curves obtained at \( V_g^- \) are less spread than those obtained at \( V_g^+ \). During each injection procedure, either from the silicon substrate or from the gate and then from the silicon substrate under a constant high electric field. This field polarity is inverted several times (see Fig. 1). This induces a change on the travel direction of injected electrons through the oxide.

III. RESULTS

Electrical damages were caused by a high electric field of 10 MV/cm. Electron injections were alternatively made from the gate and then from the silicon substrate under a constant voltage. At each gate bias alternation, the absolute value of injected tunneling current was integrated to give \( Q_{\text{period}} \). The procedure was repeated several times. Oxide defects were extracted from tunneling current during each stress alternation. Effective negative charge measurement from the Fowler–Nordheim (FN) tunneling current expression has been made by DiMaria et al.\(^9\) when they introduced the assumption that the negative charges were localized very near the injecting electrode. In the present work, the negative charges are supposed to be localized at a distance of approximately 3 nm from the injecting electrode, which roughly corresponds to the tunneling distance. Here, we think that electron trapping appears around the tunneling distance, due to the fact that we perform repeated bidirectional stress. Defect density is determined from the standard FN tunneling current expression

\[
I = AE^2 \exp(-B/E),
\]

where \( I \) is the tunneling current. It depends on time \( t \) during stress at constant gate voltage. \( I \) is sensitive to distances around the tunneling distance. \( A \) and \( B \) are the FN parameters considered to be constant. \( E \) is the electric field near the injecting electrode and its expression is given by

\[
E \approx E_0 \frac{Q_n}{e_{\text{ox}}(1 - x_n/t_{\text{ox}})},
\]

where \( t_{\text{ox}} \) is the oxide thickness, \( e_{\text{ox}} \) is the oxide permittivity, and \( x_n \) (\( \approx 3 \text{ nm} \)) is the negative charge centroid. \( E_0 \) is the oxide electric field before stress; i.e., when the potential barrier is supposed to be triangular.

Equation (2) takes into account only the charge trapped near the injecting electrode and not the one near the other electrode because, as our measurements show, the charge trapped near the anode remains weak for both oxide thicknesses. So, its contribution in Eq. (2) does not affect the field variation. Moreover, the \( (Q_n/e_{\text{ox}})/(1 - x_n/t_{\text{ox}}) \) quantity also remains weaker than the average value of \( E_0 \) (3% \( E_0 \) for 17.5 nm oxide and 4% for 11 nm oxide; if \( Q_n = q \times 10^{12} \text{C} \)). If we consider that the contribution of the created negative charges to the field variations remains relatively negligible as shown above, the oxide defect density may be given by

\[
\Delta N_n \approx - \frac{E_0^2}{B} \frac{e_{\text{ox}}}{q} \frac{1}{1 - x_n/t_{\text{ox}}} \ln \left( \frac{I(t)}{I_0} \right),
\]

where \( I(t) \) and \( I_0 \) are the FN currents during and before stress, respectively, and \( q \) is the elementary charge (1.6 \( \times 10^{-19} \text{C} \)). If \( x_n \approx 0 \) (defects would be localized at the cathode), then we find DiMaria’s expression, which underestimates the amount of negative charge. Equation (3) gives

FIG. 1. Bidirectional electric stress cycles. \( V_g^- \) and \( V_g^+ \) lead together to an average oxide field of 10 MV/cm.

FIG. 2. Tunneling current evolution during stress at a constant gate voltage for both polarities (\( V_g^- \): injection from the gate and \( V_g^+ \): injection from the substrate). Curve 1 represents the first stressing current, curve 2 the second, ...etc. Arrows indicate the decrease of tunneling current during bidirectional electron injections.
density of created traps localized near the injecting electrode at a distance $x_n$. As a consequence of bidirectional electron stress, we describe here electron trapping occurrence near both interfaces (gate/oxide and oxide/silicon substrate interfaces). Evolution of the charged trap densities is shown in Fig. 3 for thick oxide as a function of cumulated (total) injected charge $Q_{\text{inj}}$. Data of both technologies are compared.

It is shown that wet oxide contains relatively more negative charge than dry oxide. This is probably due to water incorporation in the oxide. Figure 4 shows data about thin oxide. For the two thicknesses, the oxide regions near the silicon substrate/oxide interface exhibit slightly more defects than those near the gate/oxide interface. The electron trapping is more marked in thick oxide than in thin oxide, but in this oxide asymmetry is accentuated at the beginning of bidirectional stress, for example, at $Q_{\text{inj}}=0.1 \text{ C/cm}^2$ 

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\{\Delta N(V_g^+)/\Delta N(V_g^-)\} \approx 5 \text{ for thin oxide and }\approx 1 \text{ for thick oxide.}
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\{\Delta N(V_g^+)/\Delta N(V_g^-)\} \approx 5 \text{ for thin oxide and }\approx 1 \text{ for thick oxide.}
\]

Even if the slope is reversed at about $Q_{\text{inj}}=0.4 \text{ C/cm}^2$, the $\{\Delta N(V_g^+)/\Delta N(V_g^-)\}$ quotient remains higher for thin oxide than for thick oxide. Considering inversion of the slope, asymmetry of electron trapping will either disappear for high $Q_{\text{inj}}$ or be reversed for the thin oxide. We cannot scrutinize this point for higher fluences because of sample breakdown.

**IV. DISCUSSION**

For the two oxide thicknesses used in this work, we essentially measured density of effective oxide negative charge during electron injections from the gate and from the silicon substrate. We should note that for injections under positive gate bias $V_g^+$, electron trapping essentially appears in oxide regions near the silicon substrate/oxide interface and for injections under negative gate bias $V_g^-$ it appears near the gate/oxide interface. We give some curves where defect density is represented as a function of total injected charge density, i.e., accumulated charge during bidirectional stress $Q_{\text{inj}}$. In other words, this injected charge is the sum of all injected charges during all gate bias alterations ($Q_{\text{inj}}=\sum Q_{\text{period}}$). We should keep in mind that samples are stressed under conditions where hole generation and trapping occur simultaneously, in addition to the electron generation and trapping. For this reason, the measured charge is considered to be effective negative charge. We should also note that tunneling current is very sensitive to defects present near the injecting electrode. So defects localized beyond the tunneling distance do not significantly affect its variation.

We fitted data of Figs. 3 and 4 by different laws such as logarithmic and exponential laws, but the following power law gives the relatively best fitting:

\[
\Delta N_n \propto Q_{\text{inj}}^\alpha,
\]

where $\Delta N_n$ is the density of effective negative oxide charge (lines). Data of the thick oxide are well fitted and we can see the superimposition of experimental points to the linear slope in Fig. 3. However, results obtained on trapped charges in the thin oxide are relatively spread because of the tunneling current instabilities during electron injections from the $p^+$-poly Si gate. That is why we propose two slopes as shown in Fig. 4. The parameter $\alpha$ seems to depend on oxide field polarity and on oxide thickness, but is technology independent.

As a matter of fact, the creation law was previously applied to describe the oxide negative charge buildup after a unidirectional FN stress$^{10,11}$ and used recently to describe the generalized trapping kinetic model for oxide degradation.$^{12}$ In this present study, we apply it to characterize the effective negative charge creation during repeated bidirectional elec-

![FIG. 3. Trapped effective negative charge density $\Delta N_n$ vs injected charge density $Q_{\text{inj}}$ for the two oxide technologies. Experimental results are well fitted by a simple power law as shown ($\alpha\approx0.75$ for $V_g^+$ and 0.5 for $V_g^-$).](image1)

![FIG. 4. Trapped effective negative charge density $\Delta N_n$ vs injected charge density $Q_{\text{inj}}$ for the thin oxide. Here, data are fitted by a power law applied to two different regions; for $Q_{\text{inj}}<0.5$ C/cm$^2$, $\alpha\approx0.75$ for $V_g^+$, and 0.5 for $V_g^-$ and for $Q_{\text{inj}}>0.8$ C/cm$^2$ $\alpha\approx0.3$ for $V_g^+$ and 0.75 for $V_g^-$.](image2)
electron injections under a constant electric field in the FN regime. Results of Refs. 10–12 and ours indicate that the negative charge creation has an intrinsic property, which does not depend on stress conditions either during unidirectional electron injections10–12 or repeated bidirectional stress.8 The power law quoted above always describes the negative charge creation. This leads us to suggest that the microscopic nature of created defect is the same independently of the degradation procedure or of gate bias polarity.

The more striking point revealed by Eq. (4) is that the exponent $\alpha$ value does not depend on oxide technology, but depends on oxide field polarity. Its dependence on oxide thickness is taken carefully. For thick oxide, $\alpha \approx 0.75–0.9$ for $V_g^+$ and 0.5 for $V_g^-$. However for thin oxide, the exponent depends on injected charge $Q_{inj}$ (or on the stress time). For lower $Q_{inj}(<0.5–0.8 \text{ C/cm}^2$), we find the same exponent values as for thick oxide ($\alpha \approx 0.75$ for $V_g^+$ and 0.5 for $V_g^-$), but for higher $Q_{inj} (>0.8 \text{ C/cm}^2$) values are nearly reversed since $\alpha \approx 0.3$ for $V_g^+$ and 0.75 for $V_g^-$. If electron trapping seems to be a simple process in thick oxide, it is more complicated in thin oxide during bidirectional stress.

For both $n^+$-poly.Si and $p^+$-poly.Si MOS capacitors, dependence of the exponent on field polarity means two things. On the one hand, the oxide region near the silicon substrate/oxide interface is more sensitive to bidirectional electric stress than the oxide region near the other side. Therefore, a part of the trapped effective charges near the Si/SiO$_2$ interface, which was not neutralized when this interface was the anode, would probably affect electron injection when this interface becomes the cathode. On the other hand, the energy of injected electrons from the gate would be much higher than those injected from the silicon substrate. Here, the electron energy must be referenced to an energetic position. If it is measured relative to the bottom of the oxide conduction band, energy of electrons injected from both interfaces must be the same. Because an average oxide field has been chosen to be identical for injections from the two sides, the oxide band bending will be the same for the two field polarities. This energy cannot be referenced to the bulk of polycrystalline and crystalline silicon conduction and valence bands, because there is nonnoticeable difference in their relative positions. The only difference would come from the Fermi level position at the anode/oxide interface. Under these conditions, for the $n^+$-poly.Si MOS structure (thick oxide), electrons injected from the gate would be energetically higher than from the silicon substrate, and hence they would create more traps near the silicon substrate/oxide interface. However, for the $p^+$-poly.Si gate MOS capacitor (thin oxide) there is no notable difference in energy of injected electrons relative to the Fermi level position at the anode because when the $p^+$-poly.Si gate is the cathode, the band bending of the gate is very abrupt at the gate/oxide interface. However, when this interface becomes the anode the bands are very nearly flat because the Fermi level is in the valence band. So, to explain the asymmetry appearance by the energy difference is unsatisfactory. Moreover, we have to take into account the electron–phonon interaction in the oxides used in this study.

We will present previous results to explain the asymmetry in oxide defects created during unidirectional stress. Some authors believe that the polycrystalline silicon/oxide interface is the worst due to effects from grain boundaries.13,14 Others believe that the crystalline silicon substrate/oxide interface is the worst due to the oxide transition region.15 Our results are consistent with the latter data rather than the former. However, DiMaria16 has suggested that the energy of the hot injected electrons relative to the Fermi level position at the anode/oxide interface controls the degradation rate in ultrathin oxides (3.5–4.7 nm). In other words, for either $p$-silicon or $n$-silicon substrates electrons injected from the gate (the $n^+$-polycrystalline silicon) are energetically higher relative to the Fermi level at the silicon substrate than those injected from the substrate. In our samples, the situation is much different. We make bidirectional stress; i.e., oxide field polarity is alternatively changed. In addition, we have to take into account the electron–phonon interaction because our samples are relatively thick. The difference in injected energy referenced to the Fermi level cannot explain the observed dissymmetry because it is not consistent with our data. The asymmetry observed in these oxides is caused by another phenomenon, namely the difference between the structural natures of the two oxide interfacial zones.15 Consequently, the negative charge stored near the Si/SiO$_2$ interface during the injection, for which this interface is the cathode, is higher than that stored near the other interface when the Si/SiO$_2$ is the anode. This causes a reduction of density of tunneling injected electrons and probably a reduction of their kinetic energy when the Si/SiO$_2$ interface is the cathode. Under these conditions, the density of created traps near the Si/SiO$_2$ interface increases during the bidirectional stress in comparison with generated traps near the gate/SiO$_2$ interface. Moreover, Fig. 2 shows that reduction in the tunneling current during each injection step under $V_g^-$ is significantly lower than due to the charge trapping during the previous injection in the opposite polarity $V_g^+$. This shows evidence of electron trapping dissymmetry.

We also have to take into account the presence of the positive charge. Its behavior according to the high field polarity and its location near one of the two interfaces (i.e., near the anode) can affect the tunneling electron density. Figure 2 often shows a rapid increase in the tunneling current (showing a creation of positive charge) followed by a long decrease, which is consistent with previous results. It is well known that under a constant gate voltage the tunneling current increases in the beginning of the stress, indicating creation of the positive charge and then decreases showing the apparition of the negative charge in the oxide.15 However, sometimes we observe another behavior of tunneling current variation during bidirectional stress. In the middle of Fig. 2 (at the beginning of each alternation) we notice after many stress cycles that tunneling current decreases at the beginning until a reaching a turnaround point, increases, and then decreases. This point is always situated at $q_{period}=2 \times 10^{-3} \text{ C/cm}^2$. We also notice that this decrease is more and more important during bidirectional stress, until a steady-state value. For both wet and dry thick oxides, we notice that...
this amazing behavior does not appear systematically, but occurs for some conditions. It appears a long time after the first stress cycles and not for any alternation stress. It is well known that if a sample is stressed under a constant current and then submitted to a constant current lower than the stressing one, the corresponding applied gate voltage increases, indicating the presence of electron trapping.\(^{17}\) For the two injecting electrodes (poly. Si gate electrode or silicon substrate electrode) the “extra” diminution observed during bidirectional stress leads us to suggest neutralization of the created positive charge.

The fact that “extra” reduction of tunneling current does not occur systematically at each alternation stress is related to the created positive charge density, to its location from the injecting electrode, and to the tunneling current amount. In other words, the generated positive charge, which is generally assumed localized near the anode, is more or less rapidly neutralized when the field polarity is reversed. The time of neutralization also depends on the current intensity, i.e., when the current intensity is high, the positive charge will be neutralized rapidly. For this reason, first curves do not show “extra” diminution of the tunneling current, because neutralization of positive charge was performed so abruptly that our measurement system could not detect it. These can be considered to be additional proof of the presence of amphoteric defects in the oxide as we suggested previously.\(^{8,17}\) Sometimes we find this behavior in thin oxide.

Concerning the power law exponent variation and the enhancement of the asymmetry in thin oxide, we think that they are linked to created trap distributions in the oxide. In the beginning of bidirectional stress, created traps near the two interfaces are nearly at the same distance from the injecting electrode (≈3 nm from the cathode). In Fig. 4, for \(Q_{\text{inj}}\text{<}0.5\text{C/cm}^2\), density of traps created near the silicon substrate is higher than generated near the gate as quoted above. But for \(Q_{\text{inj}}\text{>}0.5\text{C/cm}^2\), the trap creation kinetic slopes are nearly reversed. This could be explained by the fact that the oxide region near the silicon substrate is the worst region and that electron trapping extends a wide distance, leading to a shift of the negative charge centroid toward the Si/SiO\(_2\) interface. As a consequence, the electric field at the cathode and tunneling current slow down their diminution. For the other interface, we would assume that electron trapping appears predominantly beyond the tunneling distance as bidirectional stress continues, which moves the centroid toward the bulk of the oxide leading to a decrease in the field and consequently in the tunneling current. The shift of the negative charge centroid would occur in thick oxide, but this displacement remains very weak. That is why \(a\) does not vary notably with stress time for thick oxide.

We notice that experimental points for \(V_g\text{1}\) (injections from the gate) shown in Fig. 4 are relatively spread in comparison with the other points. This is related to instabilities of the tunneling current when the \(p^+\)-poly. Si gate MOS capacitor is negatively polarized (at inversion regime). These instabilities are probably caused by the positive charge creation–annihilation phenomena during bidirectional electric stress.

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An “extra” variation in the tunneling current is observed. This appears at the beginning of stress alternation when tunneling current is weak. This “extra” phenomenon is due to the neutralization of the positive charge created during the previous stress and we can assume that the curve given in Fig. 5 could describe the amount of created positive charge. In order to complete this study, it would be interesting to apply this procedure to other thicknesses and other technologies.

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