The Relaxation Phenomena of Positive Charges in Thin Gate Oxide During Fowler–Nordheim Tunneling Stress

Kow-Ming Chang, Member, IEEE, Chii-Horng Li, Shih-Wei Wang, Ta-Hsun Yeh, Ji-Yi Yang, and Tzyh-Cheang Lee

Abstract—In this study, new relaxation phenomena of positive charges in gate oxide with Fowler–Nordheim (FN) constant current injections have been investigated and characterized. It was found that the magnitudes of applied gate voltage shifts \( \Delta V_{FN} \) during FN injections, after positive charges relaxed or discharged, have a logarithmic dependence with the relaxation time for both injection polarities. The results can derive the relationship of transient discharging currents, that flow through the oxides after removal of the stress voltage, with the relaxation time. We have shown that the current has a \( 1/t \) dependence for both injection polarities which can be also derived from the tunneling front model. The effects of oxide fields (lower than the necessary voltage for FN tunneling) and wafer temperatures (373 and 423 K) for the relaxation of positive charges are also studied.

Index Terms—Fowler–Nordheim tunneling, gate oxide, positive charges, stress.

I. INTRODUCTION

The application of high electrical field to gate oxide, as used for Fowler–Nordheim (FN) tunneling, induces a degradation of this oxide film due to the generation of interface states, positive and negative charges in the oxide. It is observed that the magnitude of applied gate voltage, during constant current stress of FN tunneling, decreases at lower injection electron fluences and then begins to increase when the voltage goes through a minimum point [1]–[4]. A typical example of the variation of applied gate voltage during constant FN tunneling current stress is shown in Fig. 1. Positive charge trapping dominates during the initial period of current stressing which is denoted as region I in Fig. 1. Followed by the region I, the region II is dominated by the negative charge trapping. The positive charges in the oxide films of MOS capacitors have been largely studied [5]–[13] and have been found that they can be charged/discharged [10], [14]–[16]. To discharge (or relax) the positive charges without any applied voltage takes several minutes or more [17], [18].

The charging/discharging phenomena can be explained by the flow of electrons in and out of traps generated by the high field stress [14]. It is also found that the flat-band voltage recovery shows a logarithmic dependence in the time regime [10]. In previous studies [6], [10], [14], [16], the flat-band voltage shift and midgap voltage variations are usually used to demonstrate the discharging effect. It is also found [6] that if the first stress current of constant FN tunneling is larger than the following second stress current, the magnitude of applied gate voltage during the second FN stress will increase. However, the magnitude of the applied gate voltage shifts and their relationship with positive charges, after different relaxation times, are still not observed.

In this paper, we use the magnitude of applied gate voltage shifts \( \Delta V_{FN} \) during different constant FN current stresses, after positive charges generated and discharged, to demonstrate the relaxation phenomena. The positive charges formation and relaxation (discharging) are studied for two injection polarities (i.e., injections from the gate and from the substrate). We find that there is also a logarithmic dependence between the \( \Delta V_{FN} \) and the relaxation time. Moreover, the logarithmic dependence can derive the relationship of transient discharging currents, that flow through the oxides after removal of the stress voltage, with the relaxation time and would be proportional to \( 1/t \) which can be also derived from the tunneling front model. The effects of oxide fields (lower than the necessary voltage for FN tunneling) and wafer temperatures (373 and 423 K) for the relaxation of positive charges are also studied.

II. EXPERIMENTS

A. Device Fabrication

The devices used in this study were \( n^+ \) polysilicon gate MOS capacitors fabricated on n-type (3–5 \( \Omega \)-cm) and p-type
CHANG et al.: RELAXATION PHENOMENA OF POSITIVE CHARGES IN THIN GATE OXIDE

(8–11 Ω-cm) wafers using standard LOCOS isolation, with a field oxide of 400-nm thickness. A 25-nm sacrificial oxide was then grown and stripped. The gate oxides of 8 nm thickness were grown in diluted dry O\textsubscript{2} (N\textsubscript{2}/O\textsubscript{2} = 6/1) at 900 °C, A 300 nm thickness polysilicon film was deposited by low pressure chemical vapor deposition (LPCVD), and doped n\textsuperscript{+} at 875 °C from POCl\textsubscript{3} source for 30 min. Then, a 500 nm thickness Al film was deposited by thermal evaporation and patterned. The backsides of wafers were also deposited 500 nm thickness Al films. It has been shown that the H-related species degrade gate oxide film [19], therefore, the post metalization annealing (PMA) was done in N\textsubscript{2} ambient at 400 °C for 30 min to minimize hydrogen incorporation into gate oxide. The capacitor areas were 1 \times 10^{-8} \text{cm}^2 with circular shapes. All devices were tested in accumulation regions. This means that substrate injection was performed on n-type wafers and gate injection was performed on p-type wafers to avoid the effect of white lights which were needed when the devices were tested at inversion regions. The gate oxide thicknesses were determined from ellipsometric measurements and were consistent with the C-V measurements.

B. Electrical Measurements

First, the samples were stressed at larger FN tunneling constant current density, which was denoted as $I_{_{\text{gen}}}$ (100 mA/cm\textsuperscript{2}), to the turn-around point (0.1 C/cm\textsuperscript{2}) to ensure more positive charges generated and less negative charges generated in the oxide. The injections were performed either from the gate or from the substrate. Then the stressed samples were stressed again with smaller constant current FN tunneling density, which was denoted as $I_{_{\text{tens}}}$ (0.1 or 10 mA/cm\textsuperscript{2}) after the relaxation of 10, 10\textsuperscript{2}, 10\textsuperscript{3}, and 10\textsuperscript{4} s, to reveal the properties of traps generated by $I_{_{\text{gen}}}$. During the period of relaxation, there is no gate voltage applied. On the other hand, different temperatures (373 and 423 K) were used during FN stress and relaxation periods to investigate the temperature effects. The applied gate voltage shifts ($\Delta V_{_{FN}}$) during $I_{_{\text{tens}}}$ stress were used to demonstrate the relaxation (discharging) phenomena.

After $I_{_{\text{gen}}}$ stresses, for both injection polarities, we applied ±4 MV/cm constant field (no FN tunneling injection happened) for 20 s. Then the samples were stressed by $I_{_{\text{tens}}}$ to investigate the effect of oxide field for positive charge relaxation.

The applied gate voltage shifts ($\Delta V_{_{FN}}$) and the transient current were measured using a HP 4145B semiconductor parameter analyzer and a HP 4140B pA meter, respectively.

III. RESULTS AND DISCUSSION

A. The Relationship Between $\Delta V_{_{FN}}$ and Relaxation Time

After the generation of positive charges by $I_{_{\text{gen}}}$ (100 mA/cm\textsuperscript{2}) stressing and waiting for 10, 10\textsuperscript{2}, 10\textsuperscript{3}, and 10\textsuperscript{4} s to relax the positive charges, $I_{_{\text{tens}}}$ (0.1 mA/cm\textsuperscript{2}) was performed to investigate the relaxation phenomenon. Fig. 2(a) shows the variation of applied gate voltage for substrate injection during $I_{_{\text{tens}}}$ stress. The gate voltage shift ($\Delta V_{_{FN}}$) used in our study is defined as the difference of gate voltage at the end of $I_{_{\text{tens}}}$ stress, in which the gate voltage seems to saturate, and at the start point of the stress. If the investigation is from the viewpoint of applied gate voltage shift, as shown in Fig. 2(b), a trend of the shifts can be observed. The arrow line in Fig. 2(b) indicates this trend which is from positive to negative when relaxation time increases. If the $I_{_{\text{tens}}}$ stress (0.1 mA/cm\textsuperscript{2}) is quickly performed, the gate voltage ($V_{_{\text{tens}}}$) shift is positive which means some injected electrons are trapped in the oxide [6]. However, if the $I_{_{\text{tens}}}$ are performed after a longer relaxation time passed, the gate voltage shift becomes negative. This indicates that some positive charges are compensated in relaxation period.

It is believed that if the stress voltage is removed and there is no other applications of gate voltage to oxide film, the positive charges can be compensated (discharged) by the electrons tunneling from the electrode into the charged sites...
The amount of compensated positive charges is increased with relaxation time. Hence, the gate voltage shifts are from positive to negative and close to the value which is without the $I_{gen}$ stress.

The variations of $\Delta V_{FN}$ with relaxation time for gate and substrate injections are plotted in Fig. 3. It can be found that $\Delta V_{FN}$ has a logarithmic dependence in the relaxation time regime. The relation can be written as

$$\Delta V_{FN}(t) = \pm R_0 \times \log \left( \frac{t}{T_0} \right), \quad t > 0$$

(1)

in which $\Delta V_{FN}$, $t$, and $T_0$ are the applied gate voltage shift, the relaxation time, and the time constant when $\Delta V_{FN}$ is zero, respectively. $R_0$ is the slope of the curve which reveals the relaxation rate of positive charges. Positive sign is for gate injection and negative sign is for substrate injection. The values of $R_0$ for gate injection (p-type wafers) and substrate injection (n-type wafers) are 0.013 and 0.01, respectively. The relaxation rate of gate injection stress is slightly larger than that of substrate injection stress. Injection of electrons from poly-Si may cause more damage than from the Si substrate [21]. Hence, the energy levels, centroid or density of positive traps for gate injection are different from those for substrate injection, and different relaxation properties are revealed.

The shifts of $V_{FN}$ can be written in terms of the charge densities and their locations in the following way [1]:

$$\Delta V_{FN}(t) = \frac{Q(t)}{\varepsilon} \pi(t), \quad \text{for substrate injection}$$

(2a)

$$\Delta V_{FN}(t) = -\frac{Q(t)}{\varepsilon}(d_{ox} - \pi(t)), \quad \text{for gate injection}$$

(2b)

where $Q(t), \varepsilon, d_{ox}$ and $\pi(t)$ are the positive charge density per unit area, oxide permittivity, oxide thickness and the charge location, respectively. Equations (1)–(2) yield

$$Q(t) = -\frac{\varepsilon}{\pi(t)} R_0 \times \log \left( \frac{t}{T_0} \right), \quad \text{for substrate injection}$$

(3a)

$$Q(t) = -\frac{\varepsilon}{d_{ox} - \pi(t)} R_0 \times \log \left( \frac{t}{T_0} \right), \quad \text{for gate injection}.$$  

(3b)

If $\pi(t)$ is about constant, then we can find the discharging current

$$|J(t)| = \frac{\varepsilon}{d_{ox} - \pi(t)} R_0 \times \frac{1}{t}, \quad \text{for substrate injection}$$

(4a)

$$|J(t)| = \frac{\varepsilon}{\pi(t)} R_0 \times \frac{1}{t}, \quad \text{for gate injection},$$

(4b)

The discharging current has a $1/t$ dependence which is the same as the results derived from tunneling front model [22]. In other words, the variation of $V_{FN}$, as seen in Fig. 2(b), is due to the discharging of trapped charges in oxide film. We have taken (4) to simulate the transient discharging current. For gate injection and oxide dielectric constant is 3.9. Fig. 4 shows the transient current of MOS capacitors after $I_{gen}$ (100 mA/cm²) stress and the simulated results from (4b). It is found that the simulated results and the experimental results are matched well. Moreover, it is known that the flat-band voltage shift has a logarithmic dependence with discharging time [10] and, if interface states are assumed constant in the relaxation period, a similar equation as (4) can be also derived.

**B. The Characteristics of $\Delta V_{FN}$ Under Different $I_{Ioxos}$ Stress**

In previous study [6], as the $I_{Ioxos} < I_{gen}$, the applied gate voltage during $I_{Ioxos}$ stress increased. This was attributed to that the electrons injected by $I_{Ioxos}$ recombined with the positive charges. However, in our study, we find that the gate voltage, for $I_{Ioxos} < I_{gen}$, does not always increase during the following $I_{Ioxos}$ stress. Fig. 5 shows the $\Delta V_{FN}$ variation with stress time when the $I_{Ioxos}$ is 10 or 100 mA/cm² injected from substrate. From this figure, when $I_{Ioxos}$ is 10 mA/cm² which is smaller that $I_{gen}$ (100 mA/cm²), $\Delta V_{FN}$ is negative and is different from the observation of the earlier study [6]. However, as seen in Fig. 2(b), when $I_{Ioxos}$ is 0.1 mA/cm², a positive gate voltage shift variation is observed. These results suggest that, except the stress current, the oxide field during stress, the centroid of positive charges and their energy levels may also affect the results of $I_{Ioxos}$ stress.
Fig. 5. The variation of gate voltage shift when $I_{\text{stress}}$ is 10 mA/cm² or 100 mA/cm². The $I_{\text{gate}}$ is 100 mA/cm².

Fig. 6. (a) The schematic process of positive charge compensation during $I_{\text{stress}}$ stress. Curve (a) is for smaller $I_{\text{stress}}$ stress and (b) is for larger $I_{\text{stress}}$ stress. The electrons in the oxide conduction band can be trapped into the positively charged sites. For larger $I_{\text{stress}}$ measurement, the trapped electrons can easily escape from these traps by tunneling out or by crossing the trap barrier height due to the larger oxide field as shown in curve (b). Hence, the positive charges are not relaxed. However, for smaller $I_{\text{stress}}$ stress, the field in oxide film is smaller and the trapped electrons hardly escape from the traps. Then the positive charges are compensated by the trapped electrons. Fig. 6(b) is the relaxation of positive charges without any gate voltage applied. It is known that the centroid of positive charges is near the electrodes [1], [4], [6], [19], [20] and can be easily discharged by the electrons tunneling from electrodes [10], [14]. Hence, the amount of relaxed positive charges become larger for longer discharging time passed.

C. The Effects of Temperature and Electric Fields

Fig. 7(a) shows the $I_{\text{DOS}}$ stress curve at room temperature, 373 and 423 K after $10^2$ s relaxation for substrate injection stress. Fig. 7(b) is under the same conditions of Fig. 7(a) but for gate injection stress. It can be found that $\Delta V_{\text{FN}}$ is shifted to...
negative at higher temperature while it is positive at room temperature. A turn-around phenomenon reveals in Fig. 7 at 373 and at 423 K. We find that, at higher temperatures, negative charge generation process is more significant than the creation of positive charges in oxide film. Similar results at higher temperatures can be seen from the curves, in Fig. 8, during $I_{gen}$ stress at different temperatures. The injection polarity in Fig. 8 is from substrate. Negative charge generation region (region II as shown in Fig. 1) has been seen at 423 K while positive charge creation (region I) is still dominated at room temperature. Turn-around point is also shifted to lower electron fluence at higher temperature. Hence, the phenomena in Fig. 7 may be due to the enhanced negative charge generation at higher temperature. Similar results can be also observed on the gate injection stressed samples.

The effects of oxide field during positive charge relaxation are shown in Fig. 9. The injection polarity is from gate. Curve (a) is without any voltage applied, curve (b) is for $-4$ MV/cm applied, and curve (c) is for $+4$ MV/cm applied. After $I_{gen}$ (100 mA/cm²) stress, we applied a field of $\pm 4$ MV/cm (this field do not form FN tunneling) to the stressed samples for 20 s. Then we apply $I_{stress}$ ($0.1$ mA/cm²) to observe the variation of $\Delta V_{FN}$. After $I_{gen}$ stress, the centroid of positive charges are near the anodes [1], [6]. If the applied voltage is with the same polarity of $I_{gen}$, the relaxation of positive charges is expected to be retarded. On the other hand, if the polarity of the constant voltage is opposite to that of $I_{gen}$, the relaxation is expected to be enhanced. We find that the increase of the positive charges relaxation rate for $+4$ MV/cm applied is higher than that of the case for $-4$ MV/cm. Similar results can be also observed on the samples with substrate injection polarity. This observation is similar to the results of Lakshmananna et al. [10] and Scott et al. [14], [15].

IV. CONCLUSION

In conclusion, new relaxation phenomena of positive charges in gate oxide with FN constant current injections have been investigated and characterized. There is a logarithmic relationship between the shifts of applied FN voltage and the relaxation time. We have correlated $\Delta V_{FN}$ with the transient discharging current and have derived the relationship of transient current with relaxation time which is proportional to $1/t$. This means that the variation of $\Delta V_{FN}$ is due to the discharge of trapped charges. The result is consistent with that derived from the tunneling front model. On the other hand, under larger oxide field, electrons injected by $I_{gen}$ which are trapped with positive charged sites can escape these positive traps, and the variation of $\Delta V_{FN}$ is different with that under smaller oxide field. At higher temperature, negative charges are more easily generated than the positive charges. Moreover, the applied oxide field during charge relaxation can affect $\Delta V_{FN}$. If the applied voltage is with the same polarity of $I_{gen}$, the relaxation of positive charges is expected to be retarded. On the other hand, if the polarity of the constant voltage is opposite to that of $I_{gen}$, the relaxation is expected to be enhanced.

REFERENCES

Kow-Ming Chang (M’88) received the B.S. degree (with Great Distinction) in chemical engineering from National Central University, Chung-Li, Taiwan, R.O.C., in 1977, and the M.S. and Ph.D. degrees in chemical engineering from the University of Florida, Gainesville, in 1981 and 1985, respectively. His doctoral research concerned the processing technologies of compound semiconductors.

In 1985, he joined the Department of Electronics Engineering and Semiconductor Research Center, National Chiao-Tung University, Hsinchu, Taiwan, where he is currently a Professor. From 1989 to 1990, he was a Visiting Professor in the Electrical Engineering Department, University of California, Los Angeles, where he was engaged in research on the system design of electron cyclotron resonance chemical vapor deposition (ECR-CVD) for developing the low-temperature processing technology. He was in charge of a 500 kV ion implanter, selective tungsten LPCVD system, and two UHV-ECR-CVD systems installed in National Nano Device Laboratory (NDL) at the National Chiao-Tung University. His current research interests are in the physics, technologies, and modeling of heterojunction devices and optoelectronic devices, ULSI key technologies, CMOS devices, and MOCVD technologies. He has published over 80 articles in these fields and has served as a reviewer for international journals such as IEEE ELECTRON DEVICE LETTERS and the Journal of the Electrochemical Society.

Dr. Chang is member of Phi Tau Phi, AIChE, and the Electrochemical Society.

Shih-Wei Wang was born in Pingtong, Taiwan, R.O.C., on December 25, 1969. He received the B.S. degree in electrical engineering from National Central University, Chung-Li, Taiwan, in 1992, and the Ph.D. degree in electronics engineering from National Chiao-Tung University, Hsinchu, Taiwan, in 1997. His research interests are in the areas of the metallization and intermetal dielectric fabrication technology and reliability for VLSI back-end process.

Chii-Horng Li was born in Taipei, Taiwan, R.O.C., in 1969. He received the B.S. degree from the Department of Electronics Engineering, National Chiao-Tung University, Hsinchu, Taiwan, in 1992. He is currently pursuing the Ph.D. degree in the Institute of Electronics, National Chiao-Tung University. His research interests include fabrication technology and reliability of thin gate oxides.

Ji-Yi Yang was born in Taoyuan, Taiwan, R.O.C., in 1969. He is currently pursuing the Ph.D. degree in the Institute of Electronics, National Chiao-Tung University, Hsinchu, Taiwan. His research interests include retrograde well MOS design and the fabrication of low dielectric constant intermetal dielectrics.

Ta-Hsun Yeh was born in Taiwan, R.O.C., on August 14, 1967. He received the B.S. degree in electrical engineering from National Central University, Chung-Li, Taiwan, in 1989, and the Ph.D. degree from the Institute of Electronics, National Chiao-Tung University, Hsinchu, Taiwan, in 1997. His research interests include the CVD-W process and related metallization technologies for ULSI applications.