I. INTRODUCTION

As the oxide thickness shrinks to nanometer range (<10 nm), the reliability of these oxides has become one of the most important issues among all of the electrical and material properties. The conventional silicon dioxide grown in a furnace using the thermal oxidation method has reached its physical limitations for subquarter-micron metal–oxide–semiconductor field effect transistors (MOSFETs) with respect to gate oxide thickness in the range of 3–5 nm. As a result, various types of doped oxides have been used to replace the conventional thermal oxides. Fluorine- and nitrogen-doped silicon oxides are the most popular candidates because of their versatile advantages; the former possesses the following characteristics: decreased dielectric constant $K$, enhanced oxidation rate, relaxed oxide stress, increased transconductance $g_m$, decreased interface trap density $D_{it}$, suppressed hot-electron induced generation of $D_{it}$, increased breakdown field, improved radiation hardness, and stress hardness. 1–8 The latter has the subsequent distinctions of: increased hot-carrier immunity, decreased electron trapping due to the pileup of $N$ at the SiO$_2$–Si interface, increased current drive in MOSFETs, reduced boron (B) diffusivity caused by the formation of $p^+$-polysilicon gates, increased charge-to-breakdown, and reduced threshold voltage ($V_{th}$) shift and $g_m$ degradation. 9–14

In the literature reported so far, fluorinated silicon oxides can be fabricated using various methods such as immersing Si wafer in HF and then oxidizing the wafer, 6 ion-implanting with F 5 or using liquid phase deposition, 15 while nitrided silicon oxides are capable of being fabricated from nitridation in NH$_3$, NO, or N$_2$O gases. 16–18 In order to obtain an improved oxide film carrying the properties mentioned above, it is our strong motive to incorporate both F and N into silicon dioxide to attain an oxide of remarkable quality with mixed characteristics. In fact, many investigators have studied the possibility of incorporating both F and N into silicon dioxide by using several different techniques: (i) thermal oxidation of Si by N$_2$O and NF$_3$ gases, 19 (ii) N$_2$O plasma treatment on plasma-enhanced chemical vapor deposition (PECVD)-grown fluorinated silica glass (FSG), 20 (iii) NH$_3$-added PECVD-grown FSG, 21 and (iv) fluorination + nitridation under microwave plasma for SiO$_2$. 22 Concurrently, the Auger depth profile, the adhesion properties of SiOFN to Si, bonding network of oxide, and surface roughness of SiOFN were fully discussed. All of these results showed positive trends with excellent dielectric properties after incorporating multiform impurities into the fabrication of SiO$_2$ films.

Excluding all of these improvements, however, the incorporation of N by NH$_3$ would introduce a large amount of electron traps in the films. 23–25 It is well accepted that the presence of electron traps degrades the device performance. The incorporation of F would also lead to some oxide traps (i.e., Si dangling bonds) that increase the leakage current under moderate electric fields. 26 To keep the advantages of incorporating F and N into the SiO$_2$, the concentration of impurities must be maintained below a sufficient low level. For ultrathin oxides, the conduction mechanism has been widely discussed because it would affect the device on/off characteristics under normal operating voltages. It is well known that oxide degrades as the thickness reduces to less than 10 nm, physically limited to 3 nm. Inbetween this thickness range, many types of tunneling current are reported. 27 Some traps exist in doped oxides and then could affect the electron tunneling properties when electric fields are applied. It is essential to clarify the position and concentration of these impurities in oxides and to understand their effects on the electrical properties.
In this paper, the leakage current–voltage ($I$–$V$) characteristics of SiO$_2$ incorporated with F and/or N are discussed. The leakage current could be described by a trap-assisted tunneling (TAT) model. We have developed a generalized TAT model$^{28}$ to explain the leakage current of SiON films. This model includes trapezoidal- and triangular-barrier tunnelings under the electric fields of 4–6 MV/cm and 6–8 MV/cm, respectively. We have successfully modeled the conduction properties of nitrided oxides at 4–8 MV/cm. In this study, this model is used to simulate the $I$–$V$ curves and generate two parameters: trap energy level $\Phi_t$ and trap concentration $N_t$. The advantage of this model is to derive them to get the corresponding electric fields. It is found that the presence of both F and N in SiO$_2$ film reveals a complex property in terms of $F$. Demonstrated by different experimental conditions, i.e., an-...
the increasing slope is very different among them. This means that the detailed conduction mechanism is worth discussing. In Fig. 1(b), a Fowler–Nordheim (FN) plot is provided to extract the effective barrier height Φ₀.

\[ J = A \times E_{ox}^2 \times \exp \left( \frac{B}{E_{ox}} \right), \]

(1)

where \( A \) and \( B \) are functions of barrier height \( \Phi_B \), and \( E_{ox} \) is the oxide electric field. By plotting \( \ln(J/E_{ox}) \) versus \( 1/E_{ox} \), the slope of this straight line produces \( \Phi_B \) according to Eq. (1). The corresponding \( \Phi_B \) for each sample is listed in the inset of this graph. Pure SiO₂ has a value of \( \Phi_B = 2.98 \) eV which is close to that of the Al–SiO₂ system (= 3.15 eV).

However, other F- and/or N-doped SiO₂ films have much smaller \( \Phi_B \) values, indicating that another conduction mechanism other than FN tunneling should be considered in these cases.

In the literature, many different types of conduction processes in insulators were listed by Sze.\(^{27}\) For silicon–oxide films, four models relating to traps could be obtained; that is, ohmic conduction, Poole–Frenkel emission, Fowler–Nordheim tunneling, and trap-assisted tunneling. These conduction models will be briefly discussed in the following.

First of all, ohmic conduction is the thermally excited electron hopping from one state to another and contributing to the output current. It dominates at moderate temperatures and low fields (0–0.2 MV/cm), which can be expressed as

\[ J \sim E_{ox} \times \exp \left( -\frac{E_{act}}{kT} \right), \]

(2)

where \( E_{ox} \) is the oxide field and \( E_{act} \) is the activation energy of electrons. This model was also used to simulate the leakage current at low fields in CVD–SiOF.\(^{30}\) In this case, by carefully observing the current–voltage of LPD–SiOF films, it can be seen that this model could not simulate current at low fields because no current with electric field dependency is measurable (i.e., the current shows a noisy value and is below the sensitivity of the instrument at these fields).

Another model called Poole–Frenkel (PF) emission is described as the thermal excitation of trapped electrons into the conduction band with the assistance of field enhancement. This model is usually used to explain the conduction mechanism of Si₃N₄ (Ref. 27) or Ta₂O₅ film,\(^{31}\) which governs at high temperature and high fields:

\[ J \sim E_{ox} \times \exp \left[ -\frac{q(\Phi_t - \sqrt{qE_{ox}/\pi \varepsilon})}{kT} \right], \]

(3)

where \( \Phi_t \) is the trap density and \( \varepsilon \) is the dielectric constant. From Eq. (3), we can plot \( \ln(J/E_{ox}) \) versus \( E_{ox}^{1/2} \) to obtain \( \Phi_t \) from the intercept at the \( y \) axis and \( \varepsilon \) from the slope, respectively. Figure 2 shows an example of a current–voltage of 900 °C O₂-annealed LPD–SiOF films with oxide thickness of 9.1 nm. From the linear part of current–voltage at high fields, \( \Phi_t \) is estimated to be 1.42 eV and \( \varepsilon \) is 0.283. Clearly, this value of \( \Phi_t \) is reasonable but \( \varepsilon \) is too small and it is quite far from the normal value of \( \varepsilon = n^2 = 1.46^2 \) for silicon–oxide. It is concluded that the PF emission model is not suitable to our LPD–SiOF films.

**B. GTAT model**

Figure 3 briefly shows the energy band diagram of the Al–SiO₂–Si structure under two different tunneling processes. For pure SiO₂, the dominant tunneling process occurs at high electric field of 8 MV/cm, which is called Fowler–Nordheim tunneling (FNT). This has been verified by using curve fitting (current–voltage) in Fig. 1(b). For the second case of the TAT process, the electrons tunneling from the left are injected into the traps existing in the oxide with tunneling probability \( P_{in} \). Then these captured electrons are...
emitted again to tunnel through this oxide with tunneling probability $P_{\text{out}}$. In Fig. 3 it is found that the tunneling electrons meet either triangular barrier [denoted as TAT(Tri.)] or trapezoidal barrier [denoted as TAT(Tra.)] depending on the electric field across the oxide. In this model, we assume that the traps possess an energy level of $\Phi_i$ below the oxide conduction band and they are uniformly distributed all over the oxide. The relationship of $J$ and $E_{\text{ox}}$ can be approximated as

$$J \sim \exp \left( -\frac{4\sqrt{2qm_{\text{ox}}}}{3h} \Phi_i \sqrt{2/\varepsilon} / E_{\text{ox}} \right),$$

where $\Phi_i$ can be directly derived from the slope of the linear part in the $\ln(J/E_{\text{ox}})$ versus $1/E_{\text{ox}}$ plot. Figure 4 shows the TAT plot using our GTAT (solid line) model, while the F–N fitted curve is also shown as a dashed line. $\Phi_i$ is calculated to be 1.89 eV, $\Phi_B$ is 2.47 eV, and $N_t$ is $6 \times 10^{16}$ cm$^{-3}$. Note that $\Phi_B$ is an effective value that is different from 3.15 eV for Al–SiO$_2$. Obviously, the current–voltage curve at 5–9 MV/cm can be divided into two regions; TAT and FN tunneling. Hence TAT with uniformly distributed trap concentration is the best model to explain the conduction mechanism in medium fields (5–7 MV/cm).

**FIG. 2.** A current–voltage example of 900 °C O$_2$-annealed LPD–SiOF films with 9.1 nm oxide thickness.

**FIG. 3.** Energy band diagram of Al–SiO$_2$–Si structure under two different tunneling processes: FNT and TAT.

**FIG. 4.** TAT plot by our GTAT (solid line) model for the sample in Fig. 3. F–N fitted curve is also shown as dash line.

### C. Simulations of GTAT model

To have more insight into the effect of the trap energy level $\Phi_i$ and trap concentration $N_t$ for current–voltage curves in the GTAT model, we have performed some simulations on devices having these parameters: $\Phi_i$ = 1.2–2.6 eV, $N_t$ = $2 \times 10^{13}$–$2 \times 10^{20}$ cm$^{-3}$, $T_{\text{ox}}$ = 5 nm, and $\Phi_B$ = 3.2 eV. Figure 5(a) shows the effect of trap energy level on the leakage current and Fig. 5(b) presents the leakage current density at 6.5 MV/cm as a function of the trap energy level. From this graph, it is clear that the leakage current increases with the increase of trap energy level from 1.2 to 1.8 eV to reach its maximum value and then decreases from 2 to 2.6 eV. Basically, the leakage current is changed by 3–4 orders of magnitude in accordance with the variation of the trap energy levels. This particular phenomenon could also be seen in the ONO interpoly dielectric of erasable programmable read-only memories. The maximum value at about 1.8–1.9 eV is the result of tunneling-in probability ($P_{\text{in}}$) and tunneling-out probability ($P_{\text{out}}$). The tunneling rate $R \approx (P_{\text{in}} \times P_{\text{out}})/(P_{\text{in}} + P_{\text{out}})$; therefore, it has a maximum value of 0.5$\times$ $P_{\text{in}}$.

Figure 6(a) shows the effect of trap concentration on the leakage current and Fig. 6(b) presents the leakage current density at 6.5 MV/cm as a function of trap concentration. With the increase of trap concentration from $2 \times 10^{13}$ to $2 \times 10^{20}$ cm$^{-3}$, the leakage current increases monolithically, indicating that trap concentration has a direct relationship with tunneling currents in an oxide film. In order to reduce the leakage current, traps existing in an oxide must be sufficiently reduced.

Since the current–voltage curves of doped SiO$_2$ films (SiOF, SiON, and SiOFN) could not be adequately modeled by FN tunneling, we use the GTAT model to simulate these curves and their results are shown in Fig. 7. The table in this figure presents some values obtained from the GTAT model. One point worth noting is that the value of $\Phi_i$ extracted in our experiments is accepted when comparing it to other investigators: 1.3–1.6 eV by Ramesh et al., 2.46–2.55 eV by Cheng et al., and 2.1–2.7 eV by Fleischer et al.
concentrations are on the order of $10^{15} - 10^{17}$ cm$^{-3}$ depending on the impurity types, annealing times, and oxide thickness. It is concluded in this section that GTA T is the best model to describe the leakage current of impurity-doped SiO$_2$ films.

D. Effect of annealing temperature for SiOF

Figure 8 illustrates the effect of annealing temperature on the current–voltage curves of LPD–SiOF films. Three temperatures are used in this study: 850, 900, and 950 °C. From the simulation results, $\Phi_t$ is about 2.2 eV and trap concentration decreases as annealing temperature increases. Although curve 1 is annealed in 850 °C for 15 min (i.e., longer than others, 5 min), its trap concentration is still the highest one. This indicates that trap concentration will be much higher with short time annealing of 5 min. Therefore, high temperature annealing can effectively remove the traps in oxide films. Using the GTA T model, we would get the evolution of traps in an oxide film when different annealing temperatures or times are performed.

The initial LPD–SiOF films are grown for 10 min. From the simulation results, $\Phi_t$ is about 2.2 eV and trap concentration decreases as annealing temperature increases. Although curve 1 is annealed in 850 °C for 15 min (i.e., longer than others, 5 min), its trap concentration is still the highest one. This indicates that trap concentration will be much higher with short time annealing of 5 min. Therefore, high temperature annealing can effectively remove the traps in oxide films. Using the GTA T model, we would get the evolution of traps in an oxide film when different annealing temperatures or times are performed.
E. Effect of initial oxide thickness for SiOF

The fluorinated SiO2 can be grown from the LPD method since F is capable of being naturally incorporated in the SiO2 film as can be seen from the depth profile of Auger electron spectroscopy. As the thickness of oxide is reduced to 10 nm and below, thin oxide becomes much more leaky than the thick one within this range. Thus, it is recommended that we perform O2 annealing on LPD–SiOF film in order to reconstruct the mismatched network of oxide bonding during deposition. After this treatment, the leakage current is greatly improved so as to be comparable with thermal oxide. Figure 9 shows the current–voltage curves for different initial LPD–SiOF thicknesses with O2 annealing at 900 °C. Fluorine concentration is controlled by the initially deposited LPD–SiOF film using different times. This figure demonstrates the TA T range of $E_{ox} = 4–9$ MV/cm only. Our GTAT model is used to simulate the current–voltage curves and their results are listed in the inset. The value of $\Phi_t$ ranges from 1.62 to 1.83 eV, while $N_t$ increases ($\approx$ 4 orders of magnitude) with the increase of time for the initially deposited LPD–SiOF film. The variation of $\Phi_t$ may be attributed to the oxide thickness and annealing steps.

F. Effect of annealing time in O2 or N2O gas

Figures 10 and 11 show some results (current–voltage curves and GTAT modeling) of LPD–SiOF films annealed in O2 and N2O gases at 900 °C for 5–20 min. Annealing in O2 can substitute F with O in LPD–SiOF films and then leads to a denser structure having less dangling bonds within the oxides. Also, with the increase of annealing temperature or time, some weak Si–F bonds are driven out, leaving strong Si–F bonds in the oxides. Therefore, trap concentration relating to the incorporation of F in a SiO2 film is reduced with the increase of annealing temperature and time. The incorporation of nitrogen (annealed in NH3, NO, or N2O gases) into SiO2 is demonstrated to improve the strength of oxide’s bonding network by introducing strong Si–N bonds near the interface, and by increasing the endurance of trap creation. If nitrogen is introduced into a F-contained SiO2 system, a much more complex tetrahedral structure is
formed, F–Si(O_{1–x}N_{x}), x = 0 – 3.21 In this article, our LPD–SiOF films annealed in N\textsubscript{2}O will become SiOF:N films. Of course it is evident that longer annealing time leads to smaller trap concentration due to the N passivation effect in the Si–O–Si bonding network. In this discussion, trap concentrations between O\textsubscript{2}- and N\textsubscript{2}O-annealed LPD–SiOF films are compared.

For O\textsubscript{2} annealing shown in Fig. 10, \( N_t \) decreases from \( 8 \times 10^{17} \) to \( 1 \times 10^{16} \) cm\textsuperscript{-3} as the time is increased to 10 min. After 15 min of annealing or more, GTAT could not be used to model the current–voltage curves. \( \Phi_B \) is about 2.5 eV in this case. A second case for N\textsubscript{2}O annealing is shown in Fig. 11: \( N_t \) is as low as \( 10^{15} \) cm\textsuperscript{-3}, 2 orders lower than that in O\textsubscript{2} annealing. But \( \Phi_B \) is 1.24 and 1.85 eV for 5 and 10 min of annealing. These values of \( \Phi_B \), different from the first case, may arise from the incorporation of N in LPD–SiOF film to change its energy level (a combination of effects as a result of incorporating both nitrogen and fluorine). After a long period of annealing (15 and 20 min), \( \Phi_B \) is similar to that in O\textsubscript{2} annealing. These facts tell us that N\textsubscript{2}O annealing could substantially decrease the traps contained in LPD–SiOF films. These N\textsubscript{2}O annealed oxides show better electrical properties than those of pure thermal oxides such as flatband voltage, interface trap density, and stress-induced gate voltage shift.\textsuperscript{40}

G. Effect of initial oxide thickness for SiOFN

In order to have a deep insight into the effects of this multiimpurity system, different initial LPD–SiOF growth time and a subsequent N\textsubscript{2}O annealing at 900 °C were performed. Figure 12 shows the TAT range in the current–voltage curve at \( E_{ox} = 4–10 \) MV/cm. The leakage current increases with the increment of initial LPD–SiOF’s growth time. This is due to the increase of a large quantity of F concentration. After N\textsubscript{2}O annealing, some N is incorporated into LPD–SiOF, resulting in a value change of \( \Phi_B \). Figure 13 shows the effect of initial LPD–SiOF’s growth time on the changes of \( \Phi_B \) and \( N_t \) under N\textsubscript{2}O annealing. With the
increase of initial LPD–SiOF’s growth time, $\Phi_t$ is decreased as shown by the solid squares. On the other hand, solid rhombuses reveal the increase of $N_t$. Some possible explanations could be described in the following.

For pure SiO$_2$, the bonding network of oxide is composed mainly of Si–O bonds with Si and O being tightly bonded to each other. There are very few traps existing in this type of oxide. If a foreign atom were incorporated (for example, fluorine), it would displace oxygen in a Si–O–Si bond and result in a dangling bond on the Si atom.$^{26}$ Furthermore, if another impurity such as nitrogen is introduced into a F-contained SiO$_2$ system, a much more complex tetrahedral structure is formed, F–SiO$_2$–N$_x$,$^\_x=0–3.$ The concentration of Si–F is slightly reduced because some weak Si–F bonds are removed and stronger Si–F are left in the oxide. With the initial LPD–SiOF thickness being thin (hence smaller F concentration in quantity), the incorporation of N would bond with F to produce a mixed effect, i.e., $\Phi_t$ is lowered. This type of trap energy level is called effective $\Phi_t$ because there are two atoms contributing to this parameter. Furthermore, SiO$_2$ containing F induces defects such as –Si–O–O–Si– structures.$^{22}$ When F concentration is increased, the incorporation of N is insufficient to affect the large amounts of Si–F bonds, hence F is a dominant factor in this case, i.e., $N_t$ is increased with growth time and $\Phi_t$ is similar to that in SiOF film.

IV. CONCLUSION

For the increasing demand in quality of gate dielectrics other than conventional SiO$_2$, it is well known that adequately introducing fluorine or nitrogen atoms into SiO$_2$ could improve the oxide properties for both Si–oxide interface and bulk oxide. SiOF and SiON films have received much attention in the past 20 yr. However, SiOFN films demonstrate their potential for future gate dielectrics because of the advantages described in Sec. I. Therefore, it is our motive to investigate the electrical properties of various doped SiO$_2$ to obtain greater understanding.

First of all, the conduction mechanisms were discussed to determine which one was the best to explain the leakage current in these oxides. It was found that FNT could only model the current–voltage curve at high fields, where at moderate fields it could be well fitted by the TAT model. PF emission and ohmic conduction were excluded because they provide incorrect modeling results for current–voltage curves. Second, we have briefly discussed the GTA T model and used it to fit the current–voltage curves of doped oxides. From the results acquired, $\Phi_t$ could be derived with the simple TAT plot using $\ln(J)$ versus $1/E_{ox}$. Then, the simulated results of a trapped oxide with $\Phi_t=1.2–2.6$ eV, $N_t=2 \times 10^{13}–2 \times 10^{20}$ cm$^{-3}$, $T_{ox}=5$ nm, and $\Phi_{ox}=3.2$ eV were given to determine the suitability of this model. It was found that the leakage current has a maximum value at about 1.8 eV because tunneling-in probability is equal to tunneling-out probability. In the third part, the current–voltage modelings of SiOF and SiOFN films were investigated. The trap energy levels of SiOF films ranged from 1.62 to 2.2 eV, while trap concentrations were $7 \times 10^{14}$–$3 \times 10^{15}$ cm$^{-3}$ depending on annealing temperature, time, and initial oxide thickness. An explicit effect of annealing on trap concentration was clearly observed. As for SiOFN films, the trap energy levels ranged from 1.24 to 2.25 eV, while trap concentrations were $5 \times 10^{14}$–$3 \times 10^{20}$ cm$^{-3}$ depending on different annealing time and initial oxide thickness. By introducing N into the SiOF films, $\Phi_t$ and $N_t$ were significantly changed due to the formation of complex compounds of Si, O, F, and N in silicon dioxides. Some possible explanations were given to clarify this mixing effect. The results in this article provide a deeper insight into SiO$_2$ containing impurities in terms of their electrical behaviors. It also provides a guideline on fabricating well-controlled dielectrics for future MOSFETs.

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