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Modeling the charge decay mechanism in nitrogen-rich silicon nitride films

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The stability of negative charge in nitrogen-rich silicon nitride films deposited by plasma-enhanced chemical vapor deposition is investigated by analyzing the influence of storage temperature, postdeposition thermal annealing, and the presence of a tunnel oxide. The results are compared to a charge decay model. Comparison of experimental and modeled results indicates that (i) the tunnel oxide is almost entirely responsible for charge retention in samples with an oxide-nitride-oxide (ONO) structure, with the trap properties playing an insignificant role; (ii) thermionic emission over the tunnel oxide barrier is the limiting charge decay mechanism; and (iii) thermal annealing of the films at 800 °C leads to an increase in the oxide-nitride barrier height by ~0.22 eV, which results in a significant increase in the charge stability. Annealed ONO samples are predicted to maintain a negative charge density of $>5\times10^{12}$ cm^{-2} for well in excess of 100 years at a storage temperature of 100 °C. © *2011 American Institute of Physics*. [doi:10.1063/1.3571291]

Silicon nitride (SiN_x) is widely used in the production of commercial silicon solar cells due to its desirable optical and electronic properties.[1] It is well known that electrostatic charge can substantially reduce the recombination of excess carriers at semiconductor surfaces, by reducing the concentration of one type of carrier. Plasma-enhanced chemical vapor deposition (PECVD) SiN_x films contain a significant density of positive charge (typically several 10^{12} cm^{-2}), which is beneficial for the passivation of the n-type emitter of conventional solar cells on p type substrates. However, they do not provide good passivation for the rear of such cells, due to the formation of an inversion layer which introduces additional losses and a virtual shunt.[2] Negatively charged SiN_x films could offer the possibility of excellent passivation of p-type surfaces, and indeed, improved passivation resulting from negatively charged SiN_x films has already been demonstrated.[3] Therefore, the ability to store negative charge in SiN_x for long periods of time could be of interest for solar cell applications, particularly for the passivation of rear surfaces.

The so-called K center, consisting of a Si atom back bonded to three nitrogen atoms ($\cdot Si\equiv N_3$) is the amphoteric defect considered chiefly responsible for trapped negative charge in near stoichiometric SiN_x films.[4] The charge stability depends on the defect properties (energy level distribution) and the properties of any interfacial barrier [such as a tunnel oxide (TO)] and in particular the band alignment of the barrier layer and the nitride film. Though some work has been devoted to the effect of film deposition conditions and postgrowth processing on the K center density,[5–8] little work has been done on the influence of deposition conditions and film properties on charge stability. The aim of this paper is to investigate the impact of film postdeposition anneals and the presence of an interfacial oxide on the rate of charge decay, in order to elucidate the dominant decay processes and be able to predict charge stability under different conditions. Our previous work has found that nitrogen-rich (N-rich) SiN_x films have better negative charge storage ability and stability.[9–11] Thus, we concentrate here on N-rich films.

Czochralski, p-type, 1–10 Ω cm (100) Si wafers were used as the substrates for capacitance-voltage (C-V) measurements. After a standard RCA clean, a 20 nm SiO_2 layer was thermally grown at 900 °C on selected samples. A ~90 nm SiN_x layer was then deposited by PECVD (Oxford PlasmaLab 80) at a frequency of 13.56 MHz. The deposition parameters were a temperature of 400 °C, pressure of 1 Torr, rf power of 24.7 W and (SiH_4+5%N_2):NH_3 gas ratio of 3.7. A ~40 nm PECVD SiO_2 was subsequently deposited as a barrier layer to reduce the charge losses to the atmosphere, resulting in silicon-oxide-nitride-oxide (ONO) and silicon-nitride-oxide (NO) structures. After deposition, selected samples were rapid thermal annealed (RTA) at 800 °C for 30 s. The refractive index n, film thickness and optical bandgap were measured with a variable angle spectrophotometer.[12] The refractive index at 633 nm was 1.85 following deposition, and from this the N/Si ratio was estimated to be 1.43 using the empirical expression of Bustarret,[13] in good agreement with the value obtained from Rutherford backscattering spectrometry (RBS) measurements on the same film. The RTA treatment was found not to result in significant changes to the refractive index or stoichiometry. However, the optical band gap, increased from 4.58 to 5.21 eV after annealing. C-V measurements in the dark were used to obtain information about negative charge trapped in the films. Prior to C-V measurements, all insulator layers were removed from the rear of the samples, and ~80 nm Aluminum dots with an area of ~0.0048 cm^2 were evaporated on the front. In/Ga contacts were formed on the rear of the samples. Details of charge injection by C-V bias can be found in Ref. 11.

Figure 1(a) shows a typical charging curve (V_{fb} versus bias applied V_{app}) of a sample used for C-V measurements. The negative initial flat band voltage V_0 (~5.3 V) indicates the presence of positive charge in the as deposited film, which is caused by fixed charge at the TO-nitride interface.[14] Previous reports[15,16] showed that the amphoteric charge centers (K centers) in SiN_x film are located close to the TO-

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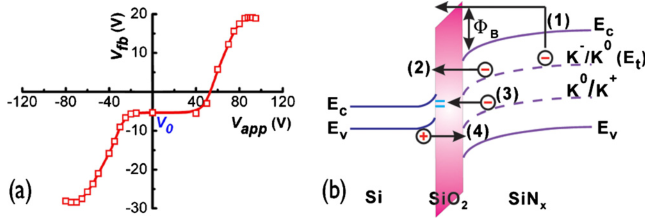

FIG. 1. (Color online) (a) Typical charging curve (V_{fb} vs V_{app}); and (b) possible charge decay paths for the excess electron state: (1) thermal emission of electrons to the nitride CB, followed by thermionic emission or tunneling across the oxide; (2) direct tunneling of electrons from traps into the silicon CB; (3) direct tunneling of electrons from traps to defects at the Si–SiO_2 interface; and (4) direct tunneling of holes in the valence band of the Si substrate to trap states in the nitride layer, followed by recombination with electrons.

nitride interface (within the first 10 nm from TO-nitride interface). Thus, the flat band voltage V_{fb} can be used to estimate the density of negative charge injected into the SiN_x films with reasonable accuracy using the following equation:

$$\sigma = -\frac{C_i}{qA}(V_{fb} - V_0), \quad (1)$$

where V_0 is the flat band voltage of the film prior to charge injection, C_i is the total capacitance of the nitride and top oxide, q is the elementary charge, and A is the Aluminum electrode area. Equation (1) was used to calculate the injected charge density in SiN_x films.

Figure 2(a) shows the decay of injected charge density in the SiN_x films with an NO structure stored at various temperatures. The charge decay rate depends on temperature, in line with our previous observations[9,10] and other reports.[17] Annealing of the films prior to charging results in a moderate increase in saturated charge density and a slight reduction in the charge decay rate. Figure 2(b) shows the decay of injected charge density in the SiN_x films with an ONO structure stored at 150 and 200 °C in atmosphere. No measurable decay was observed for samples stored at 25 °C. The presence of the TO has resulted in significantly improved charge stability compared to samples without a TO [Fig. 2(a)]. For samples with an ONO structure, annealing also leads to marked improvement in charge stability.

To understand the charge decay behavior, a simple theoretical model that describes the decay mechanisms is proposed here. Figure 1(b) shows the possible decay channels for the negative charge in SiO_2/SiN_x stacks, as identified previously.[18,19] Decay channels (2)–(4) all rely on direct tunneling of carriers through the oxide barrier, the probability of

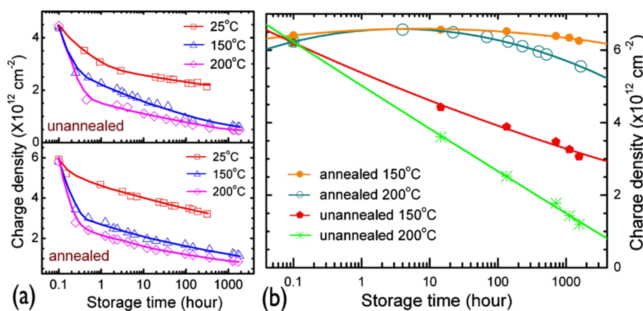

FIG. 2. (Color online) Injected negative charge density vs storage time for unannealed and 800 °C annealed N-rich SiN_x films without TO (a) and with TO (b) stored at various temperatures. The lines are a guide for the eye.

which decreases rapidly with increasing oxide thickness and is expected to be negligible for the structures studied here, which feature a thick TO. However, channel (1) involves either thermionic emission or Fowler–Nordheim (FN) tunneling for sufficiently thick oxides, and hence the transport probability becomes independent of oxide thickness. Channel (1) is, therefore, the dominant charge decay mechanism.

The thermal emission rate of electrons from negatively charged traps at an energy E below the conduction band (CB) edge of the nitride is given by[17]

$$e_{th}(E) = D(E,t)AT^2 \exp\left(-\frac{E}{kT}\right), \quad (2)$$

where $D(E,t)$ is the density of negatively charged traps of energy E at time t, A is a temperature independent constant, T is the temperature in kelvin, and k is Boltzmann's constant. The total emission rate of electrons into the nitride CB at any point in time is then given by

$$R_{th}(t) = \int_0^{\infty} D(E,t)e_{th}(E)dE. \quad (3)$$

Electrons in the nitride CB can then be transported into the silicon CB by either FN tunneling or thermionic emission. The FN tunneling probability is given by[20]

$$P_{FN} = K \exp\left[\frac{-4\sqrt{2m^*}(q\phi_B)^{3/2}}{3\hbar qE}\right], \quad (4)$$

while the thermionic emission probability is given by

$$P_{TE} = A^{**}T^2 \exp\left[\frac{-q(\phi_B - \sqrt{qE/4\pi\varepsilon_i})}{kT}\right], \quad (5)$$

where q is the electronic charge, E is the electric field strength (V/cm), ħ is the reduced Plank constant, ϕ_B is the barrier height at the nitride-TO interface, m^* is the average effective mass, and K and A^{**} are constants. The charge decay rate is then given by

$$C = N(P_{FN} + P_{TE}), \quad (6)$$

while the change rate of the charge density in the nitride CB is given by

$$dN/dt = R_{th} - C, \quad (7)$$

where N is the electron concentration in the silicon nitride CB.

In the modeling, the trap level distribution proposed in Ref. 17 (exponential decrease toward deeper trap levels) is adopted with some modifications: the traps are modeled to be distributed between levels E_1 and E_2 below the CB edge. All traps are assumed to be initially negatively charged following charge injection. So, the density of negatively charged traps with energy E below the nitride CB edge is given by

$$D(E,0) = D_0 \exp(-\lambda E), \quad (8)$$

where $E_1 < E < E_2$ and D_0 is a constant.

Figure 3(a) shows the modeling results for the unannealed NO structure. A reasonable fit to the experimental data is obtained with $\lambda = 0.31$ and $A = 0.01$. These values are quite similar to those determined in Ref. 17. In addition, for the unannealed films the best fit is obtained with $E_1 = 0.25$ eV and $E_2 = 1.3$ eV, while for the annealed films $E_1 = 0.39$ eV and $E_2 = 1.4$ eV. This indicates that the change in

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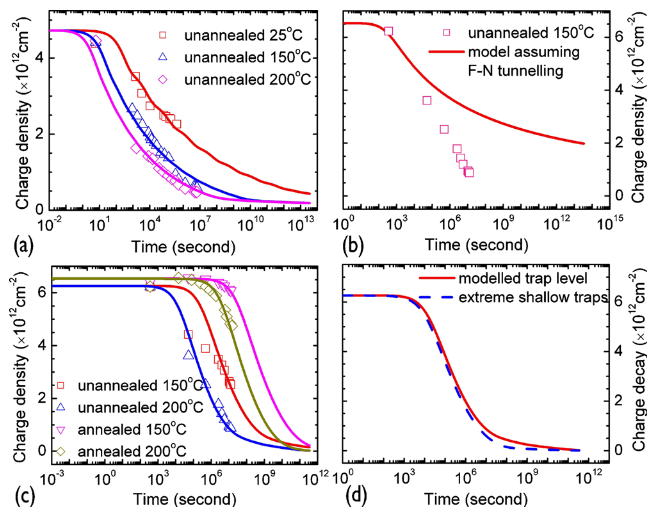

FIG. 3. (Color online) Experimental charge decay results and modeled results for unannealed NO samples at various temperatures (a); measured charge decay at 150 °C of an unannealed ONO sample and modeled result assuming FN tunneling (b); experimental charge decay results and modeled results for ONO samples (c); and modeled charge density decay using the trap parameters determined from (c) and the assumption all traps are extremely shallow, with E=0.01 eV below the CB edge (d). Symbols represent experimental data and lines are modeled results.

the trap energy distribution following annealing is much smaller than the change in the optical band gap following annealing (~0.63 eV).

To model the charge decay in ONO samples, it is assumed that the trap energy distribution is not affected by the presence of TO, and either FN tunneling or thermionic emission is the dominant mechanism of electron transport across the oxide. Retrapping of electrons has been found in our simulations to not significantly influence the charge decay and is ignored, as was the case in previous reports.[17,18]

As shown in Fig. 3(b), the enhanced stability of the ONO sample cannot be modeled by assuming FN tunneling as the dominant transport mechanism, especially at low charge densities, regardless of choice of modeling parameters. However, reasonable agreement between modeled and experimental results is achieved by assuming thermionic emission as the dominant transport mechanism, as shown in Fig. 3(c). In the absence of the unknown A^{**} value in Eq. (5), it is only possible to estimate the barrier height *difference* between annealed and unannealed samples instead of the absolute value of the barrier height. From our results an increase in barrier height of ~0.22 eV is estimated after annealing. It must be pointed out that the charge decay rate in the ONO samples is dominated by the barrier height, not the trap properties. This is illustrated in Fig. 3(d) which shows the modeled decay rate using (1) the trap parameters determined above and (2) assuming all traps are extremely shallow, with E=0.01 eV below the CB edge. This important role of oxide barrier height is further confirmed by our results (not presented here) showing a significantly enhanced charge stability of an ONO sample with a thermally grown TO compared with that with PECVD deposited silicon oxide, which is believed to be caused by the slightly higher oxide barrier height of the thermally grown TO.[21]

The model parameters can be used to estimate the charge decay rate at lower temperatures, like the maximum operating temperatures experienced by solar cells. At 100 °C, the model predicts that the charge density will remain above 5×10^{12} cm^{-2} (which value is found to result in optimum surface passivation[3]) for a period of 0.6 and >300 years for unannealed and annealed films, respectively.

In conclusion, we have demonstrated that high densities of negative charge can be stored at elevated temperatures in N-rich annealed PECVD silicon nitride films with ONO structures for long periods of time. For the structures investigated here, charge decay is dominated by thermionic emission of carriers over the TO barrier. As a result, the TO-nitride barrier height is the key parameter determining the charge stability. It is found that annealing of the films at 800 °C results in an increase in both the optical band gap and the barrier height, while the trap properties remain relatively unchanged. As a result of the increased barrier height, annealing leads to a significant increase in charge stability.

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