Effect of deposition conditions and thermal annealing on the charge trapping properties of SiN_x films

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The density of charge trapping centers in SiN_x:H films deposited by plasma enhanced chemical vapor deposition is investigated as a function of film stoichiometry and postdeposition annealing treatments. In the as-deposited films, the defect density is observed to increase with an increasing N/Si ratio x in the range of 0.89–1.45, and to correlate with the N–H bond density. Following the annealing in the temperature range of 500–800 °C, the defect density increases for all N/Si ratios, with the largest increase observed in the most Si rich samples. However, the defect density always remains highest in the most N rich films. The better charge storage ability suggests the N rich films are more suitable for the creation of negatively charged nitride films on solar cells. © *2010 American Institute of Physics*. [doi:10.1063/1.3518488]

Hydrogenated, amorphous silicon nitride (α-SiN_x:H) films have been widely used in semiconductor devices such as thin film transistors, memory devices, and solar cells. Charge plays an important role in many of these applications, and in some cases, the ability to manipulate charge is critical. In silicon solar cells, the positive charge in the as-deposited films is often beneficial as it results in field effect passivation of n type surfaces. However, for p-type surfaces, the positive charge in SiN_x induces a depletion region that increases recombination, and results in a parasitic shunt that reduces cell short circuit currents.[1] Therefore, the ability to trap negative charge in SiN_x for long periods of time could be of interest for solar cell applications, and indeed, an improved passivation resulting from negatively charged SiN_x films has already been demonstrated.[2]

The K-center defect, which consists of an Si atom backbonded to three nitrogen atoms ($Si \equiv N_3$) is the amphoteric defect chiefly responsible for trapped charge in near stoichiometric SiN_x films.[3] The ability of SiN_x films to trap the negative charge is mainly determined by the K-center density, which shows a strong dependence on film deposition conditions and postdeposition treatments. Several authors have explored the effect of deposition conditions and postdeposition thermal treatments on the film properties including the K-center density.[4–8] In these reports, the charge storage ability is indirectly measured through measurement of the neutral K-center density using electron spin resonance (ESR). Such measurements require great care to ensure that (i) all of the K centers are neutral at the time of ESR measurement (which requires UV treatment) and that (ii) the K centers are not photobleached.[9] In this paper, we present a study on the effect of deposition parameters and thermal annealing on the charge trapping properties of SiN_x films. As an alternative to ESR measurements, we measure the density of charge directly trapping centers from capacitance-voltage (C-V) measurements following the injection of negative charge.

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P-type, (100), double sided polished Si wafers were used as the substrates for Fourier transform infrared (FTIR) spectroscopy and Rutherford backscattering spectrometry (RBS) measurements. Substrates used for C-V measurements were Cz, p-type, and 1–10 Ω cm (100) Si wafers. After a standard RCA clean, 90 nm SiN_x was deposited on all samples using a plasma enhanced chemical vapor deposition (Oxford PlasmaLab 80) at a frequency of 13.56 MHz, a temperature of 400 °C, pressure of 1 Torr, and rf power of 24.7 W. For the samples used for C-V measurements, a 20 nm tunnel oxide layer was thermally grown at 900 °C before the deposition of the SiN_x films, which serves as a barrier to charge decay, and thus improves the stability of the charge in the SiN_x film.[10,11] Various (SiH_4+5%N_2):NH_3 gas ratios (R_{gas}) were used in the deposition of SiN_x films, namely, R_{gas} =3.7, 6.5, 20, 27, and 34 for samples A, B, C, D, and E, respectively. The total gas flow rate was kept constant at 420 (SCCM) (SCCM denotes standard cubic centimeters per minute at STP). After deposition, selected C-V and FTIR samples were rapid thermal annealed at various temperatures in the range of 500–800 °C for 30 s.

The refractive index n and film thickness were measured using a multiple angle reflectometer (FilmTek 4000) at a wavelength of 633 nm and an incidence angle of around 70°. The N/Si ratio x was estimated from n using the empirical expression[5,6]

$$x = \frac{[\mathrm{N}]}{[\mathrm{Si}]} = \frac{4(n_{\alpha\text{-Si:H}} - n)}{3(n + n_{\alpha\text{-Si:H}} - 2n_{\alpha\text{-Si}_3\text{N}_4})} = \frac{4(3.3 - n)}{3(n - 0.5)}, \quad (1)$$

where $n_{\alpha\text{-Si:H}}$=3.3 and $n_{\alpha\text{-Si3N4}}$=1.9 are the refractive index of amorphous silicon (a-Si:H) and nearly stoichiometric silicon nitride (a-Si_3N_4), respectively. For comparison, RBS measurements were also performed on selected as-deposited samples to determine their N/Si ratios. It was found that the N/Si ratios determined from RBS are in good agreement with the values calculated from Eq. (1) for N rich, Si rich and nearly stoichiometric films.

Information on chemical bond densities in as deposited and annealed SiN_x films was obtained from FTIR spectroscopy, using the general expression[12]

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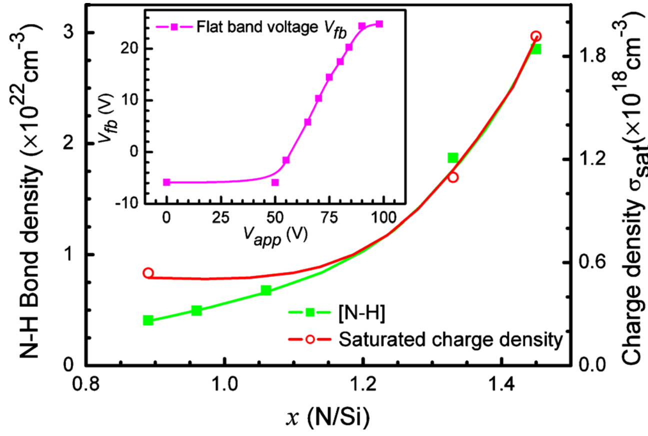

FIG. 1. (Color online) Saturated charge density σ_{sat} and the calculated N–H bond density as a function of N/Si ratio for the as-deposited films. The inset shows a typical plot of flatband voltage V_{fb} vs applied bias voltage V_{app}. Lines are guides to the eyes.

$$[A\text{-}B] = C_{A\text{-}B}\int \alpha(\omega)\omega^{-1}d\omega, \tag{2}$$

where $\alpha(\omega)$ and ω are the absorption coefficient and the wave number, respectively, and $C_{A\text{-}B}$ is the proportionality constant, where the proportionality constants of Bustarret *et al.*[5] were used.

For *C-V* measurements, Al dots with an area of $\sim$0.0048 cm^2 were evaporated on the front and In/Ga contacts were formed on the rear of the samples. To inject electrons into SiN_x film, progressively increased positive bias voltages V_{app} were applied to the front metal contacts for periods of several seconds. Following each bias voltage, a high frequency *C-V* sweep was carried out to determine the flatband voltage V_{fb}. V_{app} was increased until saturation of V_{fb} was observed. With the following two assumptions: (i) the saturated charge (with all the K centers fully charged) are roughly uniformly distributed throughout the film,[13,14] and then the charge centroid will be located in the middle of the film; (ii) the positive charge density of films prior to charge injection can be associated with interface defects carrying a fixed positive charge,[15] while the sum of charge due to K centers is assumed to be zero initially (Since the neutral state of the K center is believed to be metastable,[16] the silicon nitride film is likely to consist of roughly equal densities of positively and negatively charged K centers), the saturated flatband voltage V_{fb} following charge injection can then be used to estimate the K-center density (density of fundamental charges per unit area) in the SiN_x films

$$\sigma = -\frac{2C_i}{qA_{Al}}(V_{fb} - V_0), \tag{3}$$

where V_0 is the flatband voltage of the film prior to charge injection, C_i is the capacitance of the nitride, q is the elementary charge, and A_{Al} is the Al electrode area.

Figure 1 shows the variation of the saturated charge density σ_{sat} and the N–H bond density with N/Si ratio for the as-deposited films. The inset of Fig. 1 shows a typical plot of flatband voltage V_{fb} as a function of applied bias voltage V_{app}. An increase in σ_{sat} with increasing N content in the film is observed, which accords with the electron spin resonance measurements reported.[17,18] As reported,[17,18] the ESR spin density increases with increasing the N/Si ratio for the Si-rich and nearly stoichiometric regions. However, the ESR spin density drops with further increasing the N/Si ratio over a percolation threshold (x=1.3 and 1.1 for the films in Refs. 17 and 18, respectively). For our samples, the σ_{sat} increases all the way with increasing the N/Si ratio from 0.89 to 1.45 with no percolation threshold observed, the reasons of which are not very clear and remain to be studied further. Furthermore, it can be seen that there exists a reasonably close correlation between the σ_{sat} and [N–H], which was also observed by Garcia *et al.*[18] (It should be mentioned that [N] does not present such close correlation with σ_{sat} despite the fact that it also increases with increasing the N/Si ratio.) Mäckel and Lüdemann[4] proposed a model, whereby the formation of K centers during film deposition proceeds when a H atom is lost from an $H-SiN_3$ precursor in the presence $H-NSi_2$, with the latter catalyzing the reaction. The results of Fig. 1 support the idea that N–H bonds play an important role in the creation of K centers.

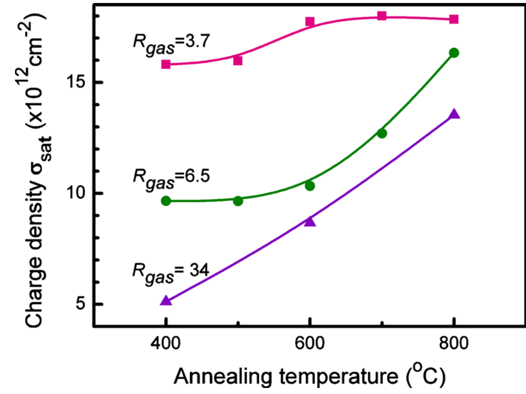

FIG. 2. (Color online) Saturated negative charge density σ_{sat} as a function of annealing temperature for sample A, B, and E. Lines are guides to the eyes. Note: 400 °C is the deposition temperature.

Following deposition, selected N-rich (sample A), stoichiometric (sample B), and Si-rich (sample E) films were annealed at 500, 600, 700, and 800 °C. Figure 2 shows σ_{sat} as a function of annealing temperature. σ_{sat} increases with increasing annealing temperature for all three samples, with the largest increase observed for the Si rich film and smallest for the N rich film. This increase of σ_{sat} with increasing the annealing temperature also accords with the ESR measurements reported.[19] As observed in Ref. 19, the spin density decreases after annealing in the temperature range of 300–600 °C. However, it increases after annealing at higher temperature (>600 °C) with the largest increase observed for the Si-rich film. The decrease of spin density after annealing in the lower temperature range was attributed to the charge transfer between two K centers, leading to the formation of non-ESR active K centers (not annihilation of K centers). The increase of spin density after annealing at higher temperatures was explained with the release of hydrogen and the resultant formation of new K centers. These models proposed agree with our observations that no evidence of a reduction in the density of chargeable defects is observed for sample A, B, and E after annealing at higher temperatures (500–800 °C).

Figure 3 shows the density of N–H and $H-SiN_3$ bonds (Si–H bonds backbonded to three N atoms) for the films annealed at various temperatures. The latter was obtained by fitting the Si–H absorption peak with the characteristic peaks

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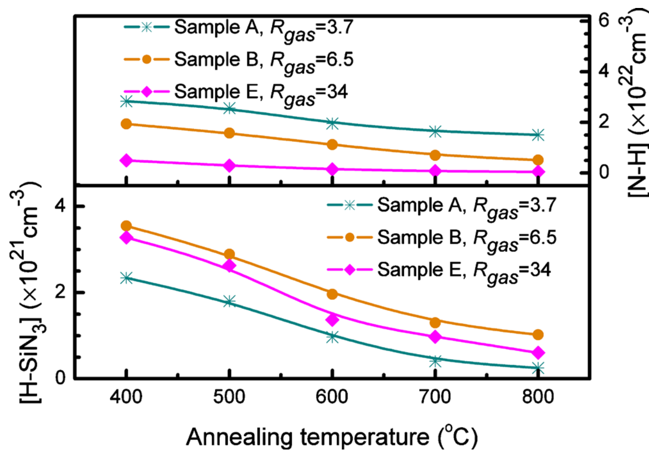

FIG. 3. (Color online) The change of [N–H] and [H–SiN$_3$] as a function of annealing temperature for samples A, B, and E. Lines are guides to the eyes. Note: 400 °C is the deposition temperature.

of the six possible backbonding configurations.[5] Possible mechanisms for the increase in σ_{sat} during annealing (at temperatures significantly above the deposition temperature) include the H–NSi$_2$ catalyzed breaking of H–SiN$_3$ proposed by Mäckel,[4] or the direct dissociation of hydrogen from H–SiN$_3$.[20,21] In the former case, the rate of formation of K centers would be expected to depend on the product of the H–SiN$_3$ and N–H densities, but in the latter case, it should depend on the density decrease of H–SiN$_3$. Analysis of the data in Fig. 3 shows that the former correlation does not exist. While Fig. 3 shows that H–SiN$_3$ bond density decreases at a comparable rate in all the films. So, in principle, a comparable increase of σ_{sat} should be induced. However, as shown in Fig. 2, the σ_{sat} shows quite different increase for three samples, which cannot be purely explained by the breaking of Si–H bonds after annealing.

To explain the larger increase of σ_{sat} for samples B and E, other formation mechanism for the K centers during annealing need to be considered. It was reported that thermal annealing can break weak Si–Si bonds in films and generate new Si dangling bonds, resulting in the formation of new K centers.[22,23] In stoichiometric and Si-rich films (sample B and E), there is a greater density of Si–Si bonds than in N-rich films (sample A). The greater increase in σ_{sat} for the films of samples B and E may therefore be the result of a greater density of weak Si–Si bonds being broken and converted into K centers. Optical measurements show that the N/Si ratio of samples A and B are virtually unchanged after annealing, while for sample E, the N/Si ratio gradually decreases from 0.85 to 0.68 for annealing temperatures between 500 and 800 °C, indicating a significant loss of N for Si rich films after annealing. This is thought to result from the reaction of Si–H and N–H bonds[19]

$$\mathrm{Si-H+H-NSi-H \Rightarrow Si-Si+NH_3}. \quad (4)$$

This indicates that in Si rich films, weaker Si–Si bonds are created during annealing. As a result, more K centers can be formed in Si rich films during the annealing process than in N rich and stoichiometric films.

In summary, we suggest that different mechanisms may be chiefly responsible for the different density of K centers in as-deposited films, and the increase in their density following annealing. This results in a relatively high density of chargeable defect centers in films with a wide range of stoichiometries following a high temperature annealing. However, σ_{sat} of the N rich films is always larger than that of the stoichiometric or Si rich films. Together with the larger optical bandgap, which is likely to result in a deeper energy level of the K center below the conduction band and therefore greater charge stability, this suggests that N rich films are most suited for application to solar cells, where a large value of σ_{sat} is important to ensure effective surface passivation.[24]

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