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Recombination and thin film properties of silicon nitride and amorphous silicon passivated c-Si following ammonia plasma exposure

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Recombination at silicon nitride (SiN_x) and amorphous silicon (a-Si) passivated crystalline silicon (c-Si) surfaces is shown to increase significantly following an ammonia (NH₃) plasma exposure at room temperature. The effect of plasma exposure on chemical structure, refractive index, permittivity, and electronic properties of the thin films is also investigated. It is found that the NH₃ plasma exposure causes (i) an increase in the density of Si≡N₃ groups in both SiN_x and a-Si films, (ii) a reduction in refractive index and permittivity, (iii) an increase in the density of defects at the SiN_x/c-Si interface, and (iv) a reduction in the density of positive charge in SiN_x. The changes in recombination and thin film properties are likely due to an insertion of N–H radicals into the bulk of SiN_x or a-Si. It is therefore important for device performance to minimize NH₃ plasma exposure of SiN_x or a-Si passivating films during subsequent fabrication steps. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907377>]

Ammonia (NH₃) plasmas have been investigated for the nitridation of bare crystalline silicon (c-Si) surfaces and dielectric materials. When the bare silicon surface is exposed to the NH₃ plasma before the deposition of a silicon nitride (SiN_x) gate insulator, Shimoda *et al.*¹ report that a metal–insulator–semiconductor field effect transistor with SiN_x as the gate insulator has a high field-effect mobility. The NH₃ plasma exposure before the SiN_x deposition was also used in several studies to improve the surface passivation by SiN_x.^{2–4}

NH₃ plasma has also been used for the nitridation of dielectrics such as thin thermal silicon dioxide (SiO₂), forming an oxynitride layer. Two groups have shown that the exposure of SiO₂-coated c-Si samples to NH₃ plasma results in a drastic increase in the amount of interface defects.^{5,6} In addition, Jin *et al.* exposed SiO₂-passivated c-Si with NH₃ plasma at room temperature, leading to a significant increase in surface recombination.⁷ The origin of the increase in defect density at SiO₂/c-Si interface upon plasma exposure has been speculated to be an interface damage induced by the penetration of energetic ions such as N–H radicals⁶ and/or H radicals.^{8,9} The SiO₂/c-Si interface may also suffer from radiation damage during plasma exposure, which is found to induce additional interface defects at amorphous silicon (a-Si)/c-Si interface.^{10–12}

In this work, the effect of NH₃ plasma exposure on the surface passivation of c-Si by SiN_x and a-Si is investigated. To understand the physical mechanism underlying the NH₃ plasma exposure, we also study its effect on the chemical structure, refractive index n , dielectric constant κ , interface defect density D_{it} , and effective insulator charge density Q_{eff} .

The lifetime samples were fabricated from n -type float-zone (FZ) {100} c-Si wafers with a resistivity of 0.45 Ω -cm and a thickness of 245 μ m. The wafers were etched in tetramethylammonium hydroxide (TMAH, 25 wt. %) at $\sim 85^\circ\text{C}$ to remove saw damage, cleaned by the RCA (Radio Corporation of America) procedure, dipped in HF to remove any remaining

oxide, and then coated with SiN_x or a-Si on both surfaces by two sequential plasma enhanced chemical vapour depositions (PECVD). The SiN_x and a-Si films were deposited using an AK400 microwave/radio-frequency (μ W/RF) PECVD reactor manufactured by Roth & Rau. A detailed description of the reactor is given elsewhere.¹³ The optimized deposition conditions reported in Ref. 13 were used, where the deposition temperature was 300 $^\circ\text{C}$, the pressure was 0.2 mbar, the μ W plasma power was 500 W, and the RF bias voltage was 150 V. The NH₃/SiH₄/Ar gas flows for SiN_x and a-Si were 20/20/20 sccm and 0/40/20 sccm, respectively. The deposition time was varied to achieve a film thickness of 60 ± 5 nm.

The symmetrically passivated samples were then exposed to an NH₃ plasma in the aforementioned AK400 PECVD reactor at room temperature (22–25 $^\circ\text{C}$) by setting the NH₃/Ar flow at 20/20 sccm and leaving the pressure, power, and voltage unchanged. The exposure time was sequentially increased from 5 to 90 min. In order to separate the effect of the radiation exposure from the penetration of N–H radicals, control samples were included in the plasma chamber but protected from the ion penetration by a 1 mm-thick glass plate. The covered samples were therefore exposed to light (although not at very short wavelengths), but were protected from the ion penetration.^{14,15}

The effective carrier lifetime was measured using a Sinton Instruments WCT-120 photoconductance tool operated in the transient mode.¹⁶ Neglecting Shockley–Read–Hall recombination in the bulk of the wafer, the upper limit of the effective surface recombination velocity $S_{eff,UL}$ was calculated according to

$$S_{eff,UL} = \frac{W}{2} \left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk,intrinsic}} \right), \quad (1)$$

where W is the Si substrate thickness and $\tau_{bulk,intrinsic}$ is the intrinsic bulk lifetime in Si parameterized by Richter *et al.*¹⁷ This approximation assumes a uniform carrier concentration

across the samples, which is justified in this study by the samples' high effective carrier lifetime.¹⁸

Reflectance and Fourier-transform infrared (FTIR) measurements were performed on double-sided polished *n*-type FZ {100} c-Si with a resistivity of 1.1 $\Omega\cdot\text{cm}$ and a thickness of 290 μm . The samples were coated with the abovementioned SiN_x or a-Si films on one side. The film thickness and *n* at 632 nm were determined from reflectance measurements using a dual-angle "reflectometer" (FilmTek 4000) at incident angles of 0° and 70°. The Tauc-Lorentz model was employed for the optical analysis.¹⁹ The FTIR transmission spectra were measured using a FTIR spectrometer (Bruker Vertex 80 V) with a resolution of 6 cm^{-1} .

Metal-insulator-semiconductor test structures were fabricated for capacitance-voltage (C-V) measurements using a 4284 A Precision LCR meter. The measurements were performed on SiN_x -coated samples that were the same as those used for reflectance and FTIR measurements. Note that high-frequency C-V curves could not be obtained on a-Si films, due to their high conductivity.²⁰ In this work, the front metal contact was formed by evaporating aluminium through a shadow mask to create circular dots of diameter $\sim 700 \mu\text{m}$ and thickness $\sim 100 \text{ nm}$. The rear contact was formed with a GaIn eutectic paste. The dielectric constant κ was determined from the measured optical thickness and insulator capacitance. Q_{eff} was calculated by assuming all charge to be located at the $\text{SiN}_x/\text{c-Si}$ interface. Quasi-static C-V measurements on typical SiN_x produced in this work could not be performed as they were too leaky. Hence, D_{it} was determined solely by applying the Terman method²¹ to high-frequency C-V measurements.

Figure 1 plots $S_{\text{eff,UL}}$ as a function of NH_3 plasma exposure time for the SiN_x and a-Si samples. The samples were either exposed directly to plasma or protected from the plasma by a glass plate. The figure shows that for the SiN_x samples, $S_{\text{eff,UL}}$ increases dramatically when exposed to the plasma, but remains constant when protected by the glass plate. This indicates that the degradation of SiN_x passivation

FIG. 1. $S_{\text{eff,UL}}$ as a function of NH_3 plasma exposure time for SiN_x and a-Si samples. The samples were either exposed directly to the plasma or protected from the plasma by a glass plate.

upon plasma exposure is induced by ion penetration rather than by light exposure.

For the a-Si samples, $S_{\text{eff,UL}}$ increases rapidly during the first 10 minutes with or without the glass plate. As the exposure continues, $S_{\text{eff,UL}}$ for the sample exposed to the plasma continues to increase but at a slow rate. By contrast, $S_{\text{eff,UL}}$ for the sample protected by the glass plate appears to be constant. The results suggest that the fast increase in $S_{\text{eff,UL}}$ is primarily induced by the light exposure, likely the Staebler-Wronski effect,²² and the slow increase in $S_{\text{eff,UL}}$ thereafter is caused by ion penetration.

In addition, the figure shows that the NH_3 plasma exposure is more detrimental to the surface passivation by SiN_x than by a-Si. Upon 90-min exposure to the plasma, $S_{\text{eff,UL}}$ for the SiN_x sample is nearly one order of magnitude higher than the $S_{\text{eff,UL}}$ for the a-Si sample.

FTIR spectra were recorded after each step of the NH_3 plasma exposure to evaluate the effect on film structure. The results are shown in Figure 2.

FIG. 2. The impact of NH_3 plasma exposure on the absorbance measured by FTIR for (a) SiN_x and (b) a-Si. The absorbance spectrum for films covered with glass plate are also included for comparison.

Before any plasma exposure, both SiN_x and a-Si films exhibit typical FTIR spectra. The SiN_x has four distinctive absorption peaks: one associated with Si–N at $\sim 840\text{ cm}^{-1}$ ($\text{N}\equiv\text{Si}_3$ asymmetric stretching), one with Si–H at $\sim 2200\text{ cm}^{-1}$ ($\text{H}-\text{Si}\equiv\text{N}_3$ stretching), and two with N–H at $\sim 1150\text{ cm}^{-1}$ (bending) and $\sim 3340\text{ cm}^{-1}$ (stretching). The a-Si has three distinctive absorption peaks, all associated with Si–H: $\sim 640\text{ cm}^{-1}$ (wag-rocking), $\sim 2000\text{ cm}^{-1}$ (Si–H stretching), and $\sim 2090\text{ cm}^{-1}$ ($\text{Si}=\text{H}_2$ stretching).^{23,24}

After 5 min of plasma exposure, a new shoulder with a peak at $\sim 1055\text{ cm}^{-1}$ appears for both SiN_x and a-Si films. This shoulder was assigned to the Si–N stretching vibrations of $\text{Si}\equiv\text{N}_3$ groups by Snmaud *et al.*²⁵ Furthermore, we note that the density of the $\text{Si}\equiv\text{N}_3$ groups increases significantly as the exposure time increases. By contrast, no obvious change in film structure can be observed for the samples protected by the glass plate. Based on these observations, the chemical bond with peak absorbance at $\sim 1055\text{ cm}^{-1}$ is likely introduced by the incorporation of N–H radicals. In addition, deconvolution of the absorbance with peaks at $\sim 1055\text{ cm}^{-1}$ shows that the increase in the density of the $\text{Si}\equiv\text{N}_3$ groups is comparable for SiN_x and a-Si films under the same duration of NH_3 plasma exposure. It is interesting to note that in Ref. 26 the $\text{Si}\equiv\text{N}_3$ groups were assigned as the bonding configuration of the so-called “K-center.” If correct, then the NH_3 plasma exposure increases the density of K-centres, thereby enhancing its capability of trapping charge.²⁷ Based on the FTIR results and the defect formation model proposed by Lucovsky *et al.*,²⁸ we discuss possible reaction pathways for the formation of the $\text{Si}\equiv\text{N}_3$ groups. In the model of Lucovsky *et al.*,²⁸ N–H related radicals are proposed to be the precursors for the formation of defects. We therefore propose that the $\text{Si}\equiv\text{N}_3$ groups are formed by an insertion of N–H related radicals into SiN_x or a-Si films in the following reaction pathways: (i) for SiN_x samples: $\text{N}\equiv\text{Si}_3 + 8(\text{N}-\text{H}) \rightarrow 3(\text{Si}\equiv\text{N}_3) + 4\text{H}_2$ and (ii) for a-Si samples: $\text{Si}-\text{H} + 3(\text{N}-\text{H}) \rightarrow \text{Si}\equiv\text{N}_3 + 2\text{H}_2$.

In addition to the alteration of the films’ structural properties, NH_3 plasma exposure also affects their optical properties. Figure 3 plots the relationship between the refractive index n at 632 nm and exposure time. It is shown that n of both SiN_x and a-Si films decreases monotonically with an increase in exposure time. The trends in decreasing n correlate with the increase in density of the $\text{Si}\equiv\text{N}_3$ groups, suggesting that the reduction in n is most likely attributable to the incorporation of N–H radicals into film network upon plasma exposure.

C–V measurements reveal how the NH_3 plasma exposure influences D_{it} at midgap, Q_{eff} , and film permittivity (i.e., the dielectric constant κ). Figure 4 plots the results and the high-frequency C–V curves are included in the inset. Note that the C–V curves in Figure 4 are solely for the SiN_x samples exposed directly to plasma, since no significant change in $S_{\text{eff,UL}}$ and film structure was observed for the sample protected by the glass plate.

It can be seen that upon 90 min of exposure (i) D_{it} increases significantly by approximately one order of magnitude; (ii) Q_{eff} decreases significantly from $+6.6 \times 10^{11}\text{ cm}^{-2}$ to $-4.2 \times 10^{11}\text{ cm}^{-2}$; and (iii) κ decreases from 7.5 to 3.6. Notably, these trends correlate clearly with a reduction in n ,

FIG. 3. Refractive indices of SiN_x and a-Si films as a function of NH_3 plasma exposure time.

which is correlated with an increase in the density of $\text{Si}\equiv\text{N}_3$ groups in the SiN_x bulk. We therefore speculate that the changes to Q_{eff} and κ are induced by the incorporation of N–H radicals into the bulk. In addition, we also think that the increase in D_{it} is caused by the incorporation of N–H radicals, introducing new defects states at the interface. We note that other energetic radicals such as hydrogen and argon can also cause interface defects.^{14,15}

In summary, we have found that a significant deterioration in surface passivation occurs when SiN_x and a-Si passivated c-Si wafers are exposed to an NH_3 plasma at room temperature. In the case of SiN_x , the degradation is solely due to the penetration of ions into the film, whereas in the case of a-Si an additional degradation due to plasma radiation also takes place. We observed via FTIR measurements that the increase in recombination correlates with an increase in the density of $\text{Si}\equiv\text{N}_3$ groups, indicating a change in film structure upon NH_3 plasma exposure. The possible reaction

FIG. 4. C–V measurements (see the inset) on SiN_x samples and the extracted D_{it} at midgap, Q_{eff} and dielectric constant κ .

pathways for the formation of $\text{Si}\equiv\text{N}_3$ groups involve an insertion of N–H radicals into the bulk of the films. We also found a reduction in film refractive index and permittivity, presumably attributable to the increase of $\text{Si}\equiv\text{N}_3$ groups. Moreover, C–V measurements revealed that NH_3 plasma exposure induced an increase in D_{it} and a reduction in positive Q_{eff} within the SiN_x , which are both responsible for the increase in surface recombination.

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