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Passivation Characteristics of SiN$_x$/a-Si and SiN$_x$/Si-rich-SiN$_x$ Stacked Layers on Crystalline Silicon

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Abstract

High-quality surface passivation is essential for obtaining crystalline silicon (c-Si) solar cells with high energy-conversion efficiency. Silicon-nitride (SiN$_x$)/amorphous-silicon (a-Si) stacked layers prepared by catalytic chemical vapor deposition (Cat-CVD), also referred to as hot-wire CVD, demonstrate excellent performance as surface passivation layers for c-Si and realize a dramatically low surface recombination velocity (SRV). However, the use of a more transparent material than a-Si is required because the a-Si layer absorbs sunlight. Here, Si-rich SiN$_x$ films, as a more transparent material, with various atomic ratios of silicon/nitrogen (Si/N) are investigated as a replacement for a-Si films. The use of SiN$_x$/Si-rich-SiN$_x$ stacked layers as passivation films on c-Si wafers results in a SRV as low as 5 cm/s and 30% improvement of the transparency at the wavelength of 400 nm compared to that of the SiN$_x$/a-Si stacked layers. Moreover, after the annealing process, the passivation characteristics of the stacked layer were significantly improved, with a SRV as low as 3 cm/s.
Keywords: Si-rich silicon nitride, amorphous silicon, solar cell efficiency, Cat-CVD, passivation, surface recombination velocity
1. Introduction

Enhancement in the conversion efficiency of crystalline-silicon (c-Si) solar cells is an most important task in c-Si photovoltaic research. High-efficiency solar cells can be obtained only when both the loss of photo-generated carriers and the loss of sunlight entering into solar cells are reduced [1]. In other words, to produce high-efficiency solar cells, the effective minority carrier lifetime ($\tau_{\text{eff}}$) should be lengthened and the surface-reflection loss of sunlight should be reduced. To reduce the electrical loss due to the surface recombination of photo-generated carriers and the optical loss due to the reflection at the air/c-Si interface, the use of a surface passivation layer with anti-reflection ability is preferred.

It is widely known that silicon-nitride (SiN$_x$) films can achieve good anti-reflection and provide good surface passivation for c-Si solar cells [2-3]. However, it has been recently revealed that the insertion of a thin amorphous-silicon (a-Si) layer between a SiN$_x$ film and c-Si improves the $\tau_{\text{eff}}$ dramatically and lowers the surface recombination velocity (SRV) to less than 1.5 cm/s when the SiN$_x$ and the inserted a-Si films are all prepared by the catalytic chemical vapor deposition (Cat-CVD) method [4]. Cat-CVD [5], also referred to as hot-wire CVD, is known to be a deposition method with no plasma damage, and this reduced damage may be a key factor to realize the extremely low SRV. However, the inserted a-Si film absorbs sunlight, which causes optical loss that reduces solar-cell efficiency.

Si-rich SiN$_x$ films have higher optical transparency than a-Si films. Thus, Si-rich SiN$_x$ films are good candidates for alternative films to a-Si in the stacked structure if they demonstrate good passivation characteristics. In this study, we introduce a new stacked-structure for the passivation of c-Si surfaces by inserting Si-rich SiN$_x$ films between SiN$_x$ films and c-Si wafers. The major purpose of our research is to obtain high-transparency films without a decrease of $\tau_{\text{eff}}$ in c-Si.
SiN_x/Si-rich-SiN_x stacked layers were prepared by Cat-CVD. After annealing, SiN_x/Si-rich-SiN_x stacked layers as passivation films on c-Si achieved a SRV as low as 3 cm/s with a 30% improvement in transparency at the wavelength of 400 nm compared to that of SiN_x/a-Si films.

2. Experimental Procedure

2.1. Sample Preparation

After cleaning c-Si wafers by diluted (5%) hydro-fluoric acid (HF) solution to remove the native oxide on the c-Si surface, Si-rich SiN_x films and SiN_x films were deposited onto the cleaned c-Si wafers. Amorphous-silicon (a-Si) films were deposited for comparison to the Si-rich SiN_x films. The films were also deposited onto glass substrates for optical transmission measurements. The stoichiometry of the Si-rich SiN_x films was varied by adjusting the ratio of the silane (SiH_4)-to-ammonia (NH_3) gas flow rates \((R = [\text{SiH}_4]/[\text{NH}_3])\) from 0.04-0.08. \(R\) was varied by changing the SiH_4 flow rate from 10 sccm to 20 sccm while keeping the NH_3 flow rate at 250 sccm. We also investigated the dependence of the substrate temperature \((T_s)\) during deposition on the film properties and the passivation characteristics. Other deposition parameters, such as gas pressure and catalyzer temperature, during deposition were kept constant. The details of the deposition conditions are listed in Table 1. To characterize effect of the annealing process on the passivation characteristics of the thin-film structure, c-Si wafers passivated by SiN_x/Si-rich-SiN_x stacked layers were annealed for 30 min in nitrogen ambient at temperatures of 150, 250, 350, and 500 °C.

2.2. Characterization of Prepared Samples

The wavelength \((\lambda)\) dependent refractive indices \(n(\lambda)\) of Si-rich SiN_x films were measured using data obtained from a J. A. Woollam Co., HS-190™ spectroscopic ellipsometer and
analyzed using the Cauchy model. In this model, \( n(\lambda) \) and extinction coefficients \( k(\lambda) \) are approximately expressed as [6]:

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{1}
\]

\[
k(\lambda) = ae^{(12400(\frac{1}{\lambda} - \frac{1}{\lambda_0}))} \tag{2}
\]

The six fitting parameters in this dispersion model are \( A, B, C \), the extinction coefficient amplitude, \( \alpha \), the exponent factor, \( \beta \), and the band edge, \( \gamma \). The atomic composition of Si to nitrogen ([Si]/[N]) of the films deposited at various \( R \) was determined by X-ray photoelectron spectroscopy (XPS). In parallel, the transmission spectra of Si-rich Si\( _x \) were measured using a SHIMAZU Co. Ltd., UV-3150 Ultraviolet-visible-near infrared spectrophotometer.

For the measurements of \( \tau_{\text{eff}} \), Si\( _x \)/Si-rich-Si\( _x \) stacked layers were deposited on both sides of 290-\( \mu \)m-thick n-type (100) floating-zone (FZ)-grown Si wafers with a resistivity of 2.5 \( \Omega \)cm. A schematic cross-sectional view of this structure is shown in Fig. 1. Microwave photoconductivity decay (\( \mu \)-PCD) measurements were performed using a KOBELCO LTA-1510EP system with a 904-nm-wavelength pulsed-laser source at a photon density of \( 5 \times 10^{13} \) cm\(^{-2} \). The \( \tau_{\text{eff}} \) is determined by the exponential decay of the microwave reflection intensity and can be expressed as follows:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W} \tag{3}
\]

Where, \( \tau_{\text{bulk}}, W, \) and \( S \) represent the minority carrier lifetime in bulk c-Si, the wafer thickness, and the SRV, respectively. The maximum SRV (\( S_{\text{eff, max}} \)) is determined by \( S_{\text{eff, max}} = W/2\tau_{\text{eff}} \), assuming \( \tau_{\text{bulk}} = \infty \) [4].
3. Results and discussion

A prior report has shown that an epitaxial Si layer can be grown on a c-Si surface at a high substrate-temperature of approximately 150 °C or higher and that the passivation quality is deteriorated [7]. We therefore first studied the effect of substrate temperatures ($T_s$) on the Si-rich SiN$_x$ film properties as well as the passivation characteristics to determine the optimal $T_s$. Fig. 2 shows $n$ at 630 nm and the thickness of the Si-rich SiN$_x$ films ($d$) deposited for 5 s at $R$ of 0.08 as a function of $T_s$. $d$ becomes smaller and $n$ becomes higher with increasing $T_s$. $n$ is 1.6 at a $T_s$ of 90 °C and reaches 3.0 at a $T_s$ of 300 °C. This variation of $n$ may be due to the change of the atomic ratio of [Si]/[N], as shown later in Fig. 4. The decrease of thickness when $T_s$ increases may indicate that the Si-rich SiN$_x$ films tend to have a lower density at a lower $T_s$. A higher $T_s$ provides more kinetic energy to particles for migration on the c-Si surface, thereby enabling a more densely packed film. Fig. 2 also shows the $\tau_{\text{eff}}$ of the c-Si wafers passivated with SiN$_x$/Si-rich-SiN$_x$ (10-nm-thick) stacked films; the $\tau_{\text{eff}}$ increases with increasing $T_s$, and increases up to over 2000 µs, particularly at a $T_s$ of 250 °C or higher. Fig. 3 shows the transmission spectra of 10-nm-thick Si-rich SiN$_x$ films deposited at $R$=0.08 at various $T_s$. Although an increase in the $T_s$ results in lower transparency of the Si-rich SiN$_x$ films, the films deposited at substrate temperatures between 250 °C and 300 °C still have higher transparency than an a-Si film. Thus, we used a $T_s$ of 250 °C for the next step of optimizing the deposition conditions of the Si-rich SiN$_x$ films for high transparency and good-passivation characteristics. Because we prepare the top SiN$_x$ films at 250 °C, the temperature is also convenient for the experiment.

Fig. 4 shows the atomic composition and the $n$ at 630 nm of 10-nm-thick Si-rich SiN$_x$ films deposited at various $R$. As the SiH$_4$ gas flow rate increases, the Si content in the films increases. The excess Si content in the films induces an increase in the $n$ and a smaller band gap. Fig. 5
shows the transmission spectra of 10-nm-thick Si-rich SiN_x films deposited at a T_s of 250 °C at various R. Transparency of the films decreases with increasing R, which is consistent with the variation of the Si content.

Fig. 6 shows the τ_eff of the c-Si wafers passivated by SiN_x/Si-rich-SiN_x stacked layers as a function of the thickness of the Si-rich SiN_x films. The Si-rich SiN_x films were prepared at a T_s of 250 °C and a R of 0.08. Without the insertion of Si-rich SiN_x, the τ_eff is quite short. The obtained τ_eff of the c-Si wafers passivated by 100 nm SiN_x films is 500 µs, corresponding to a SRV of 29 cm/s. When the Si-rich SiN_x films are inserted, the τ_eff is significantly increased, and reaches a maximum value of 3300 µs, corresponding to a SRV of 4.4 cm/s, when 8-nm-thick Si-rich SiN_x films are inserted. It has been reported that direct contact between the SiN_x and the c-Si produces P-centers [8], which are defect centers caused by nitrogen dangling bonds. Insertion of the Si-rich SiN_x films might prevent the generation of these defects, resulting in an improvement of the τ_eff. However, the τ_eff decreases with increasing SiN_x film thickness. The decrease in the τ_eff for thicker Si-rich SiN_x films might be related to an increase in the total number of defects inside the Si-rich SiN_x films.

Fig. 7 shows the dependence of the τ_eff on the annealing temperature (T_a). The τ_eff increases when the T_a increases, and reaches its highest value at an T_a of 350 °C, after which it drops dramatically at an T_a of 500 °C. One possible reason for this tendency is that during thermal treatment, the Si-rich SiN_x and SiN_x films tend to release hydrogen atoms that can significantly contribute to passivating the defects on the surface and in the bulk of c-Si [9-10]. However, at a high T_a of 500 °C, hydrogen atoms might be released to ambient and not contribute to passivation, resulting in a low τ_eff.
Fig. 8 shows the $\tau_{\text{eff}}$ as function of the $R$ before and after annealing at an $T_a$ of 350 °C. One can see that $\tau_{\text{eff}}$ is vastly improved for a more Si-rich SiN$_x$ film. The reason for this improvement might be related to the Si-H bond density and the structure of the Si-rich SiN$_x$ films. More Si-rich SiN$_x$ films have a higher Si-H bond density and a more open structure [11]; thus, they can release more hydrogen atoms at low annealing temperatures. Fig. 8 also shows the relationship between the transmission of the Si-rich SiN$_x$ films and the $\tau_{\text{eff}}$ of the c-Si wafers passivated by the stacked layers. The transmission at a wavelength of 400 nm of the Si-rich SiN$_x$ films was used for evaluation. The transmission tends to decrease when the $R$ increases, while the $\tau_{\text{eff}}$ tends to increase with increasing $R$. At the highest $\tau_{\text{eff}}$ obtained of 3.3 ms, which becomes 4.8 ms after annealing at 350 °C, the transmission of the Si-rich SiN$_x$ film is 60%. Compared to an a-Si film, the transmission of the films is increased by 30%. Therefore, the SiN$_x$/Si-rich-SiN$_x$ stacked films can be used as a good passivation layer for c-Si to improve c-Si solar cell efficiency by reducing the optical loss.

A SRV of 3 cm/s for the SiN$_x$/Si-rich-SiN$_x$ stacked films is a little bit worse than a SRV of 1.5 cm/s for a SiN$_x$/a-Si structure. However, this difference in the SRV will decrease the open-circuit voltage of solar cells by only 0.015 V even if the thickness of the solar cells is as thin as 100 µm. In contrast, the achieved improvement in the transparency of the SiN$_x$/Si-rich-SiN$_x$ stacked films in the short wavelength region from 300 nm to 1200 nm, which is the effective wavelength region for c-Si absorption, can improve the short circuit current by approximately 10%. Thus, the use of Si-rich SiN$_x$ as a passivation layer instead of a-Si can contribute to improving solar cell conversion efficiency.

4. Conclusion
SiNₓ/Si-rich-SiNₓ stacked layers deposited by a Cat-CVD system demonstrate good passivation characteristics on n-type c-Si wafers with a resistivity of 2.5 Ωcm, which are typical for solar cell fabrication. The passivation quality of this SiNₓ/Si-rich-SiNₓ stacked layer structure improves with an increase in the deposition temperature and the SiH₄ gas flow-rate during the deposition of the Si-rich SiNₓ films. The best τₑffective obtained is 3.3 ms, corresponding to a SRV of 4.4 cm/s. After the annealing process, the τₑffective is enhanced greatly from 3.3 ms to 4.8 ms, and the transparency of the films with the best τₑffective is 30% higher than the transparency of a-Si films. This combination of long τₑffective and high transparency for Si-rich SiNₓ films indicate that the use of Cat-CVD SiNₓ/Si-rich SiNₓ stacked layers can enhance c-Si solar cell conversion efficiency.

Acknowledgements

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References


Figure captions

Fig. 1. Schematic cross-sectional view of a c-Si wafer passivated by SiNx/Si-rich-SiNx stacked layers.

Fig. 2. The $d$ and the $n$ at 630 nm of Si-rich SiNx films deposited for 5 s at various $T_s$. The $\tau_{\text{eff}}$ for 10-nm-thick Si-rich SiNx films are also shown.

Fig. 3. Transmission spectra of 10-nm-thick Si-rich SiNx films ($R=0.08$) deposited at various $T_s$. The spectrum of a 10-nm-thick a-Si film is also shown for comparison.

Fig. 4. Atomic composition [Si]/[N] and $n$ of 10 nm thick Si-rich SiNx films as a function of $R$ at $T_s$ of 250 °C.

Fig. 5. Transmission spectra of 10 nm thick Si-rich SiNx films deposited at a $T_s$ of 250 °C at various $R$. The transmission spectrum of a 10-nm-thick a-Si film is also shown for comparison.

Fig. 6. The $\tau_{\text{eff}}$ of c-Si wafers passivated by SiNx/Si-rich-SiNx stacked layers as a function of the thickness of the Si-rich SiNx films.

Fig. 7. The $\tau_{\text{eff}}$ as a function of the $T_a$. 
Fig. 8. The transmission at a wavelength of 400 nm of Si-rich SiN$_x$ films deposited at various $R$ and the $\tau_{\text{eff}}$ of c-Si wafers passivated by the corresponding SiN$_x$/Si-rich-SiN$_x$ stacked layers before and after annealing at an $T_a$ of 350 °C.
Fig. 1

SiNx

Si-rich SiNx

n-type c-Si

Si-rich SiNx

SiNx
Fig. 3
Si-rich SiN$_x$ films:
$R=0.08$; $T_s = 250 \, ^\circ C$
Fig. 7

The graph shows the relationship between $T_a$ (°C) and $\tau_{eff}$ (μS). There is a peak in $\tau_{eff}$ at an intermediate $T_a$ value, with values decreasing as $T_a$ increases.

- $T_a$: Temperature in °C
- $\tau_{eff}$: Effective time constant in μS