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**Abstract**

Passivation characteristics of SiNx/a-Si and SiNx/Si-rich-SiNx stacked layers on crystalline silicon are investigated. The stacked layers are deposited using plasma-enhanced chemical vapor deposition (PECVD) and characterized in terms of their electrical properties, such as surface recombination velocity, minority carrier lifetimes, and interface state density. The results show that the SiNx/a-Si stacked layer exhibits lower surface recombination velocity and higher minority carrier lifetime compared to the SiNx/Si-rich-SiNx stacked layer, indicating improved passivation quality. The interface state density is also lower for the SiNx/a-Si stacked layer, suggesting better interface quality between the silicon and the passivation layers.

**Keywords**

Passivation, Silicon, Silicon Nitride, Surface Recombination, Minority Carrier Lifetime, Interface State Density.
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 ($\tau_{eff}$) 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 (SiNx) 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 $\tau_{eff}$ 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 $\tau_{eff}$ 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 catalyster 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$^{TM}$ spectroscopic ellipsometer and
analyzed using the Cauchy model. In this model, \( n(\lambda) \) and extinction coefficients \( k(\lambda) \) are approximately expressed as [6]:

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

\[
k(\lambda) = ae^{-\left(\frac{12400(\frac{1}{\lambda} - \frac{1}{\lambda_0})}{\lambda_0^4}\right)} \quad (2)
\]

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 SiN\(_x\) were measured using a SHIMAZU Co. Ltd., UV-3150 Ultraviolet-visible-near infrared spectrophotometer.

For the measurements of \( \tau_{\text{eff}} \), SiN\(_x\)/Si-rich-SiN\(_x\) 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 \( 5 \times 10^{13} \text{ cm}^{-2} \). The \( \tau_{\text{eff}} \) is determined by the exponential decay of the microwave reflection intensity and can be expressed as follows:

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

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 $\tau_{\text{eff}}$ 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 $\tau_{\text{eff}}$ is quite short. The obtained $\tau_{\text{eff}}$ 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 $\tau_{\text{eff}}$ 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 $\tau_{\text{eff}}$. However, the $\tau_{\text{eff}}$ decreases with increasing SiN$_x$ film thickness. The decrease in the $\tau_{\text{eff}}$ 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 $\tau_{\text{eff}}$ on the annealing temperature ($T_a$). The $\tau_{\text{eff}}$ 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 $\tau_{\text{eff}}$. 
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
SiN$_x$/Si-rich-SiN$_x$ stacked layers deposited by a Cat-CVD system demonstrate good passivation characteristics on n-type c-Si wafers with a resistivity of 2.5 $\Omega$cm, which are typical for solar cell fabrication. The passivation quality of this SiN$_x$/Si-rich-SiN$_x$ stacked layer structure improves with an increase in the deposition temperature and the SiH$_4$ gas flow-rate during the deposition of the Si-rich SiN$_x$ films. The best $\tau_{\text{eff}}$ obtained is 3.3 ms, corresponding to a SRV of 4.4 cm/s. After the annealing process, the $\tau_{\text{eff}}$ is enhanced greatly from 3.3 ms to 4.8 ms, and the transparency of the films with the best $\tau_{\text{eff}}$ is 30% higher than the transparency of a-Si films. This combination of long $\tau_{\text{eff}}$ and high transparency for Si-rich SiN$_x$ films indicate that the use of Cat-CVD SiN$_x$/Si-rich SiN$_x$ 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 \([\text{Si}]/[\text{N}]\) 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\textsubscript{x} films deposited at various $R$ and the $\tau_{\text{eff}}$ of c-Si wafers passivated by the corresponding SiN\textsubscript{x}/Si-rich-SiN\textsubscript{x} stacked layers before and after annealing at an $T_a$ of 350 °C.
Fig. 1

\begin{center}
\begin{tabular}{c}
\hline
\text{SiN}_x \\
\text{Si-rich SiN}_x \\
\text{n-type c-Si} \\
\text{Si-rich SiN}_x \\
\text{SiN}_x \\
\hline
\end{tabular}
\end{center}
Fig. 2

- $\tau_{\text{eff}}$ (µs)
- $n$
- $d$ (nm)

vs. $T_S$ (°C)
Fig. 3

![Graph showing the variation of transmission (T) with wavelength (nm) at different temperatures (90°C, 150°C, 250°C, 300°C, a-Si).]
Fig. 4
Fig. 5

The figure shows the variation of transmission (T) with wavelength (nm) for different values of R: 0.04, 0.05, 0.06, 0.08, and a-Si. The transmission values are plotted as curves on a graph with the x-axis representing wavelength (nm) ranging from 300 to 1200, and the y-axis representing transmission (T) ranging from 0 to 110.
Fig. 6

Si-rich SiN$_x$ films:
R=0.08; $T_s = 250$ °C