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# Improvement of surface passivation layers for crystalline silicon solar cells

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## 1. Introduction

Enhancement in the efficiency of crystalline-silicon (c-Si) solar cells is one of great importance in c-Si photovoltaic research. High efficiency solar cells can be obtained only when both loss of photo-generated carriers and loss of sun-light in solar cells are reduced. To reduce the electrical loss due to the surface recombination of photo-generated carriers and the optical loss due to the reflection at air/c-Si interface, the formation of a surface passivation layer with the anti-reflection ability is indispensable.

Recently, silicon-nitride ( $\text{SiN}_x$ )/amorphous-silicon (a-Si) stacked layers both prepared by catalytic chemical vapor deposition (Cat-CVD), also referred to as hot-wire CVD, are found to have excellent performance as the surface passivation of c-Si. However, since a-Si layer absorbs sun-light, the use of more transparent material is required. Si-rich  $\text{SiN}_x$  films have higher silicon contents than  $\text{SiN}_x$  films, and have higher transparency than a-Si films. Thus, in my study, Si-rich  $\text{SiN}_x$  films were used as an alternative film to a-Si in the stacked structure. The major purpose of my research is to obtain good-transparency films without decrease of passivation quality in c-Si. The use of  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as passivation films on c-Si wafers results in surface recombination velocity (SRV) of as low as 4.4 cm/s and 30 % improvement of transparency at the wavelength of 400 nm compared with that of  $\text{SiN}_x$ /a-Si stacked layers. Moreover, after annealing process, the passivation property of the stacked layers was significantly improved to SRV obtained of as low as 3 cm/s.

## 2. Experimental process

All the  $\text{SiN}_x$  and Si-rich  $\text{SiN}_x$  films were prepared by Cat-CVD. The effect of the ratio of silane ( $\text{SiH}_4$ )-to-ammonia ( $\text{NH}_3$ ) gas flow rates ( $R = [\text{SiH}_4]/[\text{NH}_3]$ ) and substrate temperature  $T_s$  during deposition of Si-rich  $\text{SiN}_x$  films on properties of the

films was firstly investigated. Then  $\text{SiN}_x/\text{Si-rich SiN}_x$  stacked layers were deposited on both sides of  $n$ -type  $c\text{-Si}$  wafers, whose schematic view is shown in Figure 1. Deposition condition of  $\text{Si-rich SiN}_x$  films and  $\text{SiN}_x$  films was listed in Table 1. The passivation quality of  $\text{SiN}_x/\text{Si-rich SiN}_x$  stacked layers were evaluated through effective minority carrier lifetime ( $\tau_{\text{eff}}$ ) measured by microwave photoconductance decay ( $\mu\text{-PCD}$ ) method.

Table 1. Deposition condition of  $\text{Si-rich SiN}_x$  and  $\text{SiN}_x$  films.

Film	$\text{SiH}_4$ (sccm)	$\text{NH}_3$ (sccm)	Gas pressure(Pa)	$T_s$ ( $^\circ\text{C}$ )	$T_{\text{cat}}$ ( $^\circ\text{C}$ )
$\text{Si-rich SiN}_x$	10-20	250	10	90-300	1800
$\text{SiN}_x$	6.9	200	10	250	1800

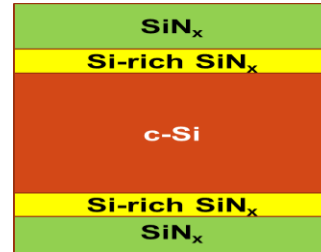


Figure 1. Schematic of cross-sectional view of a  $c\text{-Si}$  wafer passivated by  $\text{SiN}_x/\text{Si-rich SiN}_x$  stacked layers

### 3. Results and discussion

#### 3.1. The effect of $R$ and $T_s$ on the properties of $\text{Si-rich SiN}_x$ films

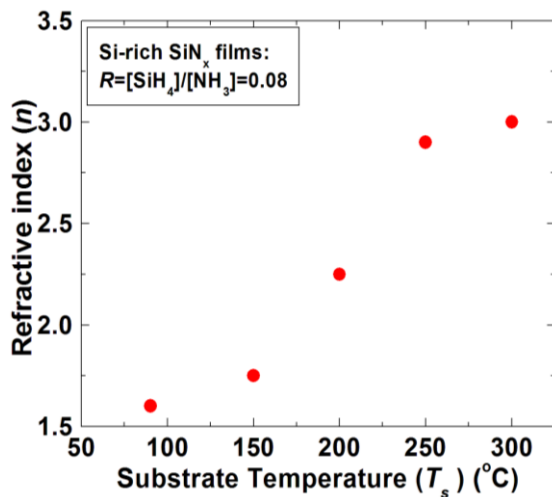


Figure 2.  $n$  at 630 nm of  $\text{Si-rich SiN}_x$  films deposited at various  $T_s$

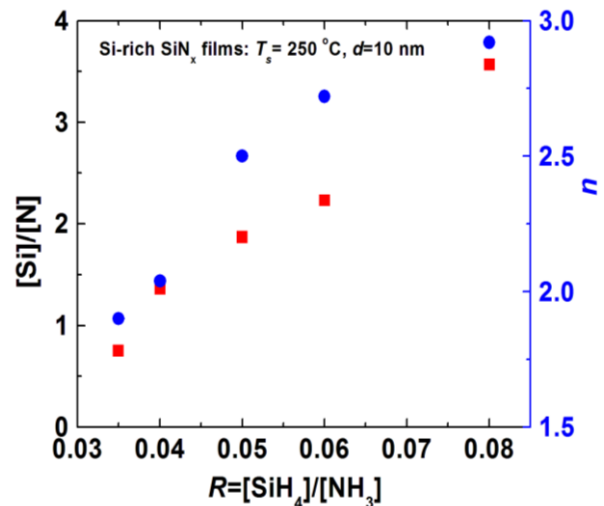


Figure 3. Atomic composition  $[\text{Si}]/[\text{N}]$  and  $n$  of 10-nm-thick  $\text{Si-rich SiN}_x$  films as a function of  $R$  at  $T_s$  of  $250^\circ\text{C}$

Figure 2 shows refractive index ( $n$ ) at 630 nm of Si-rich  $\text{SiN}_x$  films at  $R$  of 0.08 as a function of  $T_s$ .  $n$  becomes higher with increase in  $T_s$ . This variation of  $n$  may be due to the change of atomic ratio of silicon/nitrogen (Si/N) shown in Figure 3. Figure 3 shows the atomic composition and  $n$  at 630 nm of 10-nm-thick Si-rich  $\text{SiN}_x$  films deposited at various  $R$ . Si content in the films increases as  $R$  increases. The excess Si content in the films induces the increase in mass density of the films, which may contribute to increase of  $n$ .

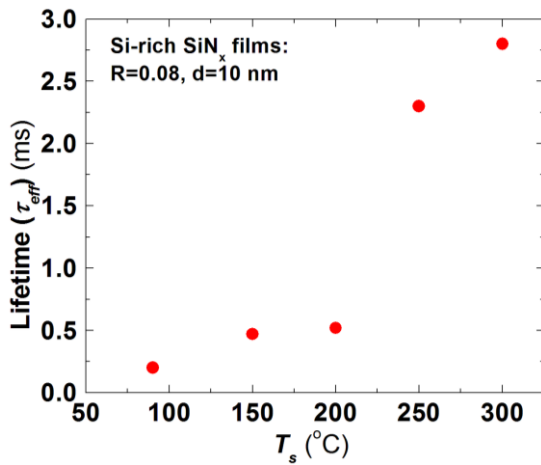


Figure 4.  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as a function of  $T_s$

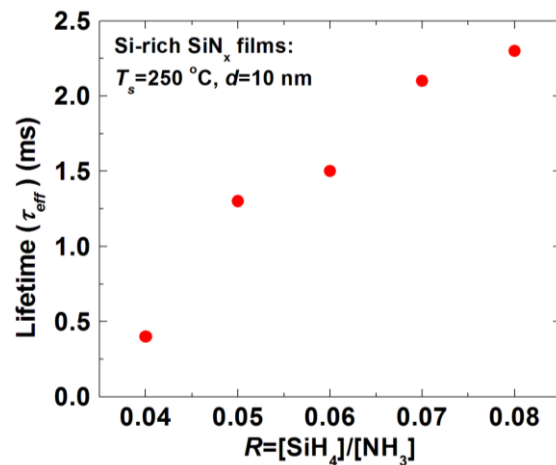


Figure 5.  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as a function of  $R$

### 3.2. Passivation quality of $\text{SiN}_x$ /Si-rich $\text{SiN}_x$ stacked layers on c-Si wafers

Figure 4 shows  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as function of  $T_s$ .  $\tau_{eff}$  improves with increase in  $T_s$ , and increases up to more than 2000  $\mu\text{s}$ , particularly at  $T_s$  of 250  $^{\circ}\text{C}$  or more. The reason is not clear at the moment. It may be due to more effective termination of unbonded Si atoms at the Si-rich  $\text{SiN}_x$ /c-Si interface and Si-rich  $\text{SiN}_x$  films at higher  $T_s$ . Figure 5 shows  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as function of  $R$ .  $\tau_{eff}$  also increases with increase of  $R$ . One possible explanation for this tendency is that the increase of  $\text{SiH}_4$  gas flow rate can provide more hydrogen atoms passivating Si wafers during Si-rich  $\text{SiN}_x$  films deposition process. Figure 6 shows  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x$ /Si-rich  $\text{SiN}_x$  stacked layers as a function of Si-rich  $\text{SiN}_x$  film

thickness. Without Si-rich  $\text{SiN}_x$  insertion,  $\tau_{eff}$  is quite low. The obtained  $\tau_{eff}$  of c-Si wafers passivated by 100 nm  $\text{SiN}_x$  films is 500  $\mu\text{s}$ , corresponding to SRV of 29 cm/s. When Si-rich  $\text{SiN}_x$  films are inserted,  $\tau_{eff}$  is significantly improved, and reaches maximum value of 3300  $\mu\text{s}$ , corresponding to SRV of 4.4 cm/s when 8-nm-thick Si-rich  $\text{SiN}_x$  films are inserted. Figure 7 shows the dependence of  $\tau_{eff}$  on annealing

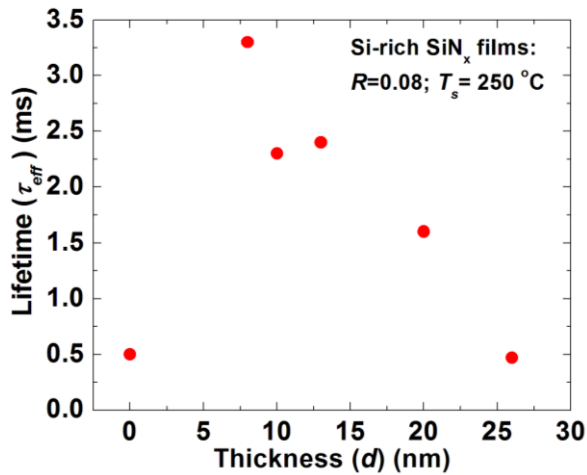


Figure 6.  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x/\text{Si-rich SiN}_x$  stacked layers as a function of thickness of Si-rich  $\text{SiN}_x$  films.

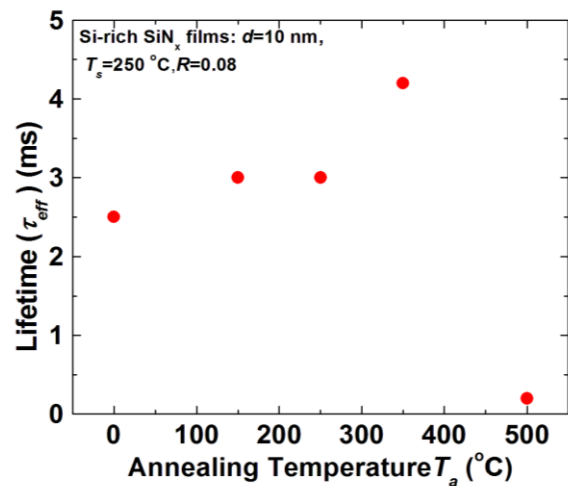


Figure 7.  $\tau_{eff}$  of c-Si wafers passivated by  $\text{SiN}_x/\text{Si-rich SiN}_x$  stacked layer as a function of  $T_a$ .

temperature ( $T_a$ ).  $\tau_{eff}$  increases when  $T_a$  increases and reaches highest value at  $T_a$  of 350 °C, and it drops drastically at  $T_a$  of 500 °C. Figure 8 shows transmission spectra of Si-rich  $\text{SiN}_x$  films at various  $R$  before and after annealing. The spectrum of a 10-nm-thick a-Si film is also shown for comparison. Transmission of Si-rich  $\text{SiN}_x$  films decreases with increase of  $R$ . However, at higher  $R$  which shows good passivation effect, transmission

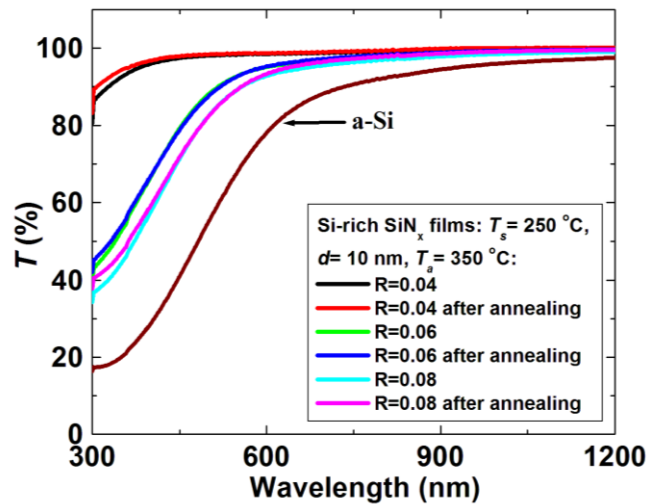


Figure 8. Transmission spectra of Si-rich  $\text{SiN}_x$  films at various  $R$  before and after annealing (The spectrum of a 10-nm-thick a-Si film is also shown for comparison).

of the films is higher than that of an a-Si film. Transmission of Si-rich SiN<sub>x</sub> films does not change after annealing process. Figure 9 shows at wavelength ( $\lambda$ ) of 400 nm of Si-rich SiN<sub>x</sub> films deposited at various  $R$  and  $\tau_{eff}$  before and after annealing. Transmission at a wavelength of 400 nm of Si-rich SiN<sub>x</sub> films was used for evaluation. Transmission tends to decrease when  $R$  increases, while  $\tau_{eff}$  tends to increase with  $R$ . At the highest  $\tau_{eff}$  of 4.8 ms after annealing at 350 °C, transmission of Si-rich SiN<sub>x</sub> film is 60 %. Compared to an a-Si film, the transmission of the films is improved by 30 %. SRV of 3 cm/s for SiN<sub>x</sub>/Si-rich SiN<sub>x</sub> stacked films is a little bit worse than that of 1.5 cm/s for a SiN<sub>x</sub>/a-Si structure.

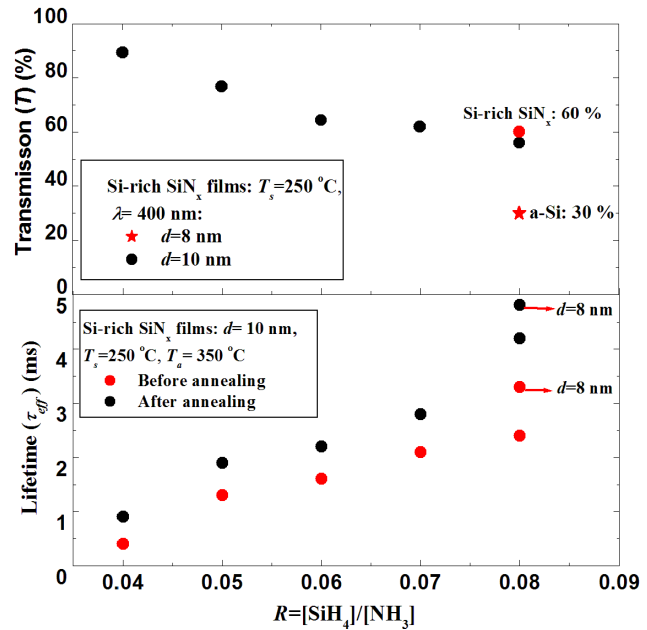


Figure 9. Transmission at wavelength ( $\lambda$ ) of 400 nm of Si-rich SiN<sub>x</sub> films deposited at various  $R$  and  $\tau_{eff}$  before and after annealing at  $T_a$  of 350 °C.

However, this difference of SRV will decrease the open-circuit voltage of solar cells only by 0.015 V. On the contrary, the improvement in transparency in short wavelength region from 300 nm to 1200 nm may improve short-circuit currents by about 10 %.

#### 4. Conclusion

SiN<sub>x</sub>/Si-rich SiN<sub>x</sub> stacked layers formed by Cat-CVD system show good passivation on  $n$ -type c-Si wafers with resistivity of 2.5  $\Omega$  cm, which are available for solar cell fabrication. Passivation quality of this structure increases with increase in  $T_s$  and  $R$  during the deposition of Si-rich SiN<sub>x</sub> films. The best  $\tau_{eff}$  obtained before annealing is 3.3 ms, corresponding to SRV of 4.4 cm/s and SRV reduces from 4.4 cm/s to 3 cm/s. After annealing process,  $\tau_{eff}$  is enhanced greatly from 3.3 ms to 4.8 ms, at which transparency is improved by 30 % in comparison with a-Si films. The results indicate that the use of Cat-CVD SiN<sub>x</sub>/Si-rich SiN<sub>x</sub> stacked layers can enhance c-Si

solar cell efficiency due to high transparency and good passivation quality of Si-rich  $\text{SiN}_x$  films.