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 (τ_{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 τ_{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 τ_{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= [SiH_4]/[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 (λ) 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]:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (1)$$

$$k(\lambda) = \alpha e^{\beta(12400(\frac{1}{\lambda} - \frac{1}{\gamma}))} \qquad (2)$$

The six fitting parameters in this dispersion model are *A*, *B*, *C*, the extinction coefficient amplitude, α, the exponent factor, β, and the band edge, γ. 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 τ_{eff}, SiN_x/Si-rich-SiN_x stacked layers were deposited on both sides of 290-µm-thick n-type (100) floating-zone (FZ)-grown Si wafers with a resistivity of 2.5 Ωcm. A schematic cross-sectional view of this structure is shown in Fig. 1. Microwave photoconductivity decay (µ-PCD) measurements were performed using a KOBELCO LTA-1510EP system with a 904-nm-wavelength pulsed-laser source at a photon density of 5×10^{13} cm^{-2}. The τ_{eff} is determined by the exponential decay of the microwave reflection intensity and can be expressed as follows:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S}{W} \qquad (3)$$

Where, τ_{bulk}, *W*, and *S* represent the minority carrier lifetime in bulk c-Si, the wafer thickness, and the SRV, respectively. The maximum SRV ($S_{eff,max}$) is determined by $S_{eff,max}=W/2\tau_{eff}$, assuming $\tau_{bulk}=\infty$ [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 τ_{eff} of the c-Si wafers passivated with SiN_x/Si-rich-SiN_x (10-nm-thick) stacked films; the τ_{eff} increases with increasing T_s, and increases up to over 2000 μs, particularly at a T_s of 250 ºC 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 ºC and 300 ºC 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 ºC 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 τ_{eff} as function of the R before and after annealing at an T_a of 350 °C. One can see that τ_{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 τ_{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 τ_{eff} tends to increase with increasing R. At the highest τ_{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 Ωcm, 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 τ_{eff} obtained is 3.3 ms, corresponding to a SRV of 4.4 cm/s. After the annealing process, the τ_{eff} is enhanced greatly from 3.3 ms to 4.8 ms, and the transparency of the films with the best τ_{eff} is 30% higher than the transparency of a-Si films. This combination of long τ_{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

[1] A. Goetzberger, J. Knobloch and B. Vob, Crystalline Silicon Solar Cells, John Wiley & Sons (1998) 87-131.

[2] A.G. Aberle, Overview on SiN surface passivation of crystalline silicon solar cells, Sol. Energy Mater. Sol. Cells 65 (2001) 239-248.

[3] F. Duerinckx and J. Szulfcik, Defect passivation of industrial multicrystalline solar cells based on PECVD silicon nitride, Sol. Energy Mater. Sol. Cells 72 (2002) 231-246.

[4] K. Koyama, K. Ohdaira, H. Matsumura, Extremely low surface recombination velocities on crystalline silicon wafers realized by catalytic chemical vapor deposited SiN_x/a-Si stacked passivation layers, Appl. Phys. Lett. 97 (2010) 082108 1-3.

[5] H. Matsumura, Study on catalytic chemical vapor deposition method to prepared hydrogenated amorphous silicon, J. Appl. Phys. 65 (1989) 4396-4403.

[6] Guide to Using WVASE32^{TM}: Software for Vase and M-44 Ellipsometers. J.A. Woollam Co., Inc. 159.

[7] J.J.H. Gielis, B. Hoex, P.J. van den Oever, M.C.M. van de Sanden and W.M.M. Kessels, Silicon surface passivation by hot-wire CVD Si Thin films studied by in situ surface spectroscopy, Thin Solid Films 517 (2009) 3456-3460.

[8] P. Aubert, F. Delmotte, M.C. Hugon, B. Agius, J.L. Cantin, H.J. Von Bardeleben, Electron-paramagnetic-resonance study of the (100)Si/Si_3N_4 interface, Phys. Rev. B 59 (1999) 10677-10684.

[9] C. Boehme, G. Lucovsky, Origins of silicon solar cell passivation by SiNx:H anneal, J. Non-Cryst. Solids 299-302 (2002) 1157-1161.

[10] M. Tucci, L. Serenelli, Metastability of SiN_x/a-Si:H crystalline silicon surface passivation for PV application, Thin solid films 516 (2008) 6939-6942.

[11] J.-F. Lelièvre, E. Fourmond, A. Kaminski, O. Palais, D. Ballutaud, M. Lemiti, Study of the composition of hydrogenated silicon nitride SiN_x:H for efficient surface and bulk passivation of silicon, Sol. Energy Mater. Sol. Cells 93 (2009) 1281-1289.

Figure captions

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

Fig. 2. The *d* and the *n* at 630 nm of Si-rich SiN_x films deposited for 5 s at various T_s. The τ_{eff} for 10-nm-thick Si-rich SiN_x films are also shown.

Fig. 3. Transmission spectra of 10-nm-thick Si-rich SiN_x 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 SiN_x films as a function of *R* at T_s of 250 °C.

Fig. 5. Transmission spectra of 10 nm thick Si-rich SiN_x 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 τ_{eff} of 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.

Fig. 7. The τ_{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 τ_{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

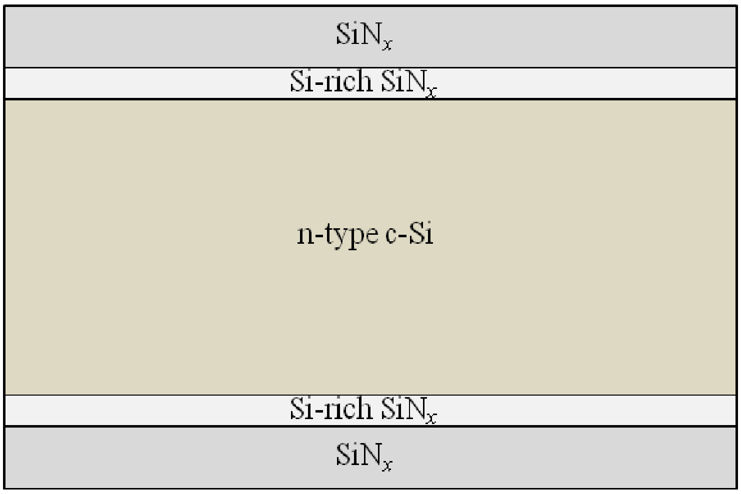
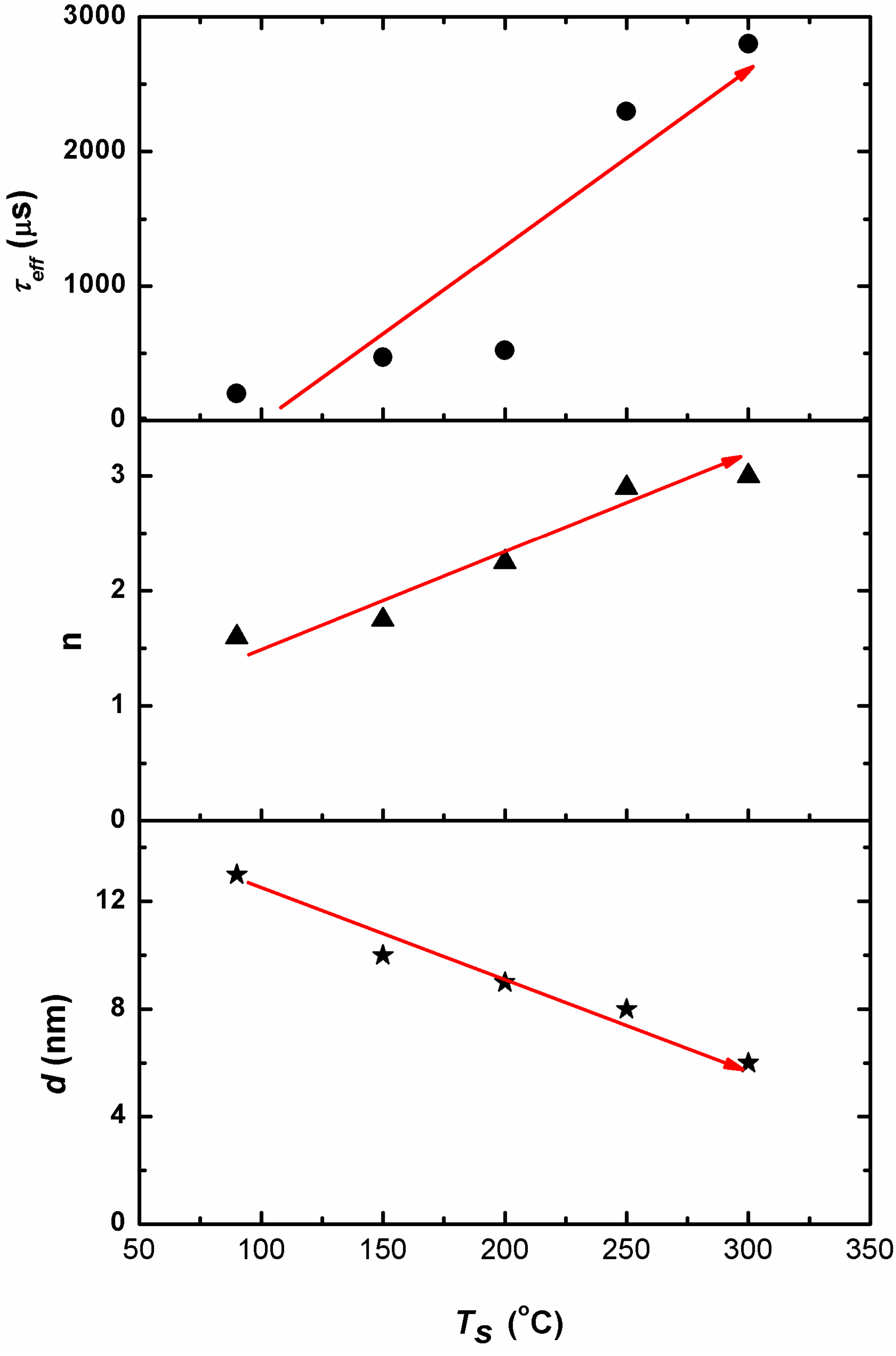


Fig. 2



3000
2000
1000
0
τ_eff (μs)
3
2
1
0
n
12
8
4
0
d (nm)
50
100
150
200
250
300
350
T_S (°C)

Fig. 3

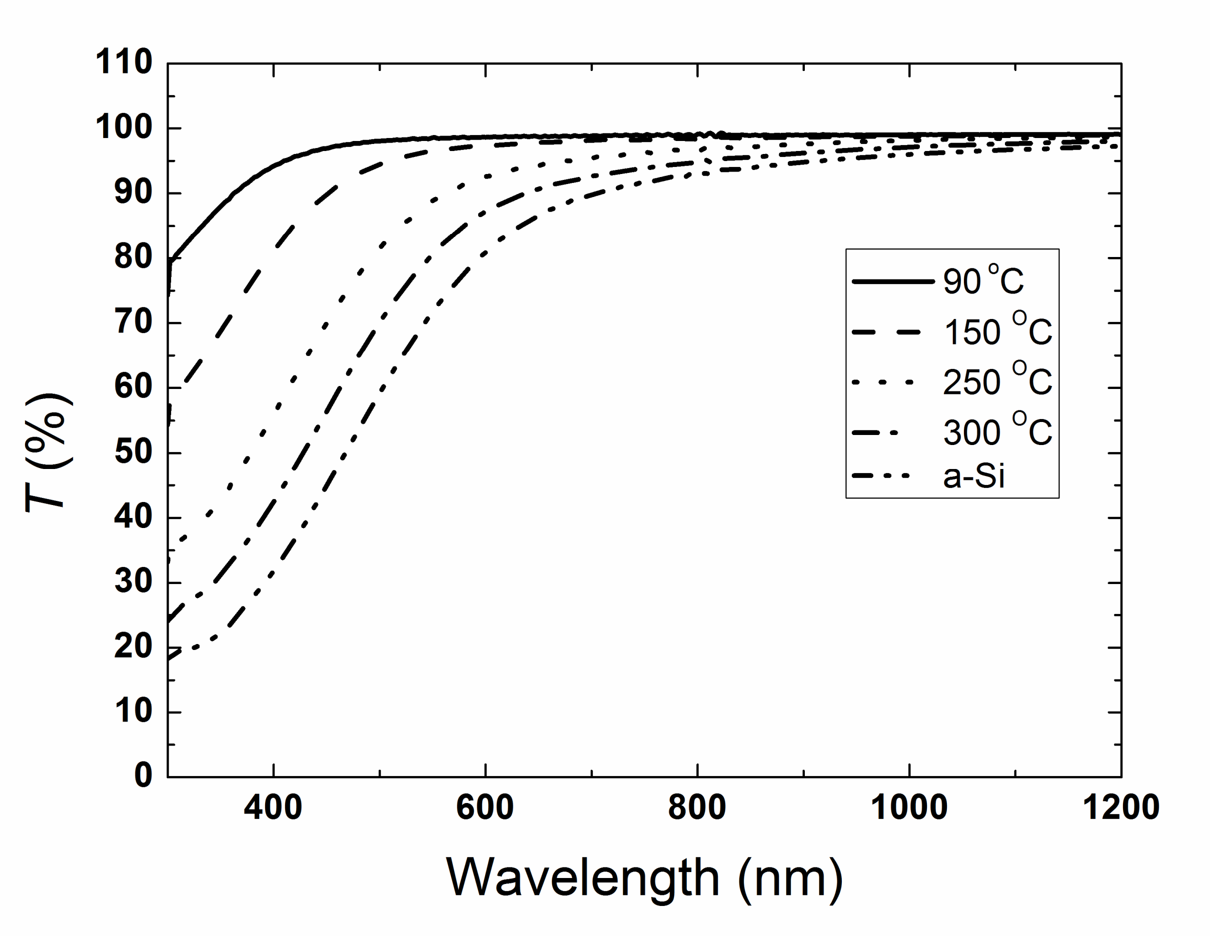
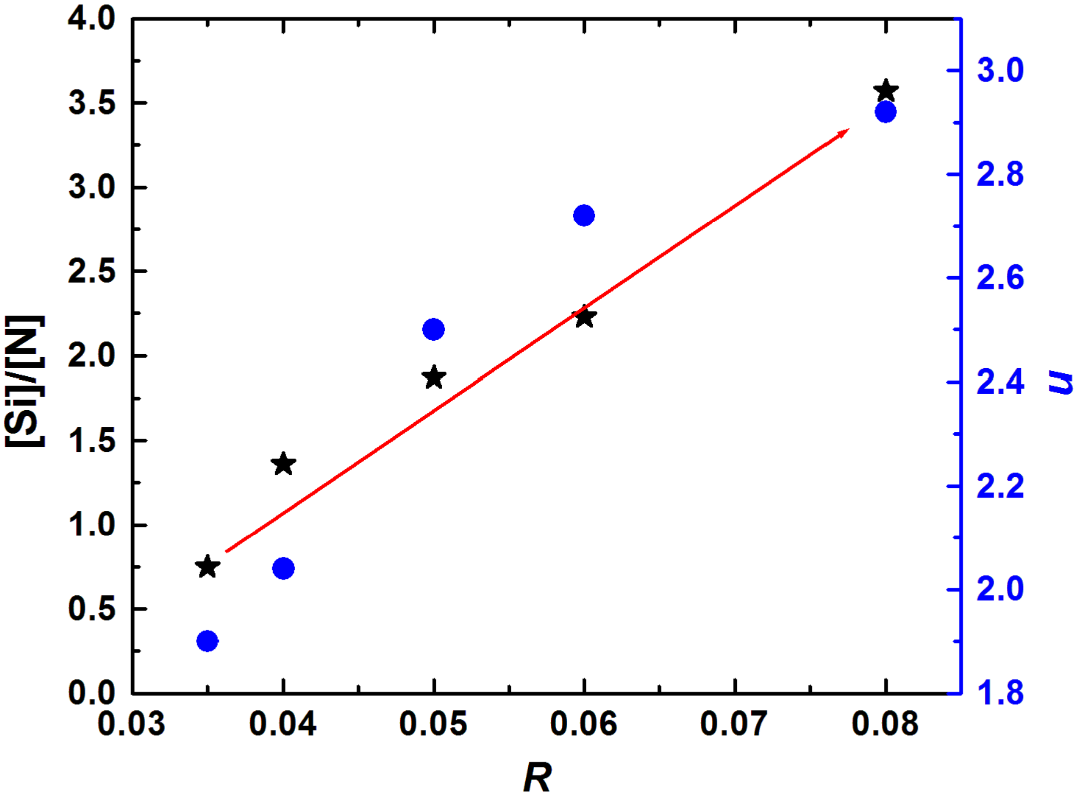
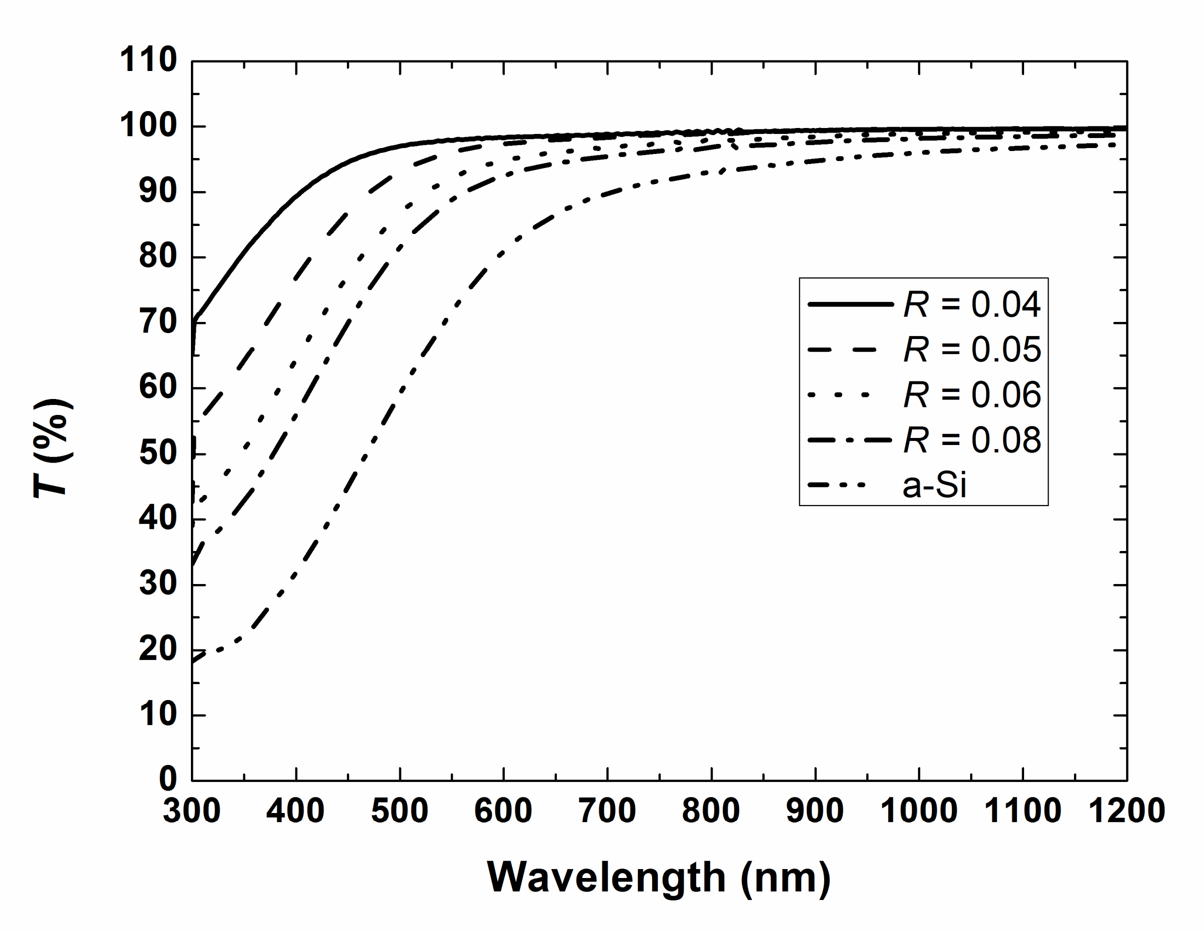

110
100
90
80
70
60
50
40
30
20
10
0
T (%)
400
600
800
1000
1200
Wavelength (nm)
90 °C
150 °C
250 °C
300 °C
a-Si

Fig. 4



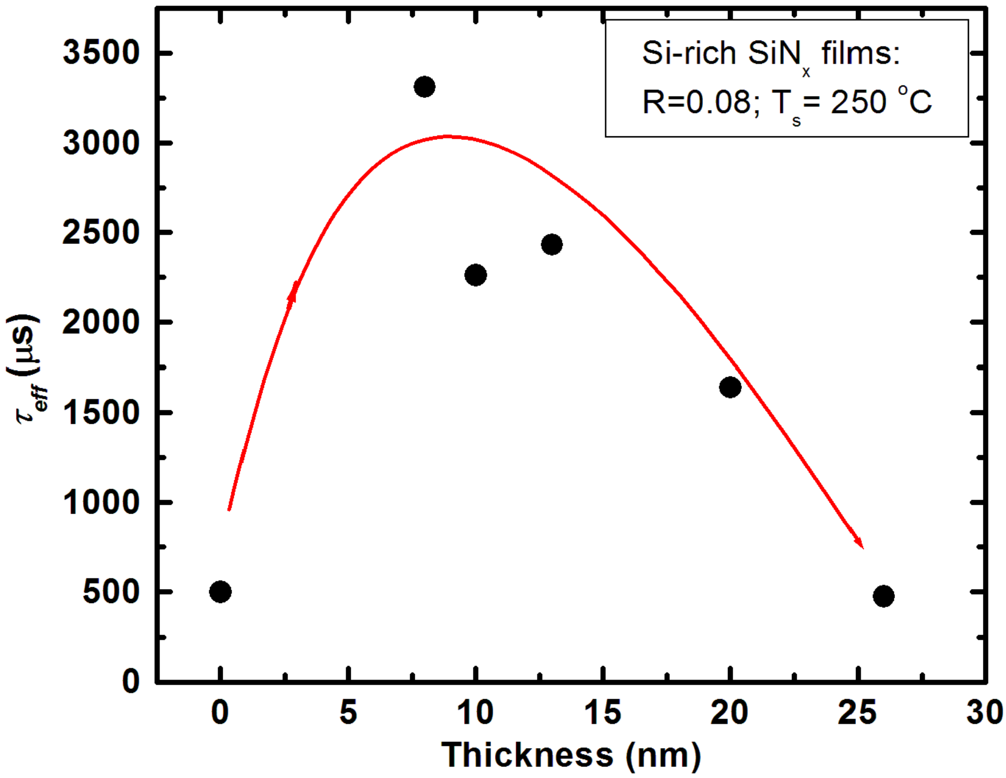
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
[Si]/[N]
3.0
2.8
2.6
2.4
2.2
2.0
1.8
n
0.03
0.04
0.05
0.06
0.07
0.08
R

Fig. 5



110
100
90
80
70
60
50
40
30
20
10
0
T (%)
300
400
500
600
700
800
900
1000
1100
1200
Wavelength (nm)
R = 0.04
R = 0.05
R = 0.06
R = 0.08
a-Si

Fig. 6



Si-rich SiN$_x$ films:
R=0.08; T$_s$ = 250 °C
τ_{eff} (µs)
3500
3000
2500
2000
1500
1000
500
0
0
5
10
15
20
25
30
Thickness (nm)

Fig. 7

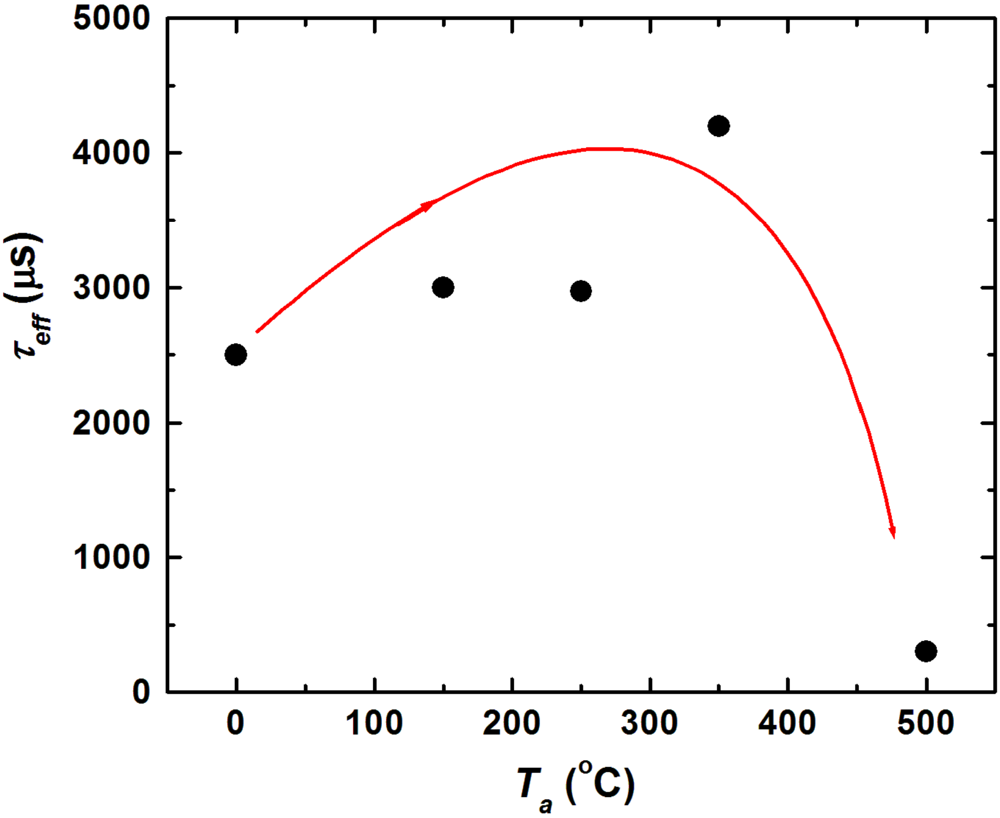
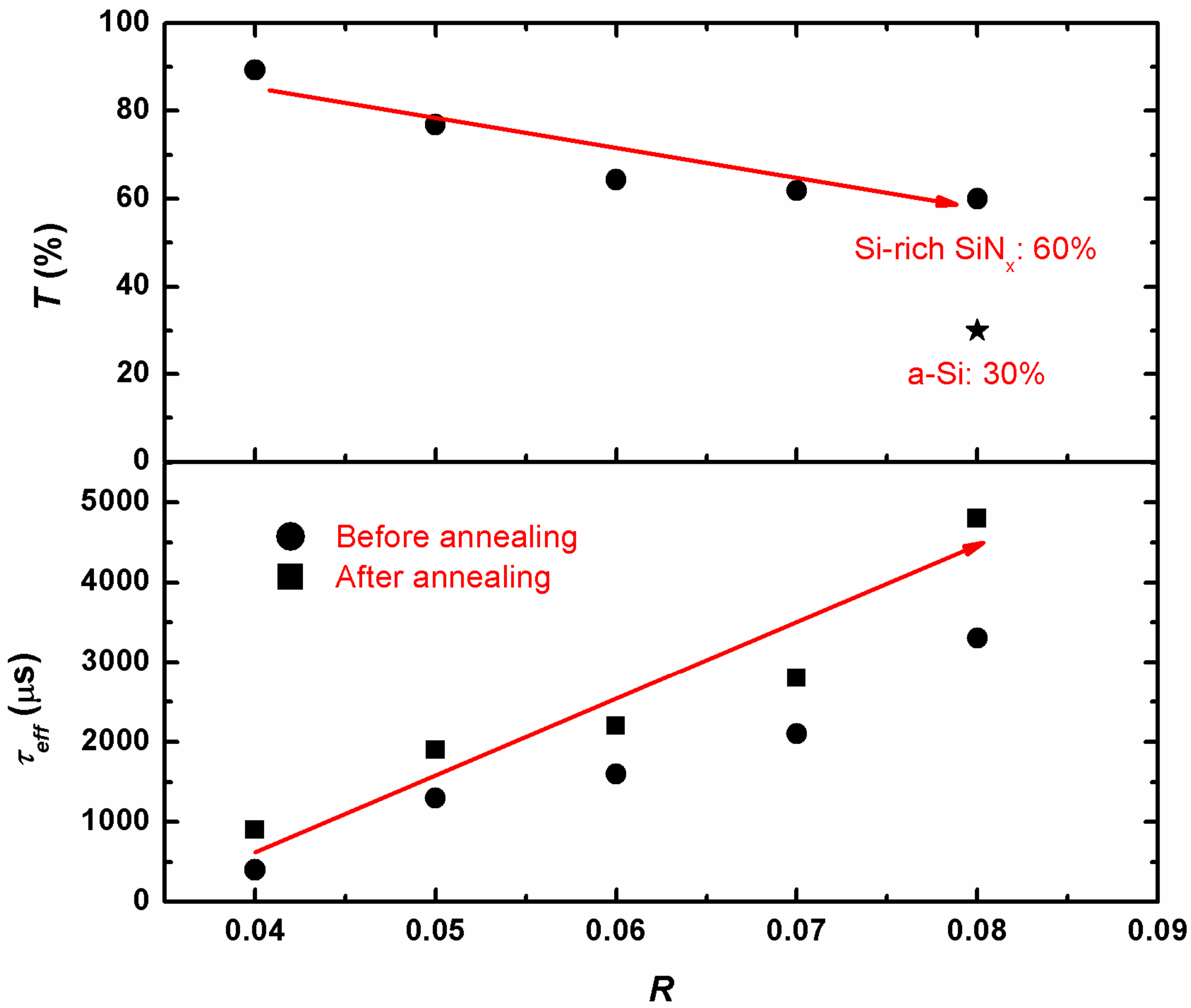


Fig. 8



100
80
60
40
20
0
T (%)
Si-rich SiNx: 60%
a-Si: 30%
5000
4000
3000
2000
1000
0
τeff (µs)
Before annealing
After annealing
0.04
0.05
0.06
0.07
0.08
0.09
R