Design of double-layer SiN_x:H film and its application in c-Si PERC solar cells

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The existing solar cell anti-reflection film technology still cannot adequately meet the light trapping needs of solar cells. In this Letter, double-layered SiN_x:H films were prepared for c-Si solar cells by plasma enhanced chemical vapor deposition (PECVD). Herein, the authors introduce a simple, convenient method to lower the reflectance in silicon solar cells by applying double-layered SiN_x:H film to increase the refractive index of such film. Compared to the single layer film devices, the reflectance of the double-layered SiN_x:H film can be significantly reduced by >30% through enhanced absorption of light in solar cells. This method has achieved an average of 0.08% conversion efficiency, with the highest being 0.18%. In addition, the double-layer film solar cells also showed a better passivation performance than that of the single-layer film, so that the minority carrier lifetime was up to 137 µs. Therefore, the improvement of solar cell efficiency mainly come from the decrease of reflectivity and the improvement in film passivation performance. The work of this Letter demonstrated the light trapping advantages and passivation enhancement performance of double-layer films applied to single crystal silicon solar cells.

1. Introduction: Solar cells which can convert solar energy to electrical energy, one of the important renewable energy sources, have a great potential to supply much power to drive the development of the modern industry which is facing the depletion of fossil energy. Especially, silicon-based solar cells have been successfully used in the commercial world and thereby dominated the solar power market. However, the energy conversion efficiency in silicon-based solar cells is far below people's expectations. With the development of solar cells technology, texturing technologies [1], SiN_x:H films [2], black silicon technologies [3–5] and Upconversion optical nanomaterials [6] were put forward to improve the optical-electivity conversion efficiency. The reported results showed that the lower reflectivity in silicon solar cells can effectively inhibit the light-loss and trap the light in the solar cells [7, 8]. In recent years, two approaches have been developed to trap the light in order to raise the silicon solar cells conversion efficiency. The first is to deposit nano-structures onto the surface of silicon wafers [3, 9, 10]. However, this method can create problems such as higher cost and lower carrier lifetime, which will cause a tremendously adverse effect on the large-scale application during industrial production. The second is to prepare anti-reflection films on the surface of silicon wafers [11, 12]. Anti-reflection films [13–16] on the one hand can passivate the silicon wafer [17] and on the other hand, lower the light reflection and enhance the carrier lifetime simultaneously. This method has been widely studied for improving the cell efficient in recent years. The relevant workers showed that a single-layer SiN_x:H film as the anti-passivation film can bring about an obvious improvement in solar cell efficiency. Gong *et al.* [18] used a double-layer film in single-crystal silicon solar cells; the solar cell with 60/20 nm SiN_x double layer anti-reflection coatings has 18.3% efficiency, while that with 80 nm SiN_x single-layer anti-reflection coating has 17.6% efficiency. The improvement of efficiency was due to the better passivation and better anti-reflection properties of double-layer anti-reflection coatings. Du *et al.* [19] used a double-layer film in polycrystalline silicon solar cells, and the double-layer silicon nitride anti-reflection coating provided a consistent enhancement in the photovoltaic performance for the multicrystalline silicon solar cell modules than the single-layer silicon nitride coating. So, depositing anti-reflection films on Si solar cells provides a significant way to increase cell efficiency. We have sorted out the research works in recent years in Table 1.

As shown in the related works listed in Table 1, to date all the available designs and studies on the double-layer SiN_x:H films are based on the conventional structure of the silicon solar cells. The passivated emitterand rear cell (PERC) solar cell is one of the most successful cases within the industry in recent years. As the transformation to the routing of a solar cell would impact its efficacy greatly, the application of double-layer SiN_x:H films to industrialised PERC solar cell production is yet to be investigated. Here, we deposited the double-layer SiN_x:H films as anti-reflection films of c-Si solar cells to effectively lower the light reflection and better passivation, which prompted a better passivation effect and improved the conversion efficiency of PERC solar cells. The novelty of our work is in the application of double-layer SiN_x:H films to industrialised PERC solar cell production, where we improved the design of the anti-reflection films, discovered the optimal conditions of such films and discussed the principles behind it.

2. Experiments and measurements: The experiment used c-Si wafers (156.75 mm × 156.75 mm, P-type, 1.5 Ω cm) as substrates. The solar cell preparation process was the standard progress of PERC solar cell. In order to reduce experimental errors, we have prepared 144 solar cells using each design parameter. The preparation of the SiN_x film was prepared by a plasma enhanced chemical vapor deposition (PECVD) apparatus. By changing the flow ratio of SiH_4 and NH_3 in PECVD, the ratio of Si to N in the film was controlled to change the refractive index of the film. The refractive index of the SiN_x:H film increased as the proportion of the silicon element increased. The thickness of the film was controlled by the processing time. The Process parameters of D_1 and D_2 films were given in Table 2.

The morphologies of as-fabricated samples were characterised using a scanning electron microscope (SEM, TESCAN, LYRA3) with an energy dispersive spectrometer (EDS) component. The reflectance of samples was acquired in the range of 300–1100 nm through the ultraviolet–visible–near infrared spectrophotometer (Shimadzu, UV-3600, with an integrating sphere). The *n* and *k* were measured by spectroscopic ellipsometry (LE-103PV, SEMLAB). Efficiencies of solar cells were measured by MAXWELL(DL-SP) and the minority carrier lifetime was acquired by Sinton WCT-120. The photovoltaic properties of the solar cells and modules were characterised at room temperature under the air mass 1.5 global solar spectrum (AM1.5G) illumination.

Table 1 Research works of double-layer film for solar cells in recent years

Year	Double film	Solar cell	Improved results (relatively)
1991 [20]	SiO_x/SiN_xO_y	p-c-Si solar cell	56% increase in I_{sc}
2001 [21]	SiN_x/SiO_2	p-c-Si solar cell	64% increase in I_{sc}
2011 [22]	SiN_x/SiN_y	p-c-Si solar cell	2.14% increase in efficiency
2017 [19]	SiN_x/SiN_y	p-c-Si solar cell	2.11% increase in efficiency
our work	SiN_x/SiN_y	c-Si PERC solar cell	0.8% increase in efficiency

Table 2 Process parameters of D_1 and D_2 films

Film	Deposition power, W	Gas flow rate (SiH_4/NH_3, sccm)	Deposition rate, nm/min
D_1	3400	200/340	0.75
D_2	3400	170/340	0.5
control group	3400	200/450	0.75

3. Results and discussions: When SiN_x:H films were grown by PECVD, those chemically reactive atoms, molecules, and groups were ionised in the RF electric field between the electrodes. These reactive particles reacted on the surface of the silicon to form SiN_x:H film. The refractive index of the SiN_x:H film was closely related to the Si/N ratio in the film. Different researchers have given approximate empirical formulas for the refractive index and Si/N ratio of SiN_x:H films prepared using different equipment. The approximate formula for the refractive index (n) and Si/N ratios given by Busarret were applicable to the SiN_x:H film prepared by PECVD [23, 24]:

$$n = 1.22 + 0.61x \tag{1}$$

where x is the Si/N molar ratio.

By adjusting the ratio of silane to ammonia to change the atomic ratio of Si and N in SiN_x:H films, the ratio of elements at different thicknesses of the SiN_x:H film was controlled to obtain different passivation properties and optical properties. The EDS results of the ratio between Si and N were shown in Fig. 1*b*. The n of the D_1 film, D_2 film and control group film were 2.15, 2.05 and 2.10 at 632 nm wavelength, respectively, while the ratio between Si and N of the D_1 film, D_2 film and control group film were 1.51, 1.26 and 1.37, respectively.

Fig. 2 shows a surface (a) and a cross-sectional view (b) of a double-layer SiN_x film coated with a silicon substrate. The Si substrate adopted a standard process of a general production line and has a pyramid-like structure with a morphology of 2–10 µm. The unevenness in the size of the structures was caused by the nucleation unevenness during the chemical etching process. The surface of the textured silicon wafer on which the double-layer film was prepared was not significantly changed, and the double-layer film was tightly covered on the surface of the pyramid-like structures. It can be seen from Fig. 2*b* that there were some small protruding structures on the surface of the coated silicon wafer, which were probably caused by uneven etching.

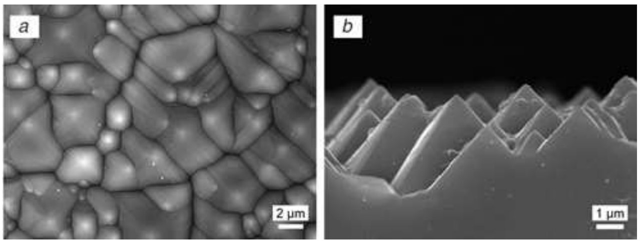

Fig. 2 *SEM images of the silicon substrate with double films*
a Surface image
b Section image

Thanks to the optical path bending effect caused by the gradient of the refractive index, the double-layer film had superior anti-reflection performance at wavelengths >600 nm. When the wavelength was <600 nm, the sample reflectance of the single-layer film was lower. This variation law was also reflected in the internal quantum efficiency curve of solar cells. In Fig. 3*b*, it can be seen that the internal quantum efficiency (IQE) curve of the experimental group and the control group have an intersection point near the wavelength of 600 nm, and the total quantum efficiency of the experimental group with double-layer films was significantly higher than that of the control group with single-layer films. The films thickness parameters of each experimental group are shown in Table 3.

We prepared three sets of samples with different total film thicknesses, and each was divided into five film thickness designs. The details of the film thickness design and the average efficiency of the corresponding solar cells are shown in Fig. 4. As can be seen from Fig. 4, the conversion efficiency of solar cells with double-layer SiN_x:H films is significantly higher than that of the samples with only single-layer films. The average efficiencies measured by the experimental groups with total film thicknesses of 65, 75 and 85 nm were 0.13, 0.08 and 0.05% higher than those of the single-layer film samples, respectively. The minority carrier lifetime test was carried out on the sample with a total film thickness of 75 nm in Fig. 4*d*. The results show that the sample life of the double-layer film is significantly higher than that of the single-layer film sample, and the minority lifetime and efficiency vary with the film thickness parameters. The high correlation proves that the design of the two-layer film shows better passivation performance than the multilayer film, which effectively improves the minority life, thereby leads to an increase in the efficiency of the solar cells.

The X-ray photoelectron spectroscopy (XPS) results are shown in Fig. 5. Due to the differences in the N/Si ratio in the film,

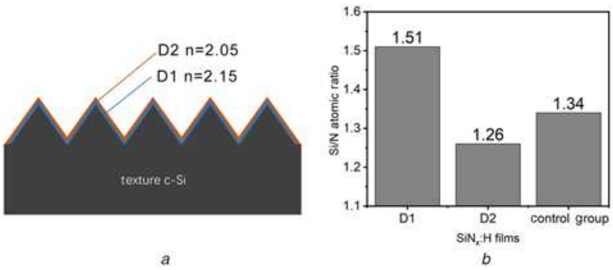

Fig. 1 *Refractive indices and the EDS result of SiN_x:H films*
a Refractive indices of SiN_x:H films
b Si/N ratio of D_1 and D_2 given by EDS

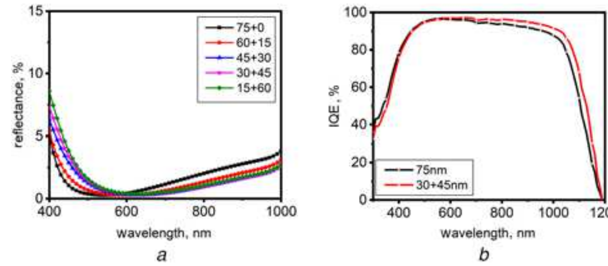

Fig. 3 *Reflectance and IQE of solar cells with different SiN_x:H films*
a Reflectance of the c-Si solar cells with different films
b IQE of solar cells with different films

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Table 3 Double-layer membrane parameters of different experimental groups

Total, nm	D_1, nm	D_2, nm
65	65	0
	50	15
	40	25
	25	40
	15	50
75	75	0
	60	15
	45	30
	30	45
	15	60
85	85	0
	70	15
	50	35
	35	50
	15	70

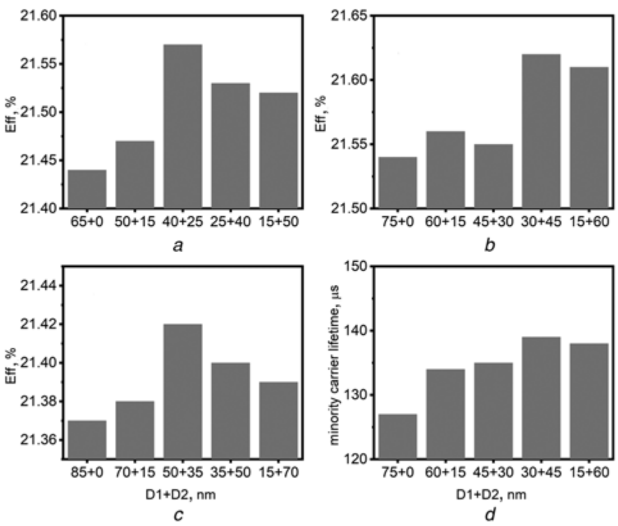

Fig. 4 *Average efficiency and monitor carriers' lifetime of c-Si solar cells with different film design*
a The average efficiencies of a total 65 nm thickness SiN_x:H film
b The average efficiencies of a total 75 nm thickness SiN_x:H film
c The average efficiencies of a total 85 nm thickness SiN_x:H film
d The minority carrier lifetime of a total 75 nm thickness SiN_x:H film

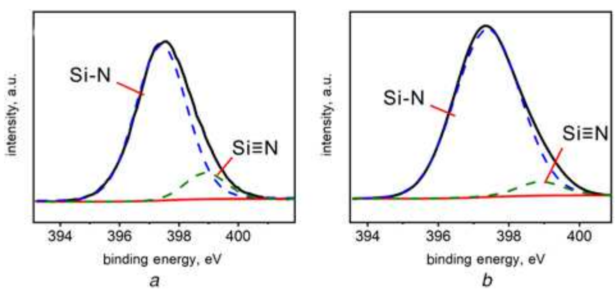

Fig. 5 *N 1s XPS results of samples*
a D_1 film
b Control group film (75 nm)

there were more Si≡N bonds (398.9 eV) in the D_1 film than in the control film, indicating that there were also more Si≡N bonds at the interface of the double-layer film and silicon. It consequently leads to an increase in passivation performance.

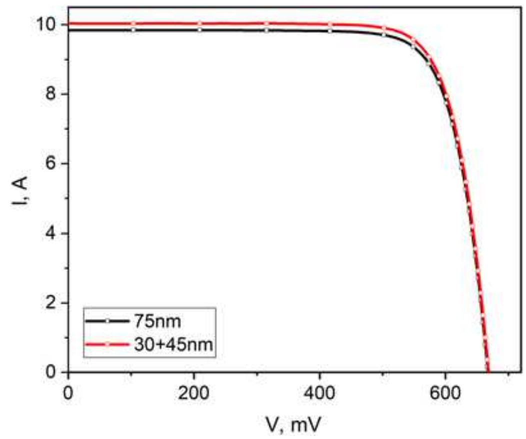

Fig. 6 *J–V curves of the solar cells with different SiN_x:H films*

Silicon suspension bonds dominated the deep level defects of SiN_x:H films, mainly $Si{\equiv}N_3$, called *K*-centre, forms a high-density defect state at the centre of the forbidden band. The stable state of the K-heart is $K^+(Si{\equiv}N_3)$, which makes the SiN_x:H films positively charged [25]. This change allowed the double-layer films to have better passivation properties than the single-layer films, resulting in improved solar cell performance. Although the minority carrier lifetime of double-layer (30 + 45) nm is higher than the (60 + 15) nm SiN_x:H, the efficiency is lower. The efficiency depends not only on the lifetime of Minority carrier but also on the reflection and some other parameters. In the case similar to the lifetime of Minority carrier, the reflection of SiN_x:H film (30 + 45) nm is higher than that of the SiN_x:H film (60 + 15) nm, resulting in higher conversion efficiency of corresponding solar cells.

From the data given in Fig. 4, the average efficiency of the solar cell with a total film thickness of 75 nm was the highest in all the experimental groups. Fig. 6 shows the *J–V* curves of the highest conversion efficiency solar cells in the experimental group and control group, respectively. Thanks to the increasing refractive index of the double-layer SiN_x:H film, the external quantum efficiency of the experimental group was significantly higher than that of the single-layer film, resulting in an efficiency increase by up to 0.18%. The performance parameters of solar cells were given in Table 4. The design of double-layer film mainly improved the light trapping effect of PERC solar cells. Under the standard lighting condition, an enhancement of electric current the light trapping effect was observed by ∼70 mA. The increase of open-circuit voltage was not significant, with the increase of only 1 mV. Hence, the short circuit current showed significant improvement, but the open circuit voltage did not.

The results of the double-layer SiN_x:H films test show that the high-refractive index SiN_x:H films, on the one hand, can increase the surface passivation effect and reduce the surface defect state, thereby reducing the probability of positive surface carrier recombination, causing the surface saturation current to decrease and enhance. The light response of the solar cell increases the open-circuit voltage. On the other hand, optical matching of the outer low refractive index to the underlying high refractive index SiN_x:

Table 4 Performance parameters of solar cells

Solar cell	Open circuit voltage, mV	Short circuit current, A	Fill factor, %	Conversion efficiency, %
75	664	9.95	79.65	21.54
30 + 45	665	10.02	79.65	21.72

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H films can reduce the reflectivity of the front surface. The enhancement of the photoresponse was effectively converted into an increase in the short circuit current. Of course, the increase in the underlying refractive index will inevitably lead to an increase in light absorption. The thickness of the underlying SiN_x:H films were only 15–75 nm, as the light absorption relative optical gain accounts for the secondary position. The surface passivation was enhanced, so the total double-layer SiN_x:H films have a positive impact on crystalline silicon solar cells.

4. Conclusion: SiN_x:H films with designed optical properties were prepared by the PECVD system. For c-Si solar cells, double-layer SiN_x:H films were designed consisting of a low index top layer and a high index lower layer. For the double-layer SiN_x:H film, the optimum total thickness was found to be 65–85 nm, and the thickness of the underlayer was about 25–45 nm. When the film thickness was within this range, the efficiency of the c-Si solar cells was relatively optimal. At the cell level, the double-layer SiN_x:H film significantly improved the photovoltaic performance of c-Si solar cells. The conversion efficiency η increased by up to 0.18% and with an average of 0.08%.

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6 References

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