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Double antireflection coating layer with silicon nitride and silicon oxide for crystalline silicon solar cell

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Abstract Anti-reflection coating (ARC) film effectively reduces the reflection of sunlight on the silicon wafer surface and then increases substantially the solar cell conversion efficiency. In this work, we carried out experiments to lessen the reflectance and thus improve the conversion efficiency with double AR coating layer with silicon nitride and silicon oxide by plasma enhanced chemical vapor deposition (PECVD) for the silicon solar cells. The optimized thicknesses and refractive indices of each ARC layer were calculated with Essential Macleod program and the theoretical method. The single antireflection layer of silicon nitride was applied with 800 Å thickness and its cell showed the conversion efficiency as 17.45 %. For the double layer AR coating (DLARC), silicon nitride layer was deposited first using SiH_4 and NH_3, and then, silicon oxide was deposited with SiH_4 and N_2O. The thicknesses of SiN_x and SiO_2 were 800 Å and 1400 Å for DLARC-1 and 500 Å and 1000 Å for DLARC-2, respectively. As a result, the reflectance of DLARCs was lower than single SiN_x and then yielded increase of short-circuit current and conversion efficiency. The completed solar cell with DLARCs showed conversion efficiencies of 17.57 % for DLARC-1 and 17.76 % for DLARC-2. This indicates that the double AR coating layer is effective to obtain the high efficiency solar cell with PECVD.

Keywords Crystalline silicon solar cell · Anti-reflection coating · Silicon nitride · Silicon oxide

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1 Introduction

Anti-reflection coating (ARC) film is necessary to reduce the surface reflection of incident light and to gain the high conversion efficiency. Usually the ARC film in the silicon solar cell is silicon nitride deposited by plasma enhanced chemical vapor deposition (PECVD). The AR coating by PECVD SiN_x in the solar cell conventional line has attracted great attention because it is operated at low-temperature (≤400 °C) and high throughput, and also provides effective surface passivation. PECVD SiN_x film contributes to the conversion efficiency improvement as AR coating maximizes the photogenerated current within the silicon substrate and passivation to reduce the surface recombination at the n^+-diffused surface. Even though SiN_x by PECVD shows unique combination of excellent electronic and optical properties, it has disadvantages of narrow wavelength range for light absorption and high absorption in the UV region reducing the short-circuit current of the cell. To solve these problems, the double layer anti-reflection coating (DLARC) is applied to the solar cell. The DLARC absorbs light in broader wavelength region and has lower reflectance, compared to single layer ARC. Due to the advantages mentioned above, DLARC process by PECVD has been studied by many groups [1–3]. The best candidate to form DLARC with SiN_x is silicon oxide (SiO_2) [3–5], as SiO_2 can be deposited by classical thermal process (CTP) or PECVD.

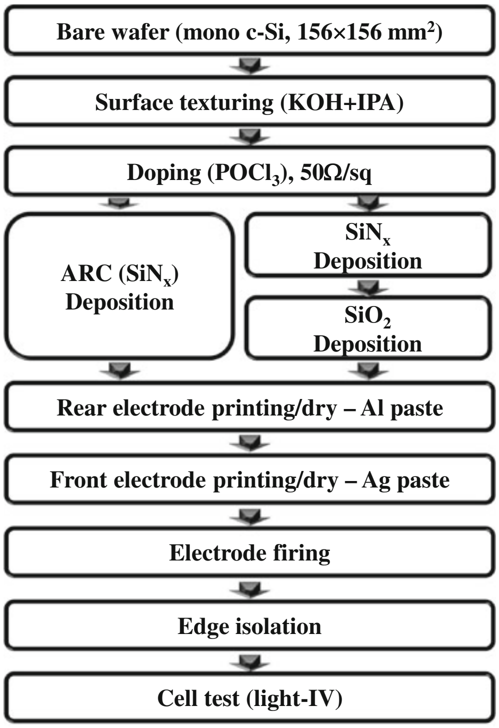


Fig. 1 Procedure of crystalline silicon solar cell fabrication

While SiO_2 by CTP has good layer properties with low density of interface trap for high conversion efficiency [1], it is known to degrade the bulk carrier lifetime of multi-crystalline silicon materials and is furthermore undesirable for its cost and throughput considerations. This indicates that the thermal silicon oxide is improper technology for the commercial solar cells. On the other hand, SiO_2 by PECVD has higher density of interface trap compared to the one by CTP [1], but is effective in throughput with short process time and enables the application for multi crystalline silicon. These are great advantages in the commercial solar cell. In this paper, we studied the double layer anti-reflection coating with silicon nitride and silicon oxide by PECVD. During fabrication of the crystalline silicon solar cell, reflectance of silicon substrate after deposited DLARC and the electrical properties of the completed cells were investigated.

2 Experimental methods

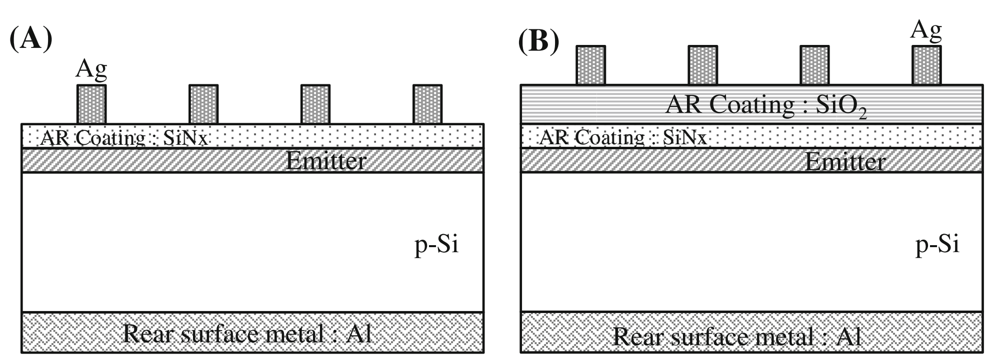
Boron doped p-type Czochralski (Cz) silicon wafers were used with 156×156 mm^2 area, 200 μm thickness, and 0.5~3 Ω•cm resistivity. Figure 1 shows the fabrication sequence and method of crystalline silicon solar cell. The wafers were textured in a mixed solution of KOH and iso-propanol at 88 °C and etched with ~12 μm in each side. The emitter then was formed by gaseous diffusion from $POCl_3$ source in a tube furnace. The temperature for pre-deposition and drive-in processes were 790 °C and 855 °C, respectively, which were the conditions obtained in the previous experiment. After dipping into HF solution to remove phosphorous silicate glass (PSG), the sheet resistance was measured as 50 Ω/□ by 4-point probe. Anti-reflection coating, SiN_x:H was deposited by PECVD using silane, ammonia and argon gases. For double layer anti-reflection coating, silicon oxide using silane, nitrous oxide, and argon gases was deposited by PECVD. The front and back electrodes were formed by the screen-printing method with Ag and Al pastes, respectively. After printing and drying with the metal pastes, the wafers were co-fired in an IR-lamp heated belt furnace in order to form the ohmic contact between metal and silicon substrate. The co-firing temperature for the single SiN_x and DLARC solar cells were same, resulting from applying various temperatures. Since the wafer was doped in all sides, the edge isolation was applied using 532 nm Q-Switched Nd:YVO_4 laser. The thickness and refractive index of AR coating film were measured by the ellipsometer from F.A. Woollam. The current–voltage characteristics of the completed cell were obtained using the solar simulator from Pasan. The electrical characteristics were averaged with 3 completed solar cells.

3 Results and discussion

3.1 Design for double layer antireflection coating

Prior to the DLARC cell fabrication, the deposition sequence and thicknesses of AR coating layers were

Fig. 2 The schematic structures for single anti-reflection coated (**a**) and double anti-reflection coated (**b**) silicon solar cells



considered. The optimal refractive index of each layer in DLARC can be determined by Eq. 1a, 1b [3, 6].

$$n_1 = \sqrt[3]{n_0^2 n_3} \quad (1a)$$

$$n_2 = \sqrt[3]{n_0 n_3^2} \quad (1b)$$

Here *n* symbols mean the refractive indices; n_o is one for silicon substrate and n_3 for air which are 3.4 and 1.0 at 630 nm, respectively [7]. The symbols of n_1 and n_2 are the inner and outer layers of DLARC film, respectively. From Eq. 1a, 1b, the ideal values for n_1 and n_2 were obtained as 2.26 and 1.5, respectively. The reflectance can be estimated using the refractive indices by Eq. 2, resulting in almost zero value at 630 nm.

$$R = \left(\frac{n_1^2 n_3 - n_0 n_2^2}{n_1^2 n_3 + n_0 n_2^2} \right)^2 \quad (2)$$

The design with low-high refractive index on silicon substrate in which the outer layer has the low refractive index and the inner layer has high refractive index is fruitful in the spectral stability of the coating and for low reflectance [2]. Stability means that the low-reflectance spectrum changes very slightly with thickness and refractive index variations. Generally, the experimental conditions affect the thickness and refractive index values of the deposited layer and consequently, the desired low reflectance value. Calculations show that the design with low-high refractive index obtained here gives more advantage than the reverse design to keep the low reflectance value with the variations of refractive index and thickness of each layer in the ARC system during deposition [2]. Thus in this study, SiO_2 and SiN_x were decided as the outer and inner layers, respectively. The thicknesses for these layers can be calculated by $n \bullet d = \lambda/4$ (d is thickness and λ is wavelength, typically 630 nm), resulting in the thicknesses of 1050 Å and 700 Å for SiO_2 and SiN_x.

The Essential Macleod software was also used to calculate the thicknesses of SiN_x and SiO_2. The Essential Macleod is comprehensive software for the design and analysis of optical thin films [6]. In particular it will calculate a wide range of performance parameters of a given coating design including the usual reflectance and transmittance magnitude and phase, but also color and ellipsometric quantities. After entering the coating materials and its range of refractive indices into the program, the proper thicknesses and refractive indices of ARC layers and the transmittance in range of 300~1200 nm were obtained. The result indicated the thicknesses and refractive indices for SiN_x and SiO_2 were 820 Å, 2.2 and 1390 Å, 1.46, respectively. The difference in thicknesses from the theoretical calculation and the Essential Macleod may have been caused by wavelength region considered because the theoretical calculation was focused on 630 nm and the Macleod was done in 300–1200 nm.

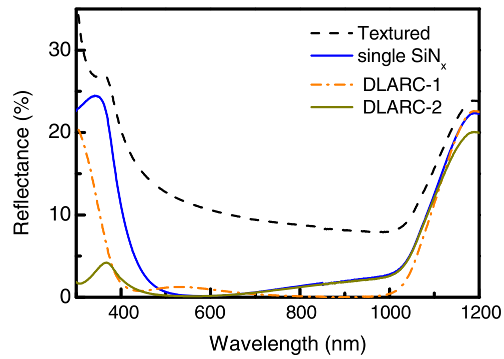


Fig. 3 The reflectance spectra of the silicon wafers with textured, single anti-reflection coated, DLARC-1 and DLARC-2

3.2 Mono crystalline silicon solar cell fabrication

Figure 2(a) shows the structure of reference silicon cell with single layer AR coating, SiN_x. The optimized thickness and refractive index of silicon nitride were obtained as 800 Å and 2.2, respectively, from the previous experiments. The 156×156 mm^2 mono crystalline silicon solar cell showed the conversion efficiency of 17.45 %, shown in Table 1. The SiN_x/SiO_2 DLARC-1 solar cell with thicknesses and refractive indices obtained from the Essential Macleod was fabricated. Double layer ARCs with SiN_x and SiO_2 in serial order were achieved on a silicon wafers by changing the deposition conditions, resulting in 800 Å and 1390 Å

Table 1 Current–voltage characteristics of 6″ monocrystalline silicon solar cell with single layer and double layer antireflection coating films

Electrical Properties	Single ARC (800 Å SiN_x)	DLARC-1 (800 Å SiN_x/1400 Å SiO_2)	DLARC-2 (500 Å SiN_x/1000 Å SiO_2)
J_{sc} (mA/cm^2)	35.15	35.51	35.63
V_{oc} (mV)	627	623	628
Fill factor (%)	79.3	79.3	79.3
Efficiency (%)	17.45	17.57	17.76

All values averaged from 3 completed cells; error range J_{sc}±0.05, V_{oc}±3 FF±0.3, Efficiency±0.05

Table 2 Reflectance measurements for monocrystalline silicon wafers with and without anti-reflection coatings

Samples	Average reflectance (%)	
	300–1200 nm	400–900 nm
Textured	13.7	10.90
Single ARC (800 Å SiN_x)	6.4	1.40
DLARC-1 (800 Å SiN_x+1400 Å SiO_2)	4.3	0.61
DLARC-2 (500 Å SiN_x+1000 Å SiO_2)	3.7	0.75

thicknesses and 2.2 and 1.46 for refractive indices, respectively. Figure 3 shows the reflectance spectrum of the silicon wafer deposited with DLARC-1. The average reflectance of DLARC-1 coated wafer was 0.61 % in range of 400–900 nm while one with single 800 Å SiN_x was 1.4 %. Figure 3 also shows the reflectance of only textured wafer without ARC and average of which was 10.9 % in 400–900 nm region. The reflectance spectrum for the wafer deposited with DLARC-2 consisting of 500 Å SiN_x and 1000 Å SiO_2 was shown in Fig. 3. The refractive indices for SiN_x and SiO_2 are 2.2 and 1.46, respectively. These values were based on the result from the theoretical calculation. The SiN_x layer was deposited thinner than the one from the calculation to avoid excessively thick ARC film. This DLARC-2 film deposited wafer also shows the dramatic decrease of reflectance, compared to textured and SiN_x-coated ones. The DLARC-2 with 500 Å SiN_x and 1000 Å SiO_2 has the average reflectance of 0.75 % in range of 400–900 nm, which is slightly higher than 0.61 % of the DLARC-1. The function of ARC film for decrease in reflectance is unquestionable. Reflectance values of both DLARCs were significantly improved over that of a single layer, indicating that DLARC film is effective for absorbing light in broader wavelength region. The reflectance spectra

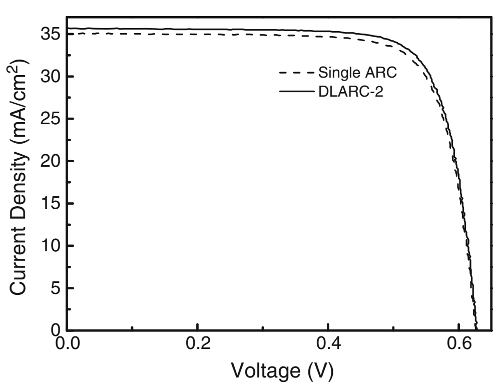


Fig. 4 The light current–voltage curve for single ARC (---) and DLARC-2 (—) solar cells

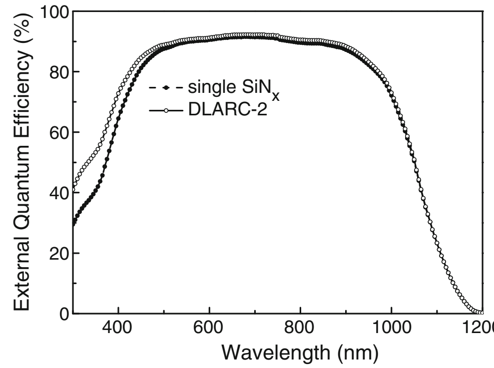


Fig. 5 External quantum efficiency of single ARC and DLARC-2 deposited crystalline silicon solar cells

for the textured wafers with DLARCs have distinguishable shape with two minima and a weak maximum between these minima while that of the single ARC has one minimum [5]. The DLARC-1 and DLARC-2 have two minima at 443 nm and 900 nm with 0.76 % and ~0 % reflectance and 305 nm and 558 nm with 1.67 % and 0.12 %, respectively, while the single ARC has one minimum at 584 nm (Fig. 3). The average reflectance for different ARC layers in different region was summarized in Table 2.

After screen printing with Ag and Al pastes for front and rear surfaces, respectively, and firing, the electrical characteristics and conversion efficiency for the completed solar cells were measured. The completed DLARC-1 and DLARC-2 solar cells showed the conversion efficiency as 17.57 % and 17.76 % with 0.12 % and 0.31 % improvement compared to single ARC solar cell (Table 1). This results from reflectance decrease of DLARC film. It can also be explained using the short circuit current (I_{sc}) equation generating under illumination (Eq. 3), indicating that I_{sc} is mainly influenced on reflectance [8].

$$I_{sc} = q\int [1 - R(\lambda)]F(\lambda)IQE(\lambda)d\lambda \tag{3}$$

where R(λ) is reflectance at the surface, F(λ) is the photon flux and IQE(λ) is the internal quantum efficiency.

The efficiency for DLARC-2 solar cell was 17.76 % with J_{sc}=35.63 mA/cm^2, V_{oc}=628 mV and fill factor=79.3 % as shown in Fig. 4 and Table 1. For comparison, Fig. 4 also shows the current–voltage curve for the single SiN_x coated solar cell. External quantum efficiency spectra shown in

Table 3 The calculated conversion efficiency from PC1D simulation with the measured reflectance spectra

	Efficiency (%)
Textured	15.9
Single ARC	17.5
DLARC-1	17.7
DLARC-2	17.6

Fig. 5 indicate that the efficiency improvement in DLARC-2 solar cell mainly results from more light absorption at the short wavelength region, compared to the single ARC cell. The DLARC-2 solar cell showed the best conversion efficiency and the current density among the cells fabricated herein. The DLARC-2 cell had slightly higher conversion efficiency than the DLARC-1 cell, but their average reflectance values were very close. This could be explained by increased absorption as the layer thickness increases in a short wavelength [9]. Even though the extinction coefficients of the ARC films are negligibly low, the absorption of SiN_x film with n=2.24 is non-negligible, especially at the short wavelength [10].

In the solar cell fabrication with DLARC, Ag paste for the front metallization might be an issue with penetration of thick film, since the commercial Ag paste was developed to optimize the common 800 Å SiN_x ARC film. As a result, the fill factor from the completed DLARC solar cells was reasonably high as 79.3 %. It means that the current commercial Ag paste is acceptable for thick ARC film. This concern was also investigated with PC1D simulation. To figure out the reflectance effect on the conversion efficiency, simulation was performed by inserting the measured reflectance spectra (Fig. 3). After setting up the SiN_x-coated cell to 17.5 %, same as the experimental data, the simulated conversion efficiency with reflectance spectra of DLARC-1 and DLARC-2 were 17.7 % and 17.6 % (Table 3). These values are very close to experimental results, indicating that the conversion efficiency difference was primarily due to reflectance. In this work, the double layer anti-reflection coating with different thicknesses by PECVD was performed in the crystalline silicon solar cell fabrication. It shows the possibility to obtain better efficiency by PECVD DLARC with various studies regarding to optimize the refractive index and thickness.

4 Conclusions

The studies reported herein have provided the conversion efficiency improvement of mono crystalline silicon solar cell with double layer anti-reflection coating consisting of SiN_x and SiO_2 deposited by PECVD. The thicknesses and refractive indices for each layer were obtained from the Essential Macleod program and theoretical calculation. The solar cells with DLARC showed the better efficiency as 17.57 % and 17.76 %, compared with 17.45 % for single SiN_x ARC. This mainly results from the current density improvement due to the reflectance decrease by DLARC.

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