

# Tri-layer antireflection coatings ( $\text{SiO}_2/\text{SiO}_2\text{--TiO}_2/\text{TiO}_2$ ) for silicon solar cells using a sol–gel technique

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## Abstract

Antireflection coatings (ARCs) have become one of the key issues for mass production of Si solar cells. They are generally performed by vacuum processes such as thermal evaporation, reactive sputtering, and plasma-enhanced chemical vapor deposition. In this work, a sol–gel method has been demonstrated to prepare the ARCs for the non-textured monocrystalline Si solar cells. The spin-coated  $\text{TiO}_2$  single-layer,  $\text{SiO}_2/\text{TiO}_2$  double-layer and  $\text{SiO}_2/\text{SiO}_2\text{--TiO}_2/\text{TiO}_2$  triple-layer ARCs were deposited on the Si solar cells and they showed good uniformity in thickness. The measured average optical reflectance (400–1000 nm) was about 9.3, 6.2 and 3.2% for the single-layer, double-layer and triple-layer ARCs, respectively. Good correlation between theoretical and experimental data was obtained. Under a triple-layer ARC condition, a 39% improvement in the efficiency of the monocrystalline Si solar cell was achieved. These indicate that the sol–gel ARC process has high potential for low-cost solar cell fabrication.

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**Keywords:** silicon; antireflection coating; sol–gel;  $\text{TiO}_2$ ;  $\text{SiO}_2$ ; solar cell

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## 1. Introduction

Antireflection coatings (ARCs) are widely used in various applications such as display panels, solar cells and optical lenses [1–3]. Thin-film ARCs can greatly reduce the optical loss in multi-element lenses by making use of phase changes and the dependence of the reflectivity on refraction index. A thin, dielectric film or several such films were applied to an optical surface to reduce its reflectance and thereby increase its transmittance. A single-layer ARC can be non-reflective only at one wavelength, usually at the middle of the visible region. Multiple layers are more effective over the entire visible spectrum. Several transparent and high refractive-index material films have already been applied to ARC techniques, e.g. SiO ( $n = 1.8$ – $1.9$ ), SiO<sub>2</sub> ( $n = 1.44$ ), Si<sub>3</sub>N<sub>4</sub> ( $n = 1.9$ ), TiO<sub>2</sub> ( $n = 2.3$ ), Al<sub>2</sub>O<sub>3</sub> ( $n = 1.86$ ), Ta<sub>2</sub>O<sub>5</sub> ( $n = 2.26$ ), SiO<sub>2</sub>–TiO<sub>2</sub> ( $n = 1.8$ – $1.96$ ) and ZnS [4–9]. Optical coatings are generally performed by vacuum processes such as thermal evaporation, reactive sputtering, and plasma-enhanced chemical vapor deposition (PECVD). All these methods are capable of producing films with uniform thickness and good optical properties. However, the conventional vacuum deposition processes are expensive and unsuitable for continuous mass production techniques in low-cost solar cells. Recently, high refractive-index and high-transparency Si<sub>3</sub>N<sub>4</sub> or TiO<sub>2</sub> single layer and SiO<sub>2</sub>/TiO<sub>2</sub> double-layer have been developed and applied in solar cell ARCs process. These favorite films are prepared by PECVD and this results in reflectance below 10% [10–12].

Recently, ARCs have become one of the key issues for mass production of mono- and multi-crystalline Si solar cells. The sol–gel technique offers a simple and low-cost process to prepare the high-quality thin films [13,14]. In this work, the TiO<sub>2</sub> single-layer, SiO<sub>2</sub>/TiO<sub>2</sub> double-layer and SiO<sub>2</sub>/SiO<sub>2</sub>–TiO<sub>2</sub>/TiO<sub>2</sub> triple-layer ARCs on monocrystalline Si solar cells were prepared by a sol–gel spin-coating technique. To achieve minimum reflection of a normal incident wave of a single wavelength, the antireflection coating may consist of a single layer, which must possess (a) a refractive index equal to the square root of the refractive indices of the materials bounding the coating, and (b) a thickness equal to one-quarter of the wavelength (i.e., the wavelength within the material of which the coating consists). However, if one wants to achieve minimum reflection of multiple wavelengths, additional layers must be added. Kern and Tracy have observed an increase of 44% in the cell efficiency after spraying TiO<sub>2</sub> single-layer ARC [15]. Green et al. have used MgF<sub>2</sub>/ZnS double-layer ARCs on Si cells with 19.1% efficiency [16]. In this paper, we present the results of calculations and experiments obtained by sol–gel method of single-layer, double-layer and triple-layer ARCs on polished silicon substrates. For an optimum ARCs design, the refractive index and thickness of each layer must be controllable to achieve the best performance along the desired spectrum. Details of the fabrication process and efficiency improvement will be described.

## 2. Experimental details

### 2.1. Sol–gel and spin coating process

The flow chart of the ARC synthesis process was performed using a sol–gel process as shown in Fig. 1. A clear solution is prepared by reacting metal alkoxide with a mixture of critical amount of water and/or acid in an alcohol diluted medium, and the SiO<sub>2</sub>, SiO<sub>2</sub>–TiO<sub>2</sub> and TiO<sub>2</sub> coatings were spin coated on the Si substrate from the above-said

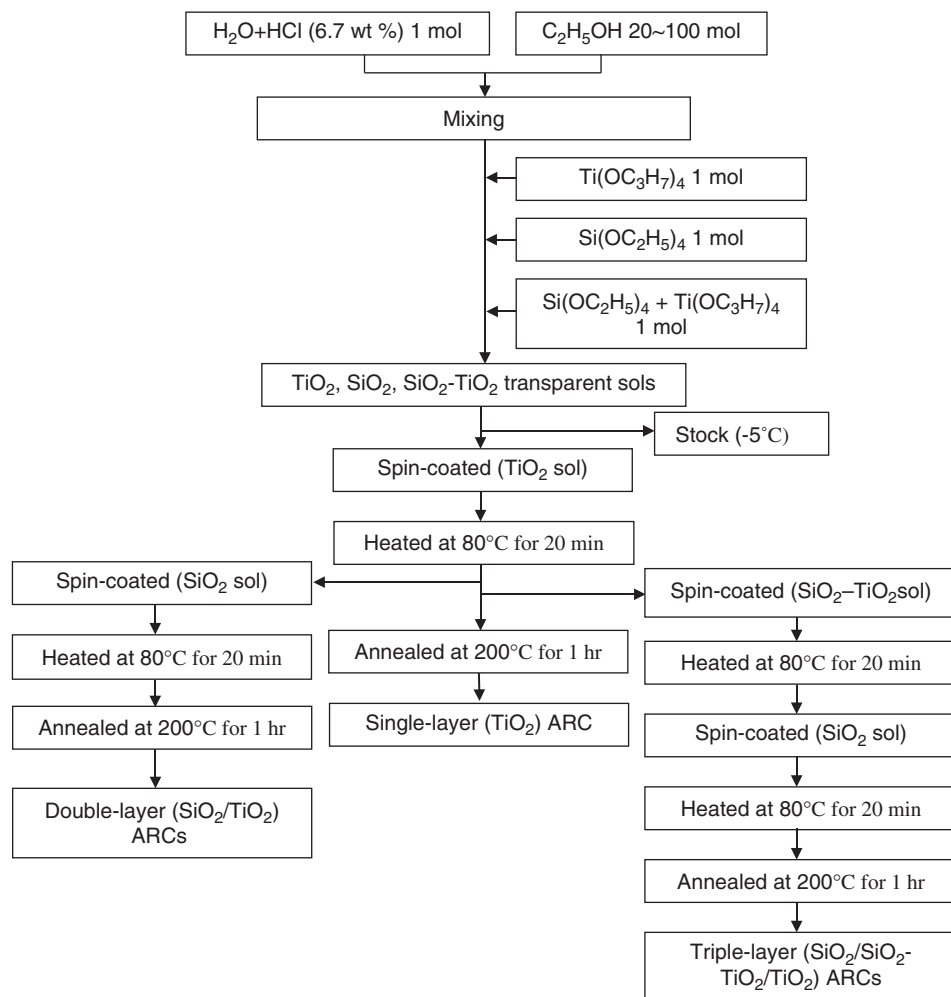


Fig. 1. Flow chart of sol-gel process for  $\text{TiO}_2$  single-layer,  $\text{SiO}_2/\text{TiO}_2$  double-layer and  $\text{SiO}_2/\text{SiO}_2\text{-TiO}_2/\text{TiO}_2$  triple-layer antireflection coatings.

solution at 2000–6000 r.p.m for 30 s. The desired film thickness can be adjusted by the spin speed. Each film was pre-baked at  $80^\circ\text{C}$  for 20 min and then post baked at  $200^\circ\text{C}$  for 1 h in atmosphere. Table 1 tabulated the sol-gel parameters and deposition results of the  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  and  $\text{TiO}_2$  films. After spin coating and post-baking processes, the refractive index, thickness and reflectance of the film were measured using an n&k analyzer (model: 1280, N&K Tech. Inc.).

## 2.2. Design of single-layer, double-layer and triple-layer ARCs

In some applications, zero reflectance is needed at a single wavelength or throughout a narrow spectrum band. The optimum thickness and refractive index with a minimum

Table 1

Sol-gel parameters and deposition results of the SiO<sub>2</sub>, SiO<sub>2</sub>-TiO<sub>2</sub> and TiO<sub>2</sub> films

|                                    | Ti(OC <sub>3</sub> H <sub>9</sub> ) <sub>4</sub> :Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> :C <sub>2</sub> H <sub>5</sub> OH (mol) | Spin rate<br>(r.p.m) | Thickness<br>(nm) | Refractive index<br>( $\lambda = 500$ nm) |
|------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|----------------------|-------------------|-------------------------------------------|
| TiO <sub>2</sub>                   | 1:0:60                                                                                                                                     | 2000–6000            | 64–33             | 2.26                                      |
| SiO <sub>2</sub>                   | 0:1:80                                                                                                                                     |                      | 93–54             | 1.45                                      |
| SiO <sub>2</sub> -TiO <sub>2</sub> | 1:1:80                                                                                                                                     |                      | 76–42             | 1.78                                      |

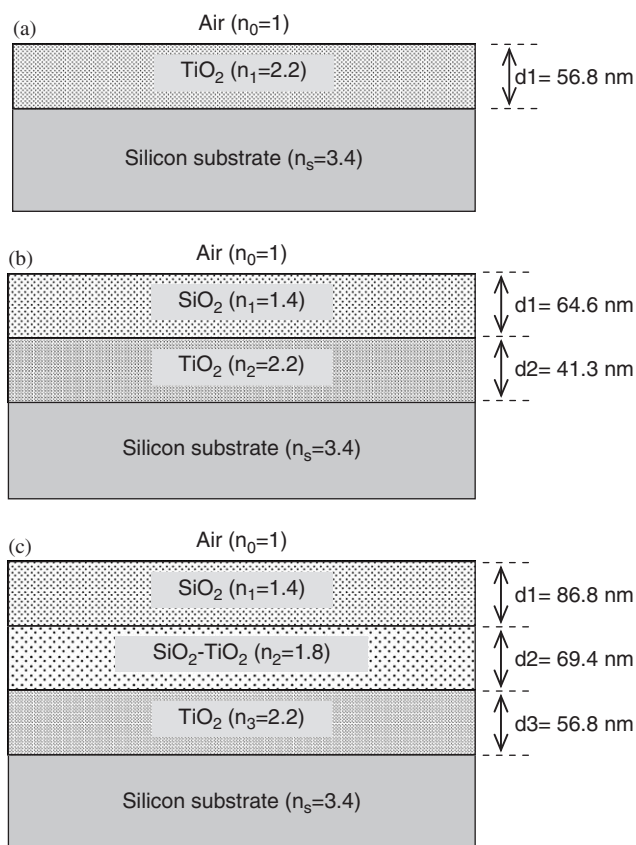


Fig. 2. Design diagram of antireflection coatings with (a) TiO<sub>2</sub> single layer, (b) SiO<sub>2</sub>/TiO<sub>2</sub> double layers and (c) SiO<sub>2</sub>/SiO<sub>2</sub>-TiO<sub>2</sub>/TiO<sub>2</sub> triple layers.

reflectance for a single-layer ARC can be deduced from

$$\lambda_0 = 4n_1 \times d_1, \quad (1)$$

where  $\lambda_0$  is the midrange wavelength of 550 nm,  $n_1$  and  $d_1$  are the refractive index and layer thickness, respectively. A schematic diagram of this case is shown in Fig. 2(a).

For the double-layer ARC design, the low-high index on the Si substrate (i.e., the outer layer has the low refractive index and inner layer has high refractive index) is used.

Fig. 2(b) shows a typical double-layer ARC structure, where  $n_0$ ,  $n_s$ ,  $n_1$  and  $n_2$  correspond to the refractive index of air, substrate, outer and inner layers, respectively. Moreover,  $d_1$  and  $d_2$  represent the thickness of the outer and inner layers, respectively. Each layer must meet Eqs. (2) and (3) in order to achieve a zero reflectance [17],

$$\frac{n_2 d_2}{\lambda_0} = \frac{1}{2\pi} \tan^{-1} \left\{ \pm \left[ \frac{(n_s - n_0)(n_0 n_s - n_1^2) n_2^2}{(n_1^2 n_s - n_0 n_2^2)(n_2^2 - n_0 n_s)} \right]^{1/2} \right\}, \quad (2)$$

$$\frac{n_1 d_1}{\lambda_0} = \frac{1}{2\pi} \tan^{-1} \left\{ \pm \left[ \frac{(n_s - n_0)(n_0 n_s - n_2^2) n_1^2}{(n_1^2 n_s - n_0 n_2^2)(n_1^2 - n_0 n_s)} \right]^{1/2} \right\}. \quad (3)$$

The design of triple-layer ARC on Si can be optimized using Eqs. (4–6) when the optimum refractive index and thickness of each layer in the stack is calculated,

$$\lambda_0 = 4n_1 \times d_1, \quad (4)$$

$$\lambda_0 = 4n_2 \times d_2, \quad (5)$$

$$\lambda_0 = 4n_3 \times d_3, \quad (6)$$

where  $n_2$  is the refractive index of the medium layer. The refractive index decreases from the high value ( $n_s$ ) to the low value ( $n_0 = 1$ ) in the order:  $n_0 < n_1 < n_2 < n_3 < n_s$ . Here each layer thickness is equal to one-quarter the wavelength in question and the multiple internal reflection of light is not been considered in these calculations. The principle of this type of ARC has been illustrated using the vector methods previously [18–20]. For a triple-layer AR stack, Fig. 2(c), shows the optimum refractive index and the thickness of each layer. A film with any medium refractive index between 1.4 and 2.4 (for 500 nm) can be obtained by mixing the starting  $\text{SiO}_2$  and  $\text{TiO}_2$  sol in different proportions. Using materials deposited by the sol–gel process [ $\text{SiO}_2$  ( $n = 1.4$ ),  $\text{SiO}_2$ – $\text{TiO}_2$  ( $n = 1.8$ ) and  $\text{TiO}_2$  ( $n = 2.3$ )], a triple-layer ARC on Si can be formed with minimum optical reflection.

### 2.3. Solar cell performance

Solar cells were fabricated using a 1–10  $\Omega$  cm boron-doped monocrystalline Si wafer ( $2 \times 2 \text{ cm}^2$  area, 300  $\mu\text{m}$  thick and one side polished). The emitter region was realized by thermal diffusion of phosphorous atoms in a quartz tube furnace at 850°C. The Al back contact was deposited by evaporation and then annealed at 800°C in order to form both effective back surface field and back contact. The  $\text{TiO}_2$  single-layer,  $\text{SiO}_2/\text{TiO}_2$  double-layer and  $\text{SiO}_2/\text{SiO}_2$ – $\text{TiO}_2/\text{TiO}_2$  triple-layer ARCs were deposited on the front of solar cells using a spin-coating technique. A front Al contact was deposited through a metallic mask (grid-type collecting electrode) and then thermal annealed at 700°C for 30 min. This grid-type correcting electrode reduces about 15% the effective illuminated area of the cell. Current density versus voltage measurements were taken under AM1.5 (80 mW/cm<sup>2</sup>) white light from a dual beam solar simulator.

### 3. Results and discussion

The thicknesses of the  $\text{TiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  and  $\text{SiO}_2$  films as functions of the spin rate are shown in Fig. 3. It was found that the film thickness decreased when the spin rate increased. Each  $\text{TiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  or  $\text{SiO}_2$  film thickness can be controlled by changing the spin rate or the alcohol concentration in the sol–gel solution. Fig. 4 shows the absorbance spectra and refractive indices of the deposited films as a function of wavelength. The refractive index of the  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  and  $\text{TiO}_2$  film was determined to be 1.45, 1.78 and

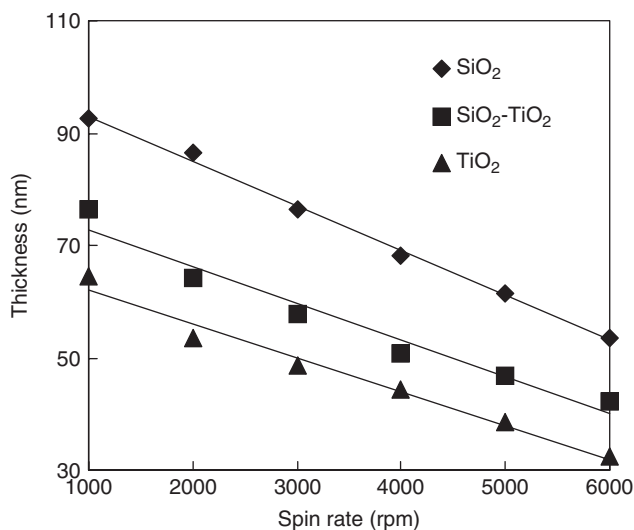


Fig. 3. Variations of  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  and  $\text{TiO}_2$  film thickness as a function of spin rate.

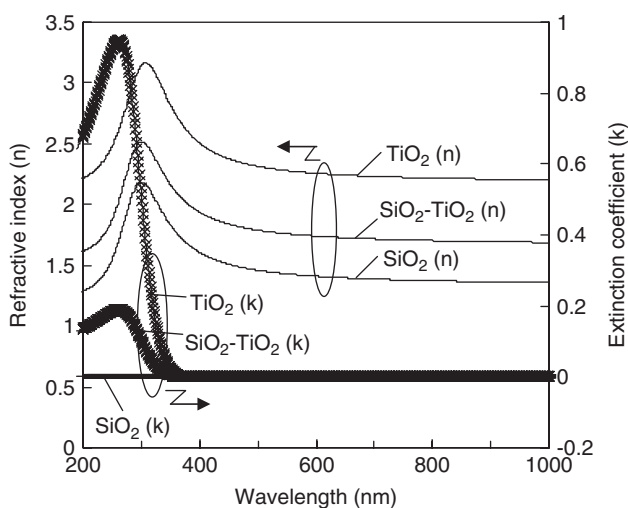


Fig. 4. Variations of extinction coefficients ( $k$ ) and refractive index ( $n$ ) of  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  and  $\text{TiO}_2$  films.

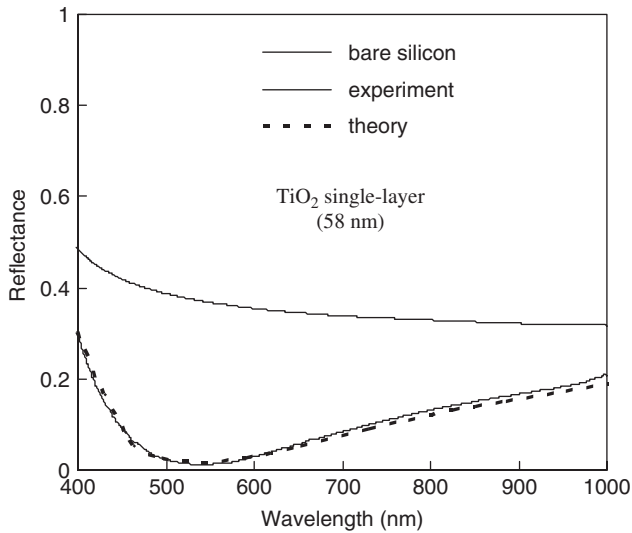


Fig. 5. Experimental and calculated reflectance data as a function of wavelength for  $\text{TiO}_2$  single-layer ARC on Si substrate.

2.26 (for wavelength at 500 nm), respectively. It was found that the extinction coefficients ( $k$ ) of each film after the annealing process almost approached to zero between 400 and 1000 nm. Furthermore, the absorbance point of the  $\text{SiO}_2$ – $\text{TiO}_2$  and  $\text{TiO}_2$  films is located at a wavelength of 340 nm. These indicate that the sol–gel deposited  $\text{SiO}_2$  and  $\text{TiO}_2$  films can be used as ARCs for Si solar cells [21,22].

Fig. 5 shows the measured and calculated reflectance spectra of the  $\text{TiO}_2$  single-layer ARC on non-textured Si substrates. It is well known that bare silicon has a high-refractive index, which leads to a solar-averaged reflectance of about 37%. The large reflection loss can be reduced significantly via a suitable ARC. A minimum value of reflectance  $R(\lambda) = 0.5\%$  can be obtained at 536 nm. The average reflectance of approximately 9.3% between 400 and 1000 nm was obtained by the  $\text{TiO}_2$  single-layer ARC on the non-textured Si substrate. The curves in Fig. 5 showed good agreement between the theoretical and experimental results for the reflectance data. The measured and calculated reflectance spectra of the optimized double-layer ARC are shown in Fig. 6. The reflectance  $R(\lambda)$  is lower than 5% in the wavelength between 550 and 900 nm, which maximizes the absorption of the incident photons and increases the photo-generated current. The  $\text{SiO}_2/\text{TiO}_2$  double-layer ARC results in a minimum reflectance of 1% at 690 nm with an average reflectance of approximately 6.2% between 400 and 1000 nm. That is, the Si absorbance increases by approximately 49.8%. Good correlation is also obtained between the theoretical and experimental results.

The experimental and theoretical reflectance data versus wavelength of the optimum triple-layer ARC structure are presented in Fig. 7. Here the theoretical  $\text{SiO}_2/\text{SiO}_2$ – $\text{TiO}_2/\text{TiO}_2$  triple-layer ARC on Si was calculated under normal optical incidence. The effective reflectance can reach 3.2% over 400–1000 nm range, indicating an increase in the absorption of the bare Si by approximately 54.6%. The difference in the short wavelength region is probably due to the dispersion of the refractive index in the wavelength region.

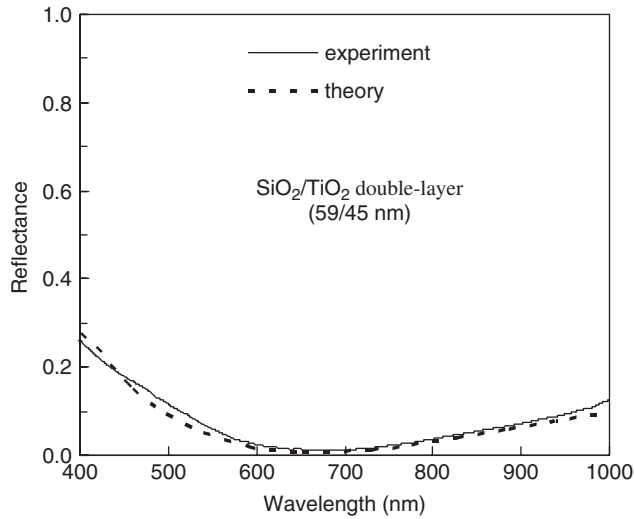


Fig. 6. Experimental and calculated reflectance data as a function of wavelength for SiO<sub>2</sub>/TiO<sub>2</sub> double-layer ARCs on Si substrate.

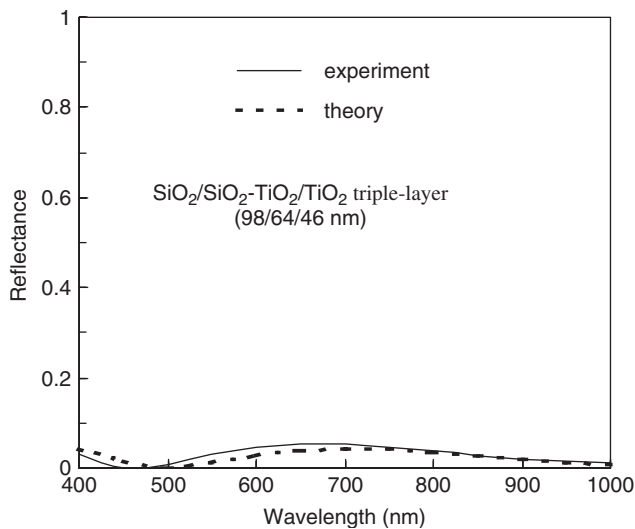


Fig. 7. Experimental and calculated reflectance data as a function of wavelength for SiO<sub>2</sub>/SiO<sub>2</sub>-TiO<sub>2</sub>/TiO<sub>2</sub> triple-layer ARCs on Si substrate.

Finally, the current–voltage characteristics of the solar cell devices with sol–gel ARCs are shown in Fig. 8. Significant improvement of the short circuit current after ARCs was observed. However, the open-circuit voltage and the fill factor were not affected by the ARCs in these measurements. It is found that the current–voltage characteristic with a triple-layer ARC is better than that with double- or single-layer ARCs. Table 2 shows the device performance of the Si solar cells with various ARC structures. The performance of

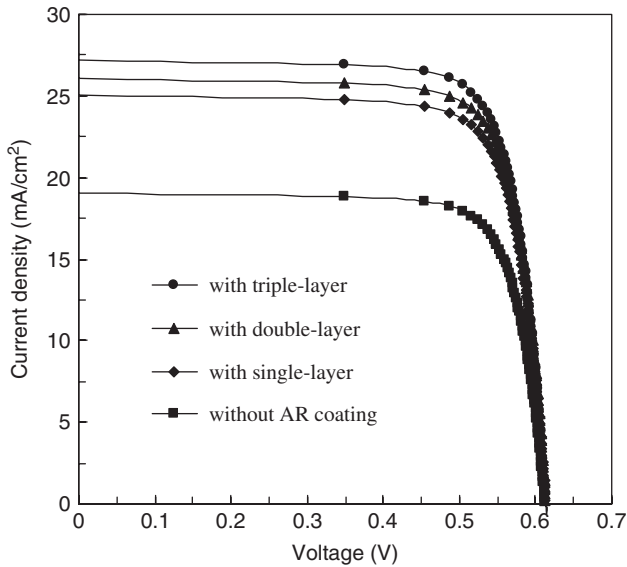


Fig. 8. Current density versus voltage characteristics of Si solar cells with triple-layer (●), double-layer (▲), single-layer (◆) and without ARCs (■).

Table 2  
Characterization of Si solar cells with various antireflection coatings

| Solar cell                                                                          | Jsc (mA/cm <sup>2</sup> ) | Voc (V) | Fill factor (%) | Efficiency (%) |
|-------------------------------------------------------------------------------------|---------------------------|---------|-----------------|----------------|
| Bare silicon                                                                        | 16.2                      | 0.61    | 76.4            | 11.36          |
| Single-layer TiO <sub>2</sub>                                                       | 24.8                      | 0.61    | 76.6            | 14.49          |
| Double-layer SiO <sub>2</sub> /TiO <sub>2</sub>                                     | 25.8                      | 0.61    | 76.2            | 14.99          |
| Triple-layer SiO <sub>2</sub> /SiO <sub>2</sub> -TiO <sub>2</sub> /TiO <sub>2</sub> | 27.1                      | 0.61    | 76.7            | 15.85          |

bare Si solar cell without any ARC has an efficiency of 11.36%. The Si solar cells with triple-, double- and single-layer ARC show an increase of efficiency of about 39, 32 and 27%, respectively. That is, the efficiency of the Si solar cell with a triple-layer ARC can increase to 15.85% in the present work by utilizing a sol-gel technique.

4. Conclusions

This work presents a comprehensive experimental study with the aim to prepare high-quality single-, double- and triple-layer ARCs on Si solar cells using a sol-gel process. The effective refractive index and thickness of the films can be easily adjusted via the concentration of the sols, spin rate and annealed temperature. The reflectance of TiO<sub>2</sub> single-layer, SiO<sub>2</sub>/TiO<sub>2</sub> double-layer and SiO<sub>2</sub>/SiO<sub>2</sub>-TiO<sub>2</sub>/TiO<sub>2</sub> triple-layer ARCs was determined to be 9.3, 6.2 and 3.2%, respectively. The optical performance of the sol-gel-deposited ARC can be compared with that of the conventional ARC using more expensive vacuum processes such as PECVD or sputtering. A 39% enhancement in conversion

efficiency was obtained in the monocrystalline Si solar cell with a triple-layer ARC. In the future, using a combination of spin coating and rapid thermal annealing processes, the sol–gel ARCs could have high potential for continuous mass production of Si solar cells at a fraction of the cost.

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