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Solar Energy Materials & Solar Cells 90 (2006) 2710–2719
Solar Energy Materials & Solar Cells
www.elsevier.com/locate/solmat

Tri-layer antireflection coatings (SiO_2/SiO_2–TiO_2/TiO_2) for silicon solar cells using a sol–gel technique

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Received 24 January 2006; received in revised form 25 March 2006; accepted 5 April 2006
Available online 12 June 2006

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 TiO_2 single-layer, SiO_2/TiO_2 double-layer and SiO_2/SiO_2–TiO_2/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.

Keywords: silicon; antireflection coating; sol–gel; TiO_2; SiO_2; solar cell

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0927-0248/$ - see front matter
doi:10.1016/j.solmat.2006.04.001

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_2 ($n = 1.44$), Si_3N_4 ($n = 1.9$), TiO_2 ($n = 2.3$), Al_2O_3 ($n = 1.86$), Ta_2O_5 ($n = 2.26$), SiO_2–TiO_2 ($n = 1.8$–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_3N_4 or TiO_2 single layer and SiO_2/TiO_2 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_2 single-layer, SiO_2/TiO_2 double-layer and SiO_2/SiO_2–TiO_2/TiO_2 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_2 single-layer ARC [15]. Green et al. have used MgF_2/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_2, SiO_2–TiO_2 and TiO_2 coatings were spin coated on the Si substrate from the above-said

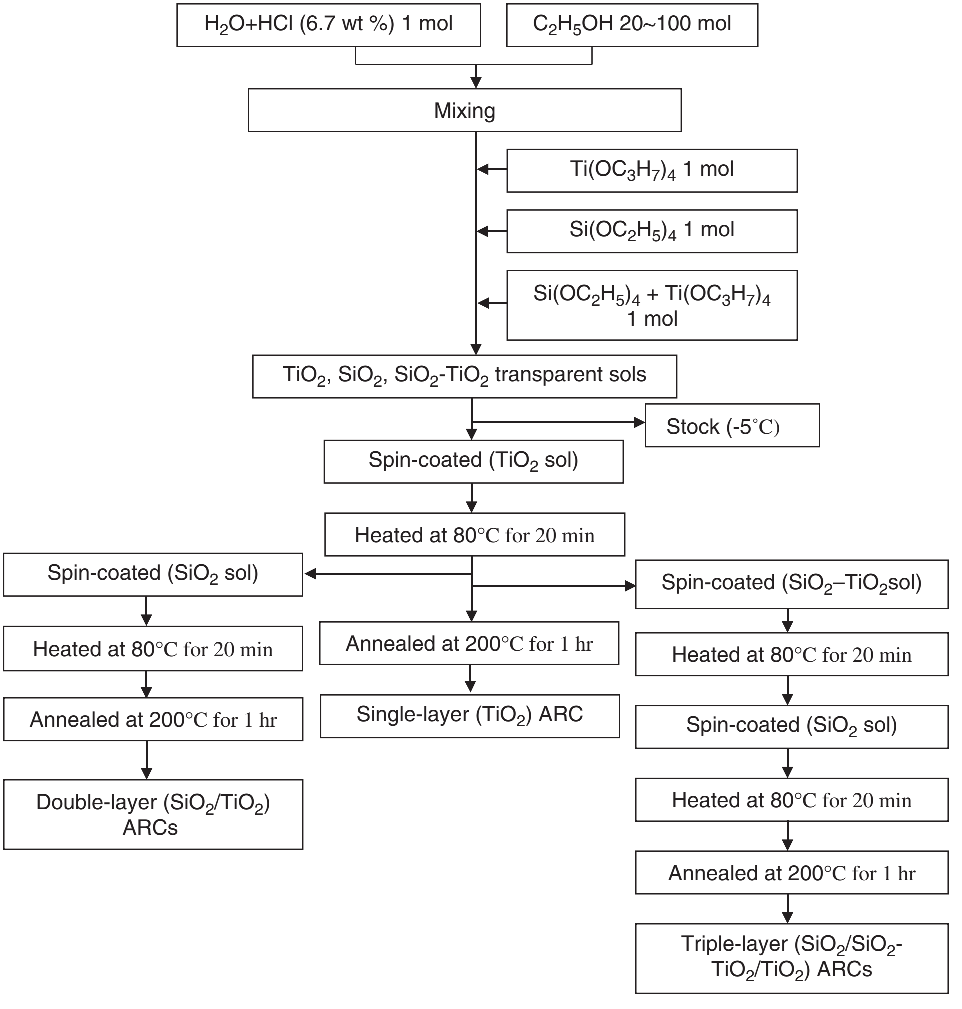

Fig. 1. Flow chart of sol–gel process for TiO_2 single-layer, SiO_2/TiO_2 double-layer and $SiO_2/SiO_2–TiO_2/TiO_2$ triple-layer antireflection coatings.

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°C for 20 min and then post baked at 200°C for 1 h in atmosphere. Table 1 tabulated the sol–gel parameters and deposition results of the SiO_2, $SiO_2–TiO_2$ and 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_2, SiO_2-TiO_2 and TiO_2 films

	$Ti(OC_3H_9)_4$:$Si(OC_2H_5)_4$:C_2H_5OH (mol)	Spin rate (r.p.m)	Thickness (nm)	Refractive index ($\lambda = 500$ nm)
TiO_2	1:0:60	2000–6000	64–33	2.26
SiO_2	0:1:80		93–54	1.45
SiO_2–TiO_2	1:1:80		76–42	1.78

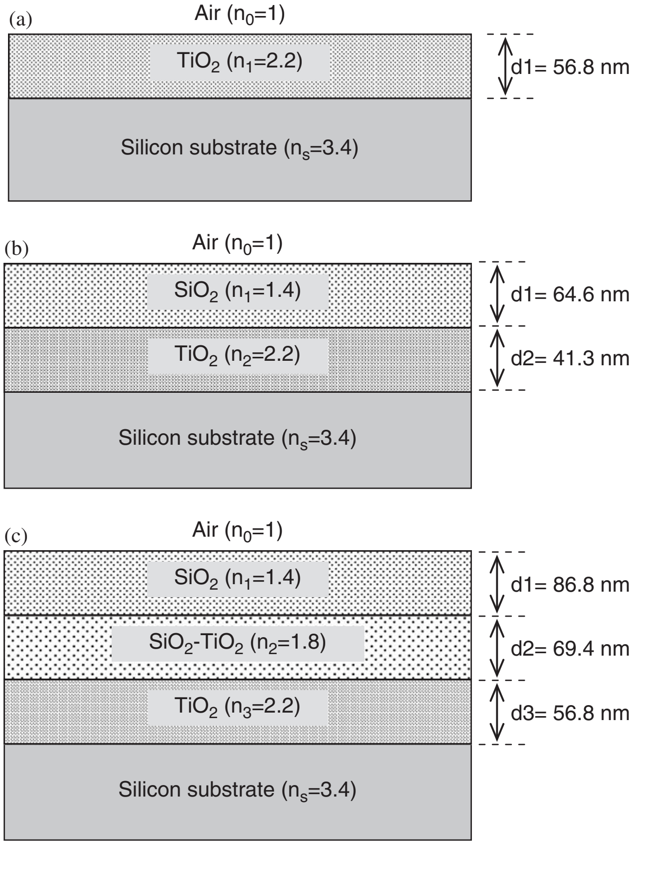

Fig. 2. Design diagram of antireflection coatings with (a) TiO_2 single layer, (b) SiO_2/TiO_2 double layers and (c) SiO_2/SiO_2–TiO_2/TiO_2 triple layers.

reflectance for a single-layer ARC can be deduced from

$$\lambda_0 = 4n_1 \times d_1, \tag{1}$$

where λ_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 SiO_2 and TiO_2 sol in different proportions. Using materials deposited by the sol–gel process [SiO_2 ($n = 1.4$), SiO_2–TiO_2 ($n = 1.8$) and 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 Ω cm boron-doped monocrystalline Si wafer ($2 \times 2\,cm^2$ area, 300 μm 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 TiO_2 single-layer, SiO_2/TiO_2 double-layer and SiO_2/SiO_2–TiO_2/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^2) white light from a dual beam solar simulator.

3. Results and discussion

The thicknesses of the TiO_2, SiO_2–TiO_2 and 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 TiO_2, SiO_2–TiO_2 or 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 SiO_2, SiO_2–TiO_2 and TiO_2 film was determined to be 1.45, 1.78 and

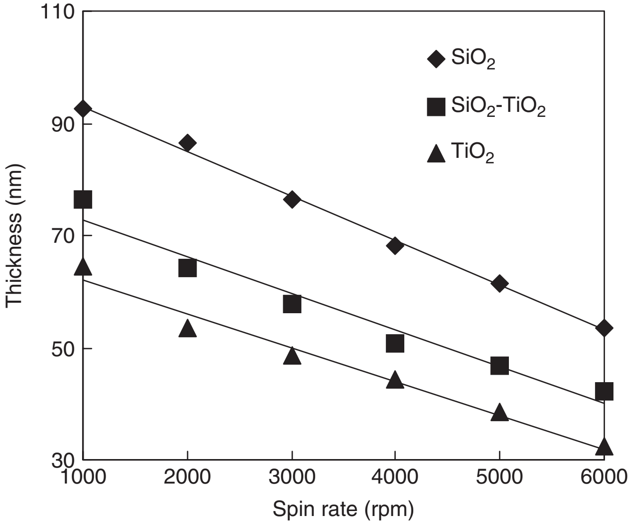

Fig. 3. Variations of SiO_2, SiO_2–TiO_2 and TiO_2 film thickness as a function ofspin rate.

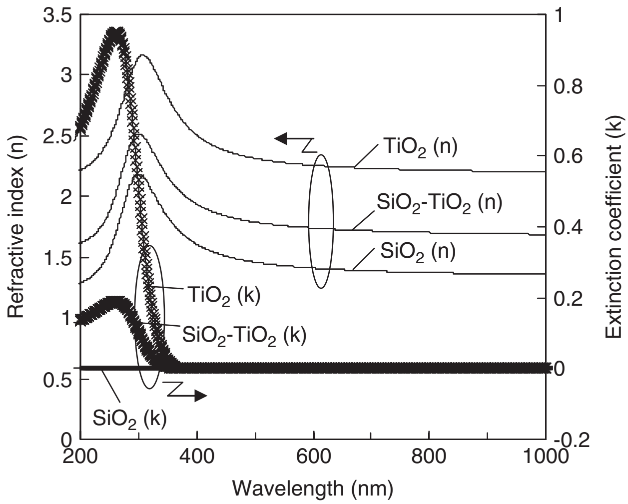

Fig. 4. Variations of extinction coefficients (k) and refractive index (n) of SiO_2, SiO_2–TiO_2 and TiO_2 films.

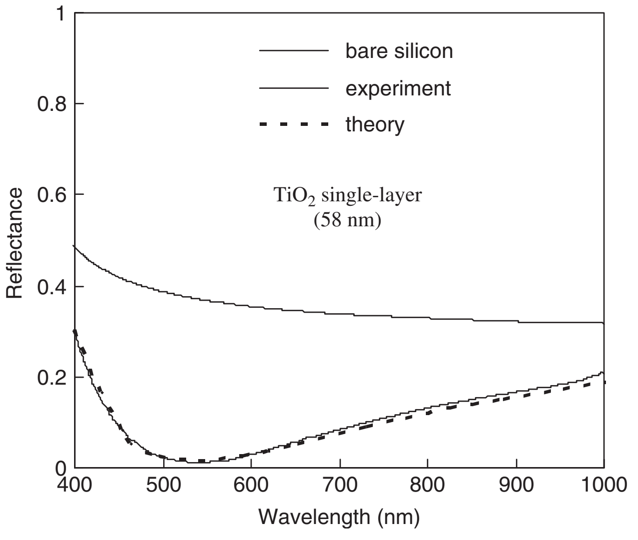

Fig. 5. Experimental and calculated reflectance data as a function of wavelength for TiO_2 single-layer ARC on Si substrate.

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 SiO_2–TiO_2 and TiO_2 films is located at a wavelength of 340 nm.These indicate that the sol–gel deposited SiO_2 and 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 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 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(λ) 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 SiO_2/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 SiO_2/SiO_2–TiO_2/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.

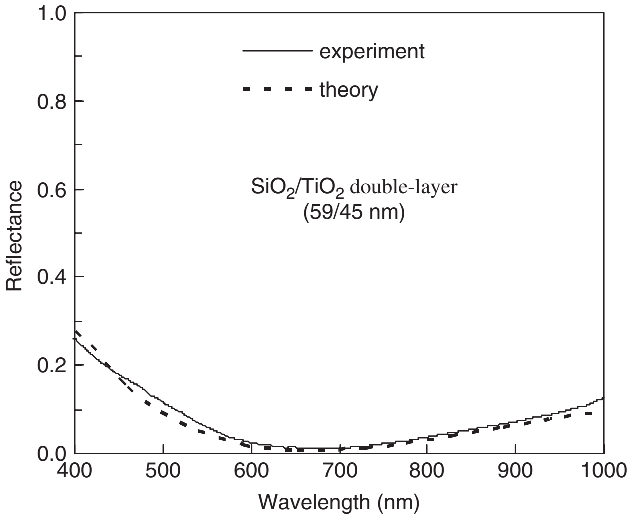

Fig. 6. Experimental and calculated reflectance data as a function of wavelength for SiO_2/TiO_2 double-layer ARCs on Si substrate.

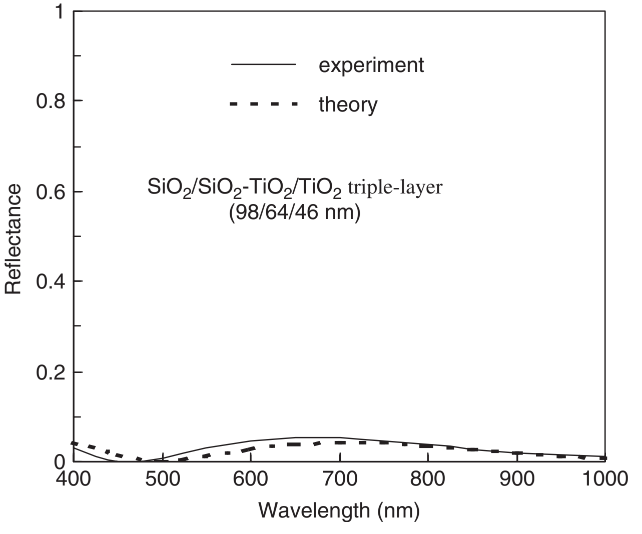

Fig. 7. Experimental and calculated reflectance data as a function of wavelength for $SiO_2/SiO_2–TiO_2/TiO_2$ triple-layer ARCs on Si substrate.

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

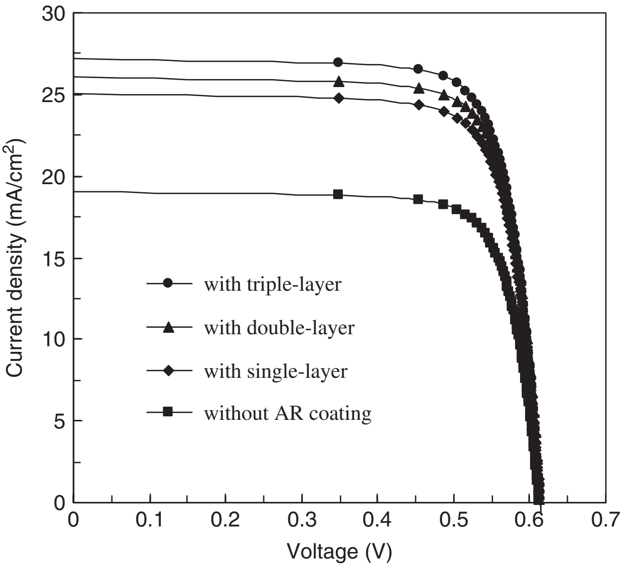

Fig. 8. Current density versus voltage characteristics of Si solar cells with triple-layer (●), double-layer (▲), single-layer (◆) and without ARCs (■).

Table 2
Characterization of Si solar cells with various antireflection coatings

Solar cell	Jsc (mA/cm^2)	Voc (V)	Fill factor (%)	Efficiency (%)
Bare silicon	16.2	0.61	76.4	11.36
Single-layer TiO_2	24.8	0.61	76.6	14.49
Double-layer SiO_2/TiO_2	25.8	0.61	76.2	14.99
Triple-layer $SiO_2/SiO_2–TiO_2/TiO_2$	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_2 single-layer, SiO_2/TiO_2 double-layer and $SiO_2/SiO_2–TiO_2/TiO_2$ 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.

Acknowledgments

This work was supported by the National Science Council of the Republic of China under contract no. NSC 091-ET-7-005-001-ET.

References

[1] D. Bouhafs, A. Moussi, A. Chikouche, J.M. Ruiz, Sol. Energy Mater. Sol. Cells 52 (1998) 79.
[2] A. Yen, H.I. Smith, M.L. Schattenbyrg, G.N. Taylor, J. Electrochem. Soc. 139 (1992) 616.
[3] J. Sczybowski, G. Brauer, G. Teschner, A. Zmelty, Surf. Coat. Technol. 98 (1998) 1460.
[4] F.W. Sexton, Solar Energy Mater. Sol. Cells 7 (1991) 1.
[5] R. Kishore, S.N. Siingh, B.K. Das, Sol. Energy Mater. Sol. Cells 26 (1992) 27.
[6] Z. Chen, P. Sana, J. Salami, A. Rohatgi, IEEE Trans. Electron Devices 40 (1993) 1161.
[7] K. Ram, S.N. Singh, B.K. Das, Renewable Energy 12 (1997) 131.
[8] C. Battaglin, F. Caccavale, A. Menelle, M. Montecchi, E. Nichelatti, F. Nicoletti, Thin Solid Films 351 (1999) 176.
[9] U. Gangopadhyay, K. Kim, D. Mangalaraj, J. Yi, Appl. Surf. Sci. 230 (2004) 364.
[10] I.O. Parm, K. Kim, D.G. Lim, J.H. Lee, J.H. Heo, J. Kim, D.S. Kim, S.H. Lee, J. Yi, Sol. Energy Mater. Sol. Cells 74 (2002) 97.
[11] C. Martinet, V. Paillard, A. Gagnaire, J. Joseph, Non-Crystalline Solids 216 (1997) 77.
[12] H. Nagel, A. Metz, R. Hezel, Sol. Energy Mater. Sol. Cells 65 (2001) 71.
[13] A. Morales, A. Duran, J. Sol-Gel Sci. Technol. 8 (1997) 451.
[14] T. Schuler, M.A. Aegerter, Thin Solid Films 351 (1999) 125.
[15] W. Kern, E. Tracy, RCA Rev. 41 (1980) 133.
[16] M.A. Green, Appl. Phys. Lett 44 (1984) 1163.
[17] H.A. Macleod, Thin-Film Optical Filters, second ed., Macmillan Publishing Company, New York, 1986.
[18] H.A. Macleod, Thin-Film Optical Filters, second ed., McGraw-Hill, New York, 1990.
[19] D. Chen, Sol. Energy Mater. Sol. Cells 68 (2001) 313.
[20] T. Mizuta, T. Ikuta, T. Minemoto, H. Takakura, Y. Hamakawa, T. Numai, Sol. Energy Mater. Sol. Cells 90 (2006) 46.
[21] M. Lemiti, J.P. Boyeaux, H.E. Omari, A. Kaminski, A. Laugier, Mater. Sci. Semicond. Process. 1 (1998) 331.
[22] G.S. Vicente, A. Morales, M.T. Gutierrez, Thin Solid Films 391 (2001) 133.