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Research Article

Sprayed and Spin-Coated Multilayer Antireflection Coating Films for Nonvacuum Processed Crystalline Silicon Solar Cells

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Using the simple and cost-effective methods, spin-coated ZrO_2-polymer composite/spray-deposited TiO_2-compact multilayer antireflection coating film was introduced. With a single TiO_2-compact film on the surface of a crystalline silicon wafer, 5.3% average reflectance (the reflectance average between the wavelengths of 300 nm and 1100 nm) was observed. Reflectance decreased further down to 3.3% after forming spin-coated ZrO_2 on the spray-deposited TiO_2-compact film. Silicon solar cells were fabricated using CZ-Si p-type wafers in three sets: (1) without antireflection coating (ARC) layer, (2) with TiO_2-compact ARC film, and (3) with ZrO_2-polymer composite/TiO_2-compact multilayer ARC film. Conversion efficiency of the cells improved by a factor of 0.8% (from 15.19% to 15.88%) owing to the multilayer ARC. J_{sc} was improved further by 2 mA cm^{-2} (from 35.3 mA cm^{-2} to 37.2 mA cm^{-2}) when compared with a single TiO_2-compact ARC.

1. Introduction

In order to achieve high efficiency silicon solar cells, reducing the optical losses and improving the absorption properties of the cell are one of the key factors. To minimize the reflection of the solar cell surface, a range of material and thin films have been used for ARC purposes for solar cells (SiO, SiO_2, SiN_x, TiO_2, Al_2O_3, ZnS thin films, etc.) depending to the type of solar cell. Although a single ARC coating layer can minimize the reflection less than 1% only at a single wavelength, a multilayer structure with gradual increase of refractive index on the light path is necessary in order to achieve improved reflectivity along the spectrum [1]. In this case, it is necessary to build multilayer structure by considering the gradual increase order of refractive indexes as air $<$ 1st layer $<$ 2nd layer $< \cdots <$ nth layer $<$ silicon. Considering the optimum refractive index for a single ARC layer between air and silicon according to $n_1 = (n_0 n_s)^{-1/2}$ (n_s, n_0, and n_1: refractive index of silicon, air, and ARC thin film, resp.), one could consider that widely in use SiN_x ($n = 1.97$) might be the optimum material for ARC layer for silicon solar cells [1]. Quality forming of ARC coating materials mostly utilizes a type of chemical vapor deposition (CVD) technique. In case of SiN_x films, for instance, typically a plasma-enhanced chemical vapor deposition (PECVD) technique [2, 3] is used. Taking the advantage of tunability of the refractive index of SiN_x by changing the deposition parameters of PECVD [4], better reflection performances with multilayer stacks of SiN_x are achievable. Although, it is a well-established technology and has advantages including the high deposition rate, the need of toxic and hazardous gases such as SiH_4 (silane), SiH_2Cl_2 (dichlorosilane), and NH_3 (ammonia) with high vacuum processing for CVD operation and considerably high costs come along as the major drawbacks. Considering these disadvantages and the fact that low-cost and high throughput are a continuous demand for silicon solar cell industry, simple low-cost technologies with high throughput, cost-effective methods need to be investigated and adapted to the solar cell manufacturing process.

In literature, TiO_2 has been widely investigated as an alternative ARC layer for crystalline silicon solar cells [5, 6], due to its good optical properties that enhance the light absorption capability because of the high refractive index for silicon solar cell. Solution processed materials for silicon solar cells including TiO_2, TiO_2-SiO_2 [5, 6], and Al_2O_3 based Ti doped mixed sol-gel sources have been introduced as well [7, 8]. Although there is a considerable amount of research regarding such alternative materials for ARC, mainly based on TiO_2 and SiO_2 solutions, the availability of proper material and combined structures is still limited. Various techniques can be used in principle to form such precursors on the substrate homogenously, including spin coating [9, 10], spray pyrolysis, or dip-coating [11–13]. These practical and low-cost techniques have advantages including simple deposition of thin films from the prepared precursor solutions. Utilizing such techniques also leads an opportunity of using a broad range of chemicals with flexible amounts for both high or low temperature applications.

Additionally, ZrO_2 thin films with good optical properties and both chemical and mechanical stabilities [14, 15] have been investigated initially for dye synthesized solar cells to enhance the properties of polymers [14], as well as improve the antireflection property of solar module glasses [16]. With the attractive optical properties, high refractive index and good thermal stability ZrO_2 films can be another promising candidate for ARC layer of silicon solar cells [17, 18].

In this work, as a low temperature and nonvacuum method, spin-coating deposition was performed for ZrO_2-polymer composite films and spray pyrolysis deposition method was performed for TiO_2-compact film and ZrO_2-polymer composite/TiO_2-compact multilayer films were introduced as an alternative ARC film for silicon solar cells. After confirming the structure of TiO_2 and ZrO_2 polymer based thin films separately, $\langle air/ZrO_2/TiO_2/Si \rangle$ multilayer structure was also built considering the gradual increase order of refractive indexes. And after the experimental evaluations, silicon solar cells were fabricated with and without using TiO_2-compact film or ZrO_2-polymer composite/TiO_2-compact film multilayer films.

2. Experimental

Spray-deposited TiO_2-compact films and spin-coating ZrO_2-polymer composite films were formed on alkaline textured crystalline silicon (c-Si) substrates for primary evaluation of the coated films in terms of optical and physical analysis. Afterwards, textured surface p-type CZ-Si solar cells were fabricated using TiO_2-compact films and ZrO_2-polymer composite/TiO_2-compact multilayer film as an antireflection coating (ARC) layer on the front surface of the c-Si wafers and were compared to those of solar cells without ARC.

For the optical measurements, square-shaped p-type silicon wafers ($25 \times 25\ mm^2$) were cut out from 6-inch CZ-Si p-type wafers. All wafers were dipped into the 20% diluted HF for 1 min and rinsed in distilled water. Afterwards, UV/O_3 surface treatment was carried out for a complete cleaning process. ZrO_2-polymer composite film was deposited on silicon substrate by spin coating using the zirconium sol (ZR-30AH, provided by Nissan Chemical Industry Co. Ltd., Chiba, Japan). The investigation and optimization of ZrO_2 based solutions were introduced in our previous works [19] in order to use them for silicon solar cell applications with flat or textured surfaces. According to these works, optimized ZrO_2 solution composed by ethyl cellulose, ethanol, and ZR-30AH in ratio of 2 : 16 : 1 (in volume) was used in this work as well. Deposition of the ZrO_2 film was carried out by spin coating with a spin speed of 1500 rpm for 25 s (acceleration time is 5 s).

TiO_2 compact films were formed on the silicon wafers by spray pyrolysis deposition using precursor solutions which was sprayed on to the surface of silicon wafers using a glass atomizer. The crystalline silicon wafers were set on a hot plate heated at deposition temperature of 450°C. The TiO_2 precursor solution was prepared by the ten-time dilution of titanium di-isopropoxidebis-acethylacetone (TAA) (prepared by mixing titanium (VI) isopropoxide and acetylacetone by 1 : 2 in mole) to ethanol. Annealing temperature was optimized for TiO_2 as 450°C and as 125°C for ZrO_2, respectively. Analyses were mainly carried out by reflection analysis (by ultraviolet-visible spectroscopy, Lambda 750 UV/VIS Spectrometer, Perkin Elmer, Waltham, MA, USA) and ellipsometer (UviselErAgms-nds, Horiba Jobin Yvon, Kyoto, Japan) and finally by the performance of the fabricated silicon solar cells with or without ARC.

Silicon solar cells were fabricated with a variety of final surface conditions: without ARC on textured surface, with TiO_2-compact film on textured surface, and with ZrO_2-polymer composite/TiO_2-compact multilayer ARC film on textured surface. For the fabrication of silicon solar cells, 25 mm × 25 mm p-type CZ-Si wafers were used as well. For textured surface, alkaline texturing was performed in KOH (5.19 g) solution in H_2O (100 mL) with Alka-Tex (0.28 mL, GP Solar, Konstanz, Germany) at 80°C (set: 100°C) for 30 min. The silicon wafers were dipped into the 20% diluted HF for 10 min and rinsed in distilled water. Then, RCA cleaning [20, 21] was carried out to remove contaminant particles on the surface of the wafers by using a $NH_4OH/H_2O_2/H_2O$ (1 : 1 : 5 in volume) solution, for 10 min at 80°C. After removal of the natural oxide films by 20% HF, a mix solution of $HCl/H_2O_2/H_2O$ (1 : 1 : 5 in volume) was used to remove metallic contaminations and mobile ions on the surface by dipping the wafers for 10 min at 80°C. In order to prevent phosphorous diffusion and to prevent the texture on the back side of the silicon wafer, polysilazane was coated using spin-coating method by two times at 1500 rpm for 20 s, succeeded by annealing at 600°C for 60 min in O_2 gas flow. $POCl_3$ diffusion was performed at 930°C for 35 min with 0.2 l/min N_2 flow, to form n^+ emitter. Afterwards, wafers were rinsed in 10% HF and pure water by dipping, successively. SiO_2 film was formed by thermal oxidation process at temperature of 800°C for 10 min under O_2 gas. Before the metallization process, wafers were set on a hot plate heated at deposition

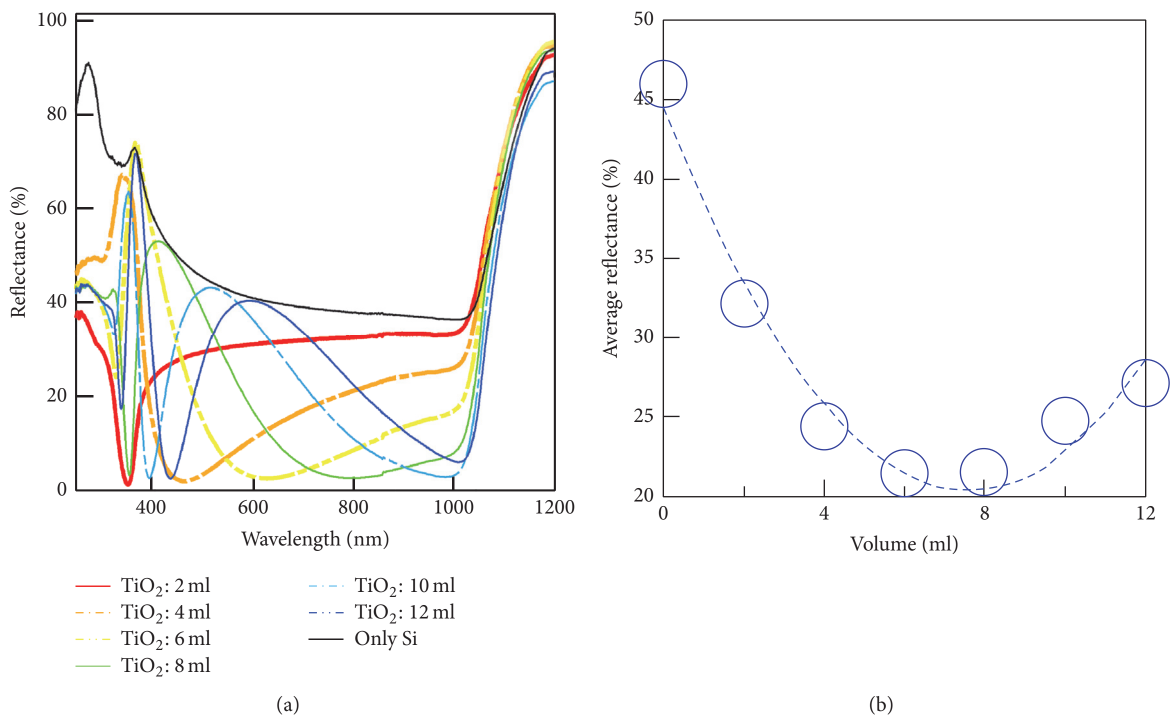

FIGURE 1: Comparison of the reflectivity of the flat samples with TiO_2 antireflection coatings by various amount TiO_2 precursor solution. (a) Reflectance spectra depending on spraying amount. (b) Average reflectance (300–1100 nm wavelength) depending on spraying amount.

temperature (450°C) and deposition of TiO_2 films were carried out by spray pyrolysis. Then, front and back contacts were formed by screen-printing Ag and Al, respectively. Cofiring was carried out at 780°C for 1 min in an oven. After evaluating the solar cells with a single layer TiO_2-compact films on the wafer surfaces, ZrO_2-polymer composite films were deposited on the finished cells and compared to those of the cells without ARC and with single layer TiO_2-compact films. Deposition of ZrO_2-polymer composite ARC films was carried out by the annealing step after spin-coating process (1000 rpm on flat surface, 1500 rpm on textured surface, 5 s acceleration + 25 s, annealing at 125°C, 5 min).

3. Results and Discussion

In order to evaluate the reflectivity performance of single layer TiO_2-compact film, flat surface silicon wafers were used. Figure 1(a) shows the comparison of the reflectivity of flat samples w/or w/o TiO_2-compact film on silicon surface. The thickness of the TiO_2 film was mainly controlled by the spraying amount of TiO_2 precursor solution in a range of 0~12 mL. Depending the film thickness, minimum of the reflectance (<2%) shifts towards to the longer wavelengths. A steep decrease before the minimum can be confirmed for all TiO_2 film coated surfaces. As can be confirmed in Figure 1(a), the minimum of the reflectance shifts to the wavelengths as high as around 1000 nm for the films coated with 10 and 12 mL TiO_2 precursors. The average reflectivity (the reflectance average between the wavelength of 300 nm and 1100 nm) was plotted by changing the spraying amount of the TiO_2 precursor as 0 mL, 2 mL, 4 mL, 6 mL, 8 mL, 10 mL,

TABLE 1: Average reflectance (between 300 and 1100 nm) of texture surface silicon substrate with ZrO_2-polymer ARC (adapted from our previous work [19]).

Spin speed (rpm)	500	1000	1500	2000	3000
Average reflectance (%)	9.15	7.77	6.91	7.1	6.84

and 12 mL, respectively (Figure 1(b)). A deposition rate of TiO_2 is defined as 10.1 nm mL^{-1} according to ellipsometry measurements. The lowest average reflectance of 21.41% was achieved by spray-deposited TiO_2 coating with a thickness of 60.6 nm.

The bottom of reflectance valley shifted to higher wavelength with increasing the solution volume from 2 mL to 12 mL, gradually. Using the 8 mL precursor solution, the second valley arouse at the lower wavelength which was close to the valley bottom of 2 mL precursor solution. The second valley at the lower wavelength was also shifted to the larger wavelength with increasing the precursor solution.

ZrO_2-polymer composite films were formed on textured silicon surface by a spin speed of 1500 rpm for 25 s (acceleration time is 5 s), based on our preliminary work of ZrO_2-polymer composite films as an ARC layer for silicon solar cells [19]. Such a ZrO_2-polymer composite film has a thickness of 102 nm on flat silicon surface and was used in combination with TiO_2-compact film in this work. The average reflectivity (the reflectivity average between 300 nm and 1100 nm) of ZrO_2-polymer films deposited on textured surface with various spin speeds was given in Table 1 where a good optical performance can be confirmed with average

TABLE 2: Photovoltaic characteristics of fabricated crystalline silicon solar cells with various surface structures with/without antireflection coating on textured surface.

Surface structure	ARC	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	R_{series} (Ω cm^2)	R_{shunt} (Ω cm^2)	η (%)
Textured	—	28.7	0.511	69.4	0.71	250	10.2
Textured	TiO_2-compact	35.3	0.581	74.1	0.40	655	15.2
Textured	ZrO_2-polymer/TiO_2-compact	37.2	0.583	73.4	0.45	535	15.9

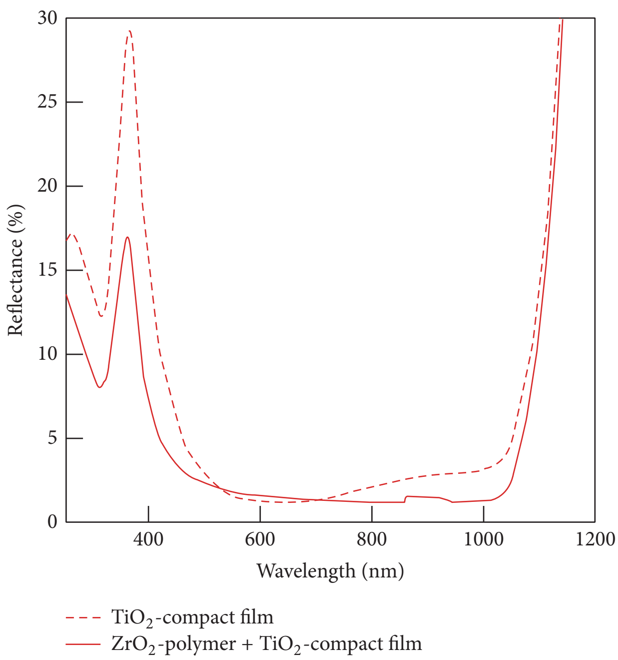

FIGURE 2: Comparison of the reflectivity of the textured silicon wafers with TiO_2 single layer and spin-coated ZrO_2/spray-deposited TiO_2 double layer.

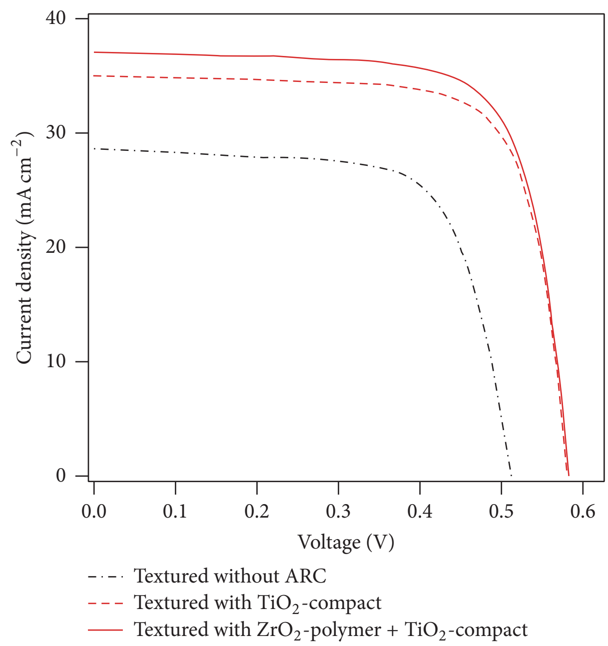

FIGURE 3: *J-V* curve comparison of the best cells with or without antireflection coating.

reflectivity of 6.91%. The slight increase of average reflectance for 2000 rpm was considered as intolerance due to the possible local inhomogeneity of the film.

In case of reflectivity measurement for ZrO_2-polymer composite/TiO_2-compact multilayer, first, TiO_2-compact single layer was formed and measured and then ZrO_2-polymer composite was formed on TiO_2 covered surface and remeasured. The comparison of reflectivity of TiO_2-compact single layer with the ZrO_2-polymer composite/TiO_2-compact multilayer formed on textured silicon wafers is given in Figure 2. The average reflectance was improved further with applying ZrO_2-polymer composite to the TiO_2-compact film, offering between 5 and 12% reflectance gain from 300 nm to 450 nm and a steady lower reflectance tendency from wavelength of around 700 to 1000 nm can also be confirmed.

Finally, silicon solar cells were fabricated using textured CZ-Si p-type wafers with and without using the ZrO_2-polymer antireflection composite layer on TiO_2-compact film. Conversion efficiency of the cells improved from 15.2% to 15.9%, where the J_{sc} also increased further from 35.3 mA cm^{-2} to 37.2 mA cm^{-2} owing to the ZrO_2/TiO_2 multilayer ARC film (the J_{sc} of the cell without ARC was 28.7 mA cm^{-2}). The electrical characteristics of the cells are summarized in Table 2.

70 mV increase of V_{oc} of the cells with ARC can be confirmed. Though SiO_2 film was formed by thermal oxidation process at temperature of 800°C for 10 min under O_2 gas, we did not compare the photovoltaic results with/without SiO_2 layer. Hence, the increase of V_{oc} is due to the compact TiO_2 layer, which can prevent excessive fire of Ag into p-n junction. The greater FF of the cells with ARC layer can be attributed to the lower contact resistances in which the effect of additional SiO_2 layer can be considerable in order to avoid internal shunts. *J-V* characteristics of the silicon solar cells fabricated with TiO_2-compact single layer and ZrO_2-polymer composite/TiO_2 -compact multilayer ARC on surface of the cells are given in Figure 3.

One can conclude that a significant improvement on J_{sc} and η could be confirmed owing to the ZrO_2-polymer composite/TiO_2-compact multilayer ARC when compared to the textured cells without ARC. The increase of the J_{sc} was related to minimizing the reflectance loses which can boost the performance of the cell. These results suggest that ZrO_2/TiO_2 based multilayer ARC films formed by spray pyrolysis deposition technique and spin-coating technique could be an attractive alternative as a low-cost, simple, and vacuum-less process for ARC coating for silicon solar cells.

4. Conclusion

TiO_2-compact and ZrO_2-polymer composite antireflection coating layers were introduced as an alternative ARC layers for silicon solar cells. Films were formed by simple and cost-effective spray pyrolysis deposition and spin-coating process. Reflectance decreased further with ZrO_2-polymer composite/TiO_2-compact layer comparing to the single TiO_2-compact film formed surface. Less than 2% surface reflectance was confirmed after applying ZrO_2-polymer composite/TiO_2-compact multilayer in a wide range of spectra, from around 550 nm to 1050 nm. Silicon solar cells were fabricated using CZ-Si p-type wafers both with and without ARC layers on the illuminated surface. Conversion efficiency of the cells improved by a factor of 0.8% with ARC and reaches 15.9% efficiency where the J_{sc} increased further by $2\,mA\,cm^{-2}$ (from $35.3\,mA\,cm^{-2}$ to $37.2\,mA\,cm^{-2}$) owing to the ZrO_2-polymer composite/TiO_2-compact multilayer ARC. These results indicate that ZrO_2-polymer composite films can be an attractive candidate as an ARC film and for multilayer ARC structures in order to produce cost-effective solar cells.

Competing Interests

The authors declare no conflict of interests.

References

[1] J. Nelson, *The Physics of Solar Cells*, Imperial College Press, London, UK, 2003.

[2] A. G. Aberle and R. Hezel, "Progress in low-temperature surface passivation of silicon solar cells using remote-plasma silicon nitride," *Progress in Photovoltaics*, vol. 5, no. 1, pp. 29–50, 1997.

[3] Y. Wan, K. R. McIntosh, and A. F. Thomson, "Characterisation and optimisation of PECVD SiNx as an antireflection coating and passivation layer for silicon solar cells," *AIP Advances*, vol. 3, no. 3, Article ID 032113, 2013.

[4] D. R. Wright, E. S. Marstein, and A. Holt, "Double layer anti-reflective coatings for silicon solar cells," in *Proceedings of the 31st IEEE Photovoltaic Specialist Conference*, pp. 1237–1240, 2005.

[5] C. J. Brinker and M. S. Harrington, "Sol-gel derived antireflective coatings for silicon," *Solar Energy Materials*, vol. 5, no. 2, pp. 159–172, 1981.

[6] B. S. Richards, "Single-material TiO_2 double-layer antireflection coatings," *Solar Energy Materials and Solar Cells*, vol. 79, no. 3, pp. 369–390, 2003.

[7] P. Vitanov, X. Loozen, A. Harizanova, T. Ivanova, and G. Beaucarne, "A study of sol-gel deposited Al_2O_3 films as passivating coatings for solar cells application," in *Proceedings of the 23rd European Photovoltaic Solar Energy Conference and Exhibition*, pp. 1596–1599, Valencia, Spain, September 2008.

[8] Z. Liang, D. Chen, C. Feng, J. Cai, and H. Shen, "Crystalline silicon surface passivation by the negative charge dielectric film," *Physics Procedia*, vol. 18, pp. 51–55, 2011.

[9] P. K. Biswas, P. S. Devi, P. K. Chakraborty et al., "Porous anti-reflective silica coatings with a high spectral coverage by sol-gel spin coating technique," *Journal of Materials Science Letters*, vol. 22, no. 3, pp. 181–183, 2003.

[10] Q. Zhang, J. Wang, G. Wu, J. Shen, and S. Buddhudu, "Interference coating by hydrophobic aerogel-like SiO_2 thin films," *Materials Chemistry and Physics*, vol. 72, no. 1, pp. 56–59, 2001.

[11] P. Nostell, A. Roos, and B. Karlsson, "Optical and mechanical properties of sol-gel antireflective films for solar energy applications," *Thin Solid Films*, vol. 351, no. 1-2, pp. 170–175, 1999.

[12] A. Gombert, W. Glaubitt, K. Rose et al., "Glazing with very high solar transmittance," *Solar Energy*, vol. 62, no. 3, pp. 177–188, 1998.

[13] D. R. Uhlmann, T. Suratwala, K. Davidson, J. M. Boulton, and G. Teowee, "Sol-gel derived coatings on glass," *Journal of Non-Crystalline Solids*, vol. 218, pp. 113–122, 1997.

[14] C. Zha, X. Luo, R. Wang, and B. L. Davies, "Effects of TiO_2 and ZrO_2 on optical properties of organic–inorganic hybrid polymers and thin films," *Journal of Materials Science: Materials in Electronics*, vol. 18, p. 331, 2007.

[15] H. H. Nwe, Y. M. Maung, T. T. Win, and K. K. K. Soe, "Photovoltaic properties of mesoporous TiO_2–ZrO_2 binary oxide electrode with sawdust organic dye for dye-sensitized solar cell application," *Journal of Science*, vol. 3, no. 1, p. 197, 2012.

[16] J. Li, Y. Lu, P. Lan et al., "Design, preparation, and durability of TiO_2/SiO_2 and ZrO_2/SiO_2 double-layer antireflective coatings in crystalline silicon solar modules," *Solar Energy*, vol. 89, pp. 134–142, 2013.

[17] A. N. Buzynin, Y. N. Buzynin, V. V. Osiko et al., "Antireflection fianite and ZrO_2 coatings for solar cells," *Bulletin of the Russian Academy of Sciences: Physics*, vol. 75, no. 9, pp. 1213–1216, 2011.

[18] M.-T. Wang, T.-H. Wang, and J. Y.-M. Lee, "Electrical conduction mechanism in high-dielectric-constant ZrO_2 thin films," *Microelectronics Reliability*, vol. 45, no. 5-6, pp. 969–972, 2005.

[19] A. Uzum, M. Kuriyama, H. Kanda, Y. Kimura, K. Tanimoto, and S. Ito, "Non-vacuum processed polymer composite antireflection coating films for silicon solar cells," *Energies*, vol. 9, no. 8, article 633, 2016.

[20] W. Kern and D. A. Puotinen, "Cleaning solutions based on hydrogen peroxide for use in silicon semiconductor technology," *RCA Review*, vol. 31, pp. 187–206, 1970.

[21] K. Reinhardt and W. Kern, Eds., *Handbook of Silicon Wafer Cleaning Technology*, William Andrew, 2nd edition, 2008.