Special Issue http://dx.doi.org/10.3786/sincs2011.03

NANO-MICRO LETTERS ARTICLE

www.nmletters.org

(Proceedings of 2011 Shanghai International Nanotechnology Cooperation Symposium, SINCS 2011, Published online 10 January 2012)

Antireflective Coatings Used in Solar Cell Prepared from Different Evaporation Solvents

Qiang Pan, Jun Shen*, Xiaodong Wang, Zhihua Zhang

Abstract: A critical review on the advancement of preparing SiO_2 antireflective (AR) coating via dip-coating method is provided. The advantages and disadvantages of sol-gel method with ethanol as solvent were considered. In order to solve the problems occurred in ethanol system, 1-methoxy, 2-propanol (PM) was used as a novel solvent to synthesize SiO_2 sol, and the AR coatings were deposited on solar glass substrates by dip-coating under industrial environment. Optical properties, surface morphology and mechanical performance of the synthesized films were investigated. The results showed that PM was an excellent solvent which could be adopted under industrial production conditions.

Keywords: Antireflective coating; Solar cell; Dip-coating; Evaporation; Industrial production

Citation: Qiang Pan, Jun Shen, Xiaodong Wang and Zhihua Zhang, "Antireflective Coatings Used in Solar Cell Prepared from Different Evaporation Solvents", Proceedings of Shanghai International Nanotechnology Cooperation Symposium, 10-14 (2011). http://dx.doi.org/sincs2011.03

Introduction

With the development of industrialization, the demand of energy source is sharply increasing. To solve the energy crisis and environmental degradation, it is necessary to seek other clean, renewable energy. The solar energy as a renewable and unexhausted energy can partly satisfy the ever-increasing demand for energy source [1].

Photovoltaic (PV) is a simple and common method to use solar energy [2]. Solar cells as the critical component in PV module directly convert the incident solar radiation into electricity. Because single piece of solar cell can't be used efficiently, several pieces should be fitted together to get desirable voltage [3]. And there is a glass baffle on the top of the combined solar cells as the protection part [4].

However, the photoelectric conversion efficiency of the solar cells is not high enough, which due to the limitation of silicon's band gap and 8∼9% reflection losses caused by the surface of protection glass. The former factor would hamper the photoelectric conversion efficiency to increase even 1%. As to the other factor, it can be satisfied by some relative simple technologies such as antireflection.

Due to the different refractive indices of the air and the protection glass, part of the solar radiation energy reflects at the air-glass interface, which leads to the loss of solar energy. Many researchers [5,6] have already shown that the reflection at the air-glass interface can be reduced by deposition of a porous SiO_2 antireflective coating. Technologies for the preparation of porous SiO_2 AR coating include the sol-gel deposition, acid etching of the glass, and direct plasma enhanced chemical vapor deposition (PEVCD), etc. Compared to the other methods, the sol-gel process has a lot of advantages, such as inexpensive, simple operation process, controllable structure [7,8], and easily adaptable to industry scale. Besides, the refractive index of the AR coating can be varied from 1.15 to 1.45, which indicates that the AR coating can be dipped on the substrate with a wide range of refractive index, and the thick-

Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, Phol Institute of Solid State Physics, Tongji University, Shanghai 200092, China

*Corresponding author. E-mail: shenjun67@tongji.edu.cn (J. Shen); phoenix0803@hotmail.com (Q. Pan)

ness of the AR coating can be controlled by changing the drawing speed, the solid content and the solution's viscosity [9].

Quite a number of preparation of different broadband AR coatings by sol-gel method are reported, such as super wide bandwidth AR coating (400~1800 nm and 2500~6000 nm) [10,11], visible region AR coating (350~850 nm) [12], and shortwave-band AR coating (~355 nm) [13]. However, few reports concern commercial applications of AR coatings. This paper focuses on the industrialization of antireflection coatings in the wavelength region of 400~800 nm, which covers the most part of the energy useful for solar cells [14].

Preparation of AR coating via sol-gel method in ethanol system

Several authors have already shown how the deposition of a thin porous SiO_2 AR coating on the glass can lead to an enhanced light transmittance by reducing reflection at the air-glass interface. These coatings could, therefore, be used to increase the performance of glasses for PV modules. Meanwhile, TiO_2 [15] or SiO_2-TiO_2 [16,17] AR coatings have also drawn researchers' attention, because of the excellent properties of TiO_2 coatings, such as mechanical performance, hydrophobic, and self-cleaning [18-20]. However, no commercial TiO_2 AR coated glass had been developed for PV application, because the possible gain in efficiency and energy output should not be offset by a high production price of the coating. Among the commonly used AR coatings, SiO_2 stands out due to its low refractive index of less than 1.45, good environmental stability and durability.

Preparation of silica sol

Teraethylorthosilicate (TEOS), ethanol, and water were used as the main precursors, and HCl and $NH_3 \cdot H_2O$ were selected as catalysts controlling the PH of the hydrolysis/condensation reaction in the sol-gel solution. Besides, trimethylamine, triethylamine, tripropylamine and tributylamine were also used as base catalysts to fabricate the base-catalyzed silica AR sol [21]. Xiao [22] has reported that SiO_2 AR coatings could be prepared by sol-gel process with acid catalysis, base catalysis, and base/acid two-step catalysis. The experimental results [23] have shown that the base/acid two-step catalysis can adjust the refractive index of the nano-porous silica coatings from 1.18 to 1.42 rapidly and continuously.

Preparation of AR coatings

There are a variety of options for depositing the AR coatings, such as dip-coating, spin-coating, meniscus-coating, spray-coating, flow-coating, and roll-coating methods. As a mature, simple and inexpensive process used to prepare thin film, dip-coating method could be applied to film deposition on substrates of arbitrary shape, and is easily adaptable to industrial scale.

The typical AR coatings could be deposited on the plate glass substrates in a stable environment (with humidity lower than 30% and temperature of 20~25℃), with the drawing speed not higher than 300 mm/min [24]. After drying in the air at room temperature, the coatings have to be baked by thermal treatment and densification temperature varies from 300℃ to 550℃ [25].

The character of the AR coatings

The average transmittance of the coated glass can reach 97.84% derived from base/acid catalyzed silica sol, which indicating an average increase of the transmittance of approximately 7.5% between 400 nm and 800 nm [26].

Figure 1 shows the surface morphology of the silica coatings prepared via sol-gel process with different catalysis. The surface of coatings from base-catalyzed sol is considerably rough with a large quantity of particles and clusters, which brings high porosity and loose

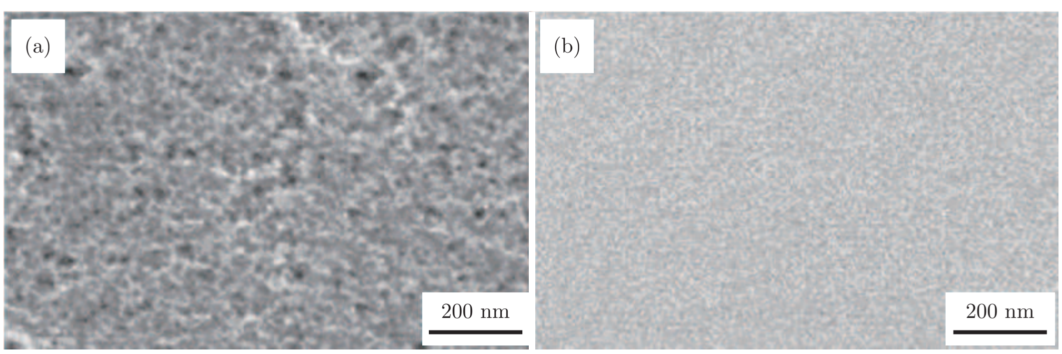

Fig. 1 SEM pattern of surface morphology of the silica coatings derived from sol-gel process with base catalysis (a) and acid catalysis (b) [22].

structure; whereas the surface of the coatings from acid-catalyzed sol is very dense and smooth with smaller particles stacking together closely. The surface of two-step catalyzed coatings is similar with that of the base catalyzed coatings, except the particles are a little bigger [22].

Due to the high porosity, the mechanical properties of the coatings from the base-catalyzed and base/acid two-step catalyzed sol are so poor that these significantly influence their commercial applications. In order to improve the properties of the nano-porous coatings, researchers [27-29] have tried to prepare scratch-resistant silica coatings by doping polymers in the silica sols, or by strengthening of the silica gels via aging in TEOS, water and ethanol solutions. On the other hand, post-treatment including ammonia and water vapor treatment [30] and modification [31] can also enhance scratch-resistant or hydrophobicity of silica coatings. Besides, Wang [14] has presented a type of high-strength SiO_2/TiO_2 AR coatings used for solar glass by dip-coating method, and the pencil hardness test has shown the coating hardness was about 5H.

Unfortunately, with a combination of the production efficiency and cost, these present methods are not suitable for industrial production. Even if changing the concentration of sol by diluted with ethanol, the drawing speed can not be increased a lot, and the surface properties of the coatings are not so ideal. Because the boiling point of the ethanol is quite low and the solvent would evaporate quickly under normal industrial environment, which leads to non-uniform of the coated layer. The disadvantages of the low boiling point solvent are not only the glass surface would become blurred, but also the transmittances in different positions are not so even. Therefore, as a solvent, ethanol can't well meet the needs of the industrial production.

Preparation of AR coating via sol-gel method in PM system

Due to the above mentioned disadvantages of whole ethanol solvent system, PM was used as a new solvent to synthesize silica sol for AR coating, whose boiling point is 120℃. The AR coatings were deposited on both side of patterned glass substrates (Matt-Matt) [3] by dip-coating method.

Experimental

Synthesis

Figure 2 shows the preparation procedure of silica sol. In the first step, TEOS, $NH_3{\cdot}H_2O$ and ethanol were mixed and stirred at room temperature with the volume ratio of 1:0.18:10, and then were aged at room temperature for several days. After refluxing at 80℃ for several hours, the sol a was prepared. Meanwhile, TEOS, HCl (PH=1), PM and deionized water with the volume ratio of 1:0.092:10:0.18 were mixed and stirred at room temperature for several hours. The sol formed here was called sol b. In the second step, sol b was added into sol a with the volume ratio of V_{sola}:V_{solb}= 2.9:1. After stirred for 2 hours, the mixed sol was diluted with PM with the volume ratio of 1:1. The new mixed sol was stirred for 2 hours and then was kept at room temperature before coating.

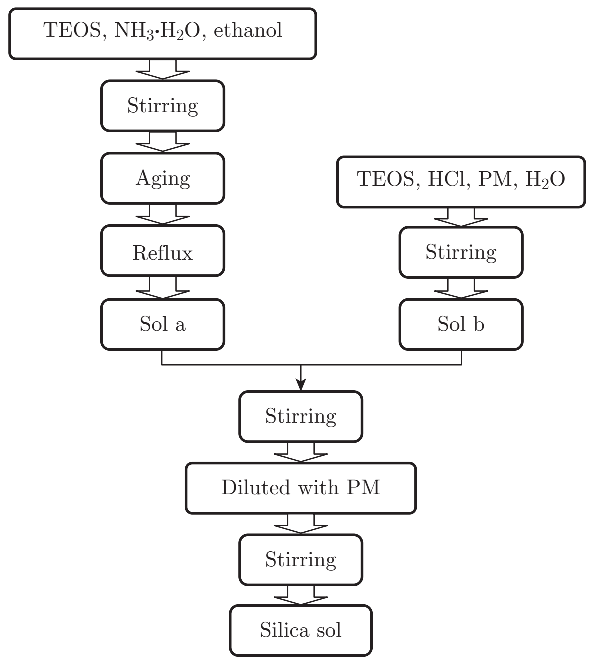

Fig. 2 Procedure of preparation of silica sol with PM.

The thin films were coated on clean patterned glass substrates by dip-coating under industrial condition (with humidity around 45% and temperature of 25∼30℃), and the desired thickness could be adjusted by the withdrawal rate (100∼1200 mm/min). Each coating was annealed at 700℃ for 3∼5 min.

Characterization

UV-VIS-NIR spectrophotometer (PE Lambda 950) was used to characterize the transmittance of the coated patterned glass. The mechanical properties of the coating were evaluated by pencil hardness tester, tape and rubber tests.

Results and discussion

Figure 3 shows the transmittance spectra of the coated patterned glasses with different drawing speeds. When the drawing speed is 600-700 mm/min, the average transmittance is about 96% in the wavelength between 400 nm and 800 nm, indicating an increase of transmitted light of approximately 4.7%. For the different surface textures between the patterned glass and the plate glass, their antireflective effect is different, and the coated patterned glass hardly gets as high transmittance as 99% [32] while the coated plate glass gets.

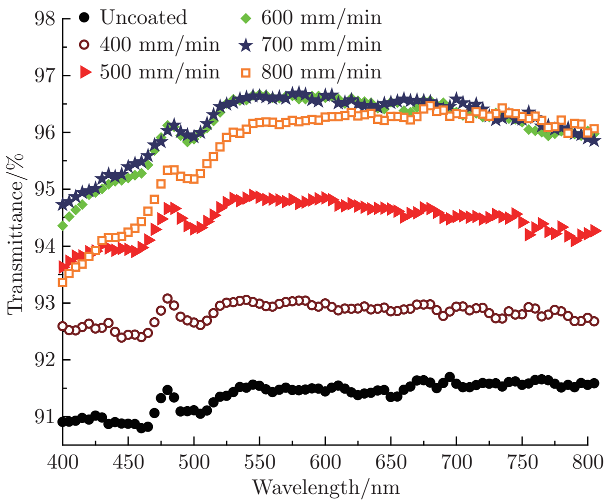

Fig. 3 Transmittance of the AR coatings.

Since the boiling point of PM is 120°C, which is much higher than that of ethanol, the solvent evaporates more slowly in the drawing process, and the solution slowly flows from top down to the bottom of the substrates. Subsequently, the solvent evaporation leads to a homogeneous gelation process and the formation of a transparent coating. The uniform coating can be formed even in the drawing speed as high as 700 mm/min. And the production efficiency with this drawing speed (600-700 mm/min) could well meet the needs of the industrial production.

It is very hard to measure the mechanical properties of the thin, soft and porous coatings. Many methods have been developed for testing hard coatings, but in general, these tests can not be applied to AR coatings since they were designed to probe under a completely different regime [33]. The properties of the coatings were therefore measured qualitatively with the pencil hardness test, tape and rubber tests [34,35].

Table 1 exhibits clearly the mechanical properties of the SiO_2 AR coatings. The result of pencil hardness test shows that the hardness of the coating is 3H. The tape tests were applied to check the layer adhesion. The tape (Brand Panda) was laid across the coated surface, and then was slowly pulled away. This process may be repeated 50 times with a fresh tape each time. Only slightly damage was observed on the films after the tape test. This indicated the good adherence of the coating to the substrate.

In the rubber test process, the surface of the coating was rubbed by the cotton ball immersed with ethanol. After 50 times of rubber tests, only slightly damage of the coating was observed.

Table 1 Mechanical properties of the coatings

Pencil hardness test	Tape test	Rubber test
3H	Slightly damage	Slightly damage

Based on the results mentioned above, as a new solvent to prepare SiO_2 AR coatings used in solar cell, PM gains lots of advantages over the ethanol, such as excellent surface performance of the coatings, and fast drawing speed. Meanwhile, the coatings can get as good mechanical performance as the coatings derived from the ethanol system.

Conclusions

AR coatings used in solar cell have been reported, in which ethanol is used as a common solvent. However, the drawing speed can't get fast enough due to ethanol's low boiling point and quick evaporation, and the surface performance of the coating is very poor under normal industrial environment.

PM, as a selected evaporation solvent has been successfully used to synthesize SiO_2 sol. The AR coatings were deposited on patterned glass substrates by dip-coating process. All the results confirmed that PM is very suitable for industrial scale production of AR coatings used in solar cell.

Acknowledgements

The authors are very grateful to the National Natural Science Foundation of China (NO. 11074189&50802064), Funds for International Corporation of Shanghai Committee of Science and Technology (NO. 10520706800), and Funds of Shanghai Committee of Science and Technology (NO. 0952nm00700&09520714300) for their financial supports.

References

[1] P. V. Kamat J. Phys. Chem. C 111, 2834 (2007).
[2] K. M. Coakley and M. D. McGehee, Chem. Mater. 16(2004) 4533-4542
[3] C. Ballif, J. Dicker, D. Borchert and T. Hofmann Sol. Energy Mater. Sol. Cells 82, 331 (2004).
[4] G. Helsch, E. Radlein and G. H. Frischat J. Non-Cryst. Solids 265, 193 (2000).
[5] L. Nikolic, and L. Radonjic, Ceram. Int. 24, 547 (1998).
[6] T. K. Bostrom, E. Wackelgard and G. Westin, Sol. Energy Mater. Sol Cells 84, 183 (2004).

[7] A. Vincent, S. Babu, E. Brinley, A. Karakoti, S. Deshpande and S. Seal, J. Phys. Chem. C 111, 8291 (2007).
[8] G. M. Wu, J. Wang, J. Shen and et al, Mater. Res. Bull. 36, 2127 (2001).
[9] S. M. Attia, J. Wang, G. M. Wu and et al, J. Mater. Sci. Tech. 18, 211 (2002).
[10] A. gombert, W. Glaubit, K. Rose and et al, Thin Solid Films 351 73 (1999).
[11] J. Shen, T. H. Yang, Q. Y. Zhang and et al, J. Sol-Gel Sci. Tech. 26, 1029 (2003).
[12] A. Beganskiene, S. Sakirzanovas, A. Melninkaitis and et al, Mater. Sci. 12, 1392 (2006).
[13] Y. Q. Xiao, J. Shen, L. F. Yao and et al, High Power Laser and Particle Beams 16, 1281 (2004).
[14] X. D. Wang and J. Shen, J. Sol-Gel Sci. Tech. 53, 322 (2010).
[15] G. S. Vicente, A. Morales and M. T. Gutierrez, Thin Solid Films 403, 335 (2002).
[16] W. M. Chen, X. J. Zhao and. J. Wuhan Uni. Tech. Mater. Sci. 16, 30 (2001).
[17] D. S. Hinczewski, M. Hinczewski, F. Z. Tepehan and et al, Sol. Energy Mater. Sol. Cells 87, 181 (2005).
[18] M. Faustini, L. Nicole, C. Boissiere and et al, Chem. Mater. 22, 4406 (2010).
[19] Z. Y. Lin, X. T. Zhang, T. Murakami and et al, Sol. Energy Mater. Sol. Cells 92, 1434 (2008).
[20] R. Prado, G. Beobide, A. Marcaide and et al, Sol. Energy Mater. Sol. Cells 94, 1081 (2010).
[21] O. Kesmez, N. Kiraz, E. Burunkaya and et al, J. Sol-Gel Sci. Tech. 56, 167 (2010).
[22] Y. Q. Xiao, J. Shen, Z. Y. Xie and et al, J. Mater. Sci. Tech. 23, 504 (2007).
[23] G. M. Wu, J. Wang, J. Shen and et al, Mater. Sci. Eng. B 78, 135 (2000).
[24] A. Beganskiene, S. Sakirzanovas, I. Kazadojev and et al, Mater. Sci. 25, 817 (2007).
[25] O. Kesmez, H. E. Camurlu, E. Burunkaya and et al, Ceram. Int. 36, 391 (2010).
[26] J. Shen, X. D. Wang, S. Z. Wang and et al, Acta Photonica Sinica 37, 34 (2008).
[27] F. T. Chi, L. H. Yan, H. B. Lv and et al, Thin Solid Films 519, 2483 (2011).
[28] S. Haereid, M. Dahle, S. Lima and et al, J. Non-Cryst. Solids 186, 96 (1995).
[29] M. A. Einarsrud and E. Nilsen, J. Non-Cryst Solids 226, 122 (1998).
[30] G. M. Wu, J. Wang, J. Shen and et al, J. Non-Cryst. Solids 275, 169 (2000).
[31] S. A. Mahadik, M. S. Kavale, S. K. Mukherjee and et al, Appl. Sur. Sci. 257, 333 (2010).
[32] I. M. Thomas, Appl. Optics 31, 6145 (1992).
[33] P. Nostell, A. Roos, B. Karlsson, Thin Solid Films 351, 170 (1999).
[34] G. M. Wu, J. Shen, T. H. Yang and et al, J. Mater. Sci. Tech. 19(2003) 299-302
[35] J. Shen, Z. Y. Xie, X. X. Wu and et al, Rare Metal Mater. Eng. 37, 47 (2008).