Design and preparation of broadband antireflective coatings with excellent mechanical properties

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Abstract: Double antireflective coatings with broadband, high-transmittance and scratch-resistance properties were prepared in this research by sol-gel method. The bottom layer was the mixture of silica nanoparticles and linear silicate polymers (SiO_2 NPs-LPs) obtained from base/acid two-step catalyzed tetraethyl orthosilicate (TEOS), while the top layer was the mixture of hollow silica nanoparticles and linear silicate polymers (HSiO_2 NPs-LPs). By optimizing the refractive index and the thickness of the double coatings, the optical performance of the double coatings was generally consistent with the results of theoretical design. The average transmittance in the wavelength range of 400-1200 nm reached 99.1%. Besides, through applying hydroxyl modification on the surfaces of silica particles and hollow spheres, the antireflective coatings exhibited excellent mechanical properties, with its pencil hardness reaching 5 H and critical load for scratch being 28.9 N. All these good features have made this coating promising in harsh outdoor conditions.

Keywords: sol-gel, broadband, high transmittance, mechanical properties;

1. Introduction

Antireflective coatings (ARCs) used on the surfaces of outdoor solar modules should meet the following requirements: 1) good broadband antireflective properties in the visible and near-infrared range to maximize the use of solar energy; 2) good abrasion-resistance and adhesion-resistance properties to adapt to harsh outdoor conditions. A common way to achieve broadband antireflective effect is to design

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double ARCs according to optical theory. And broadband antireflective effect in the visible and near-infrared range can be enhanced by optimizing the refractive index and the thickness of top and bottom layers [1]. Li et al. [2] prepared double ARCs with a M-shaped transmittance spectrum by using a top layer of low-refractive-index SiO_2 and a bottom layer of high-refractive-index TiO_2 , and the average transmittance of the coatings only reached 96% in the range of 400-1200 nm. Sun et al. [3] fabricated double ARCs by using the porous layer of SiO_2 , which consisted of a bottom and a top layer with the refractive indexes of 1.34 and 1.13 respectively. The average transmittance of the obtained double coatings in the range of 300-1200 nm reached 98.9%. However, the mechanical properties of the mesoporous SiO_2 coatings, with its porosity being up to 76%, were poor. Thus it could not be applied outdoors. Besides, ARCs can also be used in other areas, e.g. uperluminescent diodes (SLEDs) to realize high powers of SLEDs [4-6].

In this research, we designed the parameters of double broadband ARCs according to coating theory [1]. High-refractive-index SiO_2 NPs-LPs coating was adopted as the bottom layer and low-refractive-index HSiO_2 NPs-LPs coating was adopted as the top layer by sol-gel. The thicknesses of layers were controlled by withdrawal speed, so as to ensure the refractive indexes and thicknesses of the coatings were consistent with the theoretical values. Besides, through hydroxyl modification for the surfaces of SiO_2 NPs-LPs and HSiO_2 NPs-LPs, the mechanical strength of the double coatings was enhanced to balance the broadband antireflective properties and mechanical properties.

2. Experimental

2.1. Preparation of double ARCs

The synthesis of 10 nm SiO_2 NPs was done by Stöber method with the mass concentration of 4.3%.

One-step wet synthetic route controlled by polyelectrolyte [7] was used to prepare HSiO₂ NPs with the mass concentration of 1.6%. H₂O₂ was used to conduct hydroxyl modification for the surfaces of SiO₂ and HSiO₂. The molar ratio was H₂O₂: SiO₂: HSiO₂=1:6:6. After modification, acid-catalyzed TEOS [8] was mixed with the above obtained sols respectively. And then the two sols i.e. SiO₂ NPs-LPs (molar ratio of NPs: LPs=8:2) and HSiO₂ NPs-LPs (molar ratio of NPs: LPs=10:1) could be obtained. After cleaning the glass substrates [9], SYDC-100 dip-coating machine was used to coat one layer of SiO₂ NPs-LPs on the clean glass with withdrawal speed of 100 mm/min. After being dried in oven at 80 °C for 30 min, then one layer of HSiO₂ NPs-LPs was coated on the obtained layer with withdrawal speed of 160 mm/min. After being dried in oven at 80°C for 30 min and calcined at 550 °C for 2 h, the double HSiO₂ NPs-LPs/SiO₂ NPs-LPs coatings were obtained.

2.2. Characterization

The structures of SiO₂ NPs-LPs sol and HSiO₂ NPs-LPs sol were observed by a high-resolution transmission electron microscope (TEM, JEM-2100, JEOL). The surface micromorphology of the coatings was observed by a field emission scanning electron microscopy (FESEM, SUPRA55, Zeiss). The transmission spectrum of the coatings in the range of 400-1200 nm was measured by an UV-visible spectrophotometer (UV-1700, Shimadzu). The refractive index of the coatings was measured by a spectroscopic ellipsometer (E03, ELLITOP Scientific). The abrasion resistance of the coatings was investigated by a pencil hardness tester (291-type, Erichsen). And the adhesion strength between the coatings and the glass substrate was tested by a scratch tester (WS-92).

3. Results and discussion

According to the characteristic calculation of multilayer coatings [1], the corresponding characteristic

matrix of the structure of double coatings is denoted by:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \begin{bmatrix} \cos \delta_1(\lambda) & i / n_1 \sin \delta_1(\lambda) \\ i n_1 \sin \delta_1(\lambda) & \cos \delta_1(\lambda) \end{bmatrix} \begin{bmatrix} \cos \delta_2(\lambda) & i / n_2 \sin \delta_2(\lambda) \\ i n_2 \sin \delta_2(\lambda) & \cos \delta_2(\lambda) \end{bmatrix} \begin{bmatrix} 1 \\ n_g \end{bmatrix} \quad (1)$$

where B and C are the total electric field magnitude and magnetic field amplitude of optical transmission in medium respectively, n_1 and n_2 are the refractive indexes of top and bottom coating respectively, δ_1 and δ_2 are the thickness of top and bottom coating respectively, n_g is the refractive index of substrate.

The reflectance of double ARCs is denoted by [10]:

$$R = \left(\frac{n_0 B - C}{n_0 B + C} \right) \left(\frac{n_0 B - C}{n_0 B + C} \right)^* \quad (2)$$

Transmittance $T = 1 - R$.

where the incident medium is air with the refractive index of n_0 .

A series of double broadband ARCs were designed by the coating theory and the corresponding parameters are shown in Table 1.

Table 1 Parameters of some double ARCs through theoretical design

Sample number	Bottom layer		Top layer		Average transmittance (400-1200 nm)/%
	Refractive index (n_1)	Coating thickness (d_1)/nm	Refractive index (n_2)	Coating thickness (d_2)/nm	
1	1.38	110	1.24	120	99.0
2	1.38	114	1.21	122	99.2
3	1.34	120	1.21	120	99.5
4	1.34	122	1.19	129	99.2

The transmittance of the double coatings reaches the best performance when the refractive index is 1.34 and the thickness is 120 nm for the bottom layer, and the counterparts are 1.21 and 120 nm for the top layer. The average transmittance in the range of 400-1200 nm reaches 99.5%.

TEM image of the sol obtained by base/acid two-step catalyzed TEOS is shown in Fig. 1a. The size of solid SiO₂ particles is about 10 nm. Acid-catalyzed TEOS linear silicate polymers (LPs) connect the solid spheres to form a "chain-solid sphere-chain" net structure. After being coated on glass surface, the above sol could form coatings with refractive index varying from 1.22 to 1.44 depending on the proportions of SiO₂ NPs-LPs [8]. The refractive index of the SiO₂ NPs-LPs coating measured was 1.34. TEM image of the mixed sol of HSiO₂ NPs-LPs is shown in Fig. 1b. The size of the hollow sphere is 110 nm while the air sphere in the center is 60 nm. Similar to the sol obtained by base/acid two-step catalyzed TEOS, the LPs are filled in the middle of the hollow sphere to form a net structure. The relationship of the refractive index and porosity is denoted by $n_p^2 = (n^2 - 1)(1 - P) + 1$ where n_p is the refractive index of porous coating, n is the refractive index of porous coating and P is the porosity. As the hollow sphere surrounds the air whose refractive index is 1, the coatings prepared by the same proportion of the mixed sol have lower refractive index. In this research, the refractive index measured was 1.21. In the dip-coating method, the coating thickness was controlled by withdrawal speed. Through optimization, we obtained the ARCs consistent with the theoretical values where the refractive index and the thickness of the bottom layer were 1.34 and 120 nm respectively, and the counterparts of the top layer were 1.21 and 120 nm respectively, as shown in Fig. 1c.

Fig. 1. TEM images of (a) SiO₂ NPs-LPs and (b) HSiO₂ NPs-LPs. SEM images of the double ARC

coatings (c) cross-section and (d) surface morphology.

Transmittance of the double broadband ARCs is shown in Fig. 2, which is a typical M-type spectrum.

According to $\tau_T = \left(\sum_{\lambda_{\min}}^{\lambda_{\max}} T_{\lambda} S_{\lambda} \Delta\lambda \right) / \left(\sum_{\lambda_{\min}}^{\lambda_{\max}} S_{\lambda} \Delta\lambda \right)$ (where T_{λ} is the transmittance of corresponding wavelength, S_{λ} is the solar irradiance intensity for air mass 1.5 (ASTM G173-03), and $\Delta\lambda$ is the wavelength increment) [11], the weighted average transmittance of the double ARCs in the range of 400-1200 nm reached 99.1%, very close to the theoretical design value of 99.5%. The transmittance error between the experimental and theoretical values mainly occurs in the range of 400-600 nm, usually caused by the scattered incident light on the rough coating surface of particles [12]. As shown in Fig. 1d, the surface of the coating is generally flat and uniform. There are also regular stripped gaps in Fig. 1d, showing a typical morphology of nanoparticle coatings.

Fig. 2. Experimental and model transmittance spectra of the double broadband ARCs.

The transmittance and the mechanical strength of acid-base mixed sol shows "seesaw" effect. When NPs have a higher proportion in sol, coatings have good transmittance while the mechanical properties are poor (usually 4B for pencil hardness) resulting from high porosity and small number of Si-O-Si bonds respectively. When LPs have a higher proportion, the mechanical properties are good while the transmittance is poor resulting from large number of Si-O-Si bonds and low porosity respectively [13]. Based on our preliminary findings [14], after conducting hydroxyl modification for the surface of silica

nanoparticles, more hydroxyl would appear on the surface and thus the bonding strength of Si-O-Si between NPs and LPs significantly increased. According to ISO 15184, the hardness of the double coatings was measured to be 5 H. The adhesion strength between the coatings and the substrate was tested by scratch experiment [15] and the critical load, L_c was 28.9 N according to Fig. 3b, showing the excellent abrasion-resistance property.

Fig. 3. Mechanical properties. (a) Scratches by 6H pencil on the surface of the coatings. (b) Acoustic emission spectrum of scratches between the coatings and the substrate.

4. Conclusion

Based on Maxwell's equations [1], a series of broadband ARCs can be designed. Base/acid two-step catalyzed SiO_2 sol and the mixture of HSiO_2 and LPs sol obtained by sol-gel method can be used to prepare coatings with different refractive indexes. By optimizing the thickness, coatings that are very close to the theoretical design can be prepared. In this research, the double ARCs with average transmittance of 99.1% in the range of 400-1200 nm were prepared. Besides, through hydroxyl modification for the nanoparticle surfaces, antireflective coatings also exhibited excellent mechanical properties. The pencil hardness reached 5H and the critical load L_c was 28.9 N, which showed great significance for outdoor applications.

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References

- [1] H.A. Macleod, Thin-film optical filters, CRC press, Boca Raton, Florida, USA, 2010.
- [2] X. Li, X. Wang, J. Shen, Rare Metal Mat. Eng., 41 (2012) 296.
- [3] J. Sun, X. Cui, C. Zhang, et al., J. Mater. Chem. C, 3 (2015) 7187.
- [4] Z. Zang, T. Minato, P. Navaretti, et al., IPTL, 10 (2010) 721.
- [5] Z. Zang, K. Mukai, P. Navaretti, et al., Appl. Phys. Lett., 100 (2012) 031108.
- [6] Z. Zang, K. Mukai, P. Navaretti, et al., IEICE transactions on electronics, 94 (2011) 862.
- [7] Y. Wang, J. Wu, H. Wang, et al., Sol. Energy, 122 (2015) 763.
- [8] I.M. Thomas, Appl. Opt., 31 (1992) 6145.
- [9] X. Meng, Y. Wang, H. Wang, et al., Sol. Energy, 101 (2014) 283.
- [10] J. Zha, X. Lu, Z. Xin, J. Sol-Gel Sci. Technol., 74 (2015) 677.
- [11] G. Hensch, A. Mös, J. Deubener, et al., Sol. Energy Mater. Sol. Cells, 94 (2010) 2191.
- [12] K.H. Nielsen, D.K. Orzol, S. Koynov, et al., Sol. Energy Mater. Sol. Cells, 128 (2014) 283.
- [13] H. Ye, X. Zhang, Y. Zhang, et al., Sol. Energy Mater. Sol. Cells, 95 (2011) 2347.
- [14] Y. Wang, M. He, R. Chen, J. Mater. Chem. A, 3 (2015) 1609.
- [15] J. Wang, M. Liu, Mater. Chem. Phys., 129 (2011) 40.