Double-layer anti-reflection coating of SiO$_2$–TiO$_2$/SiO$_2$–TiO$_2$–PEG300 with high transmittance and super-hydrophilicity

Yong Shuai Wei$^{1,2}$, Shao Hui Xu$^{1}$, Li Gang Yuan$^{3,4}$, Biao Wang$^{1}$, Shu Li Liu$^{1,2}$, and Guang Tao Fei$^{1}$

$^1$ Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, PO Box 1129, Hefei 230031, People's Republic of China
$^2$ University of Science and Technology of China, Hefei 230026, People's Republic of China
$^3$ Science and Technology on Solid-state Laser Laboratory, North China Research Institute of Electro-Optics, Beijing 100015, People’s Republic of China
$^4$ Authors to whom any correspondence should be addressed.

E-mail: shxu@issp.ac.cn and greenlaser@sina.com

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Abstract

A highly transparent and super-hydrophilic double-layer anti-reflection coating was prepared by a simple and economical sol-gel method based on the glass substrate. The bottom and top layer were respectively made with SiO$_2$–TiO$_2$ sol and SiO$_2$–TiO$_2$–PEG300 sol. The average transmittance of the substrate coated with the double-layer coating is increased by 7% up to 97.4% in the visible light band, and the peak transmittance reaches 99% at about 550 nm. In addition, double-layer anti-reflection coating shows a good super-hydrophilic self-cleaning performance, and the transmittance of the coating can be restored by simple washing with water. Furthermore, due to the existence of anatase TiO$_2$, the composite coating can restore the super-hydrophilicity damaged by dust under UV light.

1. Introduction

Anti-reflection coatings (ARCs) have been increasingly important and widely used to reduce light reflection and increase light transmission from windows and displays to eyeglass lenses and cell phone cameras [1]. However, how to balance the transparency and the durability of ARCs is an important subject in the field of solar energy application [2, 3]. It is reported that there will be about 8% reflection loss at the interface between glass and air due to the difference in the refractive index [4]. In order to reduce the energy loss caused by reflection, one or more layers of thin films with moderate refractive index and film thickness are usually coated on the glass surface to achieve anti-reflection effect based on light interference cancellation after light reflection through two interfaces. The ideal single-layer ARC is that its refractive index is equal to the square root of the refractive index of the substrate, and many related researches have been reported. However, due to the narrow range of anti-reflection waveband for the single-layer ARC, people turn their attention to the preparation of multilayers. At present, multilayer-coating with different refractive indices have been applied to achieve a broadband anti-reflection [5–7].

As we know, for solar panels, over time, the conversion efficiency will decrease significantly due to environmental dust or organic matter adsorption on the surface [8]. Therefore, it is very important to prepare the ARC with a self-cleaning function. Generally speaking, for the super-hydrophilic film with contact angle less than 5° or the super-hydrophobic film with contact angle greater than 150°, the water drop can spread out or agglomerate into a sphere, both of which can effectively remove the dust and pollutants on the surface of the film and have a good self-cleaning performance. In order to achieve this function, one method is to adjust the micromorphology [9] or the chemical properties of the film surface, such as plating low surface energy materials on the surface [10], so as to make it super-hydrophilic or super-hydrophobic; another method is to add some materials with photocatalytic properties such as TiO$_2$ [11], which can degrade organic pollutants absorbed on
the surface under light conditions and achieve the self-cleaning effect. On the other hand, it is reported that TiO₂ itself has superhydrophilicity [12]. However, the refractive index of TiO₂ is high, leading to low transmittance in the visible range. In order to increase transmittance, porous TiO₂ films have been formed by adding organics acting as pore-forming agents, such as Triblock copolymer F127 or polyethylene glycol (PEG, molecular formula of HO(CH₂CH₂O)nH), but the improvement is limited [13–15]. SiO₂ is a commonly used low-refractive index material, and it has been achieved a higher transmittance with the self-cleaning effect by coating a SiO₂ film as the bottom layer and a thinner TiO₂ film as the top layer than pure TiO₂ film [16–18]. However, though the TiO₂ on the surface has self-cleaning property, the transmittance of this design is still unsatisfactory. Therefore, some researchers prepared SiO₂–TiO₂ hybrid films, and adjusted the refractive index by changing the content of TiO₂; however, the SiO₂ sol used in the reported SiO₂–TiO₂ hybrid films are usually acid catalysis sol [19], which make the film obtained is dense with not high transmittance. Therefore, it is still being a challenge to prepare films with both anti-reflection and self-cleaning functions.

In this research, a double-layer ARC was coated on the glass substrate. We mixed the alkaline SiO₂ particle sol, which has a lower refractive index than the acid-catalyzed SiO₂ sol, with TiO₂ sol and used it for the bottom layer. SiO₂–TiO₂ hybrid sol added the pore-forming agent PEG300, which is polyethylene glycol with molecular weight of 300, was used for the top layer. This design has several advantages as follows. On the one hand, the addition of a pore-forming agent to the top layer can adjust the refractive index in order to increase the transmittance. On the other hand, it can increase its surface area, which will be conducive to the degradation of pollutants by TiO₂. In addition, because the two layers are the same material, there is a good binding force between layers, which is beneficial to the structural stability. The obtained film with a rough surface and porous structure not only has an average transmittance of 97.4% in the visible band, but also possesses the long-term self-cleaning property.

2. Material and methods

2.1. Preparation of sol

Tetraethyl orthosilicate, anhydrous ethanol, deionized water, and ammonia water with the molar ratio of 1:20:5:0.3 were mixed and stirred for 7 h in a 40 °C water bath to obtain SiO₂ sol. After aged for 5 days, the pH of SiO₂ sol was adjusted to about 1 via nitric acid. Tetra-butyl titanate, anhydrous ethanol, deionized water, and nitric acid with the molar ratio of 1:46:4:0.11 were mixed and stirred for 2 h at room temperature and aged for 5 days to obtain TiO₂ sol. Then, the TiO₂ sol was added into the acidulated SiO₂ sol and stirred for 2 h at room temperature to obtain the SiO₂–TiO₂ hybrid sol. In our experiment, the weight ratio of SiO₂ and TiO₂ in the SiO₂–TiO₂ mixed sol is 3:1. The SiO₂–TiO₂–PEG300 hybrid sol was produced by adding PEG300 to SiO₂–TiO₂ hybrid sol with stirring for 1 h at room temperature, and the weight ratio of SiO₂–TiO₂ and PEG300 is 7:13.

2.2. Cleaning of the glass substrate

Firstly, the surface of the glass was wiped with cleaning cloth dipped in an alkaline solution, then the glass was put into absolute ethanol and deionized water in turn for about 10 min of ultrasound, respectively, and finally dried it in the oven for standby.

2.3. Preparation of film

The films were prepared with the dip-coating method. Double-layer ARC was prepared as following steps. At first, the clean glass substrate was dipped into the SiO₂–TiO₂ hybrid sol, stayed for 2 min, and then was pulled with the lifting speed of 50 mm min⁻¹. After that, the bottom layer was dried in an oven at 60 °C for 10 min. Secondly, the coated substrate was dipped into the SiO₂–TiO₂–PEG300 hybrid sol keeping the coating parameters unchanged to obtain the top layer. At last, the substrate coated with double-layers was dried in an oven at 60 °C for 10 min and then heat-treated in the tube furnace at 550 °C for 2 h. The SiO₂–TiO₂ single-layer film as a sample for comparison was pulled twice at the lifting speed of 50 mm min⁻¹ with the same SiO₂–TiO₂ hybrid sol. The hybrid sols were heated at 100 °C to volatilize, and then annealed at 550 °C for 2 h to obtain hybrid powder for XRD measurement.

2.4. Structure and morphology characterization

The crystal structure of the sample was identified by x-ray diffraction (XRD, Philips X’Pert). The surface morphology and thickness of films were obtained by field-emission scanning electron microscopy (SEM, Hitachi, SU8020). The transmittance of films was measured by Shimadzu UV–1750. The contact angle of films was measured by contact angle analyzer, and the content of hydroxyl on the sample surface was studied by Fourier-transform infrared spectroscopy (FTIR, Thermo Nicolet Corporation). The 500 W mercury lamp was used as the UV light source.
3. Results and discussion

The transmittance under normal incidence can be calculated by means of characteristic matrix theory [20–24]. The characteristic matrix for the single-layer shown in figure 1(a) and double-layer shown in figure 1(b) is given, respectively:

\[
\begin{bmatrix}
B \\
C
\end{bmatrix} = \begin{bmatrix}
\cos \delta_{layer} & i \sin \delta_{layer} \\
i n_{layer} \sin \delta_{layer} & n_{layer} \cos \delta_{layer}
\end{bmatrix}
\begin{bmatrix}
1 \\
n_{glass}
\end{bmatrix},
\]

and

\[
\begin{bmatrix}
B \\
C
\end{bmatrix} = \begin{bmatrix}
\cos \delta_{top} & i \sin \delta_{top} & i \sin \delta_{bottom} & i \sin \delta_{bottom} \\
i n_{top} \sin \delta_{top} & n_{top} \cos \delta_{top} & i n_{bottom} \sin \delta_{bottom} & i n_{bottom} \cos \delta_{bottom}
\end{bmatrix}
\begin{bmatrix}
1 \\
n_{glass}
\end{bmatrix},
\]

where the phase thickness \( \delta \) is related to the physical thickness \( d \) of the material by the expression \( \delta = \frac{2\pi}{\lambda} nd \) for the normal incidence. Then, the reflection \( R \) at the film surface can be calculated by \( R = \frac{(n_{air} - n_{glass})(n_{air} + n_{glass})}{(n_{air} + n_{glass})^2} \), where \( Y \) is given by \( Y = \frac{\lambda}{4\pi} \).

According to the effective medium formula, we can roughly calculate the refractive index of each film and \( \lambda \) is the wavelength of the incident light, there will be zero reflectivity. Base on the above relationship, for glass substrates with the refractive index \( n_{glass} \) of 1.52, we can know that \( n_{top} = 1.32 \) and \( n_{bottom} = 1.15 \) are the best choice. It is reported that the refractive indexes of SiO\(_2\) particle film and TiO\(_2\) film are \( n_{SiO2} = 1.18 \) and \( n_{TiO2} = 2.2 \) [25], respectively. In our experiment, the SiO\(_2\)–TiO\(_2\) mixed sol was selected for preparing the bottom layer. If want to obtain the top layer with a refractive index of 1.15 also with the SiO\(_2\)–TiO\(_2\) mixed sol, the TiO\(_2\) content should be very low, which will affect its catalytic self-cleaning performance. Therefore, we add pore-forming agent PEG300 into SiO\(_2\)–TiO\(_2\) mixed sol for the top layer, to form air porous in order to further decrease the refractive index of the top layer, while the amount of PEG300 should be controlled reasonably because too much pore-forming agent will affect the mechanical properties of the top layer. Comprehensive consideration of transmittance, photocatalysis, and mechanical properties, in our experiment, the SiO\(_2\)–TiO\(_2\) mixed sol with the weight ratio of SiO\(_2\):TiO\(_2\) being 3:1 was selected for the bottom layer, and the weight ratio of SiO\(_2\)–TiO\(_2\) and PEG300 being 7:13 was chosen for the top layer. The design of two layers with the same material, is also conducive to the good adhesion between the layers.

The Bruggeman effective medium approximation model is usually used to analyze the relationship between the dielectric constant and the volume of the composite material [26, 27], and the general equation form of the model is shown:

\[
\sum f_i \left( \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \right) = 0,
\]

where \( f_i \) represents the volume fraction of a component in the composite; \( \varepsilon_i \) represents the dielectric constant of the corresponding component; \( \varepsilon_m \) represents the average dielectric constant of the composite. The relationship between the refractive index \( n \) and the dielectric constant \( \varepsilon \) can be written as \( \varepsilon = n^2 \). According to the effective medium formula, we can roughly calculate the refractive index of SiO\(_2\)–TiO\(_2\) mixed film is 1.35, and the refractive index of SiO\(_2\)–TiO\(_2\)–PEG300 film is 1.28.

According to the characteristic matrix of double-layer, on account that the refractive index of the top layer and bottom layer is 1.28 and 1.35, respectively, we calculate the relationship between the transmission in the
visible light range and the optical thickness of each layer by setting the center wavelength of 550 nm, as shown in figure 2(a). It can be seen from figure 2(a), when the optical thickness of each layer is about $\lambda/7$ or $\lambda/8$, there is a better transmittance in the visible light region. Accordingly, the thickness of the top and bottom layers should be selected about 50 nm and 60 nm, respectively, i.e. the total thickness of the two layers being in the range of 100–120 nm. For other $\lambda$, the relationship between transmittance and film thickness is shown in figures 2(b)–(f). It can be seen from figures 2(b)–(f) that for different central wavelengths ($\lambda$), the best choice of the single-layer is about 50–60 nm, i.e. the total thickness being 100–120 nm. So we adjust the lifting speed to obtain the required film thickness in our experiment.

Figure 3(a) exhibits the XRD patterns of SiO$_2$–TiO$_2$ hybrid powder, pure TiO$_2$, and SiO$_2$ powder. It can be noticed that the strongest diffraction peak of pure TiO$_2$ is located at $2\theta = 25.3^\circ$ associating with (101) plane, and the other characteristic peaks at $2\theta = 37.9^\circ$, 48°, 54.1°, 55°, and 62.8° respectively correspond to (004), (200), (105), (211), and (204) planes, indicating the pure TiO$_2$ is anatase crystal structure. The XRD pattern of pure

![Figure 2](image-url)
SiO$_2$ shows an amorphous bulge, and no obvious diffraction peak of the crystal phase is observed. By comparing the XRD patterns of SiO$_2$–TiO$_2$ hybrid powder with pure TiO$_2$, the crystal plane diffraction peak of TiO$_2$ can be observed. It indicates the anatase phase existing in SiO$_2$–TiO$_2$ hybrid powder, which is a benefit for the photocatalytic properties. The morphologies of the SiO$_2$–TiO$_2$ film and the SiO$_2$–TiO$_2$-PEG300 film are shown in figures 3(b) and (c), respectively. It can be seen that both of them are all composed of uniformly distributed particles, and their particles size is not much different. However, the graininess is more obvious and the accumulation of particles is not too dense for the SiO$_2$–TiO$_2$-PEG300 film, in addition to that the pores between particles are more obvious. We speculate that this is because PEG300 has been completely decomposed after annealing at high temperature [28]. It is considered that it can adjust the refractive index of the composite films as well as be helpful to improve the hydrophilicity [29].

Figures 4(a) and (b) are the cross-section SEM images of single-layer and the double-layer ARC. It can be seen from figure 4(a) that the thickness of the single-layer ARC pulled twice with the same SiO$_2$–TiO$_2$ hybrid sol is about 108 nm, so the thickness of once pulling is approximately 54 nm. The thickness of the double-layer ARC is 116 nm, as shown in figure 4(b). Comparing with figure 4(a), it can be known that the thickness of the bottom layer and the top layer are about 54 nm and 62 nm, respectively. More importantly, it is difficult to distinguish between the top layer and the bottom layer, indicating that the two layers are well combined. Figure 4(c) is the transmittance of the single-layer ARC and the double-layer ARC. It can be seen that the double-layer ARC has a higher transmittance and its peak transmittance is up to 99% at 550 nm. What’s more, its anti-reflection band is also wider, and the waveband width with transmittance higher than 97% is twice than that of the single-layer ARC.

In addition to the high transmittance, the SiO$_2$–TiO$_2$-PEG300 shows a favorable super-hydrophilicity in nature due to its unique morphology characteristics. Figures 5(a)–(d) show the changes of contact angles for SiO$_2$ film, TiO$_2$ film, SiO$_2$–TiO$_2$ film and SiO$_2$–TiO$_2$-PEG300 film after irradiation with UV light, respectively, and the abscissa represents irradiation time. In the experiment of contact angle measurements, films were placed
outdoors for a week before the measure. On the fact that the test conditions have a great influence on the result [30], the contact angle is measured in strict accordance with the following experimental steps each time. First, the sample is placed on a horizontal platform. A spherical deionized water droplet with volume of 2 μL is suspended at the tip of the needle, and then move the tip of the needle with the water droplet down slowly towards the sample surface until the water droplet touches the sample. At last, after the water droplet on the sample is stable, measure the contact angle. It can be seen that the contact angles of SiO2 film, TiO2 film, the SiO2–TiO2 film and the SiO2–TiO2-PEG300 film before irradiation with UV light are 18.12°, 36.13°, 11.34° and 9.44°, respectively. The hydrophilicity of hybrid films shows a better weather resistance than that of pure SiO2 and TiO2 film, which can attribute to the increase of the surface roughness and the existence of microporous structure. It is noted the initial contact angle of the SiO2–TiO2-PEG300 film is slightly smaller than that of the SiO2–TiO2 film, which may be related to the increase of the porosity of the SiO2–TiO2-PEG300 film, and it is consistent with the conclusion that high porosity is beneficial to reducing the contact angle [4, 31]. When the four kinds of films are irradiated by ultraviolet light, all the contact angles decreased to some extent. The most obvious decrease of contact angle is occurred for TiO2 film, the contact angle decreased from 36.13° to 5.99° after 15 min irradiation. The contact angle of the SiO2–TiO2-PEG300 film and the SiO2–TiO2 film also shows an obvious decrease, which decreased from 9.44° to 0° and 11.34° to 0°, respectively, after 15 min irradiation. Conversely, the contact angle of SiO2 film hardly changed after irradiation.

All the situations mentioned above indicate that the presence of 25 wt% TiO2 component makes the hybrid film have the photo-induced hydrophilicity to decrease the contact angle [32]. This is attributed to the reaction of the hole with the bridge oxygen atoms on the surface to produce oxygen vacancies, and photogenerated electrons will transform Ti4+ to Ti3+, and the water in the air will be adsorbed on these defects to form chemically adsorbed water, i.e. surface hydroxyl groups [31]. The FTIR spectrum of double-layer sample is shown in figure 6, after irradiation by mercury lamp, there is some enhancement of the peak near 1100 cm−1, which may be related to the vibration of Ti-OH [33]. In addition, the hydroxyl vibration peak near 3500 cm−1 was also enhanced [34], indicating the generation of hydroxyl groups on the surface, which will help improve the
hydrophilic properties of the films. Therefore, it can be concluded that two factors will affect the contact angle, one is the porosity, and the other is the photo-hydrophilicity of the surface.

The weatherability and abrasion resistance of the film are very important for application in the outdoor environment [35]. Figure 7(a) shows that when the double-layer ARC was placed outdoors for a week, its transmittance dropped significantly due to the gathered dust on the surface. Fortunately, when the double-layer ARC was simply washed with tap-water, its transmittance almost returned to the initial state. In order to illustrate the wear resistance of the film, the sand abrasion test is used to simulate the outdoor environment on the account of solar cells being exposed to wind and sand outdoors in general [36, 37]. Although this kind of test is not a standard experiment, it can illustrate the wear resistance of the film to some extent. Figure 7(b) shows the change of the transmittance of the double-layer ARC when 100 ml of sand fell down on the film from 15 cm high referring to the measurement conditions in references [36, 37]. After the first round of sand resistance experiments, the transmittance decreased to a small extent, while the peak value of the transmittance is still around 97%. After the second and third rounds of sand resistance experiments, the transmittance unchanged. The fact that the high transmittance can be maintained by simple water cleaning and good sand resistance indicates the super-hydrophilic double-layer ARC we get here has a good weatherability and wear resistant.

4. Conclusion

A highly transparent and super-hydrophilic double-layer anti-reflection coating was prepared by a sol-gel method. The bottom and top layer were made with SiO<sub>2</sub>–TiO<sub>2</sub> sol and SiO<sub>2</sub>–TiO<sub>2</sub>-PEG300 sol, respectively. The
kind of double-layer film shows a good light transmittance in the visible light band and the average light transmittance reaches 97.4%, and the peak transmittance reaches 99% at about 550 nm. In addition, the double-layer coating shows a good super-hydrophilic self-cleaning performance, and the contact angle is still within 10° after being placed outside for one week. Furthermore, due to the existence of anatase TiO₂, the composite coating can restore the super-hydrophobicity damaged by dust under UV light.

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ORCID iDs

Shao Hui Xu @ https://orcid.org/0000-0002-1913-6288
Biao Wang @ https://orcid.org/0000-0003-3574-8388
Guang Tao Fei @ https://orcid.org/0000-0002-4657-1285

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