文章编号： 0258-7025(2009)Supplement 1-0324-06

Design and Fabrication of Multilayer SiO_2/CeO_2-TiO_2/SiO_2 Coatings with UV Absorption and High Quality Transparence Properties

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Abstract New transparence and ultraviolet (UV) absorption coatings having the sandwich structure of SiO_2/CeO_2-TiO_2/SiO_2 were deposited on the soda-lime silicate glass by radio frequency (R. F.) magnetron sputtering. The computer aid simulation for optical characterization has been used to optimize multilayer coatings to obtain high transparent and good UV absorbing properties. Optimum thickness of SiO_2 and CeO_2-TiO_2 films were obtained. Several analytical tools such as spectrophotometer, scanning electron microscopy, and digital camera were used to characterize possible changes in optical properties. These results suggest that the single addition of inner layer SiO_2 film has no distinct effect on improving transmittance and decreasing reflection rate in the visible light range, whereas the main function of this layer film is to improve the adhesion of the coating to glass substrate. In contrast, the outer layer SiO_2 film plays a main role on diminishing the interference yellow coloring and increasing transparence. Therefore the three-layered SiO_2(113 nm)/CeO_2-TiO_2(342 nm)/SiO_2(113 nm) films show good UV absorption (>99%) properties, high transparence (average value of ~89%) and low average reflection rate (as low as ~9%) in the visible light range.

Key words thin films; SiO_2/CeO_2-TiO_2/SiO_2; radio frequency magnetron sputtering

CLCN: O484 **Document Code**: A **doi**: 10.3788/CJL200936s1.0324

1 Introduction

Excessive exposure to ultraviolet (UV) rays in sunlight (~4%) can induce coloring and deterioration in paper, fabrics, and furniture. Unprotected exposure to the sun's ultraviolet rays can also cause skin damage, eye damage, immune system suppression, and even cancer. It is necessary to prevent materials and human body from damaging by UV rays. Shielding from UV irradiation is of interest in many fields, e. g., automobile application, building windows, and so on.

It is reported that CeO_2-TiO_2 coatings deposited on glass by sol-gel process showed UV absorption and exhibited high reflectance and interference coloring[1,2]. Afterward double-layered films on glass by sol-gel process with inner TiO_2-SiO_2 films and outer CeO_2-TiO_2 films were reported, and the inner TiO_2-SiO_2 films were used for diminishing the interference coloring[3]. Recently, we reported the CeO_2-TiO_2 films on glass by radio frequency (R. F.) magnetron sputtering with good UV absorption (>99%)[4]. However these materials are limited in their applications because semiconductor materials exhibit high reflectivity of the incident light. Antireflection (AR) coatings are applied at the front of the semiconductor surface to reduce losses of the reflected light as well as dissipate static charges on surface and shield against electromagnetic radiation. Usually MgF_2 and SiO_2 are used as low refractive index materials[5~7].

In this paper, we reported the results on fabrication of three-layered SiO_2/CeO_2-TiO_2/SiO_2 coatings on the soda-lime silicate glass by R. F. magnetron sputtering, which is the most common technique adapted on production line because of its high mass productivity, controllable thickness as well as high quality uniformity and flexibility. In addition, the UV absorption film with high transparence or antireflection will adapt to application in flat panel displays and architectural coating glass, automotive glass, with diminishing light pollution as well as decreasing eye fatigue and increasing comfort.

2 Film optimization design

Figure 1 shows the structure and various parameters of SiO_2/CeO_2-TiO_2/SiO_2 sandwich

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coatings used for films design. Many researchers have carried out the theoretical considerations of antireflection coatings[8~11]. We apply the optical matrix method for evaluation of the transmittance coefficient and design of these coatings[12~14]. Each thin film layer is described by a 2×2 matrix M_j of the form:

$$M_j = \begin{bmatrix} \cos\beta_j & (\mathrm{i}\sin\beta_j)/n_j \\ \mathrm{i}n_j\sin\beta_j & \cos\beta_j \end{bmatrix}, \qquad (1)$$

where β_j is related to the physical thickness d_j of the material by the expression $\beta_j = (2\pi/\lambda)n_j d_j$ for the normal incidence, $j = 1, 2$, and 3.

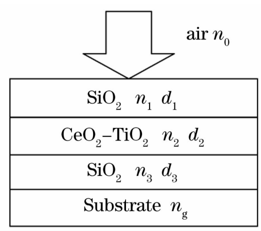

Fig.1　The various parameters of SiO_2/CeO_2-TiO_2/SiO_2 sandwich coating

The characteristic matrix for three layer films and substrate assembly shown in Fig.1 is given by Eq.(2):

$$\begin{bmatrix} B \\ C \end{bmatrix} = M_1 M_2 M_3 \begin{bmatrix} 1 \\ n_g \end{bmatrix}. \qquad (2)$$

Then, the reflectivity (R) for perpendicular incident light can be described by the expression

$$R = \left(\frac{Bn_0 - C}{Bn_0 + C}\right)\left(\frac{Bn_0 - C}{Bn_0 + C}\right)^*, \qquad (3)$$

where n_g and n_0 denote the refractive indexes of glass substrate and ambient, respectively.

The transmission (T) at normal incidence can be calculated from the R, provided that no light absorption or scattering occur.

$$T = 1 - R = \frac{4n_0 BC}{(Bn_0 + C)(Bn_0 + C)^*}. \qquad (4)$$

The reflectance and transmittance in SiO_2/CeO_2-TiO_2/SiO_2 sandwich coatings can be calculated using Eqs. (3) and (4), respectively. Optimum thickness of SiO_2 and CeO_2-TiO_2 films are determined for high transmittance in the visible light range and UV absorption by computer aid simulation. The UV absorbing properties of multilayer SiO_2/CeO_2-TiO_2/SiO_2 coatings are mainly determined by the middle layer of CeO_2-TiO_2 film. If the thickness of CeO_2-TiO_2 film is too thin, it does not form continuous layer and UV absorption capability is not strong. If too thick, the interference coloring phenomenon will become serious and transmittance of the film will decrease. So it is necessary to select an appropriate CeO_2-TiO_2 film thickness. And the role of two sided SiO_2 films (the inner and outer SiO_2 films) is mainly regulating the multilayer optical performance by the thin films interference theory.

Since the evaluation function (T) is nonlinear function about parameters of thickness and refractive index, the adjustable parameters on T are thickness d_1, d_2, d_3 and refractive index n_1, n_3.

Some necessary parameters are inputted:

1) the incident medium of refractive index n_0, due to the light in the air is perpendicular incident, $n_0 = 1$;

2) the refractive index of glass substrate, $n_g = 1.5$;

3) the refractive index of CeO_2-TiO_2 film, $n_2 = 2.0$;

4) the initial thickness of CeO_2-TiO_2 film, $d_2 = 345$ nm (by trial and error, when thickness ⩾345 nm, CeO_2-TiO_2 film has good UV absorption abilities, so the original value of d_2 is 345 nm);

5) the incident solar spectrum (380 nm ⩽ λ ⩽ 760 nm);

6) the incident angle, $\alpha = 0$;

7) the refractive index of SiO_2 film (from 1.50～1.80);

8) the film thickness of SiO_2 film (10～1000 nm).

In the fitting experiment, we made some programs using the software of Matlab[15] by computer and obtained the fitting transmittance (T_{fmax} and T_{famax}). There are three relatively ideal fitting results:

1) $n_1 = n_3 = 1.52$, $d_1 = d_3 = 113$ nm, $d_2 = 342$ nm, $T_{fmax} = 99.97\%$, $T_{famax} = 95.23\%$;

2) $n_1 = n_3 = 1.64$, $d_1 = d_3 = 79$ nm, $d_2 = 376$ nm, $T_{fmax} = 99.01\%$, $T_{famax} = 94.03\%$;

3) $n_1 = n_3 = 1.56$, $d_1 = 110$ nm, $d_3 = 188$ nm, $d_2 = 344$ nm, $T_{fmax} = 99.98\%$, $T_{famax} = 96.08\%$ (Note: T_{fmax} and T_{famax} denote the fitting maximum transmittance and fitting maximum average transmittance, respectively).

3　Experimental techniques

Three-layered SiO_2/CeO_2-TiO_2/SiO_2 films were fabricated on the soda-lime silicate glass. The glass substrate had a thickness of 1.0 mm. Before the deposition of films, the substrates were cleaned by ultrasonic washing in alcohol. Two kinds of films of low refractive index (SiO_2) and high refractive index (CeO_2-TiO_2) were deposited by R. F. magnetron sputtering.

Bulk $CeO_2:TiO_2$ targets were prepared using CeO_2 powder (C. P.) and TiO_2 powder (C. P.) as raw materials. The powders were pressed to form the pellets of mole mixture ratio for $CeO_2:TiO_2=1:1$, which were sintered at about 1373 K for 5 h and cooled down slowly in air. The obtained ceramic targets of 5.6-cm diameter were used for depositing the CeO_2-TiO_2 films by R.F. magnetron sputtering. The SiO_2 targets were purchased from the Beijing Tianrui Science and Technology Developing Center. The SiO_2 films were also deposited using SiO_2 target by R.F. magnetron sputtering.

For $CeO_2:TiO_2$ films preparation, the substrate temperature was kept at 318 K during the films growth. Before deposition, the target was pre-sputtered for 10 min to remove any contaminants on the target surface. The base pressure of the deposition system was 1×10^{-3} Pa. During sputtering, the pressure increased to 0.85 Pa as the argon gas (purity 99.999%) was introduced into the chamber. The sputtering power was 90 W. And for SiO_2 films preparation, unlike the $CeO_2:TiO_2$ films, the substrate temperature was kept at 323 K. The sputtering power was 200 W and the argon gas pressure was 0.8 Pa during sputtering process. The rate of CeO_2-TiO_2 and SiO_2 films deposition was about 3.8 nm/min and 5.5 nm/min, respectively.

The characterizations of the prepared films were as follows. The film thickness was measured by step profilometer (KLA TENCOR α-STEP500, USA). The transmittance of the films in the wavelength range of 350～800 nm were carried out using an ultraviolet-visible spectrophotometer (UV1601, SHIMADZU). The reflectance of the films in the wavelength range of 350～800nm was measured with nkd-7000 spectrophotometer (Britain AQUILA). Scanning electron microscopy (SEM, JSM-5610LV) was employed to study the cross-sectional microstructure of the films.

4 Results and discussion

Firstly, we prepared the films with different sandwich structures based on the fitting results in section 2. Figure 2 shows the transmittance curves for sample A [SiO_2(113 nm)/CeO_2-TiO_2(342 nm)/SiO_2(113 nm) film], sample B [SiO_2(79 nm)/CeO_2-TiO_2(376 nm)/SiO_2(79 nm) film], and sample C[SiO_2(110 nm)/CeO_2-TiO_2(344 nm)/SiO_2(188 nm) film]. Some optical properties were obtained from Fig.2. These three samples have no much difference in optical properties such as transmittance and cut-off wavelength. For example, the cut-off wavelengths of all three samples are about 370 nm, indicating that three kinds of SiO_2/CeO_2-TiO_2/SiO_2 sandwich coatings have excellent UV absorption. And the average transmittance of three samples is above 85% in the wavelength range of 380～760 nm. But the sample C has a big wave trough in the range of 450～575 nm, which is likely to the cause of colorful strip in surface of the film seen in the eyes. In addition, sample A has more transparency than sample B in film surface seen in the eyes. Therefore the first fitting result in section 2, the coating having sandwich structures [SiO_2(113 nm)/CeO_2-TiO_2(342 nm)/SiO_2 (113 nm)], is more reasonable in the experiments.

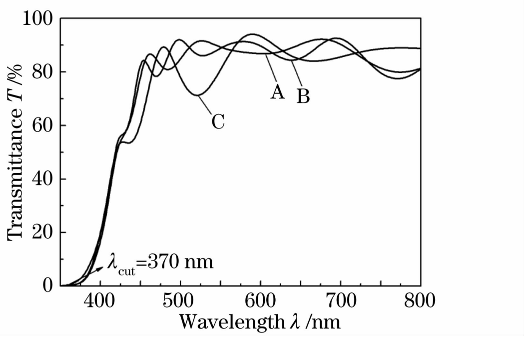

Fig.2 UV-VIS transmission spectra of three samples under different film layer thickness. A: SiO_2(113 nm)/CeO_2-TiO_2(342 nm)/SiO_2(113 nm) film; B: SiO_2(79 nm)/CeO_2-TiO_2(376 nm)/SiO_2(79 nm) film; C: SiO_2 (110 nm)/CeO_2-TiO_2 (344 nm)/SiO_2 (188 nm) film

As a result, sample A is the best film among them with high UV absorption (> 99%), transparency, and transmittance. The testing value of maximal transmittance in sample A is 92.3% at the wavelength of 525 nm, while the fitting value (T_{fmax}) is 99.97% in section 2. Ignoring its limitation, these results do suggest that the experimental fitting value is in reason.

Secondly, optical characteristics of the films having sandwich structures SiO_2(113 nm)/CeO_2-TiO_2(342 nm)/SiO_2(113 nm) film (sample B) were compared with the conventional single layer CeO_2-

TiO_2 (342 nm) film (sample A) and double-layered SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm) film (sample C) in Fig. 3 and Fig. 4. (Notes: the transmittance and reflection rate curves are non-linear function of the wavelength due to the interferential peaks resulted from film thickness. Therefore these average values of films cannot be attained directly from transmittance curve but by calculating method. The value of average transmittance: $T_{ave} = (\sum T_i)/n$ ($i = 1,2,3,\cdots,n$), 380 nm $\leqslant \lambda \leqslant$ 760 nm; the value of average reflection rate: $R_{ave} = (\sum R_j)/n$ ($j = 1,2,3,\cdots,n$), 380 nm $\leqslant \lambda \leqslant$ 760 nm, the values of T_i and R_j result from the corresponding curves in Fig. 4.)

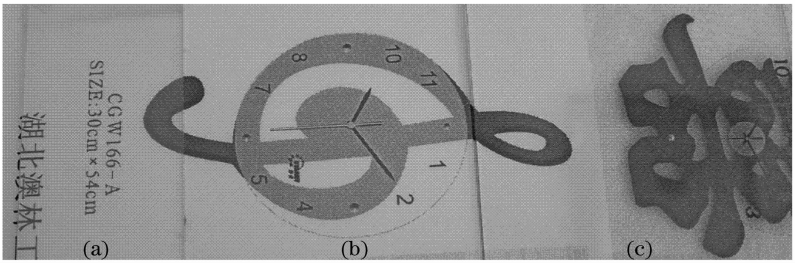

Fig. 3 Contrast photos of three samples. (a) CeO_2-TiO_2 (342 nm) film; (b) SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm)/SiO_2 (113 nm) film; (c) SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm) film. Three coating glasses were put on the picture and taken photographs, in order to contrast the transparency and interference coloring of film

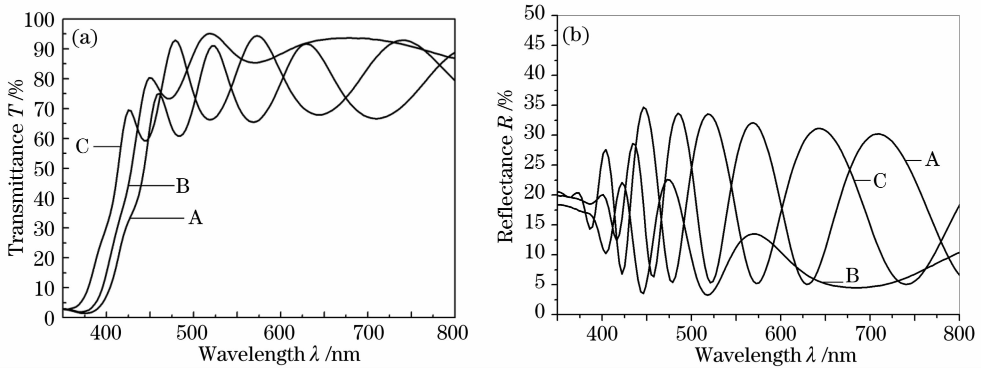

Fig. 4 Transmission (a) and reflectance (b) spectra of three samples. A: CeO_2-TiO_2 (342 nm) film; B: SiO_2 (113 nm)/ CeO_2-TiO_2 (342 nm)/SiO_2 (113nm) film; C: SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm) film

Figure 3 shows the contrast photos of sample A, B, and C. In Fig. 3, it is clearly seen that sample B has higher transparency than sample A and C; moreover, there is also interference yellow coloring of sample A and C in the films surface. The results in contrast photos show the outer SiO_2 film plays a main role on diminishing the interference yellow coloring and increasing transparency.

Figure 4 shows the transmittance (a) and the reflectance (b) of sample A, B, and C in the wavelength range from 350 to 800 nm. Some optical properties are as following. On the one hand, compared single layer film (sample A) with double-layered film (sample C) in Fig. 4(a) and Fig. 4(b), there is no significant difference on the transmittance and reflection rate except that all peaks in sample C are small 'blue shifted', which indicating the single addition of inner SiO_2 film has no distinct effects on improving transmittance and decreasing reflection rate in the visible range from 380 to 760 nm. This result is consistent with the contrast photos analysis of sample A and C in Fig. 3.

On the other hand, compared and contrasted three-layered film (sample B) with single layer film (sample A), the transmittance of sample B is much higher than that of sample A in the visible light range as seen in Fig. 4(a), and the reflectance is distinctly lower in Fig. 4(b). For example, by the calculating method, average transmittance of sample B is as high as 89% and average reflection rate is just about 9% in the wavelength range of 380～760 nm, in addition, the lowest reflection rate is nearly 3～4% at the wavelength of 700 nm, while average transmittance of sample A is about 75% and average reflection rate is almost 20% in the same wavelength range. This enhancement of light transmission and decrease of reflection rate are due to the antireflection properties of the outer SiO_2 film.

The detailed results of optical properties for singer layer film (sample A) and three-layered film (sample B) are compared in Table 1. From Table 1, we can obtain the following results. On the one hand, compared with sample A, the value of UV cut-off and absorption wavelength for sample B slightly decrease from 378 to 375 nm and 435 to 426 nm respectively, however sample B has also good UV absorption (almost 99%). On the other hand, compared with sample A, sample B has higher transparence seen from films surface coloring in Fig. 3; moreover its average transmittance increases about 14%, the average reflecting rate decreases nearly 11% in the wavelength range of 380～760 nm.

Table 1 Summarizing optical properties about single layer CeO_2-TiO_2 (342 nm) film (sample A) and three-layered SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm)/SiO_2 (113 nm) film (sample B) according to Fig.3 and Fig.4

Sample	CeO_2-TiO_2 (342 nm) film	SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm)/ SiO_2 (113 nm) film
Film coloring	Yellow transparence, relatively deep color, with color stripe	Slight yellow, high transparence, no color stripe
Visible light average transmittance /%	～75	～89
UV cut-off wavelength /nm	～378	～375
UV absorption wavelength /nm	～435	426
Average reflection rate of visible light /%	～20	～9
Remarks	There are interfere peaks, and its amplitude intensity is relatively large	The number and amplitude intensity of interfere peaks become decrease. Compared with sample A, its transmittance increase 14% and reflecting rate drops about 11% in the visible light range

Therefore the SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm)/SiO_2 (113 nm) sandwich films have the characteristics of good UV absorption as well as high transmittance and low reflection rate in the visible light range. In addition, the interference coloring of the sandwich films obviously fades away. The experimental results clearly indicate that the rational design of multilayer coatings structure using SiO_2 film as antireflection film can rapidly improve the transparency of the film and decrease reflection rate in visible light range.

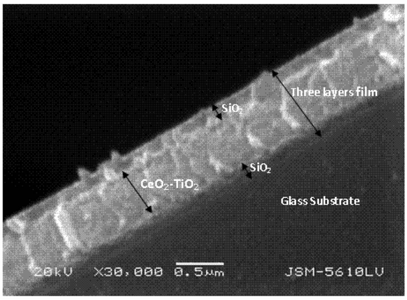

Fig.5 Cross-sectional SEM image of three-layered SiO_2/CeO_2-TiO_2/SiO_2 coating

Lastly, the structure property of sandwich structure SiO_2/CeO_2-TiO_2/SiO_2 coating is analyzed by the cross-sectional SEM image in Fig. 5. According to the SEM image of cross-section, the interface between thin films and substrate is clearly seen, which indicates that the films grow well on glass substrate. Further, we can clearly see that the first layer film is SiO_2 film, the second layer film is CeO_2-TiO_2 film, and the third layer film is also SiO_2 film. The first and the third layer film have the same film thickness. Due to the inner layer SiO_2 film is next to the glass substrate, with ion mutual penetration between this layer film and the glass substrate, the inner layer SiO_2 film can be also called the buffer layer. So the inner layer SiO_2 film can not only improve the adhesion of the coating to the glass substrate, but also prevent Ca^{2+}, Na^{+} ions in the glass substrate from entering the CeO_2-TiO_2 film layer, which may benefit the increasing of UV absorption.

5 Conclusions

In this study, we developed new UV absorption films having the sandwich structure of SiO_2/CeO_2-TiO_2/SiO_2. The optical properties of the three-layered SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm)/SiO_2 (113 nm) films were compared with those of single layer CeO_2-TiO_2 (342 nm) and double-layered SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm) films. The results show that the SiO_2 (113 nm)/CeO_2-TiO_2 (342 nm)/SiO_2 (113 nm) sandwich coatings exhibite excellent UV absorption as well as higher transmittance and lower reflectance in the visible light range. Moreover, the SiO_2/CeO_2-TiO_2/SiO_2 films have high transparency and the interference coloring of films obviously diminishes. Therefore the SiO_2/CeO_2-TiO_2/SiO_2 sandwich films are useful as window coatings such as architectural coating glass, automotive glass, and flat panel displays, since both good UV absorption and high transparence are obtainable by the conventional sputtering deposition technique at a lower substrate temperature.

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