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Single material TiO_2 double layers antireflection coating with photocatalytic property prepared by magnetron sputtering technique

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ABSTRACT

Single material TiO_2 was used to fabricate the double layers antireflection coating with photocatalytic property. TiO_2 layers with low and high refractive indices were prepared by the direct reactive magnetron sputtering technique and energy filtrating magnetron sputtering technique, respectively. The structure, surface morphology and optical property were tested by X-ray diffraction, field emission scanning electron microscope and spectroscopic ellipsometer. The photocatalytic property of the coating was evaluated by UV–vis spectrophotometer. Results suggested that the coating had both antireflective and photocatalytic performances. The refractive indices of the top and bottom TiO_2 layers were 2.10 and 2.47 (at 600 nm), respectively. The average and max transmissivities were obtained of 88.4% and 98.9% in the wavelength range of 400–800 nm and the degradation rate on Rhodamine B was obtained of 0.0034 min^{-1}.

1. Introduction

TiO_2 has been studied comprehensively because it is non-toxic, convenient to be obtained and easy to be doped by other materials. It has many excellent performances such as high energy gap, high refractive index, high electric inductivity and good chemical stability [1–3]. There are three kinds of TiO_2 including anatase, rutile and brookite [4], while the anatase and rutile TiO_2 are more widely studied and utilized for their better optical and structural properties. Anatase TiO_2 is commonly used as the photocatalytic materials for the high band gap. Also some researchers reported that the hybrid of anatase and rutile TiO_2 had better photocatalytic performance [5]. Since the discovery of photo stimulated water splitting on the TiO_2 electrodes in 1972 [9], the application of TiO_2 in the photocatalytic technology and method have been investigated [6–8]. However, TiO_2 coating with high transmissivity should also be provided in circumstances such as the application in architectural glass and glass cover for solar cells. Therefore double functional coating with both of self-cleaning and antireflective properties is required. Anatase TiO_2 was not usually used as the surface layer for the large scattering losing due to the high refractive index ($n = 2.52$) [10]. Some researchers have managed to fabricate the double functional coating [11–16]. The antireflective and self-cleaning properties were realized by the low refractive index material and anatase TiO_2. But two disadvantages exist in the fabricating process. The first one is that lattice distortion for the different material will be induced during the annealing. And the second one is that the surface modification process is complicated. TiO_2 film can be prepared by several methods such as chemical vapor deposition (CVD), dealloying and anodic oxidation, Sol-Gel, radio fraction magnetron sputtering (RFMS) and direct current reactive magnetron sputtering (DMS) [17–21]. Compared with other methods, DMS technique was used to prepare TiO_2 films in our experiment for its special advantages that the deposition parameters are stable, easy to control and high quality film with uniform distributions can be deposited in fast speed.

Double layers antireflection coating is commonly selected over single layer because two maximum can be achieved in the transmission spectrum. Furthermore the optical performance of the coating is less sensitive to the variations of the refractive index and layer thickness [22].

In this paper, single material double layers coating was fabricated by the well-matched individual TiO_2 layers with low and high refractive indices. Anatase TiO_2 with low refractive was fabricated by the DMS technique. TiO_2 with high refractive index was prepared by the energy filtrated magnetron sputtering (EFMS) technique. Both the double functional properties of antireflection and photocatalysis were investigated.

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2. Experiments

2.1. Material preparation

The glass substrates were primarily cleaned before deposition. Sequentially they were soaked in the $KMnO_4$ solution (40 g/l) for 4 h, and then were ultrasonic cleaned in proper order with the detergent solution, de-ionized water, acetone, de-ionized water, isopropyl alcohol and de-ionized water. Finally the substrates were dried in the oven.

Home made CS-300 DMS system was used to fabricate the TiO_2 films on the substrates. Ti target ($180 \times 60 \times 6$ mm^3, purity 99.99%) and the substrate with 70 mm-distance between them were set as the cathode and anode. The base pressure of below 5.0×10^{-4} Pa was realized by the mechanical pump and molecular pump. As the substrates were heated to the given temperature, high-purity gas Ar (purity 99.999%) was introduced into the chamber. Ar plasma was generated by the electric field applied between the target and substrate. After the surface of the target was purified by the bombardment of Ar^+ for 5 min, reactive gas of O_2 (purity 99.5%) was introduced in to deposit TiO_2 film.

In order to prepare films with better performances, EFMS technique was designed on the base of the DMS technique [23]. The schematic diagram is illustrated in Fig. 1. The stainless metal filtrating electrode in 0.1 mm thickness with square grid was connected with the anode (ground) in front of the substrate.

2.2. Preparation of double layers coating

The structure of the coating is illustrated in Fig. 2. TiO_2 films with high and low refractive indices are marked as TiO_2–H and TiO_2-L. TiO_2–H layer was first deposited by the EFMS technique and then TiO_2-L layer was prepared by the DMS technique on it.

Based on the matrix theory [24], the characteristic matrix for the construction of the film-substrate is given by Eq. (1).

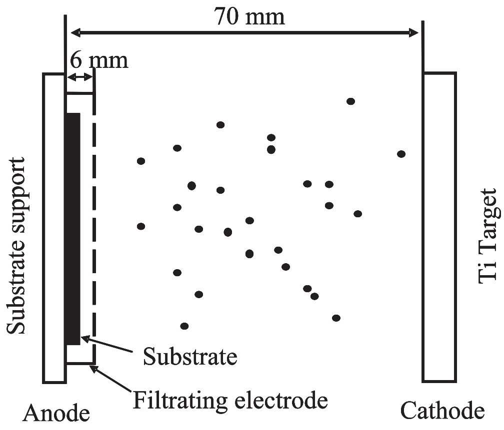

Fig. 1. Schematic diagram of the EFMS technique.

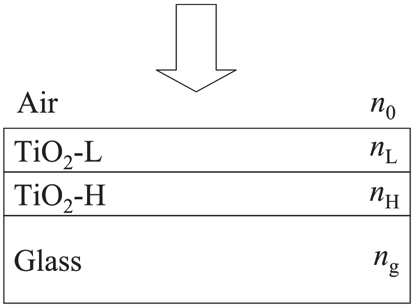

Fig. 2. Structure of single material TiO_2 double layers antireflective coating.

$$\begin{bmatrix} B \\ C \end{bmatrix} = \begin{bmatrix} \cos\delta_L & i/n_L \sin\delta_L \\ in_L \sin\delta_L & \cos\delta_L \end{bmatrix} \begin{bmatrix} \cos\delta_H & i/n_H \sin\delta_H \\ in_H \sin\delta_H & \cos\delta_H \end{bmatrix} \begin{bmatrix} 1 \\ n_g \end{bmatrix} \tag{1}$$

where n_0, n_L and n_H represent the refractive indices of the air, low refractive index and high refractive index of the TiO_2 films, respectively. δ is the phase thickness and can be described by $\delta = (2\pi/\lambda)nd$ for the normal incidence. Y given by Eq. (2) represents the admittance of the film-substrate assembly.

$$Y = \frac{C}{B} = \frac{n_g \cos\delta_L \cos\delta_H - n_L n_g \sin\delta_L \sin\delta_H/n_H + i(n_L \sin\delta_L \cos\delta_H + n_H \cos\delta_L \sin\delta_H)}{\cos\delta_L \cos\delta_H - n_H \sin\delta_L \sin\delta_H/n_L + i(n_g \sin\delta_L \cos\delta_H/n_H + n_g \cos\delta_L \sin\delta_H/n_L)} \tag{2}$$

For the normal incidence and equal phase thickness layers ($n_H d_H = n_L d_L = \lambda_0/4$), the reflectance ($R$) at the wavelength λ_0 turns into Eq. (3).

$$R = \left(\frac{n_0 - Y}{n_0 + Y}\right)^2 = \left(\frac{n_0 - n_L^2/n_H}{n_0 + n_L^2/n_H}\right)^2 \tag{3}$$

Provided that there is no light absorption or scattering occurring in the optical process, the relation of transmission (T) and R can be described as Eq. (4).

$$T = 1 - R \tag{4}$$

In order to obtain the maximum T (R minimum), the low and high refractive indices should satisfy the following relation.

$$n_H = n_L\sqrt{n_g/n_0} \tag{5}$$

W-shipped ($\lambda_0/4$–$\lambda_0/2$) antireflection coating is designed to smooth the transmission property of the coating [22]. The parameters of the optical layers are optimized by TFCalc thin film design software so that the highest calculation transmission curve can achieve.

2.3. Material characterization

X-ray diffraction (XRD, PANational X'Pert Pro) was used to determine the structure of the TiO_2 films. The field emission scanning electron microscope (FESEM, JSM 6700F) was used to observe the surface morphologies.

V-Vase spectroscopic ellipsometer (Vase 32) was used to examine the optical property (incident angles 55°, spectral range