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Photo-catalytic transparent heat mirror film $TiO_2/TiN/TiO_2$

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Abstract. Transparent heat mirror thin films have high transmittance in the visible range of wavelength and high reflectance in the infrared range of wavelength. $TiO_2/TiN/TiO_2$ films prepared via a D.C reactive magnetron sputtering method on Corning glass and Alkali glass substrates, serve as transparent heat mirrors. The outer TiO_2 layer has both the photo-catalytic and anti-reflective properties. The experiment data showed that the film thickness required for photo-catalytic properties exceeds 350nm.

In this report, we found the relationship between the thicknesses of the films via calculation and experiment. Prepared films have both catalytic and transparent heat mirror properties with an inner TiO_2 layer thickness of 40 - 300nm, a sandwich TiN layer thickness of 22 - 35nm and an outer TiO_2 layer thickness exceeding 350nm.

Keywords: Photo-catalytic, heat mirror, transmittance.

1. Introduction

The optical properties of transparent heat mirrors [1-3] consist of high transmittance in the visible spectrum (wavelength: $380 \leq \lambda \leq 760$nm) and high reflectance in the infrared spectrum (Wavelength: $\lambda \geq 760$nm). Transparent heat mirror films are obtainable via three methods [4]:

A method using multi-layer dielectric/metal or dielectric/metal/dielectric films.

A method using metal thin films with high infrared reflectance, such as silver, gold, copper, etc…

(a) A method using semiconductor materials which exhibit high infrared reflectance such as ZnO, SiN, PbO, Bi_2O_3, SnO_2, In_2O_3 etc, or doped semiconductors such as SnO_2, F, SnO_2, Sb, AZO, GZO, ITO etc.

However, metalic films are not stable in terms of heat, mechanics, and chemistry. The semiconductor films show reflectance minima located at wavelengths of $\lambda > 2{,}000$ nm, far from those of solar radiation. Multi-layer films, which can overcome the disadvantages of the doped semiconductor film, have reflectance minima located at wide wavelengths of $\lambda > 760$ nm, and are more stable in terms of heat, mechanics, and chemistry. In some reports, the multilayer films are researched on dielectric/metal/dielectric such as $TiO_2/Au/TiO_2$, $TiO_2/Ag/TiO_2$ [5] $SiO_2/Al/SiO_2$ [6] etc. However,

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the sandwich metal layer still has disadvantage of chemical durability, as mentioned. This results in variable optical properties of films over time. In this paper, we replace the sandwich layer with TiN, which has the same optical properties as gold and is stable in terms of mechanics, heat, and chemistry.

The outer TiO_2 film serves as an anti-reflection film for increasing transmission in the visible spectrum of the heat mirror, and has good mechanical, thermal, and chemical durability, and good photo-catalytic properties. Especially, glass covered by the TiO_2 film with a self-cleaning properties and anti-stagnant water, was applied to the architectural and automobile industries.

As mentioned, photo-catalytic properties as well as anti-reflection properties mainly depends on the thickness of the film [7,8]**, t**herefore, the purpose of this work is to deal with the general problem of multi-layers formulated from the Fresnel theory and matrix method [9], and to use the refractive index and extinction coefficients of TiO_2 and TiN studied via experiment, in order to formulate a theoretical system of multi-layers and apply it to experiment [1].

2. Experimental

TiO_2 films were formed by direct current magnetron sputtering of a water-cooled metallic Ti target (99.6% purity) in a mixture of pure Argon (99.999%) and O_2 (99.999%) gas with a ratio of O_2/Ar = 0.08. The TiN films in heat mirrors(TiO_2/TiN/TiO_2) were deposited by direct current magnetron sputtering of a water-cooled metallic Ti target (99.6% purity) in a mixture of pure Argon (99.999%) and N_2 (99.999%) gas with a ratio of N_2/Ar=0.1. The substrates are Corning 7059 and Alkali glasses. The gas mixture of the given ratio is introduced into a stainless steel tank, then, it is introduced into the vacuum chamber by a needle valve system. The optimum distance between the target and substrate is 4.5 centimeter, as proved in [10].

The inner TiO_2 films were fabricated at a pressure of 10^{-3} Torr, in order to ensure that the film surface morphology is smooth and the anti-reflective properties are good, because of the high refractive index of the film. The outer TiO_2 films were fabricated at a pressure of $13x10^{-3}$ Torr, in order to ensure that the film surface morphology is rough and the films have the required photo-catalytic properties [8]. Both TiO_2 films were produced at a temperature of 350^0C, in order to ensure a crystal structure.

The optical properties of the heat mirrors are shown by UV-Vis are transmittance and infrared reflectance spectra. The photo-catalytic properties of the film are determined by measuring the decomposition of methylene blue (MB) when films are exposed to the light of a mercury lamp. Then, we measured the transmission of the samples, immersed in the MB solution with a concentration of 1mM/l over one hour, and the transmittance of films T_0 and T before and after exposure to a mercury lamp. Therefore, decomposition of MB is expressed by $\Delta ABS = \ln(T/T_0)$. The thickness and refractive index

Table 1. MB decomposition versus thickness of TiO_2 films

Sample	Thickness (nm)	Grain size (nm)	RMS	ΔABS
N18	200	amorphous	1.32	0.09
M45	335	14.0, A(101)	1.94	0.146
M47	360	13.8, A(101)	3.17	0.216
M35	450	17.8, A(101)	2.6	0.11
M37	600	A(004),A(101)	1.53	0.106

of TiO_2 films, were defined by the Swanapoel method [11]. The thickness, refractive index, and extinction coefficients of TiN films, are defined by the Ellipsometry method. We used the XRD patterns to determine the structure of the film. The grain size of the TiO_2 film was determined by the Scherrer formula.

3. Results and discussion

3.1. Photo-catalytic properties of TiO_2 film

In this report, we only find the optimum thickness of the TiO_2 film with the best photo-catalytic properties under the following conditions: the intensity of sputtering is 0.45A, the pressure of sputtering is 13mTorr, the film is 4.5cm from the target, and the temperature is 350^0C, as mentioned above [10]. We observed the decomposition of MB, which depends on the thickness of the film. Our data is presented in table 1. From table 1, the thickness of the film of 360nm has the maximum decomposition of MB. From the above conditions, based on the XRD patterns in figure 1 and image of AFM in figure 2, we conclude that the film has a small amount of anatase crystal structure with a threshold thickness of 360nm, and the best photo-catalytic properties. This shows that the film has an amorphous crystal structure when the film thickness is smaller than the threshold value, and its effective surface area is small, so the photo-catalytic properties were degraded. When film thickness is large than the threshold value electrons and holes have no chance reaching its surface before recombining, since the diffusion length of the electron is smaller than the thickness of the film. In this case, the effective area of the film surface decreases because some of its crystal grains enlarge, so the photo-catalysis decreases. Thus, approaching the thickness threshold, films reduce the maximum number of electrons and holes recombined before they diffuse to the surface. In addition, the thickness threshold is large enough for the film to form an anatase crystal structure and achieve the largest effective surface area.

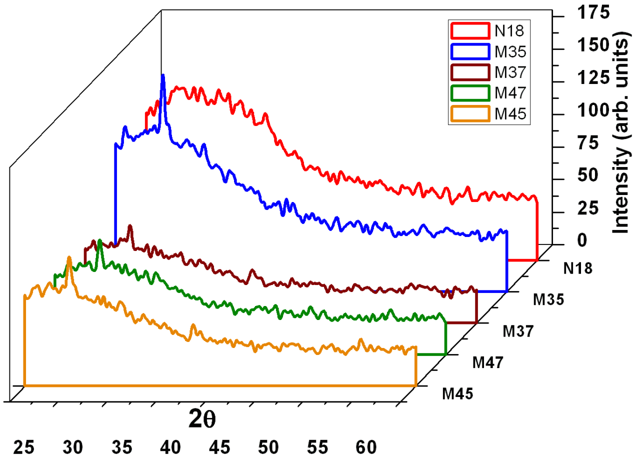

Fig. 1. XRD spectrum versus thickness of TiO_2.films.

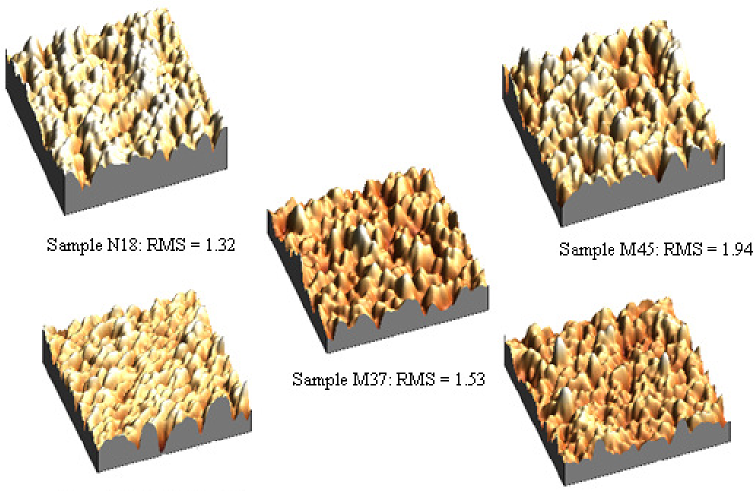

Fig. 2. AFM image of TiO_2 samples.

3.2. Optical parameters of TiO_2, TiN film

3.2.1 Defining the thickness and index of TiO_2 film

The UV-vis spectral transmission of TiO_2 films was measured by advanced technology such as the V350 spectrophotometer at the University of Natural Sciences, Ho Chi Minh City. Based on spectral transmission, we measure the thickness and refractive index of the film by the Swanapoel method [11], then, fit the film refractive index in accordance with the Cauchy model wavelength, as shown in Figure 3. The Swanapoel method is programmed by Matlab.

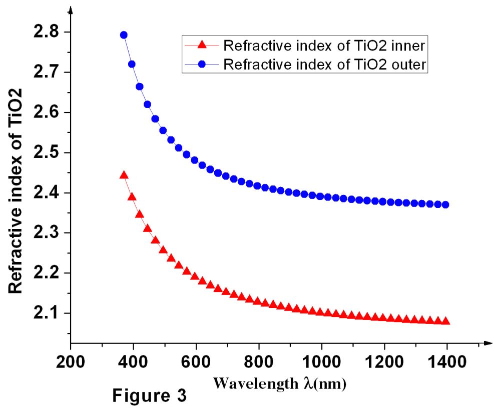

Fig. 3. Refractive index of TiO_2 films determined from Swanapoel method.

3.2.2 Defining the thickness of TiN film

The thickness, refractive index n, and extinction coefficient k of TiN films is defined by the Ellipsometry method Figure 4.

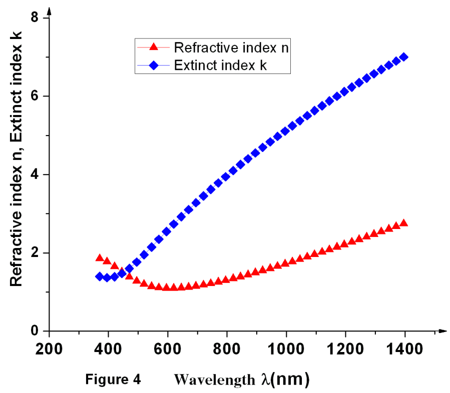

Fig. 4. Refractive index n and extinction coefficient k of TiN determined by Ellipsometry method.

3.2.3. Theoretical spectral transmittance and reflectance of multi-layer $TiO_2/TiN/TiO_2$ films

Based on the results in Sections 3.2.1 and 3.2.2 we find the refractive index n, extinction coefficient k of the outer TiO_2 layer, the TiN layer and the inner TiO_2 layer at the 550nm wavelength, as shown in Table 2. Based on the results in Table 1, the O.S.Heavens [9] matrix is used to find a suitable thickness of each layer sufficient to enable multi-layer films to effectively transmit at the 550nm wavelength, as shown in Table 3. Then, we can simulate the theoretical spectral transmittance and reflectance of the multi-layer film at the wavelengths shown in Figure 5

Table 2. Refractive index of TiO_2, TiN films at 550 nm wavelength

film	outer TiO_2	TiN	inner TiO_2
n	2.3	1.13	2.5
k	0	2.18	0

From the data in Figure 5, m3 and m4 films have high reflective coefficients, wide wavelengths including solar radiation, and transmission exceeding 40% in the visible spectrum. The best thickness of the TiN layer is smaller than 35nm. This is too large to enable the transmission of the film be smaller than 40%. Both films have the thickness of the top TiO_2 layer, which is about 360nm, and match the application of photo-catalysis, as mentioned. However, the m4 film yields a transmission 50% higher than the m3 film, even though there is interference in the spectral reflectance. Thus, the m4 film is the best the 364/26/257 thickness on glass.

Table 3. Thickness of layers in samples m_1, m_2, m_3, m_4

Layer	Outer TiO_2	Tin	Inner TiO_2	T_{ax}	sample
	368	22	38	58.49	m1
	367	24	37	56.43	m2
Thickness (nm)	365	35	34	43.21	m3
	364	26	257	54.23	m4
	368	22	38	58.49	m1

3.2.4. Experimental spectral transmittance and reflectance of multi-layer TiO_2/TiN/TiO_2 film

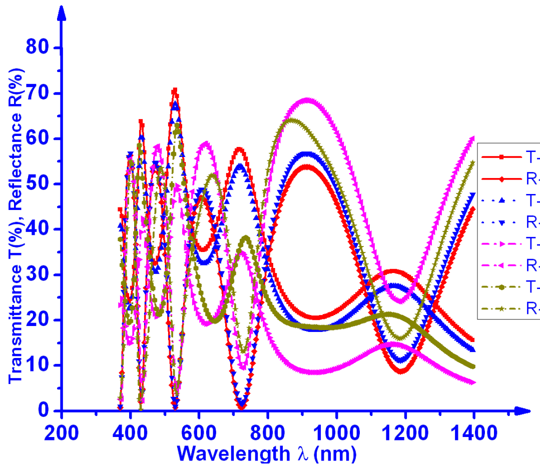

Fig. 5. Theoretical transmittance and reflectance spectra of the multi-layer films.

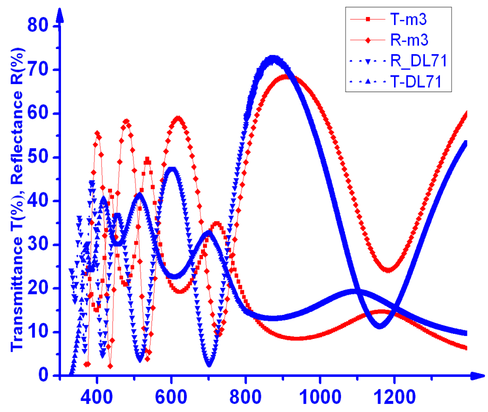

Fig. 6. Theoretical and experiment transmittance and reflectance spectra of TiO_2/TiN/TiO_2 films m3 and DL71.

From the simulated result in Section 3.2.3, we experimented with data of the m3 and m4 films. The generated film coincides quite well with the simulated results of theory. This is shown in Figure 6 and Figure 7. From the films DL71 and DL85 from Figure 6 and Figure 7 have the TiN layer which was produced under the following conditions; a threshold potential of 550 Volt, a pressure of 3.10^{-3} Torr, a ratio of N_2/Ar=10% as mentioned [10]. The outer TiO_2 layer is fabricated at the optimum sputtering intensity, which is about 0.45 Ampere, and a sputtering pressure of 13mTorr, to ensure that the film has the required photo-catalytic properties. The

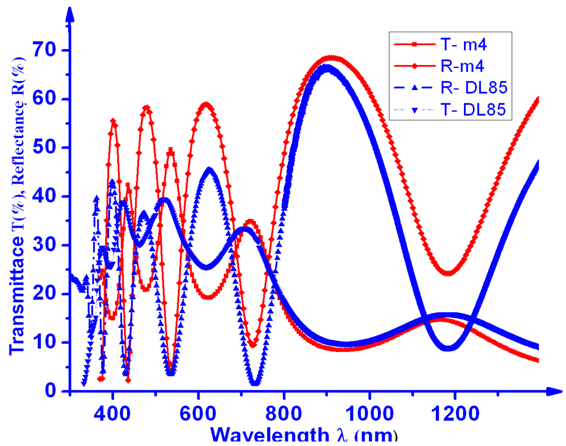

Fig. 7. Theoretical and experiment transmittance and reflectance spectra of TiO_2/TiN/TiO_2 films m4 and DL85.

inner TiO_2 layer is fabricated at an intensity of 0.5 Ampere and a pressure of 10^{-3}Torr, to ensure that the film has a high refractive index, and the surface morphology of the film is smooth. This enables an increase in the reflectance and a strong buffer layer. Both TiO_2 layers are fabricated at a ratio of O_2/Ar = 8%.

3.3. Examples of multi-layer films

The X-ray diffraction pattern and MB decomposition of some multi-layer films are described in Figure 8 and Table 4. It is clear that the specimens discovered involve a highly iterative process in terms of photo-catalytic capability, and regularity, as mentioned in Section 3.1. A (101) surface corresponding to the anatase phase, locates at 2θ = 24.6. At this position, the lower the diffractive peak of the outer is, the better the photo-catalytic capabilities of the films. The outer TiO_2 layer was grown better on the TiN layer than on glass, since glass is amorphous. Therefore, the multi-layer $TiO_2/TiN/TiO_2$ films have better crystal structure than the single layer TiO_2 on the glass substrate. This is confirmed by the appearance of the peak A(004) surface of some multi-layer films.

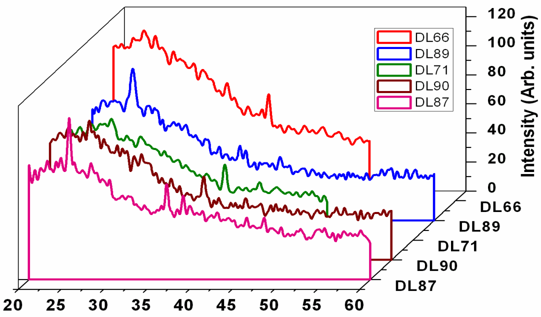

Fig. 8. XRD pattern of $TiO_2/TiN/TiO_2$ films.

Table 4. MB decomposition of $TiO_2/TiN/TiO_2$ films

Sample	ΔABS
DL87	0.17
DL89	0.19
DL90	0.25
DL71	0.23
DL66	0.18

4. Conclusion

We found that the thickness threshold is about 360 nm for the outer TiO_2 layer, which enables the last exhibit best photo-catalytic and transmittance heating mirror properties; the theoretical matrix problem of multi-layer film is formulated, then, computed using the experiment data for the refractive index n, and the extinction coefficient k of each layer. The spectral reflectance and the transmittance of the heat mirror $TiO_2/TiN/TiO_2$ determined from the experiment, perfectly coincides with the theoretical simulation, and the results can be replicated. The fabricated transmittance heat mirror films $TiO_2/TiN/TiO_2$ have both the transparent heat mirror property and the same photo-catalysis properties as the single-layer films TiO_2.

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