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High transmittance superhydrophilic thin film with superior mechanical properties

Ya-Chen Chang [a,b], Hung-Sen Wei [a,b,*], Chien-Cheng Kuo [b,c], Wei-Bo Liao [a,b], Sing-Rong Huang [a,b], Cheng-Chung Lee [a,b,*]

[a] Department of Optics and Photonics, National Central University, Taoyuan 320, Taiwan
[b] Thin Film Technology Center, National Central University, Taoyuan 320, Taiwan
[c] Graduate Institute of Energy Engineering, National Central University, Taoyuan 320, Taiwan

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A two-layer structure of superhydrophilic thin film with high transmittance and superior mechanical properties was fabricated and developed. Superhydrophilic thin film has been deposited on a pre-coated anti-reflection coating substrate. The average transmittance in the visible range (400–700 nm) was increased from 91.3 ± 0.1% to 94.2 ± 0.1%, because an anti-reflection coating was inserted between the superhydrophilic thin film and substrate. In particular, the mechanical properties of the high transmittance superhydrophilic thin film were also deeply investigated in this paper. The hardness of the thin film was greater than 3H. The superhydrophilic property was maintained after the thin film was pressed by a 500 g weight steel wool and moved back and forth for more than 100 times. According to ISO 2409 standard, the adhesion of the thin film is given a quality of rank 1. The water contact angle of the thin film was less than 10° after ultraviolet light irradiation and the superhydrophilicity was maintained for 76 h when stored in a dark place. The high transmittance superhydrophilic thin film with superior mechanical properties can be utilized in optical, environmental, superhydrophilic and photocatalytic applications.

1. Introduction

In 1972, the research on the semiconductor photocatalyst of TiO_2 was presented by Honda-Fujishima and named as the Honda-Fujishima effect [1]. It was found that when the TiO_2 thin film was irradiated by ultraviolet, UV, light, the water contact angle, WCA, decreased gradually and finally, it became almost 0° [2–4]. The phenomenon was called superhydrophilicity. The superhydrophilic property of the surface allows water to spread across the surface rather than remaining as a droplet [5]. The superhydrophilic phenomenon brings about self-cleaning and anti-fogging properties [6]. In addition, transparent TiO_2 thin films have a high potential for practical applications such as on windows and windshields of automobile, mirrors [7]. Many methods have been used to fabricate superhydrophilic thin films, such as chemical vapor deposition [8,9], plasma-enhanced chemical vapor deposition [10,11], sputtering [12,13] and so on. However, they are expensive and bulky. Moreover, the shapes and species of substrates that can be coated using these methods are limited [14]. Sol–gel process is widely known as practical and effective for fabricating superhydrophilic thin films on various substrates [15–17]. Sol–gel technique provides unique benefits such as fabrication on large-area substrates and low-temperature synthesis, and it is simple to implement [18,19].

The solar flux of UV incidents at the earth's surface is less than 5%. To establish the fully developed superhydrophilic state, the superhydrophilic thin film had to be irradiated for several days. Besides, the superhydrophilic thin film is not always irradiated by UV light such as in a rainy or cloudy day. Therefore, it is desirable that the WCA stays low for a long time in dark. In general, a superhydrophilic thin film which consists of only TiO_2, the WCA increases quickly in a dark place. It was found that adding SiO_2 to TiO_2, WCA was lower and the hydrophilicity was maintained longer in a dark place. However, the transmittance and mechanical properties were not investigated in [20].

For the optical applications, the transmittance is an important factor to be considered. Optical reflection is a fundamental phenomenon occurring when light propagates across a boundary between different refractive index media. Anti-reflection, AR, coatings play a pivotal role in a wide variety of optical technologies by reducing reflective losses at interfaces [21]. Optical elements based on glass and common plastics have refraction indices (n) in the range of 1.45–1.7 [22]. As the results, there are 4% to 6.5% reflectance from each air–substrate interface. The reflection of substrate can lead to a blur image and the reduction of

* Corresponding authors at: Department of Optics and Photonics, National Central University, Taoyuan 320, Taiwan.
E-mail addresses: hswei@dop.ncu.edu.tw (H.-S. Wei), cclee@dop.ncu.edu.tw (C.-C. Lee).

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transmittance. The reduction of surface reflection can be achieved by applying an AR coating on the substrates [23–25]. It is therefore necessary to reduce the intensity of reflected light to improve the overall quality of systems. Macleod software was used to simulate the thickness of each layer of the AR coating. Not only transmittance but also the mechanical properties of superhydrophilic thin films such as adhesion, hardness and abrasion resistance must be considered for practical applications. However, the research of $TiO_2 + SiO_2$ composite thin film about mechanical properties is seldom discussed. In previous studies, Fateh et al. [26] reported that the thin film made by different molar ratio of TiO_2 and SiO_2 on PC. Although the adhesion of the film was measured, the other mechanical properties were not discussed in their study. Besides, several works have shown that the addition of SiO_2 into TiO_2 films and focus on the characterizations of function group, surface analysis, crystalline and the ratio of $TiO_2 + SiO_2$ [3,5,27]. Damchan et al. [28] reported the WCA change of $TiO_2 \pm SiO_2$ composite film in different mol% of SiO_2 and investigated the photocatalytic activity and hydrophilicity fraction. Yu et al. [29] studied the anatase peak change of X-ray diffraction, XRD, of a $TiO_2 \pm SiO_2$ composite thin film in different mol% of SiO_2. Tricoli et al. [30] reported that the WCA and anti-fogging property of SiO_2, TiO_2 and $TiO_2 \pm SiO_2$ with different thickness. Eshaghi et al. [31] prepared nanocomposite $TiO_2 \pm SiO_2$ thin film by sol–gel process and reported the surface analysis of the film by XRD and X-ray photoelectron spectroscopy, XPS. Pakdel et al. [32] used TiO_2 and $TiO_2 \pm SiO_2$ nanocomposites to coat on wool fabrics and studied the self-cleaning property and hydrophilicity of the $TiO_2 \pm SiO_2$ nanocomposite films based on different molar ratio percentages of $TiO_2 \pm SiO_2$. Liu et al. [13] also reported XRD patterns and XPS characterization of $TiO_2 \pm SiO_2$ films. Unfortunately, these studies had never focused on mechanical properties. In this work, the paper deeply studied and discussed mechanical properties including hardness, adhesion and abrasion resistance and the transmittance of superhydrophilic thin film which was increased when an AR coating was inserted.

2. Experiment

2.1. Chemicals and materials

Titanium dioxide nanoparticles (Sachtleben Hombikat UV100) that were smaller than 10 nm were obtained from Sachtleben Chemie. Tetraethoxysilane (TEOS) was purchased from Seedchem. Hydrochloric acid (HCl) and anhydrous ethanol (EtOH) were purchased from Showa Chemical Co., Ltd. and Champion Yuan Co., Ltd., respectively. Sodium dodecyl sulfate (SDS) was obtained from Acros Organics. The water used herein was deionized. The above chemicals were all used without further purification.

2.2. High transmittance superhydrophilic thin film structure

The SEM image of structure of high transmittance superhydrophilic thin film was formed on a Si wafer/AR coating/superhydrophilic thin film, as displayed in Fig. 1. The superhydrophilic thin film and AR coating was fabricated by sol–gel process and electron gun evaporation, respectively.

2.3. Preparation of AR coating

The structure of AR coating is substrate/$(HL)^2$/air. Ta_2O_5 ($n = 2.21$) and SiO_2 ($n = 1.46$) were selected as the high (H) refractive index and low (L) refractive index materials at the central wavelength $\lambda_0 =$ 550 nm, respectively. AR coating was produced by electron gun evaporation with ion-beam-assisted deposition. From substrate to air, the thicknesses of each layer were 13.24 nm, 33.71 nm, 119.92 nm and 87.65 nm. And the optical thickness was monitored by an optical monitor.

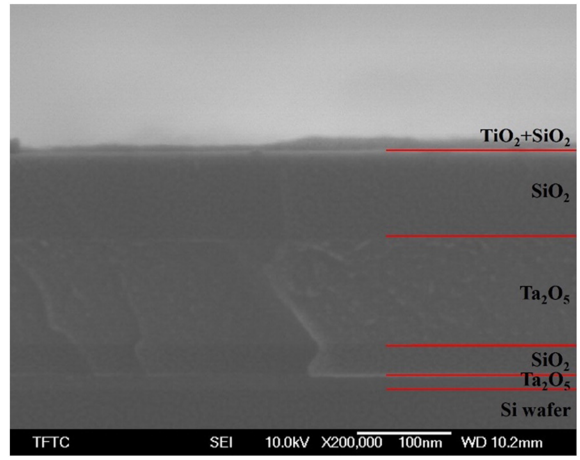

Fig. 1. SEM image of high transmittance superhydrophilic thin film.

2.4. Preparation of $TiO_2 + SiO_2$ superhydrophilic thin film

Superhydrophilic thin film was fabricated by $TiO_2 + SiO_2$ solution which was prepared by mixing a TiO_2 dispersion solution and a SiO_2 sol. To obtain a good TiO_2 dispersion solution, the pH value of EtOH was adjusted to pH = 1 and the surfactant (SDS) was added to the EtOH. Additionally, SiO_2 sol was typically prepared by the sol–gel process. The molar ratio of SiO_2 sol was TEOS:EtOH:deionized water = 1:7.88:5. Subsequently, a 0.02 ml volume of HCl (3.6%) was added into above SiO_2 sol to catalyze the hydrolysis followed by stirring the solution 1 h at room temperature. Finally, $TiO_2 + SiO_2$ solution was obtained by TiO_2 dispersion solution mixing with SiO_2 sol. The optimized molar ratio of TiO_2:SiO_2:EtOH was 1:1.78:371.

2.5. High transmittance superhydrophilic thin film preparation

Substrate (B270 glass) was cleaned in acetone and isopropanol for 10 min by ultrasonic bath and then dried by using a N_2 gun. The $TiO_2 + SiO_2$ solution was deposited onto a pre-coated AR coating glass by dip-coating with 2 mm/s withdrawal rate. And then the thin films thus formed by dried in an oven at 150 °C for 1 h.

2.6. Instrumentation and measurements

WCA was measured by a water contact angle measurement apparatus (Pentad Scientific Corporation, FTA-125) and the volume of deionized water droplets was 2 μL. The transmission spectra were measured using a UV–vis spectrophotometer (Hitachi, U-4100). The adhesion and hardness of the film were estimated quantitatively by using ISO 2409 standard and the pencil test by using ASTM D 3363 standard, respectively. The film was illuminated by UV light with a UV intensity of 4 mW/cm^2 under germicidal lamps that efficiently transmit ultraviolet rays at 253.7 nm (Sankyo Denki, G10T8).

3. Results and discussion

3.1. Optical properties of the high transmittance superhydrophilic thin film

For the practical application of the superhydrophilic thin film, the transmittance is an important factor to be considered. The transmittance was reduced when a $TiO_2 + SiO_2$ superhydrophilic thin film was coated on a substrate. The refraction index of $TiO_2 + SiO_2$ superhydrophilic thin film is 1.75 as calculated by using Macleod software from the transmittance spectra. In this work, AR coating was the key point to eliminate the reflection from the substrate and to increase the transmittance of the substrate. Macleod software

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