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Research Paper

Preparation of hydrophobic broadband antireflective SiO_2 coating on flexible poly(methyl methacrylate) substrates

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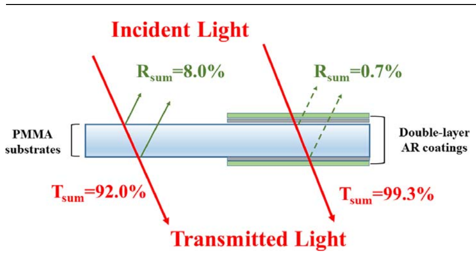
GRAPHICAL ABSTRACT



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ABSTRACT

The double-layer broadband antireflective coatings is crucial for optical devices, e.g. plastic eyeglass lenses and the solar cell system. Among optical situation, the wide wavelength range of light is one of the most demanded. Here we designed a double-layer broadband antireflective (AR) coating with excellent average transmittance at visible region for poly (methyl methacrylate) (PMMA) using thin film design software. A template-free sol–gel process was developed to prepare the SiO_2/PMHS coating with ultralow refractive index of 1.13 for top layer. By combining the colloidal silica and poly (methyl hydrogen) siloxane (PMHS), the coating with adjustable refractive index that vary between 1.13 and 1.37 was obtained. The formation mechanism of the ultralow refractive index was proposed. Meanwhile, using PMHS to partially substitute the hydrophilic groups in the coating, the hydrophobicity of the coatings was improved, and its static water contact angle was as high as 126°. Besides, the coating had excellent mechanical property and refractive index of 1.22–1.42 can be well prepared by combining base-catalyzed silica sol and acid-catalyzed silica sol together for bottom layer. Then, using the two raw materials base/acid -catalyzed mix SiO_2 sol and the PMHS-SiO_2 sol and optimizing the thickness, the prepared double-layer coatings with average transmittance of 99.30% in the 400 nm to 800 nm wavelength on PMMA substrate was successfully obtained. Those prepared hydrophobic broadband AR coatings represented excellent transmittance and had enormous potential application in the optical devices.

1. Introduction

Antireflective coatings for substrates surfaces not only limit unwanted reflections effectively, but also improved the performance of optical devices by increasing transmission. According to different requirements of optical devices, the application of antireflective coatings can be divide into two main areas. The first area are picture glass, art glazing, eyeglasses and museum [1–4], where the AR coatings were used to reduce reflections of sunlight or artificial lighting and improve the view of art works. The second area are lenses and devices that

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performance is improved through using AR coatings, like photovoltaic (PV) modules, lasers fusion systems, organic light-emitting diodes (OLEDs) and green house [5,6]. In the context of development of AR coatings, continuous efforts has been made in technological development for preparation and use of AR coatings [7]. For instance, Kido et al. added an AR coating to white OLEDs, the efficiency was risen from 36 lm/W to 57 lm/W [8,9]. S. Hemming et al also reported that using of AR coatings increased 8.6%more light transmission in the photosynthesis active region from 400 to 800 nm, resulting in a significant increase in crop yield[10]. In these above studies, the single-layer coating was used, which can only optimize one wavelength.

Compared with the single-layer porous AR coating, the multi-layer AR coating can apply to other cases of the displaying system and the solar cell system where requires a wide wavelength range of light [11]. Nevertheless, the simplest multilayer coatings is double-layer AR coatings and it have applied to glass for many decades [12]. Kawamura et al. developed a double-layer AR coating for optical lens applications for the first times, it achieved a transmittance of approximately 98.5% from two-side of the substrate surface [13]. After that, Zou et al. successfully designed and prepared broadband double-layer AR silica coatings by block copolymer assisted sol–gel method, it realized a high transmittance at optimized waveband [14]. However, few of double-layer AR coating are applied to plastic substrates, e.g. such as plastic eyeglass lenses, optical lenses, components for photographic equipment, flexible electronics, optoelectronics, and lighting. Among optical functions, wide wavelength range of light is one of the most demanded. Furthermore, owing to plastic substrates have light weight, low cost and flexibility, it have already replaced glass materials in some special optical component, such as flexible display, light emitting diode and organic photovoltaic devices. Therefore, it is most desirable to prepare double-layer broadband AR coating on plastic substrate to fulfill their optical function. However, the low glass-transition temperature and chemical structures of plastics substrate, which seriously limit the use of subtractive techniques involving thermal treatments at temperatures or chemical solvent etching [15]. As a consequence, the coating process with fairly low temperature was required. In general, many methods have been applied to prepared double-layer AR coatings, such as sputtering [16], chemical vapor deposition (CVD) [17], self-assembly of block-angle deposition [18], sol–gel process [19]. Among these methods, the sol–gel process method has been demonstrated to be one of the most popular and suitable choices for preparation of double-layer on plastic substrates. Because it has good flexibility to control in the porosity for preparation of coating and it with moderate coating process. More importantly, sol–gel process suitable for large-scale production.

In this paper, we successfully achieved broadband double-layer AR coatings with average transmittance of 99.3% on PMMA substrate by simple template-free sol–gel process. The refractive index of top layer and bottom layer used in the calculations were setting to 1.13 and 1.34, respectively. The outcome of calculations illustrates that the coating with ultralow refractive index for top layer is a key factor of the high quality double-layer broadband AR coatings preparation. Recently, the template technique were most commonly methods to prepare the ultralow refractive index coatings [20,21]. However, this approach suffer from drawback that the cost too high, and optical components are likely to be damaged during the annealing process. Here, we developed a simple template-free sol–gel process to prepare SiO_2/PMHS ultralow refractive index coating of 1.13. By using the poly (methyl hydrogen) siloxane (PMHS) to modify the SiO_2 particles, the coating with refractive index vary between 1.13 and 1.37 was obtained and the hydrophobicity of the coatings was improved. Moreover, in order to clear the formation mechanism of the ultralow refractive index, we proposed a formation process model to explain the effect PMHS on the refractive index of coating in detail. In the meantime, a schematic sketches of the double layers AR coating was also established to demonstrate the formation of coating on PMMA substrate.

2. Experimental section

2.1. Preparation of base-catalyzed silica sol

The base-catalyzed sol were prepared by mixing tetraethyl orthosilicate (TEOS), ethanol and ammonia at 5:46:1 vol ratio. The solution was stirred at 30 °C for 2 h and aged at room temperature for 7 days. After that the new sol was refluxed at 80 °C for 24–36 h to remove ammonia.

2.2. Preparation of PMHS/SiO2 sol

The PMHS/SiO_2 sol were prepared by adding PMHS and tiny amount of Karstedt catslyst into base-catalyzed pure sol. After the strong stirring for more than 20 h. The mass ratio of PMHS: SiO2 was range from 0%–250% to yield the coating with different refractive index.

2.3. Preparation of acid-catalyzed silica sol

The TEOS, ethanol, deionized water and hydrochloric acid were mixed at 1:2.5:4:0.5 mass ratio. Then it was stirred at 30 °C for 2 h and aged at room temperature for 2 weeks.

2.4. Preparation of base- and acid-catalyzed mixed silica sol

The mixed sol were prepared by the process of combining base-catalyzed silica sol and acid-catalyzed silica sol in different proportions. Then it was stirred for more than 12 h to ensure it to mix.

2.5. Preparation of AR coatings

PMMA substrates of size of 75 mm × 25 mm × 1.0 mm (HC-PMMA, hardness of 4H,) were cleaned in ultrasonic bath in detergent solution for at least 15 min and then in deionized water for an additional 15 min. The base- and acid-catalyzed mixed silica sols and PMHS/SiO_2 sol were deposited on both sides of well-cleaned PMMA substrates at relative low humidity by dip coating at a withdraw rate of 1.4 mm/s and 0.4 mm/s, respectively. The volume ratio of acid-catalyzed silica sol to base-catalyzed silica sol in the mixed silica sol was approximate 43% for bottom layer. The weight ratio of PMHS to silica sol was about 10% for top layer. The double-layer coating were heated at 60 °C for 2 h.

2.6. Characterization

The theoretical transmittance measurements were performed by TFCalc program (Software Spectra Inc). The double-layer coating is deposited on well-cleaned PMMA substrate by using the dip-coating machine (SYDC-100, Shanghai SAN-YAN Instrument Co., Ltd). The UV-vis-NIR spectrophotometer (Hitachi U-4100) was used to measure the optical transmittance of the coatings. The refractive index values of the coatings were determined by spectroscopic ellipsometer (SENTECH SE800PV). Surface contact angle was evaluated with an angle measurement instrument (KRUSS DSA100). The morphology of a coating surface and cross-section were investigated by using scanning electron microscope (ZEISS Gemini SEM500). The diameter of SiO_2 particles was measured by Malvern Zataszier (Nano-ZS90). Transmission electron microscopy (JEOL-2010) was performed at an acceleration voltage of 200 kV.