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Fabrication of optical reflectors by using of elastomer with self-organized undulations

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ABSTRACT

Back-surface diffusive reflectors have been widely applied in many optical systems to promote the efficiency used in system. In this work, we propose a novel way to fabricate a soft diffusive reflector by using of silicone (polydimethylsiloxane, PDMS). High-reflectance substrates were first fabricated by mixing nanoscaled TiO₂ powders with PDMS polymers, and then microscale wave-like undulations were spontaneously developed after the substrates were dipped into H₂SO₄/HNO₃ solutions. After optical examination, a TiO₂/PDMS plate comprising microscale undulations, which can surely serve as a reflector, could reflect and diffuse light effectively. Besides, all fabrication processes can be executed in the ambient environment and at low temperature. This proposed method has a potential for mass production in the future. © 2008 Elsevier B.V. All rights reserved.

1. Introduction

Back-surface diffusive reflectors have been widely applied in many optical systems, such as liquid crystal displays (LCDs), lighting systems and solar cells. The main functions are used to reflect light departed from these systems and subsequently promote the light efficiency used in systems. Recently, we reported that PDMS silicone elastomer mixed with nanoscale TiO₂ powders could serve as highreflectance materials due to the scattering effect of TiO₂ [1]. The reflectance of TiO₂/PDMS mixtures was close to 98% in the range of visible-light wavelength. The reflectance of TiO₂/PDMS mixtures was almost equal to that of silver films, but the cost is cheaper.

In order to reflect light uniformly from these systems, microstructures on the reflector surfaces play important roles. Various microstructures such as microlens [2], V-groove [3], pyramid [4], rough surface [5], and other microstructures could change the trace of light when the light is illuminating on these microstructures. Although these microstructures are quite common, the fabrication cost is still expensive especially on large areas. However, self-organized undulations on the surface of an elastomer are often observed as the elastomer was exposed on oxygen plasma or coated by hard films. Compared with the techniques often used [2–5], self-organized undulations on elastic materials have a potential to generate large-scaled and low-cost microstructures. However, the metal films on an elastomer [6] were easily broken under mechanical deformation, causing the poor performance for optics. Therefore, oxygen plasma treatment [7] could only generate wrinkles on smaller areas. In our previous work, a simple novel way to self-generate microscale wrinkles by chemical oxidization methods was demonstrated. Oxidization layers, the product of chemical reaction, were capped on the surface of PDMS after acid treatment and subsequently undulations were spontaneously developed due to the large difference in volumetric contraction rates on a bilayer system [8].

In this study, high-reflectance substrates were fabricated by mixing nanoscaled TiO_2 powders with PDMS polymers, and then microscaled surface undulations were formed after acid treatment, regarding as optical reflectors. Therefore, the periodicity of undulations could be controlled by the volume ratio of H₂SO₄/HNO₃ solutions and the dipped duration. The optical performance of reflectors was also discussed. Because the orientation of undulations was always disordered, the reflectors could be used as back surface reflectors (BSR) applied in LCD system to reflect light uniformly form the light guide plate (LGP).

2. Experiment

Two steps for fabricating soft reflectors are described as follows:



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Fig. 1. Schematic illustration showing the fabrication process of soft reflectors.

- (a) The liquid silicone pre-polymers, Sylgard 184 from Dow Corning, were mixed in a weight ratio of 10:1 with the curing agent. Nanoscaled TiO₂ powders of which the averaged size could be selected from 40 nm to 400 nm were directly mixed with the resultant polymers [1]. After mixing, the TiO₂/PDMS liquid polymers poured into a mold and cured at 70 °C for 1 h. The solidified PDMS plate with 1 mm thickness could be easily fabricated. The resultant TiO₂/PDMS substrate is shown in Fig. 1a.
- (b) A strong acid solution that mixed sulfuric acid solutions (95% H_2SO_4) and nitric acid solutions (66–71% HNO_3) with an appropriate volume ratio was prepared. The TiO₂/PDMS plate, obtained in Step 1, was dipped into the strong acid solution from few seconds to several minutes. The acid-modified PDMS substrate is shown in Fig. 1b. The acid-modified PDMS plate was then dipped into clean water to remove the residual acid liquids from the surface of substrate. Finally, undulations were found on the surface of TiO₂/PDMS plate. The TiO₂/PDMS plate with undulations is shown in Fig. 1c.

3. Results and discussions

3.1. The control of self-organized undulations

The formation mechanism of undulations of bilayer systems such as Al/PS films [9], Au/PDMS films [10] and SiO_x/PDMS films [11] have been demonstrated by several research groups. Hence, oxidization layers generated by dipping PDMS polymers into the H_2SO_4/HNO_3 solution, were capped on the PDMS surface. This could result in the formation of surface undulations. Fig. 2a shows the real view image of TiO₂/PDMS plate with undulations and the





Fig. 2. (a) The real view image showing a TiO₂/PDMS plate with undulations and the inserted image showing random undulations located on the TiO₂/PDMS plate. (b) The AFM image of 3D surface topography of reflectors. (c) The dipped time as a function of the wavy periodicity under different volume ratios of H₂SO₄/HNO₃ solutions.

magnification image photographed by the use of inverted microscope is inserted in it. Based on the image, it could found that the orientation of surface undulations was random. Fig. 2b shows the 3D AFM image of surface topography on the TiO₂/PDMS plate. The configuration of each undulation is like a sinusoidal wave. The generation of wave-like structures was because compressive stresses on an oxidization layer were induced into an elastic PDMS layer

 $\lambda = 4.36t \left(\frac{E_{\rm o}(1-v_{\rm p}^2)}{E_{\rm p}(1-v_{\rm o}^2)} \right)^{1/3} \tag{1}$

by the large difference in volumetric contraction rates on a bilayer

system. For undulations on bilayer systems, the periodicity (λ) of

the waves can be expressed as Eq. (1) [10],

where *t*, v_o , E_o , E_p and v_p are the thickness of oxidization layer, the elastic modulus and Poisson's of the oxidization layer and the soft PDMS layer. Based on Eq. (1), the periodicity of waves depended mainly on the thickness of oxidation layers. To modulate the volume ratio of H₂SO₄/HNO₃, the thickness of the oxidation layers would be changed, causing the variation of the morphology on the TiO₂/PDMS plate. Fig. 2c shows the dipped time as a function of the wavy periodicity under different volume ratios of H₂SO₄/HNO₃. The periodicity of undulations could range from 3 to 130 µm by controlling the dipped duration and the H₂SO₄/HNO₃ solutions ratio. As shown in Fig. 2c, the periodicity increases with

the increase of the ratio of H_2SO_4/HNO_3 solutions from 1:1 to 4:1. On the other hand, the surface undulations were hardly developed when the volume ratio of H_2SO_4/HNO_3 solution was below 1:1. It indicates that the oxidization layers increased with the quantity of H_2SO_4 as the quantity of H_2SO_4 exceeded certain amount. Therefore, the effect of HNO_3 was only used to promote the oxidized ability of the acid solution. Besides, the increase of dipped duration would result in the nonuniform distribution of waves' periodicity since some growing wrinkles would merge together.

3.2. The optical performance of reflectors

Additionally, the optical performance of the TiO₂/PDMS plate with oxidization layers was examined experimentally. The reflectance of oxidized TiO₂/PDMS plates (shown in Fig. 3a), dipped into H₂SO₄/HNO₃ solutions with the ratio of 3:1 during four durations (t = 0, 10, 20 and 30 s), was respectively characterized by the use of UV–Vis spectrophotometer. Experimental results indicate that the reflectance decreased obviously from 98% to 94% while oxidization layers were formed. However, the reflectance decreased slightly with the increase of oxidization layers. Compared to common Al coatings (the reflectance was about 90% in the visible-light wavelength) [12], the oxidized TiO₂/PDMS plates were able to substitute for Al coatings. Then, the optical spot of reflector was examined by a simple setup consisted of a laser beam as a light source,



Fig. 3. (a) The reflectance of oxidized TiO₂/PDMS plates, which were dipped into H₂SO₄/HNO₃ solutions with the ratio of 3:1 during four durations, *t* = 0, 10, 20 and 30 s as a function of incident wavelength ranged between 200 and 1100 nm. (b) A schematic diagraph of the experimental setup. (c) The related brightness as a function of a whole hemispherical solid angle on the reflector surface.

the self-made reflector, and a light meter. Fig. 3b shows a schematic diagraph of the experimental setup. When a laser beam was illuminating on the reflector, the laser beam was reflected and the light meter would measure the luminous flux around the reflector with a fixed distance. In this study, three reflectors were respectively examined: (1) a smooth $TiO_2/PDMS$ plate; (2) a $TiO_2/$ PDMS plate with 12–15 μ m undulations; (3) a TiO₂/PDMS plate with 53–60 μ m undulations. Fig. 3c shows the related brightness as a function of a whole hemispherical solid angle on the reflector surface, wherein the related brightness is defined as the measured flux divided by the maximum flux. When the surface of reflector is smooth, the reflected beam keeps the original shape without any broadening phenomenon. Hence, the pattern in Fig. 3c is quite narrow. The smooth TiO₂/PDMS plate is like a mirror. As the undulations were developed on the surface of a TiO₂/PDMS plate, the reflected beam would spread to form a larger optical spot when the laser beam was illuminating on the reflector. Here, these surface undulations were considered to be like microscaled convex reflective optical elements located on the surface of a reflector. As light was reflected by convex reflective optical elements, the reflected light would be divergent. Hence, the pattern in Fig. 3c is broad. Experimental results showed that the distribution and scale of waves' periodicity was increased, and the spread spot would become bigger one. It implies that the reflective beam would be uniformly diffused. Hence, the diffusivity of reflectors could be controlled by surface undulations.

4. Conclusions

High-reflectance substrates were fabricated by mixing nanoscale TiO_2 powders with PDMS polymers, and then the microscale wave-like undulations were self-developed after the substrates were dipped into H_2SO_4/HNO_3 solutions, regarding as optical reflectors. Therefore, the periodicity of undulations could be controlled between 3 and 130 µm by the control of the dipped duration and the ratio of H_2SO_4/HNO_3 solutions. After optical examination, a TiO₂/PDMS plate with microscaled undulations can reflect and diffuse light effectively. Hence, the novel way has a potential for the fabrication of low-cost and large-area reflectors.

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