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Effect of self-assembled monolayer and aluminum oxide ALD film on a PMMA substrate

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The antireflective (AR) coated poly methyl methacrylate (PMMA) substrate was deposited by atomic layer deposition (ALD) on a self-assembled monolayer (SAM) to improve hydrophobicity and mechano-chemical properties of organic thin films. The water contact angles (WCA) were tested to characterize the surface wettability of SAM octadecyltrichlorosilane (OTS) films. Results showed that a contact angle of 105.9 ° was obtained for the SAM films with an annealing process, and the highest WCA of 120° was achieved for the films prepared by the SAM and ALD multi-process. The surface morphology of the SAM films with different assembly times and varying number of ALD cycles was obtained by atomic force microscopy (AFM). The maximum light transmittance for the SAM films on the PMMA substrate reached 99.9% at a wavelength of 450 nm. It was found that the SAM surfaces were not affected at all by the ALD process.

Key words: PMMA, Self-assembled monolayer (SAM), ALD, Water contact angle, AFM.

Introduction

A hydrophobic surface with a water contact angle larger than 90° has attracted a great deal of attention. [1] However, for applications such as self-cleaning widows, optical devices, and solar cells, high optical transparency is an additionally requirement, as well as resistance to mechanical wear. The water contact angle of about 100° can be obtained for a nominally flat surface with a low surface energy coating [2].

Surface composition and surface roughness are the two main factors that govern the wettability of a solid surface. Commonly, a hydrophobic surface can be prepared by a combination of lowering the surface energy and enhancing the surface roughness [3].

The dual requirements of hydrophobicity and transparency pose a challenge. The surface must be sufficiently rough to obtain high water contact angles (WCA), but the dimensions of the roughness features must be small enough to allow high transmittance of light. It is usually suggested that the size of surface features should not exceed roughly one quarter of the wavelength of visible light [4-7].

Glass is the most common optical material for lenses, architectural windows, and so forth, but transparent polymers such as polycarbonate (PC) and poly methyl methacrylate (PMMA) are also of great engineering importance. PC and PMMA are used for a wide-range of applications such as aircraft canopies, bullet-proof windows, solar cell panels, and many high-performance optical devices. Compared with a glass substrate, PMMA has higher transmittance, flexibility and volume productivity, with applications for optical components [8].

Self-cleaning, antireflective coatings on a PMMA substrate may be used in some special applications where glass is not suitable, such as in Fresnel lenses or the wall of space telescope lenses. The coating process on PMMA requires deposition at a fairly low temperature due to its low glass-transition temperature [8].

The self-cleaning coating layer applied to the smart spectacle lens, which is attracting attention as a functional optical lens, presents issues with respect to the characteristics of organic material. The ITO coating layer with an antistatic effect for removing dust is not economical [9-11].

The selection of the SAM precursor is determined by considering the substrate of interest upon which the SAM must be deposited, and the specific desirable properties (hydrophilic, hydrophobic, etc.) of the functionalization. In general, the head group of the SAM is determined by the substrate, and typically silanes (trichlorosilanes and alkylsilanes) are used for OH-rich oxide surfaces. Thiols (organosulfurs) are typically chosen for noble metal surfaces that do not offer hydroxyl ligands on the surface. The functional groups determine the surface properties of the SAM layer: non-polar groups (alkyl, phenyl) for hydrophobicity, polar groups (-OH, -COOH) for hydrophilicity, and fluorinated chains for oleophobicity

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[12].

In this study, an ALD/SAM multi-process to prepare a hydrophobic surface on AR-coated PMMA was reported. The self-assembled monolayer was deposited on an AR-coated PMMA substrate by a selected solution in various solution concentrations and immersion times. The ALD process was then performed at low temperatures on various surfaces of the SAM to prevent damage to the underlying organic material. To investigate the hydrophobicity, morphology, surface roughness, mechanical and chemical properties of the films, we measured the static water contact angle (WCA) by atomic force microscopy (AFM). The light transmittance of the coating was measured using ultraviolet-visible (UV-Vis) spectroscopy.

Experimental Methods

The AR coated PMMA substrates were cut into 2 cm \times 2 cm samples. The substrates were pretreated before the self-assembled OTS film preparation in a Piranha solution (Deionized water 100 ml, H₂O₂ 20 ml, H₂SiO₄ 1 ml) for 10 min to remove the oxide layer from the surface.

The solution of octadecyltrichlorosilane (OTS) and heptane (C_7H_{16}) with a volume ratio of 0.1:136 was prepared. The AR-coated PMMA was immediately immersed in the solution prepared at 60 °C for 5-30 min to investigate the effect of self-assembled OTS film time on the surface properties. After the SAM formed, the samples were heated at 150 °C for 1 hr in a vacuum. Then the Al₂O₃ ALD process was repeated for 300-1200 cycles at 150 °C, leading to the deposition of a 9-36-nm film of Al₂O₃.

Surface WCA was evaluated by using an angle measurement instrument (CAM-200). Optical transmittance of the coating was determined by spectroscopic UV-Vis (JASCO V-650). Atomic force microscopy (AFM) analysis was carried out using an XE-100 at room temperature.

Results and Discussion

The surface wettability of AR-coated PMMA substrates coated with self-assembled monolayer (SAM) OTS films were judged by WCA measurement, as shown in Fig 1. The WCA of substrates coated with SAM (OTS) films were found to increase significantly when assembly time increased from 5-30 min, as seen in Figs. 1(a) and 1(b). The static water droplets on the SAM (OTS) films for 20 min, from which we could identify that the WCA were 105.9 °, implying that more hydrophobic surface can be obtained. Fig. 1(b) shows no significant change in the WCA measurements after the annealing process.

To proceed with the ALD/SAM multi-process, it was necessary to conduct a thermal stability test of the



Fig. 1. Water contact angle (WCA) of AR coating on PMMA coated SAM (OTS): (a) Before annealing. (b) After annealing.

SAM (OTS) organic molecules because of the ALD process temperature.

As shown in Fig. 2, when SAM (OTS) specimens were annealed at room temperature to 200 °C, abrupt WCA reduction was observed due to organic molecule desorption at around 200 °C. Also, the contact angles of SAM (OTS) specimens without annealing and those with heat treatment were not significantly changed. Thus, the ALD process temperature was set at 150 °C. [13]

Fig. 3 shows the WCA applied with the ALD/SAM multi-process. The SAM (OTS) was at 5 and 20 min, and the ALD process was applied from 300 to 1200 cycles.

The SAM (OTS) films immersed for 5 min yielded a water contact angle of 90.3 °, and with additional ALD application, and this angle increased to 108.2 ° after 300 cycles. After immersion for 20 min the water contact angle was 105 °, and with additional ALD application, the angle increased to 120 ° after 900 cycles. Therefore, the self-assembled OTS films immersed for 5 min showed that the WCA value gradually decreased with



Fig. 2. Water contact angle (WCA) of the SAM (OTS) coatings on the 0 to 200 °C annealing.



Fig. 3. Water contact angle (WCA) of AR coating on PMMA coated SAM (OTS) 5 and 20 min. with the ALD 300-1200 cycle.

 Table 1. Surface roughness and water contact angles of SAM immersion time with different ALD cycle.

OTS Immersing time	ALD cycle	R _a (nm)	R _q (nm)	WCA (°)
5 min.	300	1.743	1.208	110.2
	600	1.372	1.299	108.7
	900	1.208	1.208	106.7
	1200	0.924	0.924	106.5
20 min.	300	0.420	0.420	110.7
	600	0.939	0.973	110.9
	900	0.980	0.980	120
	1200	1.163	1.624	119.2

increasing ALD cycle and increased at 20 min as the number of ALD cycles increased. As the immersion time increases, the coverage increases and the space of Al_2O_3 deposition decreases; hence the effect of ALD seems to be minimal.



ALD 1200 cvcle

Fig. 4. AFM 3D images of SAM (OTS) 5 and 20 min. with the ALD 300-1200 cycle. (a) SAM 5 min./ALD 300-1200 cycle, (b) SAM 20 min./ALD 300-1200 cycle.

ALD 900 cycle

The samples coated with SAM (OTS) films after annealing and the ALD process were studied with respect to surface morphologies by AFM in tapping mode to determine if the assembly and number of ALD cycles had an effect on the surface morphology and surface wettability.

Fig. 4 shows a series of AFM images taken over regions of 2 μ m × 2 μ m specimens at different stages of the film formation, where Fig. 5a presents the 3D morphology images of SAM OTS films immersed for 5 min with the number of ALD cycles from 300 to 1200, while Fig. 5b presents the 3D morphology images of SAM (OTS) films immersed for 20 min with the number of ALD cycles from 300 to 1200.

The WCA is determined by the surface energy (chemical effect) and the roughness (structural effect). When the ALD is deposited on the SAM specimen, the chemical effect is slightly reduced (Surface energy: organic molecule $> Al_2O_3$) and roughness increased as it filled.

As a result, ALD increases both the chemical effects and structural effects of specimens with large voids. Therefore, for specimens with long immersion times, the change in roughness is also reduced.

The surface roughness values and water contact angles of SAM (OTS) immersed at 5 and 20 min with different ALD cycles are listed in Table 1. R_a and R_q are used to evaluate the surface roughness, which can be calculated by Eqs. (1) and (2).

$$R_{a} = \frac{1}{l} \int_{0}^{1} |z(x)| dx$$
(1)

$$\mathbf{R}_{\mathbf{q}} = \sqrt{\frac{1}{l}} \int_{0}^{1} z^{2}(x) dx \tag{2}$$

Here, R_a is the arithmetic mean deviation of the assessed profile, 1 is the sampling length, z(x) is the height of the assessed profile at any position x, and R_q is the mean square deviation of the assessed profile [14].

Significant changes in the surface roughness have been observed along different assembly times and ALD cycles. When the assembly time was 5 min/600 ALD cycles, the samples exhibited a surface roughness as $1.372(R_a)$ and $1.299(R_q)$ together with a water contact angle of 108.7 °. When the assembly time was 20 min/ 900 ALD cycles, the sample exhibited surface roughness as $0.980(R_a)$ and $0.980(R_q)$ together with a satisfactory water contact angle of 120 °.

The optical transmittance of the PMMA substrate is about 92.0%. [15] The measured optical properties of AR-coated PMMA substrates are presented in Figs. 6(a-c). When the SAM (OTS) 5 and 20 min coating was applied on the PMMA substrate, its maximum optical transmittance value reached 99.9% at a wavelength of 450 nm. Additionally, the ALD cycle does not seem to affect the light transmittance in the ALD/SAM multiplexing process.

Conclusions

In this study, we evaluated octadecyltrichlorosilane to form self-assembled coatings on AR-coated PMMA substrates by the method of liquid phase deposition, followed by the ALD process.

ALD/SAM multi-process were found to have a larger WCA than those without the ALD application process. In addition, SAM immersed for 20 min and ALD 900 cycles had the highest WCA of 120 °. The surface morphology of AR-coated PMMA with self-assembled film showed that the sharp peaks grew gradually with the extension of assembly time and the number of ALD cycles, resulting in a rougher and more hydrophobic surface. The maximum optical transmittance was 99.9% at 450 nm. The optical transmittance did not change for SAM time or number of ALD cycle applications.



Fig. 5. Optical transmittance of the AR coating on PMMA surface. (a) AR coating on PMMA, SAM (OTS) 5 and 20 min. (b) with the SAM 5 min./ALD 300-1200 cycle (c) with the SAM 20 min./ALD 300-1200 cycle.

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