


Article

Surface Modification of Sol-Gel Silica Antireflective Coatings by F-PMHS: A Simple Method for Improvement of Amphiphobicity

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Abstract: Sol-gel silica antireflective coatings (ARCs) with improved amphiphobicity were simply fabricated on BK7 glass substrates via fluorinated-poly(methylhydrogen)siloxane (F-PMHS) surface modification by the dip-coating method. The results of Fourier Transform Infrared (FTIR) and X-ray Photoelectron Spectroscopy (XPS) showed that F-PMHS were covalently bonded to the surface of ARCs. F-PMHS modification significantly improved hydrophobicity and oleophobicity of silica ARCs by increasing their water contact angles from 27° to 105° and oil contact angles from 17° to 45°. In addition to the improved amphiphobicity, the modified ARCs also possessed excellent transmittance. Most importantly, it was found that with increasing F-PMHS content the atom amounts and porous property of modified ARCs were almost unchanged. This result had been shown to be associated with the changes of optical property and amphiphobicity for silica ARCs, and the details were discussed.

Keywords: amphiphobicity; surface modification; sol-gel method; antireflective coating; fluorinated-poly(methylhydrogen)siloxane

1. Introduction

Sol-gel silica antireflective coatings (ARCs) have captured a considerable amount of attention in the past few decades, since they exhibit outstanding properties, such as superior homogeneity, controllable structure, adjustable refractive index, and have a wide variety of potential applications in solar panels, light sensors, and high-powered laser fusion systems [1–6]. However, sol-gel silica ARCs are usually porous and polar and apt to absorb contamination from the working environment [7]. This leads to gradual decrease in transmittance of sol-gel silica ARCs. This phenomenon is generally called poor AR stability. Sol-gel silica ARCs are the most commonly used ARCs in high-powered laser fusion systems, in which there are thousands of transmissive optics. An obvious decrease in transmittance will seriously decrease the final output energy of lasers. Therefore, the AR stability is very important for sol-gel silica ARCs used in high-powered laser fusion systems. It was reported that the hydrophobic modification of sol-gel silica ARCs was an effective method for improving their AR stability [8]. Many scholars have reported different methods to prepare hydrophobic ARCs [9–12]. These hydrophobic sol-gel silica ARCs show good hydrophobicity and AR stability to hydrophilic

pollutants. However, the hydrophobic modification of sol-gel silica ARCs incorporates a great number of hydrophobic groups into the silica. These hydrophobic groups make the modified ARCs difficult to absorb polar contaminants, but easy to absorb organic pollutants [13,14]. There are also some oleophilic pollutants in high-powered laser fusion systems and, therefore, it is desirable to improve the amphiphobicity of sol-gel silica ARCs to afford them good AR stability to hydrophilic and oleophilic pollutants simultaneously.

In our previous work [15], PMHS surface modification was reported as an ultra-fast and effective method for hydrophobic modification of sol-gel silica ARCs. However, the PMHS-modified ARCs also suffer from poor AR stability to the oleophilic pollutants. In this work, surface modification of sol-gel silica ARCs by F-PMHS was reported to improve the hydrophobicity and oleophobicity simultaneously. The resultant F-PMHS modified ARCs exhibited not only improved amphiphobicity, but also good transmittance.

2. Materials and Methods

2.1. Materials

High purity tetraethyl orthosilicate (TEOS) was purchased from Kermel (Tianjin, China). Analytical grade ammonia-water with an NH_3 content of 25–28% was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Analytical-grade ethanol and hexane were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China. F-PMHS and Kastredt catalyst (platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane) were purchased from Chengguang Research Institute of Chemical Industry (Chengdu, China).

2.2. Fabrication of Silica Sols

TEOS, ethanol and ammonia-water were added in a sealed glass container and then magnetically agitated for 2 h at 30 °C. Then, the sol was aged at 25 °C for 7 days. The molar ratio of $\text{TEOS}:\text{NH}_3:\text{EtOH}:\text{H}_2\text{O}$ was 1:0.73:37.74:1.98.

2.3. Preparation of Sol-Gel Silica ARCs

BK7 glass substrates with a diameter of 30 mm and thickness of 3 mm were dipped into 0.5% HF solution for several seconds and then immediately washed with deionized water. Finally, the substrates were washed with a hydrous ethanol and wiped carefully with a cleanroom wiper. Silica ARCs were obtained by dipping BK7 glass substrates in sols and subsequently withdrawing at a constant speed of 100 mm/min. The obtained ARCs were heated at 120 °C for 1 h. In this work, the dip-coater (SYDC-100N) was purchased from SANYAN Instrument Co., Ltd. (Shanghai, China). The humidity was well controlled to 40% with a nitrogen atmosphere.

2.4. Surface Modification of Silica ARCs

The modifier solutions with weight ratio of F-PMHS of 0.125%, 0.25%, 0.5%, 0.75%, 1.0%, and 1.25% were obtained by mixing hexane, F-PMHS and Kastredt catalyst together. The F-PMHS surface-modified silica ARCs were fabricated by immersing the sol-gel silica ARCs into the modifier solution and immediately removing at a withdrawal rate of 100 mm/min. The modified ARCs were flushed with hexane to remove unreacted F-PMHS and then heated at 120 °C for 1 h.

2.5. Characterization

The xerogel for FTIR characterization was obtained by rotary evaporation with a further heat-treatment at 120 °C for 1 h. The F-PMHS-modified xerogel was realized by immersing xerogel into the modifier solution with a weight ratio of F-PMHS of 0.5% for 1 min. The F-PMHS-modified xerogel was heat-treated at 120 °C for 1 h and then extracted with hexane for 48 h to remove F-PMHS which does not covalently bond to silica particles. FTIR spectra of xerogels before and after F-PMHS

modification were analyzed by a Bruker Tensor 27 (Bruker Optik, Ettlingen, Germany) using the KBr pellet method with transmission mode in the mid-IR range from 500 to 4000 cm^{-1} . XPS spectra of AR coatings were obtained by using a Thermo SCIENTIFIC ESCALAB 250Xi (Thermo Fisher Scientific, Pittsburgh, PA, USA) with AlX-radiation ($K\alpha$, $h\nu = 1486.8$ eV). The water and oil contact angles (WCA and OCA) of ARCs were obtained on a Krüss DSA100 (Hamburg, Germany). The surface morphology of the coating was analyzed by scanning electron microscope (SEM, ZEISS Z500, Jena, Germany). The refractive index and film thickness of the ARCs were determined using an ellipsometer at 633 nm (Horiba UVISEL, Longjumeau, France). The transmittance spectra were measured with a UV-VIS spectrophotometer (Mapada, 3200PC, Shanghai, China).

3. Results and Discussion

3.1. FTIR Characterization

FTIR spectra of silica xerogels before and after F-PMHS modification were recorded and represented in Figure 1. Before FTIR characterization, the modified silica xerogel has been extracted with hexane for 48 h to remove F-PMHS which did not covalently bind to the silica particles. For pure silica xerogel, there are absorption bands observed at around 3450 cm^{-1} , 2964 cm^{-1} , 1630 cm^{-1} , 1090 cm^{-1} , 954 cm^{-1} , and 800 cm^{-1} . The broad absorption band at around 3450 cm^{-1} is attributed to Si–OH bonds or absorbed water [16,17]. The three peaks around 2964 cm^{-1} corresponds to the stretching vibration of C–H bonds from $-\text{CH}_3$ [18]. The water deformation band appear at about 1630 cm^{-1} [19]. The absorption bands at around 1090 cm^{-1} and 800 cm^{-1} are the characteristic absorption band of Si–O–Si bond due to the asymmetric and symmetric vibration, respectively [20,21]. The absorption band at 961 cm^{-1} is attributed to $-\text{Si}-\text{OH}$ [22]. After F-PMHS surface modification, there are two new absorption bands at 900 cm^{-1} and 2167 cm^{-1} corresponding to $-\text{Si}-\text{C}$ and $-\text{Si}-\text{H}$ of F-PMHS, respectively [23]. In addition, the intensity of absorption band at 2964 cm^{-1} is strengthened while that of absorption band at 961 cm^{-1} is weakened gradually with the increasing F-PMHS concentration. The latter demonstrates convincingly that $-\text{Si}-\text{H}$ groups of F-PMHS react with the hydroxyl groups of silica particles by dehydrogenation and, hence, F-PMHS chains are covalently grafted onto the surface of silica particles.

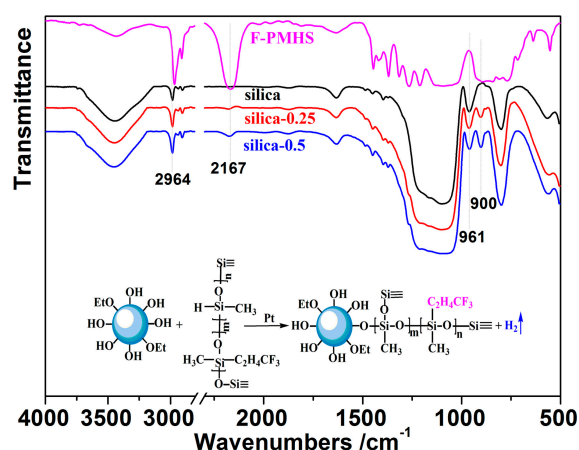


Figure 1. FTIR spectra of PMHS, pure silica xerogel, and xerogel modified with F-PMHS content of 0.25% and 0.5%.

3.2. XPS Analysis

It is difficult to demonstrate the existence of amphiphobic $-\text{CF}_3$ groups by FTIR because its absorption bands are similar to those of $-\text{CH}_3$ [23]. So the characterization of XPS is carried out further. And before XPS characterization, the modified SiO_2 ARCs were washed with hexane three times to

remove unreacted F-PMHS. XPS spectra of ARCs and corresponding atomic amounts of O, Si, C, and F as a function of F-PMHS content are represented in Figure 2a,b. As shown in Figure 2a, the ARCs consists of O, Si, and C elements before F-PMHS modification [24,25], while there is an additional F element after F-PMHS modification [26]. As shown in Figure 2b, the atomic amounts of C and F for silica ARCs are 13.35% and 0, respectively, which are increased to 21.53% and 10.71% after being modified by 0.125% F-PMHS. At the same time, the atomic amounts of O and Si decrease from 63.43% and 23.22% to 47.4% and 20.07%, respectively. This is in good agreement with the results from FTIR. It is the F-PMHS grafted onto the ARCs that results in this change in atomic amounts.

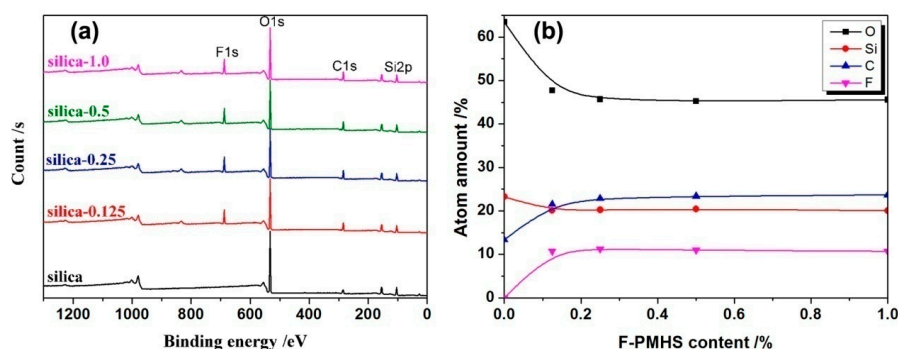


Figure 2. XPS spectra of silica ARC before and after F-PMHS modification (a), and the effect of F-PMHS content on the atom amounts of ARCs (b).

Most importantly, a very interesting phenomenon can be found in Figure 2b. The atomic amounts are very different before and after F-PMHS modification; however, they are almost unchanged for modified ARCs, no matter what the F-PMHS content in modifier solution is. This can be explained from the ultra-fast reaction between F-PMHS and silica particles. As shown in the schematic representation in Figure 3, sol-gel silica ARC consists of silica particles which randomly stack on the substrate [27]. Silica AR coating is polar and abundant in hydroxyl groups. As long as ARCs being immersed into the modifier solution which contains F-PMHS and Karstedt catalyst, the dehydrogenation happens immediately. Thus, even if at very low F-PMHS content, the surface of porous silica ARC would be easily modified by F-PMHS. With increasing F-PMHS content, the penetration deep of modification also increases. However, the deep modification has no contribution to the XPS characterization because the testing deep of XPS is only 2–10 nm [28]. This is the reason that the atom amounts for modified ARC is unchanged.

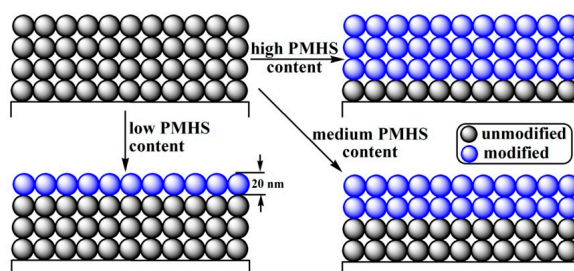


Figure 3. Schematic representation of F-PMHS modification at different F-PMHS content.

3.3. Morphology of ARCs

It is very important to investigate the morphology of ARCs before and after F-PMHS surface modification. Figure 4 shows the top-view and cross-sectional SEM images of ARCs modified by F-PMHS with increasing content. It can be found from the top view that the unmodified sol-gel silica ARC is porous. This is benefit for sol-gel silica ARCs because the nano-pores lower the refractive

index of ARCs to the square root of that of substrate and, therefore, nearly 100% transmittance can be realized [29,30]. Suppose that, during F-PMHS modification of ARCs, most of the nano-pores in ARCs are replaced by F-PMHS chains, the porosity of sol-gel silica ARCs would be decreased obviously, which would result in a remarkable reduction of transmittance [31]. However, fortunately, the top view shows that the modified ARCs are also porous, indicating that the F-PMHS surface modification does not significantly affect the pore structure of ARCs. It can be also revealed from the cross-sectional SEM images that the thickness of ARCs does not increase significantly after F-PMHS modification.

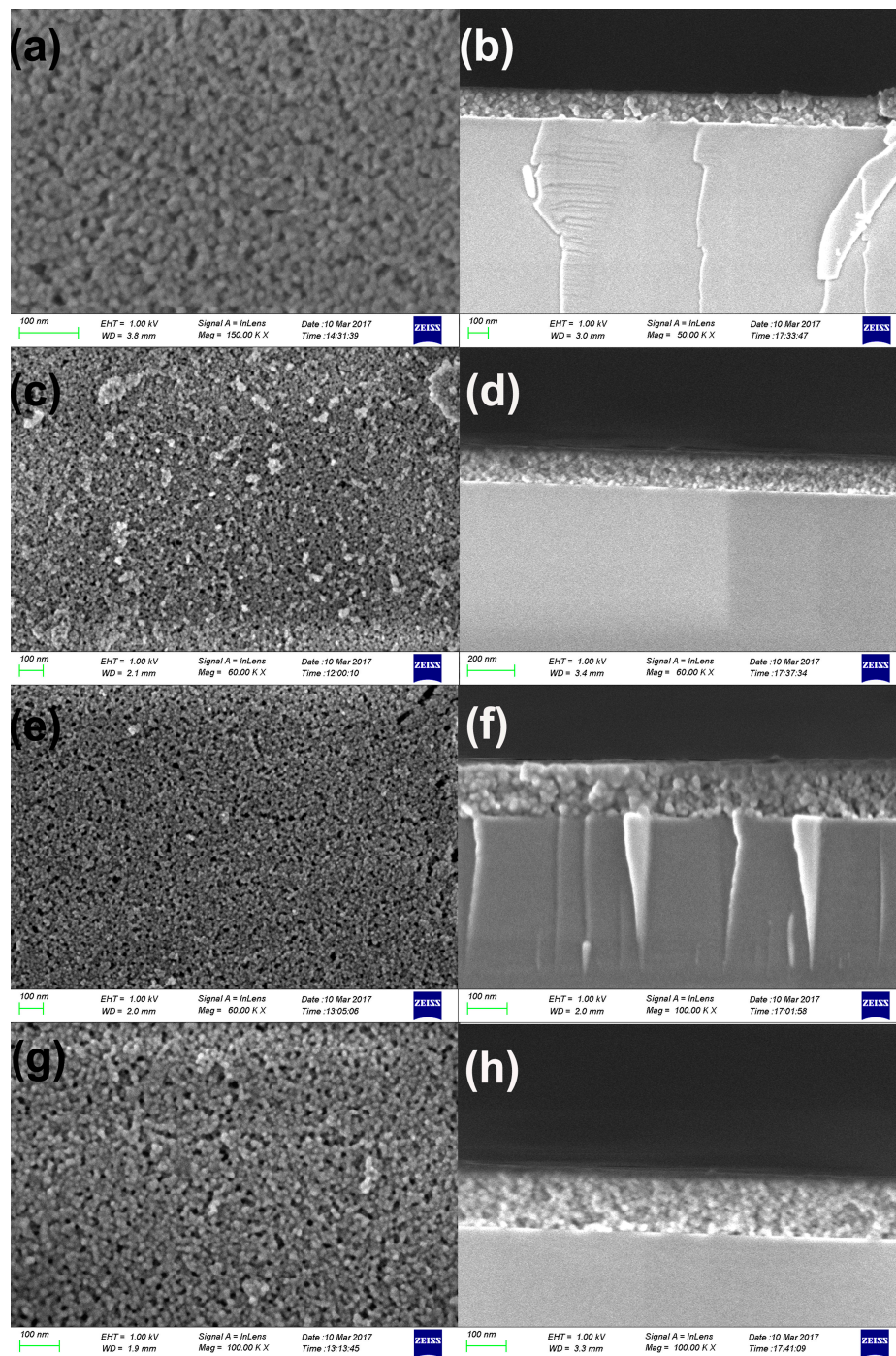


Figure 4. Top-view and cross-sectional SEM images of ARC modified F-PMHS at content of 0.0% (a,b), 0.25% (c,d), 0.5% (e,f), and 1.0% (g,h).

3.4. Hydrophobicity and Oleophobicity

According to the FTIR and XPS analysis, the chemical composition is quite different for ARCs before and after F-PMHS modification. There are amounts of hydrophobic $-\text{CH}_3$ and many amphiphobic $-\text{CF}_3$ groups incorporated onto the surface of ARCs. Therefore, the wettability of sol-gel silica ARCs can be adjusted by F-PMHS modification. It is well-known that WCA and OCA measurements can be applied to assess the wettability properties of silica ARCs [32]. Figure 5 shows the WCA and OCA of silica ARCs with and without F-PMHS modification. The WCA and OCA of pure silica ARC is 27° and 17° , respectively, indicating that it is very hydrophilic and oleophilic. After modification, the WCA and OCA increase significantly to about 105° and 45° , respectively. In agreement with the XPS analysis, the WCA and OCA does not change with increasing F-PMHS content because the surface chemical property is unchanged.

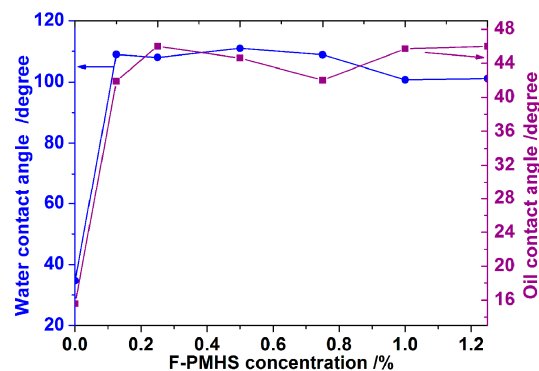


Figure 5. Effect of F-PMHS content on the water and oil contact angles of ARCs.

3.5. Optical Property of ARCs

The transmittance spectra of sol-gel silica ARCs before and after modification with different F-PMHS content were recorded and shown in Figure 6. As shown in Figure 6, the central wavelength shifts to the longer wavelength, while the maximum transmittance at central wavelength decrease slightly after F-PMHS modification. The change in maximum transmittance and central wavelength is named as ΔT_{\max} and $\Delta\lambda$. The effect of F-PMHS content on ΔT_{\max} and $\Delta\lambda$ can be also read from Figure 6. The ΔT_{\max} and $\Delta\lambda$ increases gradually with increasing F-PMHS content. The relationship between reflection and refractive index of ARCs is as follows Equation (1) [33]:

$$R = (n_c^2 - n_s)^2 / (n_c^2 + n_s)^2 = (1 - T) / 2 \quad (1)$$

where n_c and n_s are the refractive indices of ARC and substrate, respectively; and R and T are the reflection and transmittance of ARC.

The change in refractive index, thickness and porosity as a function of F-PMHS was showed in Table 1. The refractive index of sol-gel silica ARC is 1.25 to give nearly 100% transmittance. After being immersing in modifier solutions with increasing F-PMHS concentration, the refractive index of modified ARCs increases gradually from 1.25 to 1.32. This leads to the decrease in transmittance and, hence, an increase in ΔT_{\max} . After being immersed into the modifier solutions with higher F-PMHS content, more F-PMHS chains penetrate into the pores of ARC. The F-PMHS chains partially replace the air in the pores, resulting in a decrease in porosity and a corresponding increase in refractive index. However, the ΔT_{\max} is small and, therefore, the transmittance of modified ARC is still very high. For example, for ARC modified by 0.5% F-PMHS, the ARC coated glass exhibits much better readability for the characters below it because of its antireflective property at visible wavelengths. This is in agreement with the discussion in morphology characterization.

The relationship between central wavelength, refractive index and physical thickness of ARC can refer to Equation (2) [34]:

$$\lambda = 4n_c d \quad (2)$$

where n_c and d are the refractive and physical thickness of ARC, respectively.

The increase in refractive index is one of the reasons for the increase of central wavelength. On the other hand, during modification, the surface of silica AR coating was grafted with F-PMHS chains. This will probably increase the physical thickness of ARC to a certain extent. Both of these factors lead to an increase in $\Delta\lambda$ as a function of F-PMHS concentration.

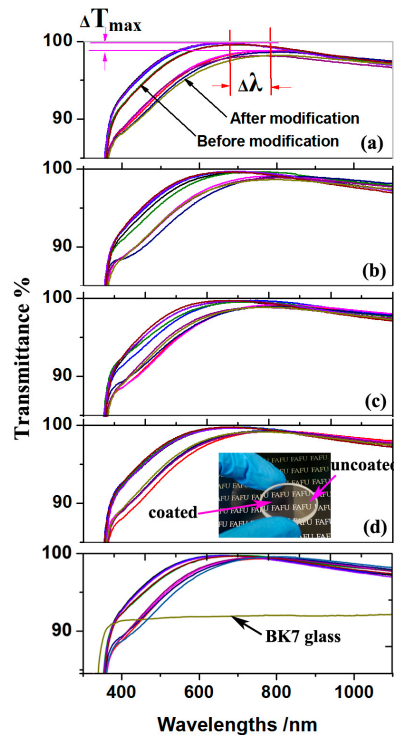


Figure 6. Transmittance spectra of ARCs before and after being modified by F-PMHS in different content of 1.25% (a), 1.00% (b), 0.75% (c), 0.50% (d), and 0.25% (e).

Table 1. Change in refractive index, thickness and porosity as a function of F-PMHS concentration.

F-PMHS Concentration/%	Refractive Index	Thickness/nm	Porosity/%
0	1.25	136	50.3
0.25	1.28	140	43.6
0.5	1.29	142	41.3
0.75	1.30	141	39.0
1.0%	1.31	140	36.7
1.25	1.32	141	34.4

4. Conclusions

In summary, we present a simple route to improve the amphiphobicity of sol-gel silica ARCs. The surface modification process can be achieved simply by immersing silica ARCs into the modifier solution and then immediately withdrawing. The hydrophilic ARCs can be easily switched to hydrophobic after F-PMHS modification and its oleophobicity was improved simultaneously. In addition, modified ARCs also possess good transmittance. The resultant F-PMHS modified sol-gel silica ARCs may find important application in high-powered laser fusion system due to its amphiphobic property and high transmittance.

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