Effect of the Treatment Quantity of Hexamethyldisilazane-ammonia Water on Environment Resistance of Silica Antireflective (AR) Coatings

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Abstract

The sol–gel single-layer silica antireflective coatings on the fused silica substrates were prepared with the dip method, and after that treated modified with different amounts of hexamethyldisilazane (HMDS)-ammonia atmosphere. The contamination resistance of silica antireflective coatings with and without hexamethyldisilazane (HMDS)-ammonia modification was measured by dibutyl phthalate (DBP). The evolution of silica antireflective coatings properties before and after modification was analyzed by ultraviolet - visible - near infrared spectrophotometer (UV), ellipsometry, water contact angles (WCAs), atomic force microscopy (AFM), and FTIR spectra. The ultraviolet - visible - near infrared spectrophotometer test showed that the transmittance of the silica antireflective coatings treated with HMDS-ammonia water was 99.80%, while that of the untreated silica antireflective coatings was only 96.28%. When the treatment capacity of HMDS-ammonia exceeds 10ml, the silica antireflective coatings have excellent environmental stability. The results show that: HMDS-ammonia water modification can significantly improve the anti DBP pollution performance, transmittance, and service life of silica antireflective coatings, and provide a guarantee for the smooth operation of high power laser.

Keywords

Silica antireflective coatings; Hexamethyldisilazane (HMDS)-ammonia; Dibutyl phthalate (DBP); Environmental stability.

1. INTRODUCTION

During the operation of high power laser system, the performance of the optical element is an important index to evaluate the laser device [1-4]. However, when the laser passes through the optical element, the loss of laser energy is due to reflection, scattering and absorption. For many years, silica antireflective coatings on optical elements was used to increase the transmittance of optical elements surface for ensuring the smooth operation of laser devices. Single-layer silica antireflective coatings are composed of randomly deposited nearly spherical silicon dioxide particles that are about 20nm. The refractive index of silica antireflective coatings can be adjusted to be about 1.2, which is close to the square root of the refractive index (1.46) of fused silica substrate, and meets one of the requirement that the transmittance of ideal single layer coating is close to 100%. The silica antireflective coatings are suitable for large-sized and irregularly shaped optical elements, since its excellent optical performance and high laser damage threshold. It has been widely used in high-power solids large-aperture optics for

laser devices [5]. However, due to the large specific surface area, high surface energy and sizable amount of hydroxyl groups on the surface of silica antireflective coatings, it is easy to adsorb moisture and organic matter in the vacuum environment and be contaminated. Contamination can cause a decrease in optical efficiency and even damage to optical components, severely restricting the use of antireflective coatings. Contamination not only changes the refractive index and reduces the antireflective efficiency of coating, but also decreases the anti-laser damage ability of coating [6]. Therefore, maintain high luminous flux of optical elements and enhance the environmental stability of optical elements has become a major challenge.

At present, a variety of solutions have been proposed to solve these problems. The main solution is to substitute the hydroxyl group on the silica particles with the group on the organic compounds to improve the properties of the coatings. For example, the methyl group on the hexamethyldisilazane (HMDS) or tetramethyldisilazane (TMDS) can replace the free hydroxyl group on the coatings to reduce the polarity of the surface of the coatings, so as to improve contamination resistance of the antireflective coatings[7-8]. In addition, ammonia treatment can promote the dehydration and condensation of hydroxyl groups on the surface of the coatings, form the Si-O-Si bond, harden the coatings and reduce its thickness and specific surface area [9-10]. In order to ensure the stable application of AR coatings in optical engineering, other researchers also modified the AR coatings with ammonia and HMDS. The research shows that contamination resistance of antireflective coatings can be substantially improved after modified by HMDS and ammonia water [11-12]. However, it is necessary to ensure stable performance of the antireflective coatings in engineering application.

In this work, we used different treatment quantity of HMDS-ammonia to modify the antireflective coatings, and tested them in a low-vacuum dibutyl phthalate (DBP) polluted environment, so as to provide a strong guarantee for the application of antireflective film in optical engineering.

2. EXPERIMENT

2.1. Preparations of SiO_2 Colloid and Anti-reflective Coatings

Monodisperse SiO_2 sol-gel is prepared with tetraethylorthosilicate (TEOS) as the precursor, ammonia (25-28%) as the catalyst, and anhydrous ethanol (EtOH) as the solvent. At room temperature, 150ml anhydrous ethanol was divided into two parts. In one part, 10ml ethyl orthosilicate was added to stir evenly, which was denoted as solution #1; The other part was added to 1ml ionized water and 3ml ammonia water (NH_3 content in ammonia water is 25.0%-28%) and stirred evenly, which is denoted as solution #2. Then, the solution #2 was slowly added to the solution #1, which was stirred evenly and recorded as solution #3. The Solution # 3 was sealed and aged for 7 days under normal temperature and pressure. After 7 days, the solution # 3 was refluxed at 50°C for 8 hours to remove NH3 from the solution, and monodisperse SiO2 sol-gel with average diameter which was about 20nm was prepared for use.

In clean environment with temperatures of 23°C and relative humidity of about 45%, the coating with peak transmittance of about 380nm was obtained by dipping and pulling at a speed of 8.5cm/min.

2.2. Surface Modifications of SiO_2 Antireflective Coatings

Figure 1 is the schematic diagram of the modification of silica antireflective coatings. At a environment of 23 °C, the samples were put into a 6L closed glassware which was put into hexamethyldisilazane (HMDS) with the quantity of Rx ml (x = 5, 10, 15, 30, 50) , and modified in the atmosphere formed by the natural volatilization of HMDS. Then, the samples were put into a container with My ml (NH_3 content in ammonia water is 25% ~ 28%, Y = 5, 10, 15, 30, 50) ammonia water, and the samples were modified in the atmosphere formed by the natural

volatilization of ammonia water for 24 hours. The untreated and HMDS-ammonia treated silica coatings with the quantity of Rx -My ml (x = y) were labeled as I, II, III, IV, V and VI respectively.
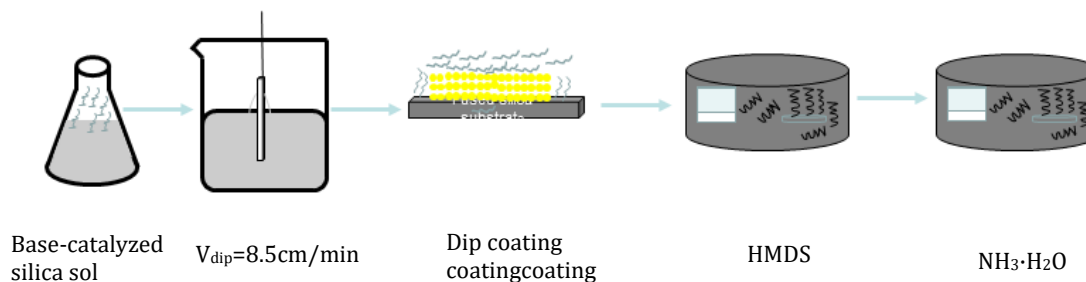

Base-catalyzed V_{dip}=8.5cm/min   Dip coating   HMDS $NH_3 \cdot H_2O$
silica sol   coatingcoating

Figure 1. Schematic diagram of SiO₂ coatings treated with HMDS - ammonia water modification

3. RESULT AND ANALYSIS

3.1. Transmittance Analyses

The transmission spectra of the silica antireflective coatings before and after HMDS-ammonia water modification are shown in Figure 2. The figure showed that the transmittance curve of the treated silica antireflective coatings has a blue shift and the peak transmittance remains unchanged. The transmittance of silica antireflective coatings modified by 15ml~ 50ml HMDS-ammonia water remained above 99.69% which indicated that the modified optical coatings still had excellent transmittance. After modified by HMDS-ammonia water, the chemical structure of the silica antireflective coatings changed, resulting in the peak position of curve moving towards the short-wavelength direction. Moreover, with the increase of the amount of HMDS-ammonia water, the shift of the peak position towards the short wavelength direction is more obvious [11]. The movement of peak position provides reference for the use of specific wavelength peak.
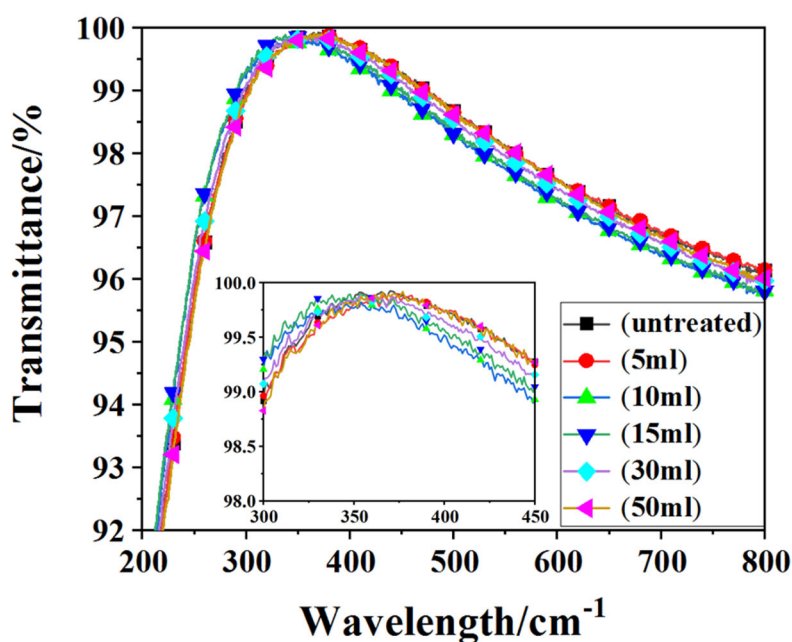

Figure 2. The transmittance spectra of the silica antireflective coatings before and after modification with HMDS-ammonia water

Table 1 shows the changes of thickness and refractive index of HMDS - ammonia water before and after modification. After the modification, the thickness of the coatings shrinks, and the amount of shrinkage increases gradually. The refractive index is about 1.20. The change of the thickness and refractive index of the coatings satisfies the requirement of the ideal single layer antireflective coatings: The optical thickness of the silica antireflective coatings is 1/4 of the incident wavelength; The refractive index of a silica antireflective coatings is the square root of the product of the refractive index of the incident medium and the substrate [13-16]. The refractive index of the substrate fused silica and air are 1.46 and 1, respectively, while the refractive index of the ideal silica antireflective coatings is 1.208.

Table 1. Changes of thickness and refractive index of chemical films before and after HMDS and NH3 treatment

HMDS/ Ammonia /ml	T before treatment/nm	T after treatment/nm	Relative shrinkage/%	n before treatment	T after treatment
5/5	80.27	78.02	2.80	1.191	1.2010
10/10	80.81	77.26	4.39	1.194	1.2011
15/15	80.61	77.02	4.14	1.193	1.2012
30/30	80.34	76.11	5.26	1.198	1.2023
50/50	80.14	75.35	5.97	1.2002	1.2024

The above experimental results show that the silica antireflective coatings modified by HMDS-ammonia water can meet the conditions of ideal monolayer antireflective coatings and maintain a high transmittance, showing a good application prospect.

3.2. Environmental Stability Analysis

The surface properties of the silica antireflective coatings were characterized by Water contact angles (WCAs), as showed in Figure 3. The contact angles of the coatings and water after HMDS-ammonia water treatment are obviously improved, and the contact angle increase from 27.56 ° to 121.12 °. With the increase of HMDS-ammonia water treatment, the final contact angle with water gradually increases to be about 120°. This is can be explained as follows: Firstly, a part of the polar Si-OH groups on the surface of the silica antireflective coatings are transformed into Si-O-Si $(CH_3)_3$ during HMDS treatment, which reduces the surface polarity and surface energy, the adsorption of water, and improves the hydrophobicity of the silica antireflective coatings. Secondly, the Si-OH groups on the surface of the silica antireflective coatings were further dehydrated and condensed to form Si-O-Si bonds with lower polarity, which further improved the hydrophobicity [17-19]. After two-step post-treatment, the silica antireflective coatings can reduce the absorption of water in the air and enhance the environmental stability. Table 2 shows the changes of peak transmittance of untreated and HMDS-ammonia water treated silica antireflective coatings under the condition of air humidity of 80%, respectively. After treatment, the environmental stability of the silica antireflective coatings was improved obviously. Among them, the peak transmittance of the silica antireflective coatings basically remained unchanged after 4 months after treatment with 15ml~50ml HMDS-ammonia water, showing excellent environmental stability.
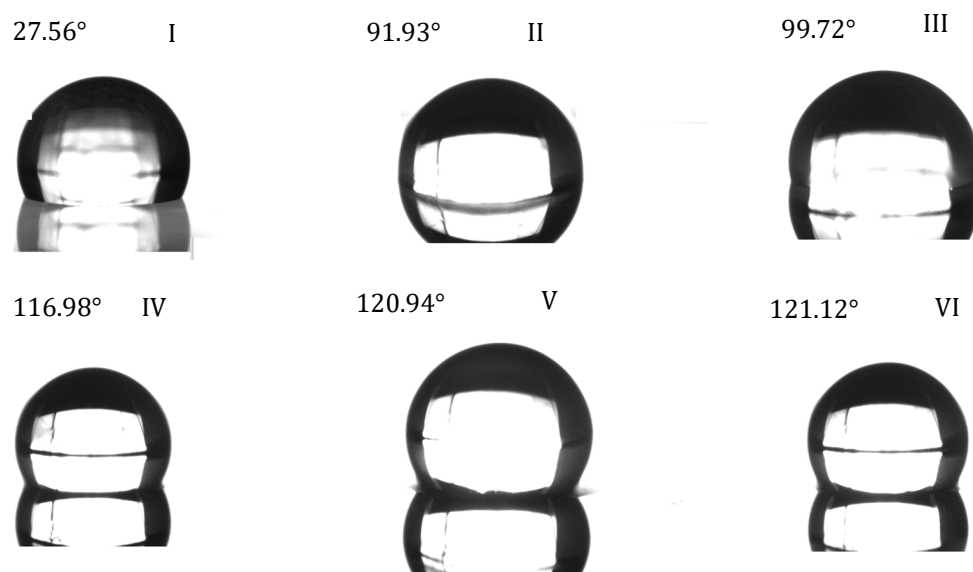
Figure 3. Contact angle of the silica antireflective coatings before and after treatment with HMDS and ammonia water

Table 2. Changes of peak transmittance of the chemical film of samples I ~ VI with time

Sample	$T_P\%$						
	Initial	5days	10days	1month	2months	3months	4months
I	99.98	99.87	99.56	99.27	98.97	99.75	98.53
II	99.97	99.91	99.85	99.61	99.57	99.58	98.56
III	99.96	99.90	99.83	99.72	99.63	99.61	99.61
IV	99.97	99.92	99.93	99.95	99.90	99.93	99.90
V	99.98	99.95	99.96	99.92	99.94	99.89	99.91
VI	99.97	99.93	99.85	99.84	99.87	99.86	99.84

In order to verify the effect of HMDS-ammonia water modification on improving the environmental stability of silica antireflective coatings, DBP contamination test was carried out. Figure 4 shows of the transmittance of the untreated silica antireflective coatings and HMDS-ammonia water treated silica antireflective coatings in the low vacuum (10-4Pa) environment of DBP contamination for 24h. After DBP contamination, the transmittance of the unmodified silica antireflective coatings decreased by 3.70%. When the HMDS ammonia water treatment amount exceeded 10ml, the modified silica antireflective coatings showed excellent contamination resistance, and its transmittance remained basically unchanged. This indicates that modification of HMDS - ammonia water can improve contamination resistance of the silica antireflective coatings and enhance the environmental stability.

Figure 5 shows in the surface morphology of the silica antireflective coatings before and after HMDS - ammonia water modification by atomic force microscope. We can know that the silica antireflective coatings before modification is loose and porous with large surface roughness, while the particles in the surface of the modified silica antireflective coatings become larger and the surface becomes smooth. The root mean square roughness Rq values of samples (I) ~ (VI) before and after HMDS - ammonia water modification were 7.7 nm and 4.4 nm and 3.4 nm, 2 nm, 1.9 nm and 1.8 nm, it suggests that HMDS - ammonia water modification can effectively reduce the roughness of the silica antireflective coatings, and with the increase of HMDS -

ammonia water, the roughness of the silica antireflective coatings gradually reduced, surface is becoming more and more smooth.
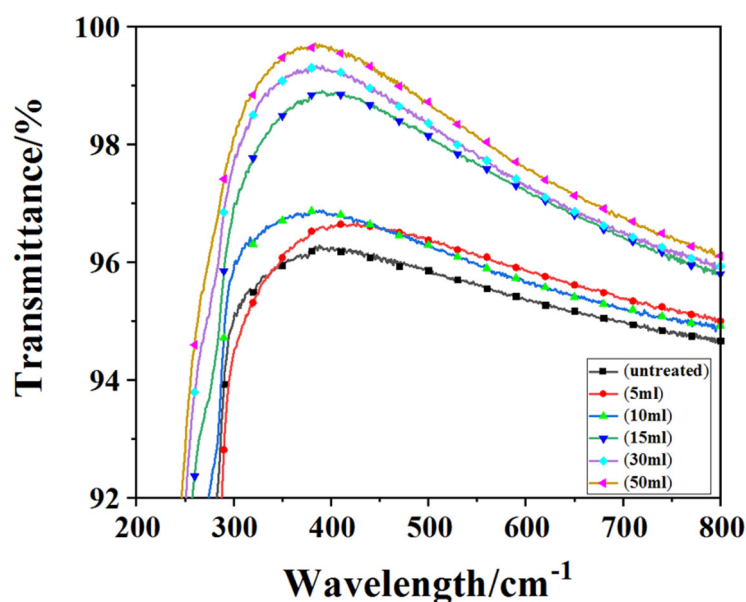

Figure 4. DBP contamination test of modified silica antireflective coatings

(I) untreated   (II) 5ml   (III) 10ml

(IV) 15ml   (V) 30ml   (VI) 50ml
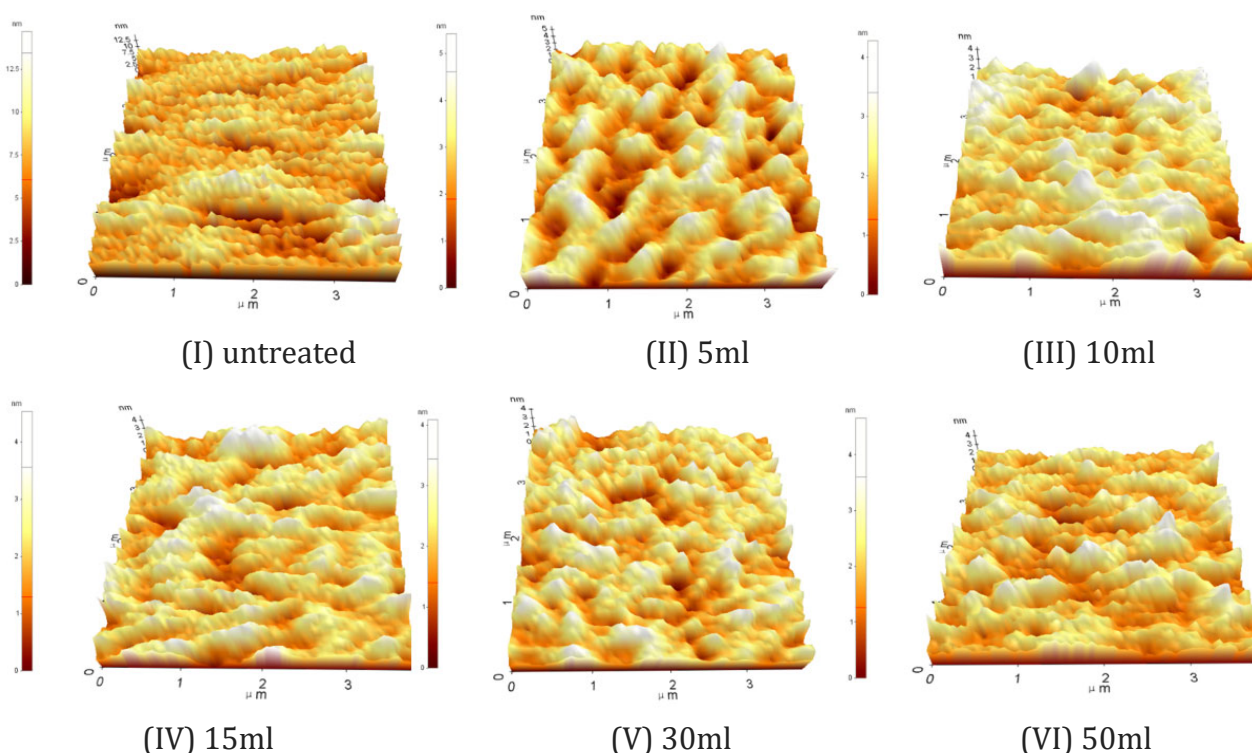
Figure 5. Atomic force microscope (AFM) images of silica antireflective coatings before and after HMDS - ammonia water modification: (I) untreated; (II) 5 ml; (III) 10ml; (IV) 15 ml; (V) 30 ml; (VI) 50 ml

Figure 6 is FTIR spectra of samples before and after silica antireflective coatings modification. The bending vibration of Si-O-Si group is near 472 cm^{-1}, the stretching vibration of Si-OH is near

960 cm^{-1}, and the antisymmetric stretching vibration of Si-O is near 1050 cm^{-1} [10]. With the increase of HMDS - ammonia water treatment, the stretching vibration intensity of Si-OH decreases gradually. The stretching vibration intensity of Si-O-Si increases and Si-CH$_3$ appears near 853cm^{-1}[20]. The results show that the chemical structure of the modified silica antireflective coatings has changed, the Si-O-Si group increases and the Si-OH group decreases. This is due to the formation of Si-O-Si group in the silica antireflective coatings through dehydration condensation, and then the formation of network structure [1,15]. The appearance of Si-CH$_3$ is caused by the conversion of Si-OH group into Si-O-Si (CH$_3$)$_3$ during HMDS treatment.
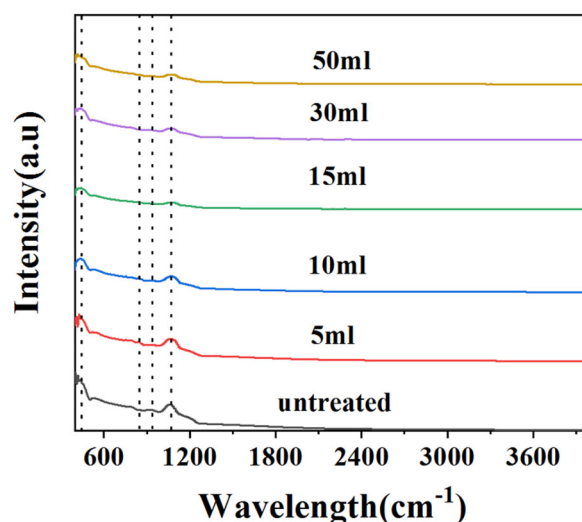

Figure 6. FTIR spectra of the silica antireflective coatings before and after modification with HMDS - ammonia water modification

From the analysis of the above results, it can be seen that contamination resistance of the silica antireflective coatings is significantly improved after HMDS - ammonia water modification. Among them, the effect is remarkable when the treatment quantity of HMDS - ammonia water is more than 10ml. On the one hand, due to the silica antireflective coatings in the process of HMDS modification, the hydroxyl groups on the surface are replaced by non-polar -Si (CH$_3$)$_3$, the polarity and energy of the surface of the silica antireflective coatings are reduced, the surface pores are modified and filled, and the adsorption of DBP is reduced. When the ammonia water is modified, the residual hydroxyl groups are further dehydrated and condensed to form Si-O-Si chemical structure, resulting in the enhancement of the gel network cross-linking. The pore size of the coatings becomes smaller. The silica antireflective coatings become thinner and the surface becomes smooth, which reduces the adsorption of DBP. On the other hand, the Rq of the modified silica antireflective coatings decreases, which is beneficial to reduce the adsorption of BDP.

4. CONCLUSION

In this paper, the silica antireflective coatings modified with different amounts of HMDS-ammonia water at room temperature was studied to explore its contamination resistance under low vacuum conditions. The results showed that the Rq of the modified coatings decreased, the surface became flat, the thickness of the coatings became thin and the refractive index increased, but the transmissivity of the modified coatings remained high, its contamination resistance and the environmental stability have been significantly improved. The results of paper can provide reference for practical appli-Resistant Antireflective Coatings for Flexible Polymeric Glasses via Embedding of Silica Nanoparticles and HMDS Modification. [J].

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