

# Improvement of Environmental Stability of the Antireflective Coating by PEG Modified SiO<sub>2</sub> Sol

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## Abstract

As the antireflective coating prepared by sol-gel method had poor environmental stability, sol-modified method was used to improve its performance. The alkaline silica sol was prepared in ethanol solvent by using tetraethyl orthosilicate (TEOS) as precursors and aqueous ammonia as catalyst (content ~ 28%). Polyethylene glycol (PEG200) was used to modify the silica sol and the antireflective (AR) coating was prepared by dip-coating from the modified sol. The transmittance, composition, refractive index, and hydrophobicity of AR coating were discussed by combining the spectrophotometer, FTIR, Coating Wizard 32 coating design software, optical microscopy imaging system and JC2000A static droplet contact angle measurement software. Finally, the environmental stability of the AR coating was tested. The results showed that AR coating transmittance decreased by less than 0.1% after UV light for 20 hours and its transmittance decreased by about 0.57% in the humid environment for 2 months. Resistance to environmental stability has been improved.

## Keywords

Environmental Stability, Hydrophobicity, AR Coating, Sol-Gel

## 1. Introduction

Sol-gel technology has attracted wide attention in the field of nanoporous materials because of its simple process, high purity of products, normal temperature and pressure operation and so on [1]. And it has shown its strong use value in the field of coating preparation [2] [3]. This kind of coating is a product of silica sol prepared using Stober method [4], in which silicon alkoxides hydrolyze and condense in alcohol solvents in the presence of water and a catalyst (e.g., NH<sub>3</sub>). The nanoporous properties of this AR coating impart a higher transmittance and laser damage threshold while limiting the environmental stability of the coating [5] [6]. Therefore, the appropriate treatment must be carried out before the use

of the coating, so that it has a certain degree of environmental stability in order to cope with the needs of the environment.

At present, the modification method for the AR coating is mainly divided into two kinds of sol-modification [7]-[18] and coating surface treatment [19] [20] [21]. Coating surface treatment is through the coating surface effective group grafting and other means to change the performance of the coating surface and thus improve the coating's environmental stability. Sol-modification is the introduction of modifier in the aging stage of sol by adjusting the microstructure and chemical composition of SiO<sub>2</sub> particles in the sol, so as to effectively resist the pollution of the external environment. Li xiaoguang *et al.* [22] [23] [24] obtained sol-gel silica coatings with high laser damage threshold and the stability in vacuum with organic contaminants by adding PEG in the sol. However, the stability of the environment for humid environments and UV light has not been reported. In this paper, by adding PEG200 in the sol to adjust the sol structure [25], we explored the environment stability of the AR coating combined with the change in transmittance. The environmental stability of the AR coatings in humid environments and UV light environments has been improved.

## 2. Experimental Details

### 2.1. Materials

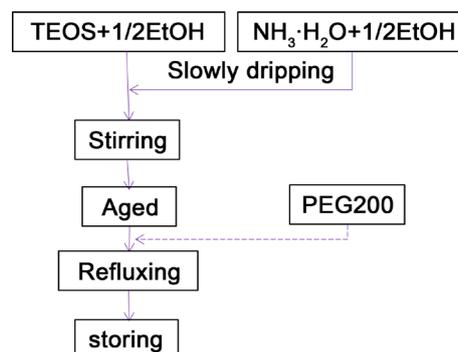
Tetraethyl orthosilicate (TEOS), anhydrous ethanol (EtOH, 99.9%), aqueous ammonia (28%) and Polyethylene glycol (PEG200) were purchased from Sino-pharm Chemical Reagent Co. Ltd. All chemicals agents were directly used without further purification.

### 2.2. Preparation of PEG-Silica Sol

The base-catalyzed silica sol was prepared using the Stober method [4]. A solution of aqueous ammonia and the half of the prescribed amount of EtOH was first added into a solution consisting of TEOS and the other half of the prescribed amount of EtOH under stirring. The final molar ratio of the base-catalyzed silica sol was TEOS: EtOH:NH<sub>3</sub>·H<sub>2</sub>O = 1:38:2.45. Then, the resultant sol was sealed in a glass container and stirred for 2 h at 25°C. In order to obtain silica particles suitable for coating, the resultant sol was aged in an appropriate environment with 20°C - 25°C and relative humidity (RH) lower than 50% for 4 days, followed by the slow addition of The molar ratio of 0.1 (PEG200/TEOS = 0.1), stirring for 1 hour to continue aging for 3 days. In the end, it had to be refluxed for 24 h to remove the ammonia at 80°C and stored to use (Figure 1).

### 2.3. Coating Preparation

The sol was deposited on the well-cleaned BK7 substrates and silicon wafers (using for FTIR) by dip-coating apparatus (CHEMAT Dip Master-200) with a fixed withdraw rate (0 - 12 inch/min) in a super clean room with the temperature of 25°C, and relative humidity (RH) was less than 50%. The substrate was placed in a muffle stove at 100°C heat treatment for 2 h to get the final sample.



**Figure 1.** Preparation process of PEG200 modified SiO<sub>2</sub> sol.

The samples were prepared and referred as: unmodified silica coating (Base-SiO<sub>2</sub>) and PEG modified coating (PEG-SiO<sub>2</sub>), respectively.

## 2.4. Characterization

The transmittance and reflection spectra of silica AR coatings were measured with an UV-vis-NIR spectrophotometer (JASCOV-570). The refractive index of silica AR coatings was determined using Coating Wizard 32 (SCI, Scientific Computing International) software. The chemical composition of silica AR coatings was obtained using Fourier transform infrared (FTIR) spectrometer (BRUKER TENSOR-27). The water contact angle (WCA) of silica AR coatings was measured using an optical contact-angle meter system (home-made). Resistance to environmental stability test is carried out, including the following simulated environment: 1) in the closed dryer to store distilled water to create a humid environment (RH > 90%); 2) in the UV irradiation box (power 1 kw) to achieve UV radiation environment.

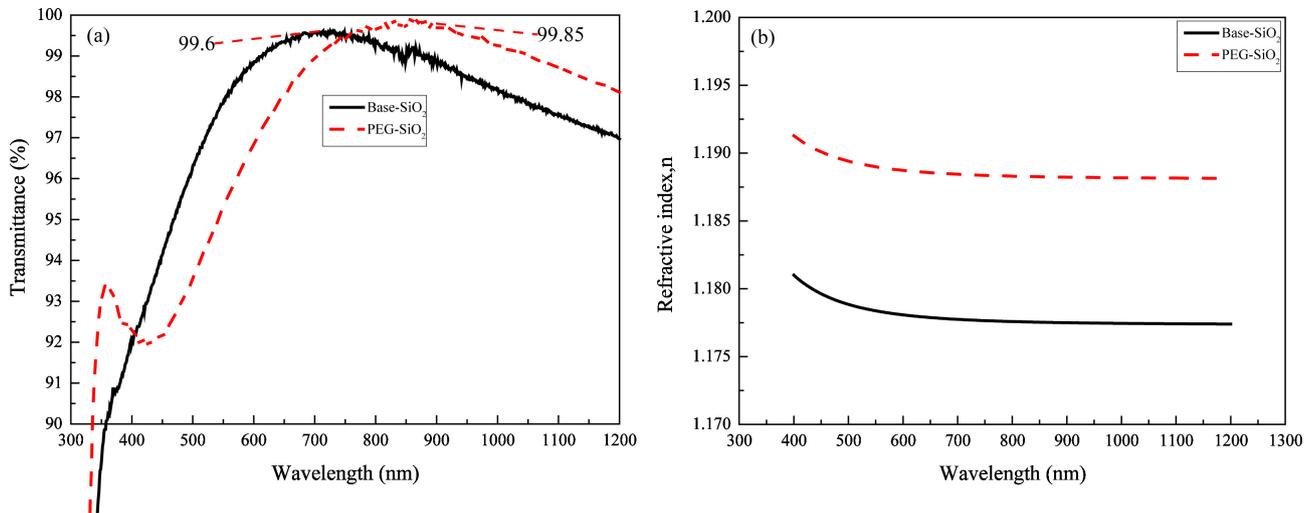
## 3. Results and Discussion

### 3.1. Optical Properties of the Coating

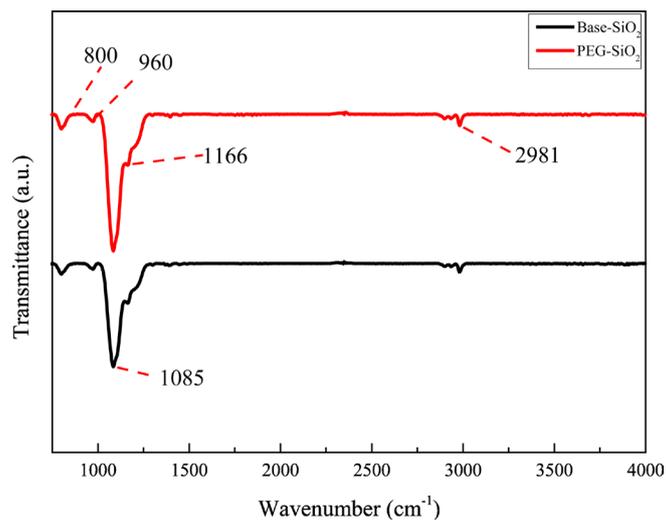
**Figure 2** shows the transmittance (a) and refractive index (b) of AR coating of Base-SiO<sub>2</sub> and PEG-SiO<sub>2</sub>. As can be seen from **Figure 2(a)**, the transmittance of PEG-SiO<sub>2</sub> is more than 99.8%, which is more excellent than Base-SiO<sub>2</sub>. It is also found that the refractive index (**Figure 2(b)**) of PEG-SiO<sub>2</sub> is closer to 1.22, so that the coating has more excellent optical performance.

### 3.2. Chemical Analysis by FTIR Spectroscopy

**Figure 3** shows FTIR spectrum of AR coatingsofBase-SiO<sub>2</sub> and PEG-SiO<sub>2</sub>. Several characteristic absorption bands were observed in the range between 750 and 4000 cm<sup>-1</sup>. The absorption band observed around 2981 cm<sup>-1</sup> is due to stretching and bending of C-H bonds. The most intense absorption peak centered at 1085 cm<sup>-1</sup> is an asymmetry stretching vibration of Si-O-Si bonds and the peak observed at 800 cm<sup>-1</sup> is due to a symmetric stretching vibration of Si-O-Si bonds. The peak at 960 cm<sup>-1</sup> is attributed to the Si-OH groups and a shoulder around 1166 cm<sup>-1</sup> is related to stretching of Si-O-groups. It can be seen from the figure



**Figure 2.** Transmittance spectra (a) and curve of refractive index (b) for the substrate coated with silica AR coatings of Base-SiO<sub>2</sub> and PEG-SiO<sub>2</sub>.



**Figure 3.** FTIR spectrum of AR coatings of Base-SiO<sub>2</sub> and PEG-SiO<sub>2</sub>.

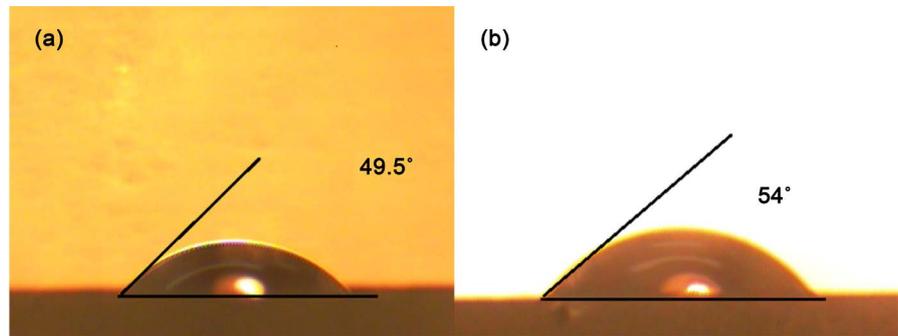
that there is no significant difference between the two coatings. Because the PEG200 does not contain special functional groups or its content is less (has been decomposed), no obvious absorption peak appears in the FTIR.

### 3.3. Analysis of Water Contact Angle

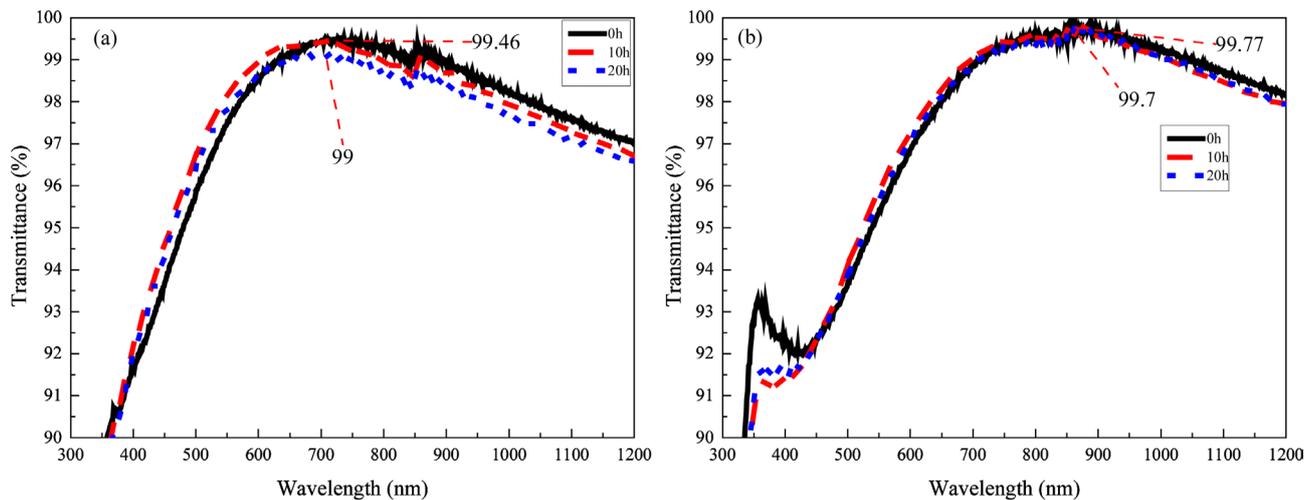
Figure 4 is the picture of water contact angle of AR coatings of Base-SiO<sub>2</sub> (a) and PEG-SiO<sub>2</sub> (b). It can be seen from the figure that the water contact angle between Base-SiO<sub>2</sub> (49.5°) and PEG-SiO<sub>2</sub> (54°) is almost the same. This is because PEG200 in the sol is to control the growth of sol particles [25] and does not introduce hydrophobic functional groups, the water contact angle does not change much (only 5°).

### 3.4. The Environmental Stability of UV Light for PEG-SiO<sub>2</sub>

Transmittance change spectra of AR coatings of Base-SiO<sub>2</sub> (a) and PEG-SiO<sub>2</sub> (b)



**Figure 4.** Picture of water contact angle of AR coatings of Base-SiO<sub>2</sub> (a) and PEG-SiO<sub>2</sub> (b).



**Figure 5.** Transmittance change spectra of Base-SiO<sub>2</sub> (a) and PEG-SiO<sub>2</sub> (b) in the UV light environment for 20 h.

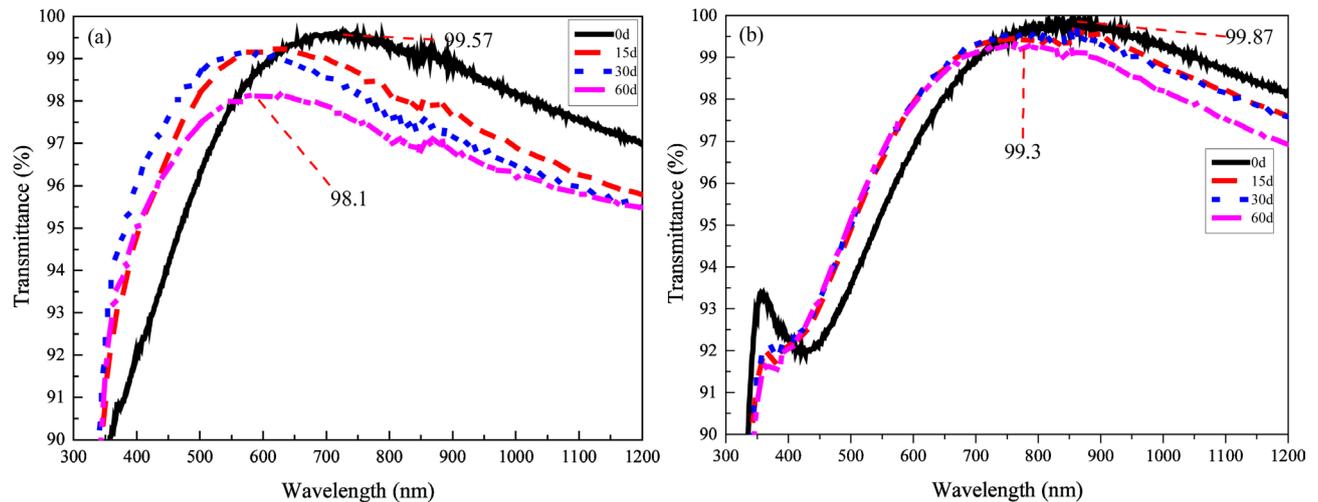
in the UV light environment for 20 h are shown in **Figure 5**. Base-SiO<sub>2</sub> and PEG-SiO<sub>2</sub> were put in UV irradiation box (power 1 kw) to achieve UV light environment. After 20 hours of UV light, the transmittance of Base-SiO<sub>2</sub> decreases greater than 0.45%, while the transmittance of PEG-SiO<sub>2</sub> decreases less than 0.1%.

### 3.5. The Environmental Stability of Humid Environment for PEG-SiO<sub>2</sub>

**Figure 6** shows Transmittance change spectra of Base-SiO<sub>2</sub> (a) and PEG-SiO<sub>2</sub> (b) in a humid environment for 2 months. Base-SiO<sub>2</sub> and PEG-SiO<sub>2</sub> were put in a closed drier with deionized water (RH > 90%) to achieve humid environment. After 2 months of humid environment, the transmittance of Base-SiO<sub>2</sub> decreases greater than 1.47%, while the transmittance of PEG-SiO<sub>2</sub> decreases less than 0.57%. Significantly, the environmental stability of AR coating is improved on the humid environment.

## 4. Conclusion

In this study, alkaline silica sol was prepared by sol-gel method and modified by adding appropriate amount of PEG200 to alkaline silica sol to obtain the cor-



**Figure 6.** Transmittance change spectra of Base-SiO<sub>2</sub> (a) and PEG-SiO<sub>2</sub> (b) in a humid environment for 2 months.

responding modified sol. The changes of transmittance, refractive index, FTIR and water contact angle of AR coatings of Base-SiO<sub>2</sub> and PEG-SiO<sub>2</sub> were discussed. The coating of the corresponding modified sol has a better transmittance than that of the unmodified sol. And finally, good environmental stability of AR coating is obtained in the UV light and humid environment.

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