Preparation of silica antireflection film based on sol-gel method

Zheyu Jiang¹, Qiuyi Wan¹, Jiarong Liu² and Xiujun Tian^{3*}

¹ Environmental Engineering, Lancaster University at Beijing Jiaotong University, Weihai, Shandong, 264200, China

² Environmental Engineering, Lancaster University at Beijing Jiaotong University, Weihai, Shandong, 264200, China

³ Environmental Engineering, Lancaster University at Beijing Jiaotong University, Weihai, Shandong, 264200, China

Abstract. Glass antireflection membrane can effectively increase the collection and utilization of sunlight by daylighting equipment, and has been widely used in solar energy related fields. Therefore, exploring the development of high-performance glass antireflection membrane is an essential topic in the current energy utilization research. This paper introduces the general situation of the preparation technology of antireflection membrane internationally, especially the specific method of producing antireflection membrane of silica by sol-gel method in the research. According to the analysis of the results, the significance of membrane surfactant which is similar to Triton X-100 was obtained, and the development prospect of this technology was discussed.

1 Introduction

With the development of the society, the development and utilization of new energy has become the focus of social attention. Among them, the collection and utilization of solar energy is one of the most significant topics. In order to protect the environment and improve the quality of production and life, the efficient utilization of solar energy is particularly important. Due to the reason of interface reflection, the optical system without coating treatment will weaken the intensity of the transmitted light, the optical system cannot operate efficiently consequently. Antireflection film is a kind of optical film with the widest application range and the largest output. The interference cancellation phenomenon generated when light propagates inside the film is used to effectively reduce the intensity of reflected light on the surface of the element, so that more light passes through the element in the form of transmission. Therefore, in order to solve the problem of interface reflection and improve energy utilization efficiency, it is necessary to coat antireflection film on the surface of the corresponding optical devices to improve the transmission, so as to significantly improve the operating efficiency of the optical system.

Since the 1950s, with the increase of the demand for antireflection film, the technology of high-performance antireflection film preparation has developed rapidly, and the types of antireflection film are becoming more and more abundant. Different types of anti-reflection membranes have different characteristics to meet the needs of different fields:

The SiO₂ antireflection film coating prepared by Hot Wire Chemical Vapor Deposition (HWCVD) has the properties of high rate and low residual stress. This antireflection film coating can be used for broadband gap materials and dielectric materials of solar cells^[1]. The SiO₂

antireflection film produced by introducing SiO₂ hollow nanospheres (SiO₂-HNSS) into flexible transparent conductive film (TCF) based on silver nanowires (AGNW) has excellent flexibility, adhesion and thermal stability, which can be widely used in wearable electronic products^[2]. The SiO₂ antireflection film prepared by liquid phase deposition method can change the concentration of H₂SiF₆ to control the surface characteristics and grain structure of the film to achieve lower reflectivity. This antireflection film has become a suitable antireflection film for polycrystalline silicon solar cells^[3].

In addition to the foregoing, sol-gel method is used in the preparation of new materials such as multifunctional synthetic membranes. Using Sol-gel method to prepare anti-reflection film requires lower reaction temperature, and the reaction is easier to meet the needs of practical application and promotion. Additionally, the component elements can achieve uniform doping on the molecular level. In the meantime, sol-gel method can also effectively adjust the microstructure of thin films. Therefore, with the development of laser technology and applications, sol-gel method has been used as a common method to prepare nanomaterials and thin films with special structures^{[4]-[7]}.

The purpose of this research project is to prepare silica antireflection film by sol-gel method under the condition of acid catalysis, and test the performances of transmittance and friction resistance, so as to explore the methods to improve these relevant performances. Therefore, based on the traditional sol-gel method to prepare glass antireflection film, this research project explores the feasibility of improving various properties of antireflection film, in order to promote the progress of the performance of glass antireflection film, and then improve the yield, so as to facilitate the application of glass antireflection film in a wider range.

* Corresponding author's e-mail: xjtian@bjtu.edu.cn

2 Materials and Methods

2.1 Introduction to sol-gel method

Sol-gel method is a kind of material preparation method which developed in the 1960s. It was not until 1971 that the German scholar H. Dislich first obtained multi-component solid materials by sol-gel method that the sol-gel process attracted extensive attention of the scientific community and was rapidly developed, and accordingly, various optical films, such as antipermeability films and high reverse films, were prepared gradually^[8]. In this method, metallic inorganic substances or metal alkyl salts are used as raw materials, which are mixed uniformly in

liquid phase. Then, a stable transparent sol system is formed in the solution through hydrolysis reactions and condensation reaction. After aging, the colloidal particles polymerize slowly, and the gel with three-dimensional space network structure formed. After drying, sintering and curing, the gel whose networks are filled with solvent that has lost the fluidity, can be prepared into molecular and even nanometer substructure materials.

2.2 Experimental Reagent and Instrument

The main raw materials and chemical reagents used in this experiment are shown in Table 1.

Table 1. List of raw materials and chemical reagents.

Reagent	Chemical formula	Purity	Manufacturer
Tetraethyl orthosilicate	$\text{Si}(\text{OC}_2\text{H}_5)_4$	AR	Sinopharm Shanghai Chemical Reagent Co., Ltd
Tetrabutyl titanate	$\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$	AR	Sinopharm Shanghai Chemical Reagent Co., Ltd
Anhydrous ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	AR	Sinopharm Shanghai Chemical Reagent Co., Ltd
Hydrochloric acid	HCl	AR	Sinopharm Shanghai Chemical Reagent Co., Ltd
Deionized water	H_2O	Primary distillation	Self-control
TritonX-100	$\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$	AR	Sigma Gade chemical plant

The main instruments and equipment used in this experiment are shown in Table 2.

Table 2. List of the equipment and instruments in the experimental process.

Name	Model	Manufacturer
Magnetic stirrer	JK-SMS-HS	Shanghai Jingxue Scientific Instrument Co., Ltd
Uniform speed lift coater	Self-made	Huiyin Group
Box incinerator	S12 09-10	Weihai Golden sun solar thermal power generation equipment Co., Ltd
Spectrophotometer	UV-3600	Shanghai Optical Instrument No.5 factory
Metallurgical microscope	4XC	Shanghai Optical Instrument No.5 factory
Linear abrasion tester	5750	Changzhou Sanfeng Technology Co., Ltd
Polyvinylidene fluoride 0.22 micron filter membrane (F model)	Q/IEF J01-1997	Shanghai Xingya purification material factory
Biochemical incubator	SPX-100B-Z	Shanghai Boxun Industry & Commerce Co.,Ltd. Medical Equipment Factory
Taber rubber friction head	MIL-E-12397	Shenzhen Guangxinda Trade Co., Ltd

2.3 Preparation of sol-gel

2.3.1 Preparation of SiO_2 sol-gel (method 1)

Mix $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{C}_2\text{H}_5\text{OH}$ reagent proportionally and stir for 30 minutes. Also mix H_2O , $\text{C}_2\text{H}_5\text{OH}$ and HCl reagent proportionally and stir for 20 minutes. The volume ratio of the final monolithic sol preparation reagent is $\text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O} : \text{HCl} : \text{Si}(\text{OC}_2\text{H}_5)_4 = 53.4:8:0.088:20$. Mix the above solution and stir for 2 hours. The speed of

magnetic agitator is controlled at 800~1000 r/min, so that the reaction can be fully contacted between reagents. After obtaining the colorless and transparent SiO_2 sol, it was aged in a biochemical incubator for seven days and the aging temperature was controlled at 30°C. Finally, SiO_2 plating solution was obtained for testing.

2.3.2 Preparation of SiO_2 sol-gel (method 2)

Mix $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{C}_2\text{H}_5\text{OH}$, H_2O and HCl reagent proportionally and stir for 2 hours, and the volume ratio of the final monolithic sol preparation reagent is $\text{C}_2\text{H}_5\text{OH} :$

$\text{H}_2\text{O} : \text{HCl} : \text{Si}(\text{OC}_2\text{H}_5)_4 = 200.14 : 6.68 : 0.012 : 20.65$. The speed of magnetic agitator is controlled at 800~1000 r/min, so that the reaction can be fully contacted between reagents. After obtaining the colorless and transparent SiO_2 sol, it was aged in a biochemical incubator for seven days and the aging temperature was controlled at 30°C. Finally, SiO_2 plating solution was obtained for testing.

2.3.3 Preparation of SiO_2 sol-gel with different Triton X-100 content

Mix $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{C}_2\text{H}_5\text{OH}$, H_2O , HCl and Triton X-100 reagent proportionally and stir for 2 hours, and the volume ratio of the final monolithic sol preparation reagent is $\text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O} : \text{HCl} : \text{Si}(\text{OC}_2\text{H}_5)_4 = 237.77 : 7.936 : 0.0143 : 31.482$. The speed of magnetic agitator is controlled at 800~1000 r/min, so that the reaction can be fully contacted between reagents. After obtaining the colorless and transparent SiO_2 sol, it was aged in a biochemical incubator for seven days and the aging temperature was controlled at 30°C. The final SiO_2 plating solution containing the Triton X-100 is obtained for testing.

2.4 Practical Operation Procedure of Coating

2.4.1 SiO_2 sol-gel coating prepared by two methods

Wash the glass sheet with detergent and deionized water for 15 minutes, then dry with blower.

Method 1: The SiO_2 sol-gel coatings were subjected to four different tensile speeds of 2 mm/s, 2.2mm/s, 2.4mm/s and 2.5 mm/s, respectively. Put the coated glasses into the

muffle furnace at 400°C to be solidified for 1 hour. The transmittance was measured after a short cooling time.

Method 2: The SiO_2 sol-gel coatings were subjected to four different tensile speeds of 7 mm/s, 7.2mm/s, 7.33mm/s and 7.5 mm/s, respectively. Put the coated glasses into the muffle furnace at 400°C to be solidified for 1 hour. The transmittance was measured after a short cooling time.

2.4.2 SiO_2 sol-gel coatings with Triton X-100

By the preparation and transmittance measurement of silica gel in the first two methods, it is found that the average transmittance of silica gel prepared by method 2 is high, and the optimum tensile speed is 7 mm/s. Therefore, the second method of preparing silica sol and its solvent ratio are used to prepare it. The prepared sols were divided into 6 groups and the Triton X-100 was added from 1 to 6 mL, respectively.

Clean the glass sheet in the same way. 6 groups of sols with 7 mm/s pull-up speed. Put the coated glasses into the muffle furnace at 400°C to be solidified for 1 hour. The transmittance was measured after a short cooling time. Finally, suitable samples are selected for friction analysis.

3 Results & Discussion

3.1 Experimental results of acid-catalyzed silica sol-gel and discussion

Table 3 shows the average transmittance of each SiO_2 sol-gel film layers catalyzed by acid.

Table 3. Average transmittance of SiO_2 sol-gel layers catalyzed by acid.

Sample	1-SiO ₂ -1	1-SiO ₂ -2	1-SiO ₂ -3	1-SiO ₂ -4	2_SiO ₂ _1	2_SiO ₂ _2	2_SiO ₂ _3	2_SiO ₂ _4
Average transmittance (%)	94	93.9	93.7	93.7	94.5	93.8	94.3	94

As can be seen from Table 3, when the traction speed is 7 mm/s, the average transmittance is the highest. And from figure 1 the transmittance is the highest when the

wavelength is about 1800 nm. The solar transmittance is good in the visible range of 400-760 nm, and the transmittance between 400-440 nm is high.

Figure 1. Transmittance of method 1.

Figure 2. Transmittance of method 2.

3.2 Experimental results of silica sol-gel membrane layer with Triton X-100 and discussion

Table 4. Average transmittance of the SiO₂ sol-gel films containing the Triton X-100.

Sample	2_SiO2_1	3_SiO2_1	3_SiO2_2	3_SiO2_3	3_SiO2_4	3_SiO2_5	3_SiO2_6	3_SiO2_2_5
Average transmittance (%)	94.5	95.2	95.5	95.5	95.3	95.9	94.5	93.2

It can be seen that Triton X-100 improves the overall transmittance of the antireflection film.

Figure 3. Transmittance of sol with Triton X-100.

By comparison, the average transmittance increased significantly after the addition of Triton X-100. When the amount of Triton X-100 is 5 ml, the average transmittance is close to 96%. When the transmittance of each sample was measured, the sample 2 was rubbed with MIL-E-12397 plate friction head for 5 times, and the sample 3_SiO2_2_5 was obtained in Table 4. All samples have good

transmittance in the infrared region. In addition, its transmittance in visible light range is also increased compared with the original transmittance. The transmittance of silica gel film before and after friction is compared, as shown in figure. 4.

Figure 4. Transmittance before and after friction.

Then, the changes of the film surface before and after friction are observed, as shown in graph 1, respectively.

Figure 5. (a) Surface of film before friction; (b) Surface of film after friction

After five times of friction, some tiny cracks caused by friction caused a slight decrease in the transmittance of the coating.

4 Conclusions

(1) For silica sol-gel prepared under acid-catalyzed conditions, when the traction speed is 7mm/s, the average transmittance of the prepared antireflection film is the highest for visible light between 400 and 440 nm.

(2) Regarding silica sol-gel, due to the addition of Triton X-100, the overall transmittance is higher than that of the enhanced film without Triton X-100 (when the addition of Triton X-100 is 5 mL, the average transmittance reaches 96%), and it is obviously improved in the visible wavelength range.

Therefore, in the process of preparing SiO₂ antireflection membrane by sol-gel method under acid catalytic conditions in the future, researchers can consider adding membrane surfactants similar to Triton X-100 to explore the best ratio of related reagents in order to prepare a more perfect multifunctional antireflection membrane.

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