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Study on the Preparation and Properties of Inorganic Silica Single-Layer Film

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The silica single-layer film catalyzed by hydrochloric acid was prepared on the glass matrix with tetraethyl orthosilicate and absolute alcohol as main raw materials by sol-gel method. The reaction mechanism of sol-gel method included hydrolysis reactions and polymerization reactions. The samples were characterized by visible spectrophotometer, X-ray diffraction and thermal analysis (TG and DTA). Results showed that the light transmittance of the silica single-layer film was enhanced remarkably. X-ray diffraction results indicated that the single-layer film possessed amorphous characteristic. Adhesion tests showed that the adhesion force between the silica single-layer film and the glass matrix was very strong. Thermal analytical results demonstrated that silica would absorb heat when it transformed from amorphous structure to crystal structure.

Keywords: Sol-gel method, Tetraethyl orthosilicate, Silica film, Transmittance, Property.

INTRODUCTION

Silica films are widely used in photoelectric materials, isolation techniques, chemical sensors and biosensors, preservative treatments, *etc.*[1-4]. There are various kinds of preparation methods about silica films, such as oxidization, chemical vapor deposition(CVD), sol-gel method and condensation polymerization[5,6]. The sol-gel method is one of the most promising methods for its easy operation, low operating temperature and uniform composition of the film, which has been utilized broadly in preparing glass, ceramic, film, coating, fibre, composite materials and nanoparticles. Thin films can be produced directly from the solution by some simple techniques, such as dip-coating, spin-coating and spin-drawing. Due to the simple equipments needed, high efficiency and the uniform film produced, dip-coating method is often employed in preparing films through sol-gel method. The thickness of a film depends on the concentration of the sol, the viscosity and the pulling rate.

Antireflection film can enhance the transmittance of light in certain wavenumber range and its applications have been involved in medical science, military science, space exploration and other fields[7,8]. A good antireflection film not only has high transmittance, but also possesses proper hardness, heat-resisting properties and strong adhesion force between the film and the matrix. According to the existing literatures, magnesium fluoride, titanium dioxide, lead sulfide, lead selenide and silica are common materials for antireflection films[9,10].

In this paper, the silica single-layer film catalyzed by HCl was prepared on the clean glass matrix with tetraethyl orthosilicate and absolute alcohol as main raw materials by the sol-gel method. We obtained silica sol first and then used dip-coating technique to prepare silica single-layer film on glass matrix. The reaction mechanism of sol-gel method were also discussed. The transmittance, structure, thermostabilities of the silica single-layer film were investigated by visible spectrophotometer, X-ray diffraction, Fourier transform infrared spectroscopy and thermal analysis.

EXPERIMENTAL

In 1st step, 30 mL absolute alcohol was poured into a beaker and then 5.5 mL tetraethyl orthosilicate was added. The mixture solution was stirred for 10 min. This is component A. In 2nd step, 20 mL absolute alcohol, 0.5 mL concentrated HCl and 1 mL double-distilled water were measured, mixed together and stirred for 5 min. This is component B. In 3rd step, the component B transferred into a separatory funnel was added into the component A slowly and the mixture solution obtained was stirred for 0.5 h. Finally, the solution of third step was shifted into a flat bottom flask and was refluxed for 0.5 h under the action of the condenser pipe. After the mixture solution was cooled to room temperature and silica sol was prepared. The silica sol was aged for 4 days before preparing the silica single-layer film.

The silica single-layer film was prepared by dip-coating technique. The glass matrix was cleaned by ultrasonic cleaning with detergent, water and absolute alcohol, respectively. The glass matrix was dipped into the silica sol and placed for 10 min. Next, the glass matrix was put out of the silica sol at a speed of 3.5 cm min^{-1} using a self-prepared coating machine. The silica single-layer film was prepared successfully on the glass matrix.

722E visible spectrophotometer was used to measure the transmittance of the silica single-layer film. X-Ray diffraction (XRD) (model: Shimadzu maxima XRD-7000) was employed to investigate the crystallinity of the film using CuK_α target at 40 kV and 30 mA. ZRY-2P thermal analyzer was used to analyze the thermostability with a heating rate of 10 ºC min^{-1}. TJ270-30 Fourier transform infrared spectrometer (FTIR) was introduced to analyze the structure of the film. The method of cross-shaped frame was used to evaluate the adhesive force between the silica single-layer film and the glass matrix.

RESULTS AND DISCUSSION

Reaction mechanisms of sol-gel method: In the existing of acid catalyst, hydrolysis reactions and polymerization reactions will occur for tetraethyl orthosilicate[3]. The hydrolysis reactions are as follows:

$$Si(OC_2H_5)_4 + H_2O \rightarrow Si(OH)(OC_2H_5)_3 + C_2H_5OH$$
$$Si(OH)(OC_2H_5)_3 + H_2O \rightarrow Si(OH)_2(OC_2H_5)_2 + C_2H_5OH$$
$$Si(OH)_2(OC_2H_5)_2 + H_2O \rightarrow Si(OH)_3(OC_2H_5) + C_2H_5OH$$
$$Si(OH)_3(OC_2H_5) + H_2O \rightarrow Si(OH)_4 + C_2H_5OH$$

After the hydrolysis reactions of TEOS proceed thoroughly, silica sol is prepared. Then, the polymerization reactions occur on the glass matrix as follows:

$$\equiv Si\text{-}OC_2H_5 + C_2H_5O\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Sia\equiv + C_2H_5OC_2H_5$$
$$\equiv Si\text{-}OC_2H_5 + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Sia\equiv + C_2H_5OH$$
$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$$

Transmittance of the silica single-layer film: Fig. 1 shows the transmittance of the glass matrix and the silica single-layer film. It is clear that the transmittance of the silica single-layer film is higher than that of the glass matrix in the wavelength range of 400-800 nm. The transmittance of the glass matrix and the silica single-layer film are both increasing first and then decreasing with the rise of the wavelength. The transmittance of the silica single-layer film reaches the utmost, 95.5 %, at the wavelength, 540 nm. According to the classic optics theory[8], the coating will decrease the transmittance of the matrix when the refractive index of the coating is higher than that of the matrix. On the contrary, the coating will increase the transmittance of the matrix when the refractive index of the coating is lower than that of the matrix. The silica single-layer film prepared by sol-gel method had lower transmittance. As a result, it improved the transmittance of the glass matrix remarkably.

FTIR spectra of the silica single-layer film: Fig. 2 shows the FTIR spectra of the silica single-layer film. The absorption peaks, 455, 809 and 1083 cm^{-1}, represent the antisymmetry stretching vibration, symmetry stretching vibration and bending vibration of the Si-O-Si bond, respectively. The absorption peaks, 3400 and 965 cm^{-1}, are the antisymmetry stretching vibration and the symmetry stretching vibration of the Si-OH functional group. The absorption peak of 1631 cm^{-1} is caused by the water in air it is noted that the absorption peak of 2450 cm^{-1} represents the vibration of $Si\text{-}O\text{-}C_2H_5$, which showed that there was a minor of not hydrolyzed $Si\text{-}O\text{-}C_2H_5$ groups and the hydrolytic reaction of TEOS was not thoroughly in this study.

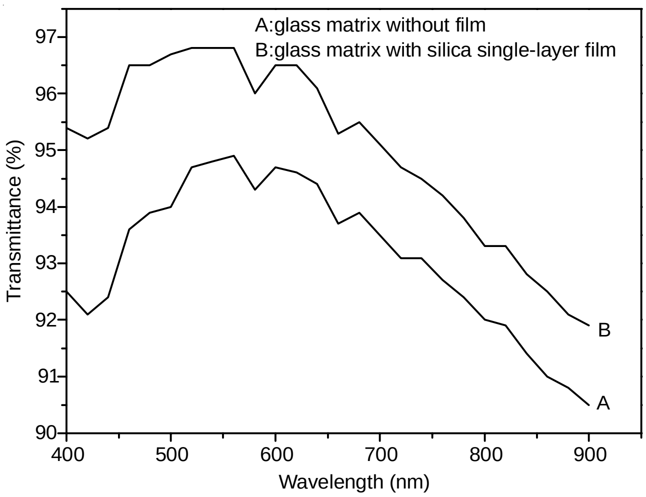


Fig. 1. Transmittance of the glass matrix and the silica single-layer film

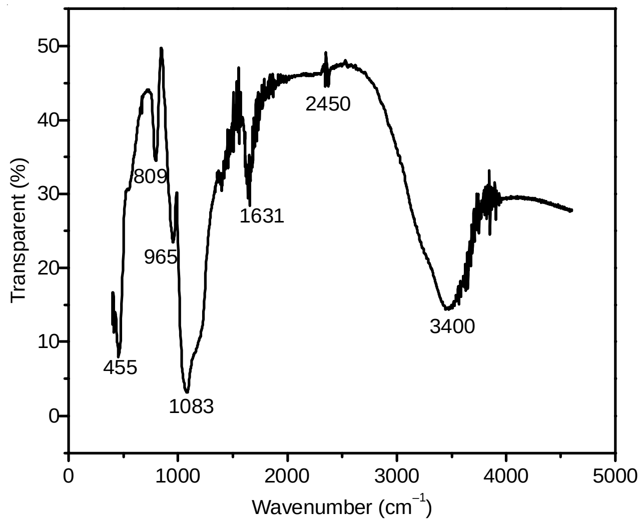


Fig. 2. FTIR spectra of the silica single-layer film

X-Ray diffraction of the silica single-layer film: Fig. 3 shows the X-ray diffraction of the silica single-layer film. There was a wide peak in the range of 15 and 30º, which was the standard amorphous diffraction peak of silica. Although there were four strong diffraction peaks ((201), (202), (312), (401)) in the X-ray diffraction patterns, the silica single-layer film prepared possessed disorder and network structure and had amorphous characteristic . It is well known that the structure of a material can determine the properties of the material. Similarly, this amorphous structure is beneficial to improve the light transmittance properties of the glass.

Thermal stability of the silica sol: Fig. 4 shows the TG and DTA curves of the silica sol. There are three weight loss periods in the TG curve. The first break a 50 and 100 ºC was the serious weight loss, which referred to the evaporation of adsorption water and absolute alcohol. The second break in 100 and 450 ºC region and the weight loss became slow. In this temperature region, some chemical reactions happened

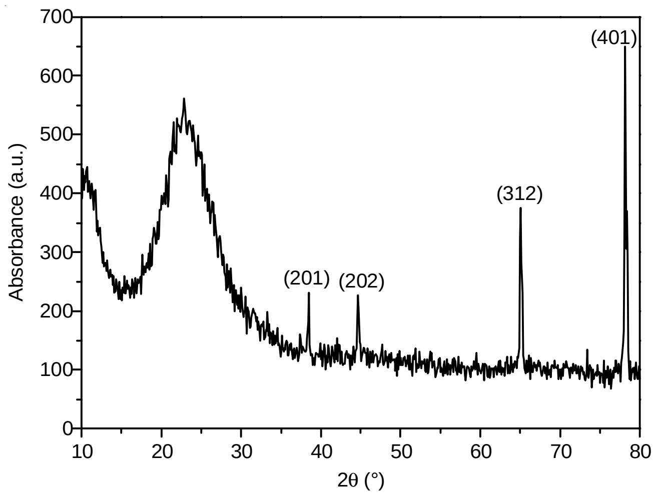
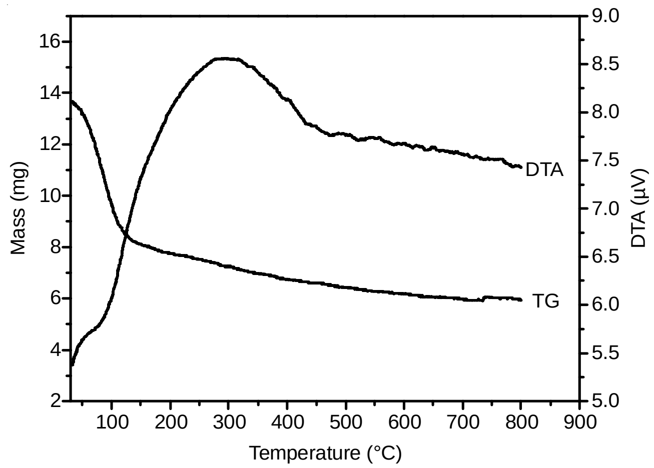


Fig. 3. X-Ray diffraction patterns of the silica single-layer film



F ig. 4. TG and DTA curves of the silica single-layer film

between the organic materials in the silica sol and these reactions would let out heat. Therefore, a big exothermic peak occurred on the DTA curve. The third change occurred in 450 and 800 ºC temperature region and the weight loss became stable, which means the silica has transformed into silica gel and there is no chemical reactions. The thermal properties of silica gel is excellent and its mass remains stable with the rising of temperature. So, in this period, DTA curve is almost a straight line.

Adhesion force between silica single-layer film and glass matrix: The comparison chart of adhesion force between a film and matrix is shown in Fig. 5. In this study, we used a special tool to draw many cross frames on the surface of the silica single-layer film. Then, a adhesive tape for a special purpose was employed to determine the adhesion force between the silica single-layer film and the glass matrix. After the adhesive tape was taken down, the surface images were observed. Results showed that the adhesion force between the silica single-layer film belonged to 0 class. This is because a chemical bonding between the TEOS and Si-OH of the glass matrix was formed. A lot of network with ≡Si-O-Si≡ functional groups existed on the surface of the glass matrix. This strong chemical bonding is responsible for the high adhesion force between silica single-layer film and glass matrix.

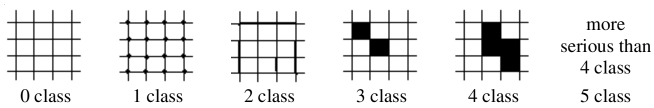


Fig. 5. Comparison chart of adhesion

Conclusion

The silica single-layer film with obvious antireflection effect was successfully prepared on the glass matrix by sol-gel method. The light transmittance of the silica single-layer film was higher than that of blank glass matrix in the range of visible light. The reaction mechanisms included hydrolysis reactions and polymerization reactions. The silica single-layer film possessed amorphous characteristic and good thermo-stabilities. The adhesion between the silica single-layer film and the glass matrix was very strong.

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