Preparation and Optical Properties of TiO$_2$-SiO$_2$ thin films by Sol-gel Dipping Method

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Abstract. TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ thin films were prepared by sol-gel dipping method on glass substrates. The pyrolysis behavior of TiO$_2$ and SiO$_2$ dry gel were tested by differential thermal analysis (DTA). The microstructure and optical properties of the TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ were studied by X-ray diffraction (XRD) and ultraviolet and visible spectrophotometer. The results showed that the phase structure of the films was affected by the composition. All the films were transparent in the visible region. Meanwhile, the transparency of SiO$_2$ was better than TiO$_2$ and TiO$_2$-SiO$_2$ composite film. The band-gap of the TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ thin films were 3.79, 4.01 and 3.91.

1. Introduction
TiO$_2$ has attracted much attention due to its non-toxic, stable chemical properties, excellent optical properties, and super hydrophilicity under UV irradiation [1, 2]. Moreover, anatase TiO$_2$ has photocatalytic activity [3]. As surface modification materials, TiO$_2$ film has been widely investigated in self-cleaning application [4]. SiO$_2$ is another kind of surface modification materials. SiO$_2$ film has super hydrophilicity because of the abundant hydroxyl groups on the surface. The refractive of SiO$_2$ is about 1.45, which is close to that of glass. SiO$_2$ film is often used as transparent anti-fogging materials [5, 6].

In recent years, in order to combine the advantages of TiO$_2$ and SiO$_2$, many experiment works on TiO$_2$-SiO$_2$ composite materials has been reported. Chemin et al. reported transparent, anti-fogging and self-cleaning anatase TiO$_2$-SiO$_2$ films on polymer substrates at low temperature by APCVD [7]. Liu et al. reported a facile soft templating rout for preparing TiO$_2$-SiO$_2$ nanospheres [8]. Besides, Vázquez-Velázquez et al. found polymer nanocomposite coatings based on TiO$_2$-SiO$_2$ films has high transparent and super hydrophilicity [9]. TiO$_2$-SiO$_2$ composite films can act as multifunction coatings in surface modification.

So far, the comparison of microstructure and optical properties of TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ materials is scarcely reported. Many films method has been used in composite films preparation. Among them, sol-gel method has the easy control composition and formation uniform film in large area. Here, we prepared TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films on glass substrates by sol-gel dipping coating method. The microstructure and optical properties were investigated.

2. Experimental

2.1. Materials
Tetrabutyl titanate (C₁₆H₃₆O₄Ti, CP), and ethyl silicate (C₈H₂O₄Si, AR) were provided by Sinopharm Group Co. Ltd, China. Acetone (CH₃COCH₃, AR), nitric acid (HNO₃, AR) and alcohol (C₂H₅OH, AR) were purchased by Xilong chemical co. Ltd, China. The sail brand glass slide substrates made in China was used in our experiment. The distilled water was self-made in our laboratory.

2.2. Sample preparation and characterization
Tetrabutyl titanate and ethyl silicate were used as Ti and Si source. Ethanol is used as solvent and nitric acid as catalysts. The detail process of TiO₂ or SiO₂ sol can be found elsewhere [1, 10]. The mole ratio of Ti and Si was 1:1 in TiO₂-SiO₂ solution. After 24h, the solutions were used to prepare film.

The glass substrates were ultrasonically cleaned in Acetone, alcohol and distilled water. The films were prepared by dip coating with the withdraw speed of 2000 μm/s. The wet films were dried at 100°C for 10 minutes. The process was repeated twice for increasing the film thickness. The dried TiO₂, SiO₂ and TiO₂-SiO₂ films were annealed at 500°C for 60 minutes.

Differential thermal analysis (DTA) was used to investigate the thermal decomposition of TiO₂ and SiO₂ xerogel. To evaluate the microstructure of TiO₂, SiO₂ and TiO₂-SiO₂ materials, the TiO₂, SiO₂ and TiO₂-SiO₂ powders were prepared by the corresponding sol. The annealing process of the powders was the same as that of the films. The microstructure of the powders were analyzed by X-ray diffraction (XRD) measurement with Cu Kα radiation (λ=0.154056 nm) in the 2θ range of 10-80°. Transmittance and absorption spectra of the films were characterized by ultraviolet and visible spectrophotometer in the wavelength range of 190-1100 nm. The optical band gap of the films was studied based on the absorption spectrum.

3. Results and discussion
Figure 1 was the DTA curves of TiO₂ and SiO₂ xerogel. The endothermic peak about 100°C was in TiO₂ and SiO₂ DTA curves due to the evaporation of alcohol and water. The exothermic peak about 210 °C and 310 °C for TiO₂ DTA curve, 358 °C for SiO₂ DTA curve was because of decomposition of organic compounds. A sharp exothermic peak about 510 °C for TiO₂ DTA curve was corresponding to crystallization. No other peaks appeared in the DTA curves.

To determine the microstructure of TiO₂, SiO₂ and TiO₂-SiO₂, XRD was carried out. Figure 2 shows the XRD patterns of TiO₂, SiO₂ and TiO₂-SiO₂ powders in the 2θ range of 10-80°. The corresponding diffraction index has been marked out in the graph. For pure TiO₂, anatase phase (JCPDS No. 21-1272) was detected and no other phase was observed. The broad weak peak around 23° indicated that SiO₂ was amorphous. SiO₂ cannot crystallize when anneal at 500°C. This is consistent with DTA results. For the TiO₂-SiO₂ composite film, only peaks associated to anatase TiO₂ were appeared. The diffraction peak of TiO₂ in the composite film was broadened and weakened. It means that the crystallization degree of TiO₂-SiO₂ composite film decreased slightly. The (101) peak
of TiO$_2$-SiO$_2$ composite film has strong background. It indicated that the TiO$_2$-SiO$_2$ composite film was composited of antase TiO$_2$ and amorphous SiO$_2$.

Figure 2. XRD patterns of TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$

Transmittance spectra of TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films were shown in Figure 3. For compassion, the transmittance spectrum of glass was also shown in Figure 3. The transmittance of the films was more than 75% in the wavelength range between 400-800 nm. It means that all the films were transparent in visible range. The SiO$_2$ film has largest transmittance, which is slightly lower than that of glass substrate. This behavior may be attributed to the refractive index of SiO$_2$ is similar to glass substrate. Therefore, SiO$_2$ is often used to antireflection material [11, 12].

The wavy nature in the transmittance spectra of TiO$_2$ and TiO$_2$-SiO$_2$ film is due to interference effect. There was shifting in the position of maximal and minimum transmittance for TiO$_2$-SiO$_2$ film to shorter wavelength. This is due to the refractive index of TiO$_2$-SiO$_2$ film is lower than TiO$_2$ film. The preparation process of the films in our experiment is the same. There is no significant difference in thickness of the films. Therefore, smaller refractive index results in the blue shift of the interference peak by the equation $2nd = m\lambda$ (where $n$ is the refractive index, $d$ is the thickness of the film, $m$ is the interference number, $\lambda$ is the interference wavelength).

Figure 3. Transmittance spectra of TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films

Figure 4 gives the absorbance spectra of TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films. All the films have strong absorption at wavelength below 300 nm. The absorbance decreased sharply between 300 nm and 350 nm. The absorption edge of the films can be obtained by making tangents (point lines in the figure), which is 321.9 nm, 331.0 nm and 341.2 nm for SiO$_2$, TiO$_2$-SiO$_2$ and TiO$_2$ film. The relation between the optical band gap and absorption edge is as follow: $E_g = \frac{1293}{\lambda}$, where $E_g$ is the band gap, $\lambda$ is the absorption. Based on the equation, the band gap is 3.79 eV, 3.91 eV and 4.01 eV for TiO$_2$, TiO$_2$-SiO$_2$ and SiO$_2$ film.
Figure 4. Absorption spectra of TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films

4. Conclusion
In the present work, highly transparent stable sols were prepared for coating TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films by sol-gel method. DTA and XRD reveals that pure TiO$_2$ can crystallize as anatase phase at 500°C, but SiO$_2$ was amorphous. Meanwhile, anatase TiO$_2$ and amorphous SiO$_2$ appeared in TiO$_2$-SiO$_2$ composite material. TiO$_2$, SiO$_2$ and TiO$_2$-SiO$_2$ films were successfully prepared on glass substrates. All films showed good transmittance in the visible wavelength range. The transmittance of SiO$_2$ is higher than that of TiO$_2$ and TiO$_2$-SiO$_2$ composite film. This may be due to the refractive index of SiO$_2$ is close to that of glass substrate. The optical band gap of TiO$_2$, TiO$_2$-SiO$_2$ and SiO$_2$ film is 3.79 eV, 3.91 eV and 4.01 eV, respectively.

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