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ARTICLE

Hydrothermal Synthesis and UV Irradiation Shielding Performances of Nanometer Cerium (IV) Oxide Thin Films

Liu Lianli, Liu Yujing, Sun Tong, Xu Shuying, Wang Lili, Zhou Li

Bohai University, Jinzhou 121013, China

Abstract: The cerium oxide films with high refractive index and good UV irradiation shielding performance were synthesized on the glass substrates by a hydrothermal method using $Ce(NO_3)_3 \cdot 6H_2O$ and $CO(NH_2)_2$ as raw materials. The films and the powders prepared at the same time were characterized by SEM, XRD, FT-IR, ellipsometer and UV-vis. The influences of original Ce(Ⅲ) concentration and urea dosage on cerium oxide films were researched. The results show that the films are smooth and the particles are small at low Ce(Ⅲ) concentration and urea dose. The sediments are cerium oxide and $Ce(CO_3)_2O \cdot H_2O$ crystal, and silicon of substrate is involved in hydrothermal reaction. Meanwhile, the film refractive indexes are affected by film compact and chemical composition. Both of absorbance and absorption wavelength edge become big with increasing of Ce(Ⅲ) concentration and urea dose, and the main influence factors are the film thickness and composite semiconductors. The optimal Ce(Ⅲ) concentration is 0.008 mol/L, and the optimal urea dosage is 0.06 g.

Key words: cerium oxide film; hydrothermal synthesis; refractive index; ultraviolet irradiation

Excessive exposure to ultraviolet rays (UV) in sunlight could induce skin cancer and paper, fabrics and furniture to fading and deteriorating. And it causes harmful damage to the human body such as premature and skin cancer [1, 2]. Shielding from UV irradiation was of interest in many fields, e.g. museum windows, commercial high-resolution displays and so on. Therefore, excellent sunscreen materials for UV-shielding have received considerable attention, and some progresses have been made [3,4]. Recently, the synthesis of inorganic nano-materials has attracted substantial attention from many of the researchers because of the potential of inorganic materials [5]. Ultrafine ceria (CeO_2) has ideal characteristics for using as a broad-spectrum inorganic sunscreen in personal-care products. It is relatively transparent to visible light, however, its ultraviolet radiation absorption properties are excellent[6, 7].

In recent years, various successful strategies are used for the fabrication of inorganic nanometer films onto glass including hydrothermal synthesis [8], sol-gel[9], plasma spray physical vapor deposition [10], chemical solution deposition method[11] and spray pyrolysis method [12, 13]. Among all the solution methods, the hydrothermal process is considered to be a promising method. In general, the hydrothermal process could significantly shorten the required reaction time and low the temperature [14-16]. Moreover, materials in the form of film were important in many practical uses. Therefore, it was highly desirable to fabricate a material into thin film.

In this paper, thin films of cerium oxide deposited on K9 glass substrate were synthesized by a hydrothermal method. The main objective is to determine the influences of cerium (III) nitrate hexahydrate concentration and urea dosage on the growth of cerium oxide films. And the performances of the samples were assessed by refractive index and UV-Vis.

1 Experiment

Cerium(Ⅲ) nitrate hexahydrate and urea was chosen as precursor for cerium oxide films synthesis, both of which were analytical reagents, and they were prepared to solution by distilled water. The K9 glass with a dimension of 30 mm

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Corresponding author: Sun Tong, Ph. D., Professor, College of Chemistry, Chemical Engineering and Food Safety, Bohai University, Jinzhou 121013, P. R. China, Tel: 0086-416-3400302, E-mail: jzsuntong@sina.com

×30 mm served as substrates, which were ultrasonically cleaned in advance by distilled water and absolute ethyl alcohol. The deposition process was performed under hydrothermal conditions in a teflon-lined stainless steel autoclave. First of all, $Ce(NO_3)_3 \cdot 6H_2O$ and urea are dissolved in 70 mL distilled water. Six drops of 10% H_2O_2 was dropped into precursor solution. Then, the precursor solution was added into the autoclave, and a substrate was set vertically in the solution. The autoclave was sealed tightly and kept at 130 °C for 7 h. The autoclave was cooled down to room temperature. Afterwards, the substrate coated with thin solid films was taken out, rinsed with distilled water to remove soluble impurities, and finally dried at 60 °C. The powders were cleaned in distilled water for three times and then dried at 80 °C.

The powders were characterized by means of X-ray diffraction (D-max-RB, Rigaku, D8-Advance, 40 kV and 20 mA, Cu Kα) and FT-IR (scimitar 2000 near FT-IR spectrometer, Varian). The films were characterized by scanning electronic microscopy (SEM-505, Philips) and atomic force microscope (AFM XE-70, Park Systems), elliptic polarization thickness gauge (SGC-2, Gang dong), ultraviolet and visible spectrophotometer (UV-2550, Shimadzu Corporation).

2 Results and Discussion

2.1 SEM analysis of the films

Cerium(Ⅲ) nitrate solution with different Ce(Ⅲ) concentrations and 0.10 g urea were thoroughly mixed and hydrothermally heated at 130 °C for 7 h. SEM was used to investigate surface morphologies of the cerium oxide films, and the results are shown in Fig.1.

From Fig.1 it can be seen that the morphologies of the samples are affected by Ce(Ⅲ) original concentration. The film is smooth and the particles are small at low concentration, however, there are big and non-uniform particles on the films at high concentration. This may be that low Ce(Ⅲ) concentration makes reaction slow, and the particles are deposited on the substrates tardily, so small particles are uniformly distributed on the film surface. Whereas, a high reactant Ce(Ⅲ) concentration will accelerate reaction velocity, and the particles are deposited on the substrates too fast, so there are big and non-uniform particles under the same hydrothermal reaction condition. The film morphologies are similar at Ce(Ⅲ) concentration of 0.008 mol/L and 0.011 mol/L. To further research the film morphology, we measured these two films using AFM, and the roughness data (*R*q) from AFM images are 33.107 and 33.256 nm, respectively. So the film morphologies and roughness are nearly identical.

0.005 mol/L cerium(Ⅲ) nitrate solution and different dosage of urea were thoroughly mixed and hydrothermally heated at 130 °C for 7 h. SEM is used to investigate the surface morphologies of the cerium oxide films, and the results were shown in Fig.2.

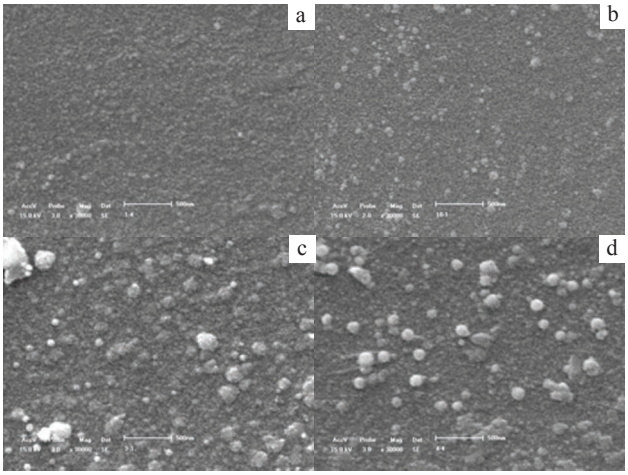

Fig.1 SEM images of cerium oxide films prepared with different $Ce(NO_3)_3 \cdot 6H_2O$ concentrations: (a) 0.002 mol/L, (b) 0.005 mol/L, (c) 0.008 mol/L, and (d) 0.011 mol/L

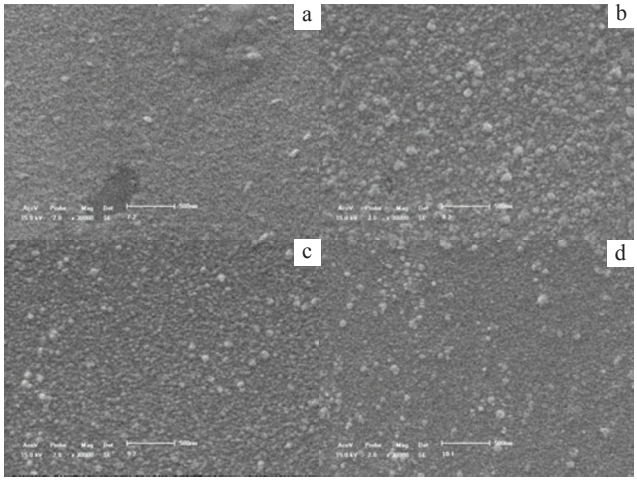

Fig.2 SEM images of cerium oxide films prepared with different urea dosages: (a) 0.04 g, (b) 0.06 g, (c) 0.08 g, and (d) 0.10 g

As Fig.2 shown, the sizes of particles become big and the films become coarse with increase of the urea dose, and the particles are the biggest at 0.06 g of urea dose. Continuing to increase urea dose, the particles become small and the film become smooth. The possible reaction equations are as followed:

$$CO(NH_2)_2+3H_2O=CO_2\uparrow+2NH_3 \cdot H_2O \quad (1)$$

$$Ce(NO_3)_3 \cdot 6H_2O+3NH_3 \cdot H_2O \rightarrow Ce(OH)_3\downarrow+3NH_4NO_3+6H_2O \quad (2)$$

$$2Ce(OH)_3+H_2O_2 \rightarrow 2Ce(OH)_4\downarrow+O_2 \quad (3)$$

$$Ce(OH)_4 \rightarrow CeO_2+2H_2O \quad (4)$$

Because $NH_3 \cdot H_2O$ formation increases with the increase of urea dosage, the formation of CeO_2 particles are accelerated and the particles become big. However, when the urea