

# Morphology and photoluminescence properties of SrWO<sub>4</sub> films prepared by the anodization method

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In this paper, we report on the morphology and optical properties of SrWO<sub>4</sub> films prepared by constant voltage anodization of tungsten foils in Sr(OH)<sub>2</sub> solution. These films are analyzed by scanning electron microscopy (SEM), X-ray diffractometer (XRD) and photoluminescence measurements (PL), respectively. SEM micrographs indicate that the SrWO<sub>4</sub> films with dense and large particles in uniform size can be prepared at appropriate anodization voltage, temperature, and electrolyte concentration. XRD patterns show that the SrWO<sub>4</sub> films present a scheelite-type tetragonal structure and are free of secondary phases. PL spectra verify that a maximum emission situated at around 360 nm is obtained when the SrWO<sub>4</sub> films are excited at 200 nm.

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## 1. Introduction

Strontium tungstate (SrWO<sub>4</sub>), a classic luminescent material of scheelite-type tungstate [1, 2], has been investigated as one of the important inorganic materials due to its attractive applications in photoluminescence, humidity sensors, solid-state lasers, optical fibers, and scintillating materials [3-6]. Traditionally, tungstates have been prepared by solid-state reaction, hydrothermal, microwave-hydrothermal, cyclic microwave, co-precipitation, sputtering or sol-gel processes [7-14]. All these methods could not directly get crystallized tungstate films and further treatment at high temperature is necessary, which would influence the surface structure and uniformity of tungstate films [15]. Anodization is a new kind of fabrication technology for photoluminescence films [16]. Crystallized tungstate films can be directly fabricated by the anodization method without further heat treatment. Anodization method has many advantages including simple technique, low cost, and easy for industrial production.

Therefore, in this paper, we report on the fabrication of SrWO<sub>4</sub> films with scheelite-type tetragonal structure by constant voltage anodization. The influences of anodization voltage, temperature, and electrolyte concentration on the morphology of the films are investigated in detail and the photoluminescence properties are also tested.

## 2. Experimental

Tungsten foils (99.9 % purity, 25 mm × 15 mm × 0.18 mm) were used in the experiments. Prior to the anodization treatment, the tungsten foils were mechanically polished with abrasive paper to eliminate

oxide film. Then the tungsten foils were cleaned through ultrasonic washing in acetone, 2-propanol, and deionized water respectively for 5 min. 0.1 M Sr(OH)<sub>2</sub> electrolyte prepared with boiled deionized water and analytical Sr(OH)<sub>2</sub> were put in a hermetic plastic cell. The pretreated tungsten foil was used as anodic electrode and platinum was used as cathodic electrode. Anodization experiments were carried out at certain temperature and voltage with N<sub>2</sub> protection.

After anodization, the samples were rinsed in deionized water and dried in air. Then the surface morphologies of the films were observed via scanning electron microscopy (SEM); S-4800, Japan Hitachi Inc. The structures were analyzed by X-ray diffractometer (XRD); D8 FOCUS German Bruker Inc. The photoluminescence (PL) properties were studied by photoluminescence measurements at room temperature; F-7000, Japan Hitachi Inc.

## 3. Results and discussion

Fig. 1 shows the SEM micrographs of the SrWO<sub>4</sub> films prepared at 15 °C and different voltages for 40 min. With increasing anodization voltage, the particle sizes of the products increase firstly and then decrease. And the largest particles with a size of 2.1 μm were fabricated at 40 V. When the anodization voltage is low, increasing anodization voltage would raise the reaction speed and the temperature at reacting interface, which is favorable for crystallization and growth of products. Consequently, the particle sizes of the products gradually increase. When the voltage is excess high, the reaction speed is too fast and the number of crystal grains increases [17]. This results in the decrease of particle size on the contrary.

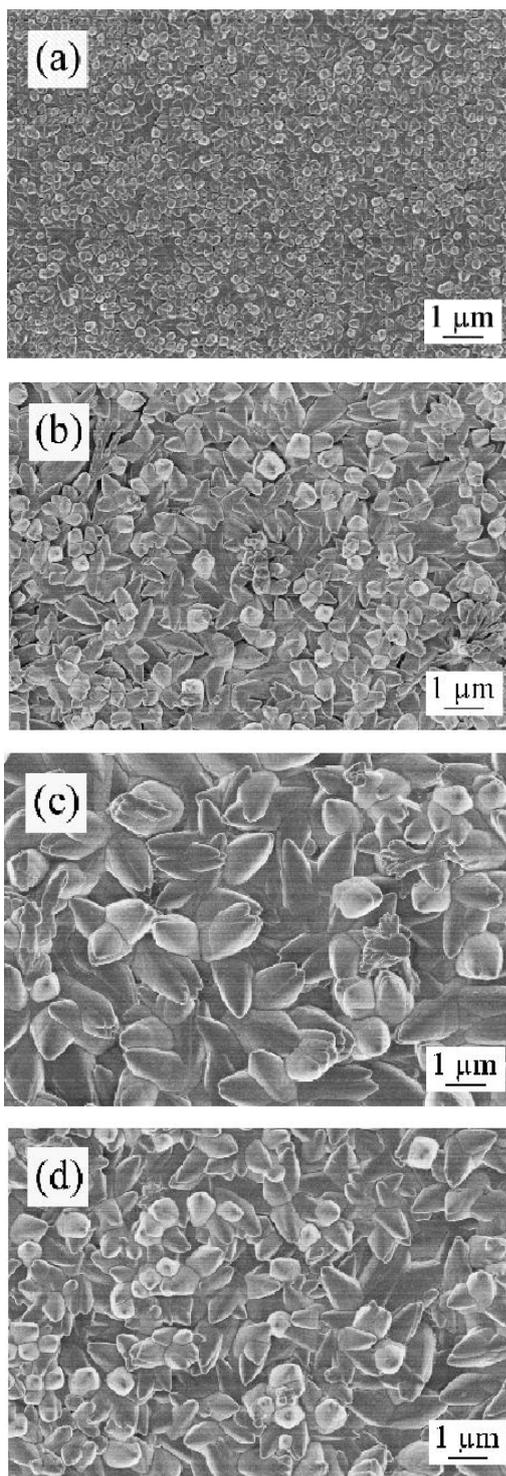


Fig. 1. SEM micrographs of  $\text{SrWO}_4$  films prepared at different anodization voltages (a) 10 V, (b) 20 V, (c) 40 V, (d) 60 V

Anodization time also has effects on particle size and the shape, which is in agreement with similar tungstate crystals [17, 18].

Fig. 2 shows the SEM micrographs of the  $\text{SrWO}_4$  films prepared at 10 V and different temperatures for 40 min. The increase of anodization temperature would elevate the particle sizes and uniformity of the products.

The morphology of the product with a size of  $0.9 \mu\text{m}$  and a shape of square pyramid is best at  $45^\circ\text{C}$  (Fig. 2c). When the temperature is  $55^\circ\text{C}$ , there are some holes in the film and the particle sizes are uneven. A rise in temperature can improve crystallization and uniformity of the products. When the temperature is overly high ( $55^\circ\text{C}$ ), increased solubility of the products results in the decrease of the film quality.

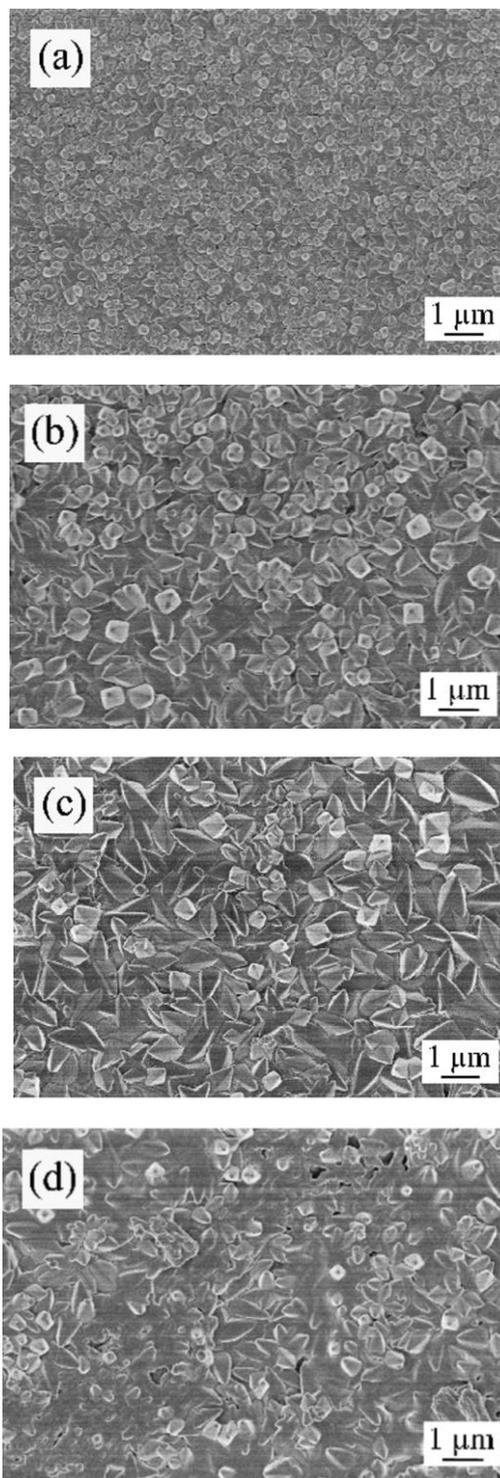


Fig. 2. SEM micrographs of  $\text{SrWO}_4$  films prepared at different anodization temperatures (a)  $15^\circ\text{C}$ , (b)  $35^\circ\text{C}$ , (c)  $45^\circ\text{C}$ , (d)  $55^\circ\text{C}$

Fig. 3 shows the SEM micrographs of the SrWO<sub>4</sub> films prepared at 10 V, 15 °C for 40 min in 0.0125 M, 0.025 M, 0.05 M, and 0.1 M Sr(OH)<sub>2</sub>, respectively. With the increase of electrolyte concentration, the particle size of the products becomes small. The lower electrolyte concentration is unfavorable to the formation of crystal nucleus. Therefore the number of the crystal particles decreases and their volume becomes larger, which is similar with the work reported in the literature [19].

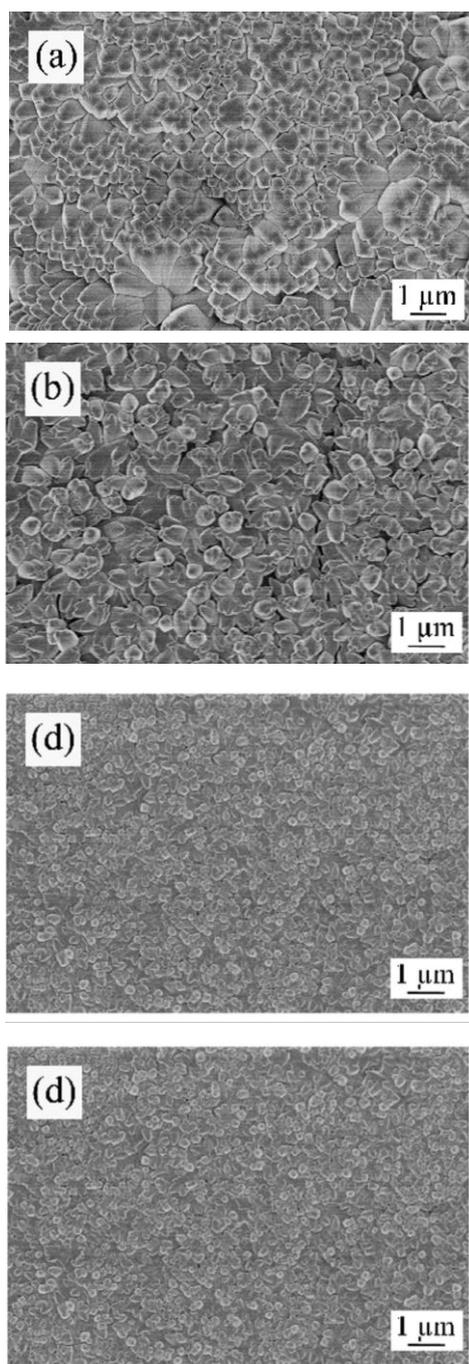


Fig. 3. SEM micrographs of SrWO<sub>4</sub> films prepared in different Sr(OH)<sub>2</sub> concentrations (a) 0.0125 M, (b) 0.025 M, (c) 0.05 M, (d) 0.1 M

The XRD patterns of the SrWO<sub>4</sub> films prepared at different voltages and temperatures are shown in Fig. 4. XRD patterns reveal that all the diffraction peaks of the SrWO<sub>4</sub> films can be indexed to the scheelite-type tetragonal structure, in agreement with the “Joint Committee on Powder Diffraction Standards” (JCPDS) card no. 08-0490. These results indicate that the SrWO<sub>4</sub> films prepared by constant voltage anodization are highly crystallized. With the increase of the anodization voltage and temperature, the diffraction peaks are enhanced and the crystallization of the film is improved.

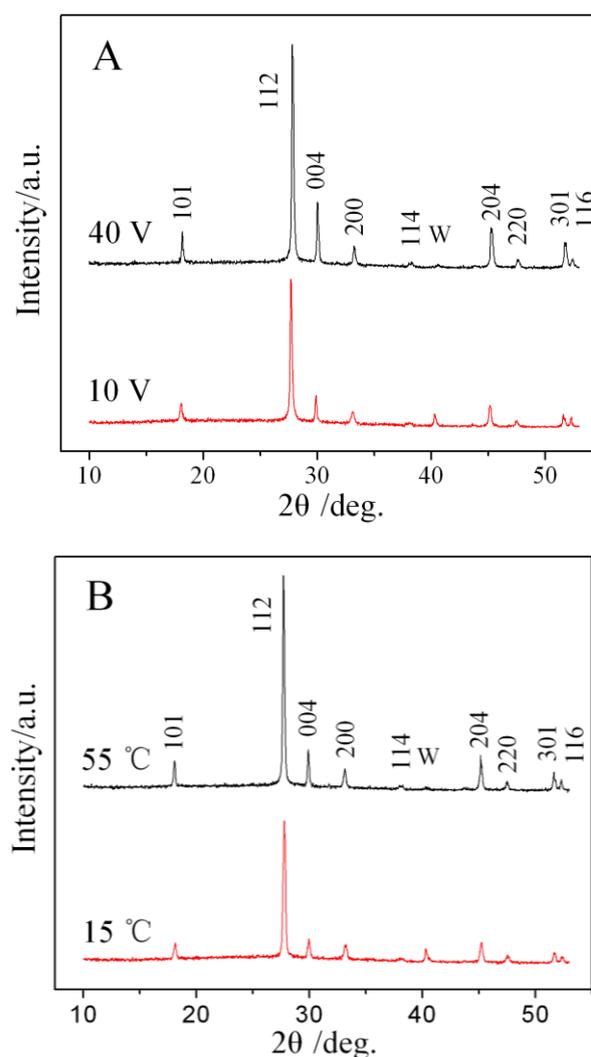


Fig. 4. XRD patterns of SrWO<sub>4</sub> films prepared at different voltages and temperatures

Photoluminescence analyses were carried out on the films prepared at different conditions. A maximum emission situated at around 360 nm was obtained when the sample was excited at 200 nm. Relative intensities of emission light are shown in Fig. 5. When the anodization voltage and temperature are raised, the emission intensities increase at first and then decrease (Fig. 5A, B). PL emission intensity of SrWO<sub>4</sub> films depends on their uniformity and crystallization. Better crystallization results

in the higher intensity of photoluminescence while more defects in the  $\text{SrWO}_4$  films result in the lower intensity of the photoluminescence. Overly high reaction speed or

temperature will make defects increase and intensity of the photoluminescence decrease.

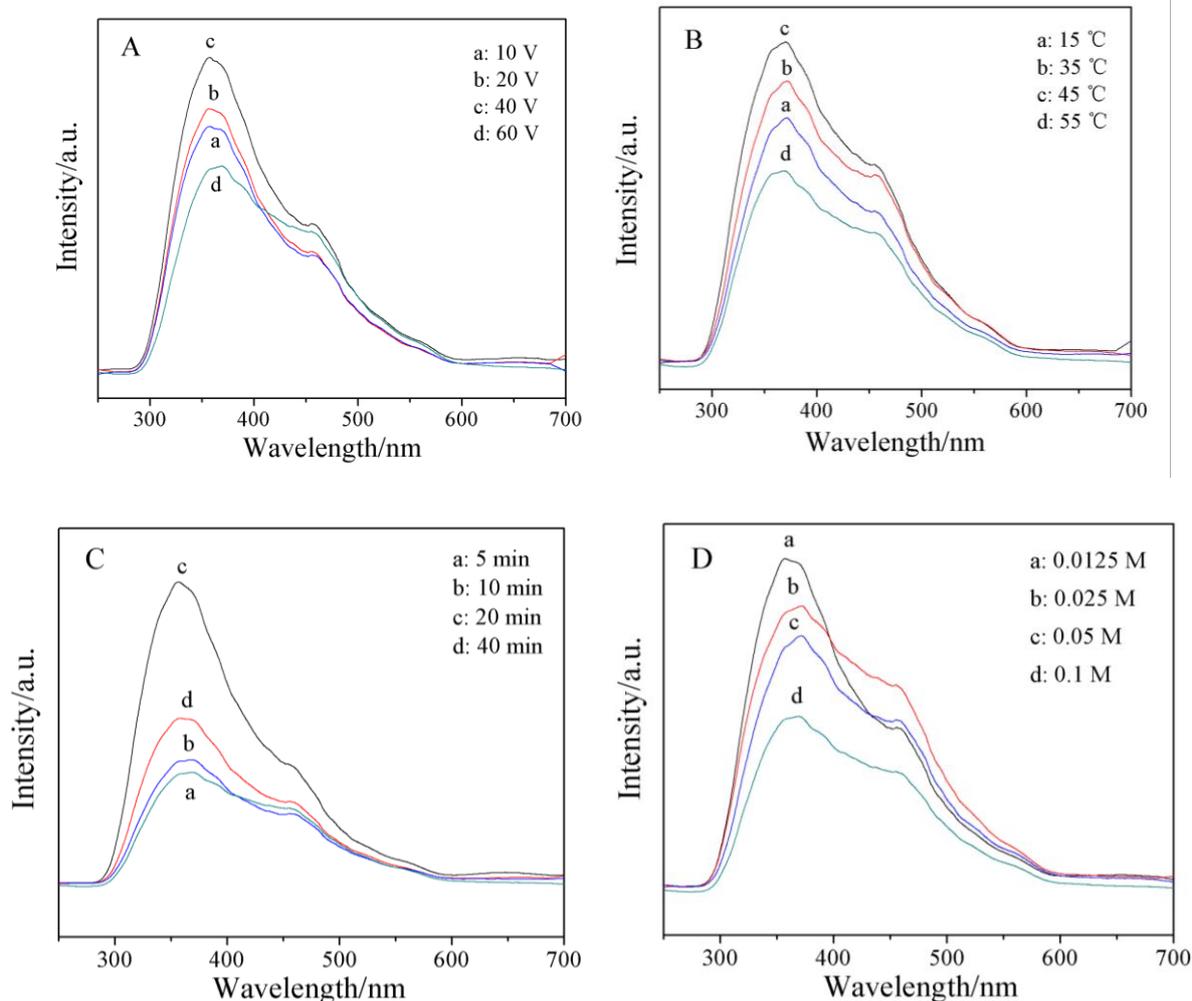


Fig. 5. PL spectra of  $\text{SrWO}_4$  films prepared at different conditions.

The anodization time and electrolyte concentration have a great effect on the photoluminescence properties of the  $\text{SrWO}_4$  films. With increasing anodization time, the relative intensities of the emission increase firstly, and then decrease. The relative intensity is strongest when anodization time is 20 min (Fig. 5C). The relative intensity of the emission decreases with the increase of electrolyte concentration. The relative intensity is strongest in 0.0125 M  $\text{Sr}(\text{OH})_2$  (Fig. 5D). As the anodization time extends, the  $\text{SrWO}_4$  films become uniform and dense gradually and relative intensities are enhanced. After films in high quality are formed, further reaction results in the generation of the defects and decrease of the photoluminescence intensity due to the expansion of the products. The decrease of electrolyte concentration is favorable to the formation of high quality films. Consequently, photoluminescence properties are enhanced. In Fig. 5, the positions of the main peak around 360 nm

are slightly different and the intensity sequence of the main peak is different from that of the small shoulder peak around 450 nm. This is probably caused by the structural defects and/or distortions on the  $[\text{WO}_4]$  tetrahedron groups [17, 20].

#### 4. Conclusions

In summary,  $\text{SrWO}_4$  films with scheelite-type tetragonal structure were prepared by constant voltage anodization in  $\text{Sr}(\text{OH})_2$  solution. SEM micrographs suggest that the anodization voltage, temperature and electrolyte concentration have a great effect on the morphology of the  $\text{SrWO}_4$  films and the films with dense and large particles in uniform size can be prepared at appropriate conditions. XRD patterns indicate that the  $\text{SrWO}_4$  films are highly crystallized and present a

scheelite-type tetragonal structure. PL spectra verify that a maximum emission situated at around 360 nm is obtained when the SrWO<sub>4</sub> films are excited at 200 nm, the anodization voltage, temperature and electrolyte concentration also have a great effect on the emission intensity. The PL behavior is related with the structural defects and/or distortions on the [WO<sub>4</sub>] tetrahedron groups.

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