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Fabrication and morphology control of $BaWO_4$ thin films by microwave assisted chemical bath deposition

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ABSTRACT

Highly crystallized barium tungstate ($BaWO_4$) thin films with dumbbell-like, kernel-like, bowknot-like and cauliflower-like microstructure were synthesized from an aqueous solution containing barium nitrate, ethylenediamine tetraacetate acid disodium and sodium tungstate, via mild microwave assisted chemical bath deposition process. The resulting $BaWO_4$ films with different morphologies were characterized by X-ray diffraction spectrum, scanning electron microscope, Raman and photoluminescence spectra. The results indicate that the morphologies of final products significantly depend on the reaction conditions including the reaction time, the initial concentration of precursor reagent and the physicochemical characteristics of the substrates. Furthermore, the oriented aggregation mechanism is proposed as a possible formation mechanism of the films with specific morphologies.

1. Introduction

The shape, phase, and size of inorganic nanocrystals and microcrystals are important elements in varying their electrical, optical, and other properties [1–5], so rational control over these elements has become a hot research topic in recent years [6]. Many efforts have been made in the controllable methods for synthesizing nano- and microcrystals with specific size and morphology, in order to contrive new materials and devices in various fields such as catalysis, medicine, electronics, ceramics, pigments, cosmetics [7–10], etc.

As an one-step, environment-friendly and low-energy-consumption aqueous technique, chemical bath deposition (CBD) has been wildly applied for depositing large-area semiconductor films with particular shape, orientation and thickness [11,12]. In fact, microwave assisted chemical bath deposition (MA-CBD) is a fascinating film preparation method, since it combines all the merit of CBD and the high time efficiency with enhanced film adherence [13]. It is generally accepted that constant reorientation caused by the response of electric dipoles materials to mutative electric field creates friction and collisions between molecules, which subsequently generates heat. In the case of applying microwave irradiation in chemical bath, the fast, homogeneous heating and the formation of active spots on the conducting substrate can lead to a faster and more simultaneous heterogeneous nucleation on the supporting surface than conventional heating [14–17]. However, Only a few kinds of thin film materials have been successfully deposited by MA-CBD until now, such as ZnO [18], ZnS,CdS [19], TiO_2 [20], and Eu:YVO_4 [21].

There has been a recent highlighted interesting in scheelite structured $BaWO_4$ which is a high quality material in electro-optical manufacture. Its interesting emission of blue luminescence and stimulated Raman scattering (SRS) properties render $BaWO_4$ as a suitable candidate for the design of solid-state lasers that can emit radiation within a specific spectral region. Also, $BaWO_4$ can be used for medical laser treatment applications, up-conversion fiber lasers, and analogous spectroscopic [22–24]. Various techniques has been employed to synthesize $BaWO_4$ crystals, i.e., Czochralski method for bulk $BaWO_4$ [25], micro-emulsions and hydrothermal method for nano- and micro-powder (nanowire [26], cylinders, rods [27], hollow sphere [28], double-taper, scissors, fasciculus, flower, shuttle [29] etc.); It is generally accepted that a thin film phosphor has superior resolution compared with the powders because of their inherently smaller grain size and less lateral scattering. However, less study focus on the preparation of those films. And the film deposition methods mainly fasten on chemical vapor deposition (CVD) [30], evaporation [31], sputtering evaporation [32], and dip coating process [33]. All of these methods are highly energy consuming and inevitably destroy the film morphology due to high temperatures above 500 °C [34]. Recently, Yoshimura et al. successfully prepared $BaWO_4$ film by some soft solution process, such as hydrothermal [35], electrochemical [35,36] and hydrothermal–electrochemical [35] deposition. However, up to now, little focus has been exerted to the controllable morphology of $BaWO_4$ thin film. In this paper, we introduce a facile and fast microwave route to obtain highly

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crystallized uniform $BaWO_4$ films with controllable morphology and orientation on glass and FTO glass barely within 25 min. Studies found that some related experimental parameters including the reaction time, the initial concentration of the precursor reagent and the property of substrate had great influences on the morphologies of films. By carefully controlling these experimental parameters, $BaWO_4$ thin films consist of dumbbell-like, kernel-like, bowknot-like, and cauliflower-like microstructure can be successfully obtained, respectively. This method may satisfy the requirements of thin films with different morphologies and orientation in a fast and energy saving route, and provide important theoretical reference to the controlled synthesis of other inorganic thin films.

2. Experimental section

The $BaWO_4$ films were deposited on the commercial ($1.5 \times 1 \times 0.1$ cm) microscope glass slides and ($1.5 \times 1 \times 0.2$ cm) F: SnO_2 (FTO) coated glass substrates. Before deposition, the substrates were cleaned by ultrasonic treatment in toluene, acetone, and ethanol in turn, rinsed with deionized water, and then dried in air. All reagents were analytical grade and used without further purification. In a typical procedure, $Ba(NO_3)_2$ and ethylenediamine tetraacetate acid disodium salt (EDTA-2Na) solutions were mixed in a 150 ml beaker with constant stirring. The pH value of the mixed solution was adjusted to 8 with NaOH. Then, under continuous stirring, the $Na_2WO_4 \cdot 2H_2O$ solution was put into the former beaker in the molecular ratio of Ba^{2+}: $EDTA^{2-}$: $WO_4^{2-} = 1:1:1$, and the concentration of these species was defined as the precursor concentration. By continuous stirring, the solution became clear and homogenous. Then the pre-treated substrates were floated on the surface of the above solution to farthest facilitate heterogeneous nucleation on the substrate surface [21]. The solution was then placed in a domestic microwave oven of 2.45 GHz and a maximum power of 700 W, and the reaction was performed under ambient air for different times with 17% power export. All experiments were carried out initially at room temperature (about 20 °C) without further temperature control. After deposition, the films were washed by deionized water and dried in air.

The X-ray diffraction (XRD) analysis was performed on a Bruker Advance D8 diffractometer equipped with graphite-monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54062$). A scanning rate of 0.1/s was used to record the pattern in the range of 10–70°. Scanning electron microcopy (SEM) images were taken on a Hitachi S-3500N scanning electron microscope. Raman spectra were recorded on a JY-HORIBA T64000 spectrometer at room temperature and with an excitation wavelength of 514 nm. Photoluminescence (PL) spectra were measured on a SLM48000DSCF/AB2 fluorescence spectrometer made by American SLM Inc. at room temperature.

3. Results

3.1. Characterizations of films deposited on glass substrate

Fig. 1 shows the XRD patterns of the as-prepared films on glass substrates at different precursor concentration with the same pH value (pH = 8) and reaction time (25 min). The diffraction peaks of the products can be all indexed to a pure tetragonal scheelite structure with cell parameters $a = 5.61$ and $c = 12.70$ Å, which are in good agreement with the literature values (JCPDS Card Number 43-0646). However, the relative peak intensity of the four films varies significantly, which indicates different crystallinity. The

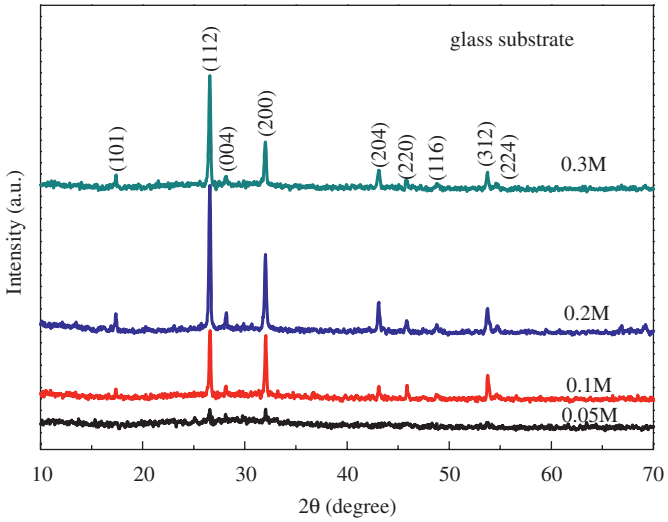

Fig. 1. XRD patterns of the as-prepared films on glass substrate at different precursor concentration with the same pH value (pH = 8) and reaction time (25 min).

samples prepared at 0.1–0.3 M show better crystallization than the one made at 0.05 M. No noticeable impurities can be detected. These XRD patterns indicate that well-crystallized $BaWO_4$ films can be easily prepared under the current synthetic conditions. However, if oven heating is employed instead of microwave heating, nearly nothing can be obtained on the substrates within 25 min. According to our related work, if oven heating was employed, at least 12 h was indispensable to achieve the same crystallinity of the samples which deposited within 25 min of microwave heating at the same concentration level. The results indicate that sluggish kinetics of oven heating can be overcome by using microwave heating, which enhances the reaction rate considerably.

The morphologies of these films were observed by SEM. Fig. 2a shows that the film prepared at 0.05 M is composed of symmetrical four sides kernel-like crystals with dimension of 3–4 μm in length and 0.8–1 μm in width. At a precursor concentration of 0.1 M, a few tiny quartered pricks appear at both ends of the four sides kernel-like crystals and the length of the crystals increases to about 8 μm (Fig. 2b) with a slight decrease in the films density. New nucleus and growth elements tend to gather on the existent "shaft" rather than the bare glass substrate [37]. If the precursor concentration further increased to 0.2 M, the two ends of the products further luxuriate and the film density comes up as shown in Fig. 2c. By the concentration added to 0.3 M, the microstructure of the film turns out to be perfect multilayer bowknot-like microcrystal (the insert of Fig. 2d). However, the density of this film decreases again, which maybe attribute to the poor grasping ability of glass substrate since it was floating on the solution surface.

3.2. Characterizations of films deposited on FTO coated substrate

The $BaWO_4$ films were also deposited on F: SnO_2 (FTO) coated substrates at the same precursor concentration as on glass substrates. The SEM images shown in Fig. 3 clearly reveal the crystallite structures of $BaWO_4$ films obtained from the alkalescent aqueous solution (pH = 8) with various precursor concentration under microwave irradiation for 25 min. The low magnification images (Fig. 3a, c, e, g) indicate the high yield of uniform $BaWO_4$ microcrystals morphologies at each level of precursor concentration. The high magnification images (Fig. 3b,