



Oxidant-assisted preparation of CaMoO_4 thin film using an irreversible galvanic cell method

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ARTICLE INFO

Article history:

Received 21 June 2008

Received in revised form 14 August 2009

Accepted 26 August 2009

Available online 4 September 2009

Keywords:

Calcium molybdate

Thin films

Galvanic cell

X-ray diffraction

Scanning electron microscopy

Photoluminescence

ABSTRACT

CaMoO_4 thin films were prepared by an irreversible galvanic cell method at room temperature; the crystalline phase structure, surface morphology, chemical composition and room temperature photoluminescence property were characterized by X-ray diffraction, Raman spectroscopy, scanning electronic microscopy, X-ray photoelectron spectroscopy as well as photoluminescence spectroscopy. Our results reveal that it is very difficult to directly deposit dense and uniform CaMoO_4 thin films in saturated $\text{Ca}(\text{OH})_2$ solution at room temperature by the irreversible galvanic cell method. After adding some oxidant (NaClO solution or H_2O_2 solution), the growth of CaMoO_4 grains has been promoted, and well-crystallized, dense, and uniform CaMoO_4 films were obtained. The as-prepared CaMoO_4 films exhibit a good green photoluminescence, with the excitation of various wavelengths (220 nm, 230 nm, 240 nm, 250 nm and 270 nm) of ultraviolet irradiation.

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1. Introduction

CaMoO_4 with a scheelite-type structure has been of practical interest for a long time because of its attractive luminescence property [1,2], which provides green emission as available optical fibers, solid-state optical masers and electrochromic materials [3,4]. Recently, various technologies including hydrothermal method [5,6], complex polymerization method [7,8] and microemulsion method [9,10] were used for the preparation of alkaline molybdate and tungstate single crystals and particles. It is generally agreed that the thin film phosphor has superior resolution when compared with powder because of its inherently smaller grain size and less lateral scattering. Nevertheless, less extensive investigations have been made on preparation of these films. A variety of physical and chemical deposition techniques such as polymeric precursor method [11,12], spray pyrolysis [13], chemical bath deposition [14] and spinning technique [15,16] have been reported for the preparation of those films. However, those synthetic methods still have some shortcomings. For example, some of them require highly energetic species like molecules, atoms or ions with sophisticated equipment, and some of them need expensive precursors. In addition, some of them also exhaust gaseous species during and/or after the reaction and require firing at high temperature to produce crystalline films. Therefore, from the view of sustainable development of society, it is of great need to develop an economical and environmental friendly process. An electrochemical technique seems to be one of the promising

candidates for those films [17–19]. Recently, molybdate polycrystalline films with scheelite structure have been prepared by galvanostatic electrochemical deposition technology at room temperature [20–22]. Although the conventional electrochemical technique is convenient and mild, it also requires precise electrochemical apparatus, and it easily generates concentration polarization and electrochemical polarization under applied electric power. To overcome these drawbacks, an irreversible galvanic cell method was put forward to prepare ceramic thin films, and serials of molybdate and tungstate luminescent thin films have been obtained by this simple electrochemical method [23–27]. Compared with other preparation methods, this irreversible galvanic cell method has the obvious advantages of simple instrumentation, easy manipulation, low energy consumption and relatively less impact on the environment [23,25].

The present work is devoted to prepare CaMoO_4 films with scheelite-type structure via the irreversible galvanic cell method with oxidant assistance. The crystalline phase structure, surface morphology, chemical composition as well as room temperature photoluminescence property of the as-prepared films were investigated. From the point of crystal chemistry, the formation mechanism of CaMoO_4 film under the irreversible galvanic cell reaction was discussed in detail.

2. Experimental details

2.1. Thin film preparation

Molybdenum and nickel metal substrates with 99.9 wt.% purity and dimension of $15 \times 30 \times 0.1$ mm were used as working electrode

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(anode) and counter electrode, respectively. Prior to electrochemical treatment, the substrates were pretreated in strong alkaline solution. Constant volume of saturated $\text{Ca}(\text{OH})_2$ solution and some oxidant (NaClO or H_2O_2) solution were added into a sealed polytetrafluoroethylene electrolytic bath, and then the molybdenum and nickel substrates were inserted in the solution and connected with silver lead. All the galvanic cell electrochemical reactions were carried out at room temperature, and detailed experimental conditions are shown in Table 1.

The prepared CaMoO_4 films were immersed in tepid water for 5 min, and then dried in air for characterization.

2.2. Characterization

Phase purity and crystal structure of the obtained films were determined using X-ray diffraction (XRD) and Raman spectroscopy. The XRD patterns were recorded with a standard diffractometer (XD-2, Beijing Purkinje General Instrument Co. Ltd., China) equipped with a graphite monochromator using $\text{CuK}\alpha$ ray ($\lambda = 1.5406 \text{ \AA}$) operating at 30 mA and 40 kV, and employing a scanning rate of 4° and counting time of 60 s per step, in the (2θ) range from 10° to 80° . The Raman spectra in the range from 100 to 4000 cm^{-1} were recorded at room temperature by using Almaga XR spectrometer (Thermo Nicolet Corporation, USA) with 532 nm laser (25 mW).

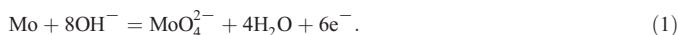
The morphology of the thin films was observed by scanning electron microscopy (SEM), which was performed using a JSM-5900 electron microscopy (JEOL, Japan) operated at accelerating voltage of 20 kV. The chemical composition of the thin films was studied by X-ray photoelectron spectroscopy (XPS). XPS experiments were performed using a XSAM-800 spectrometer (KRATOS, UK) with a monochromatic X-ray source (Aluminium $\text{K}\alpha$ line of 1486.6 eV energy and 400 W), and all the binding energies at various peaks were calibrated using the binding energy of C_{1s} (285.0 eV). The room temperature photoluminescence property of the as-prepared CaMoO_4 films was measured by photoluminescence spectrum (Fluoroscpectrophotometer, LS55, UK).

3. Results and discussion

The SEM morphologies of the as-prepared CaMoO_4 thin films are shown in Fig. 1. One can see that when the galvanic cell reaction time is 280 h, there are only few sporadic CaMoO_4 grains formed on the surface of molybdenum substrate (CM1). When electrochemical reaction is up to 500 h, although a lot of taper-like CaMoO_4 grains produced, the surface of molybdenum substrate still obviously appeared (CM2). The above SEM results imply that a dense and uniform CaMoO_4 thin film is very difficult to be deposited only by the irreversible galvanic cell electrochemical reaction at room temperature, even though the galvanic cell electrochemical reaction lasts for a long time. The SEM micrographs of sample CM3 and sample CM4 show that the compactness and the uniformity of the as-deposited CaMoO_4 films have been enhanced significantly after adding some oxidant, and the morphology of the films is unanimous with the

results reported in literatures [21,24]. This indicates that the added adequate oxidant can effectively promote the growth of CaMoO_4 grains and the formation of CaMoO_4 films.

In the irreversible galvanic cell technique, the formation of the CaMoO_4 films may include a dissolution–oxidation reaction and a solution deposition reaction. Due to the standard electrode potential $E_{\text{MoO}_4^{2-}/\text{Mo}}^0 = -1.05 \text{ (V)}$, $E_{\text{Ni}(\text{OH})_2/\text{Ni}}^0$ respectively [28], when a molybdenum electrode and a nickel electrode are connected with a silver conductor, molybdenum substrate has a tendency to dissolve and convert into MoO_4^{2-} ion in alkaline solution as following Eq. (1):



At the same time, the nickel electrode is accompanied by a charge transfer reaction between the electrode and the solution as shown in following Eq. (2):



At room temperature, the solubility product of $\text{Ca}(\text{OH})_2$, i.e. $K_{\text{spCa}(\text{OH})_2}$ is 5.5×10^{-6} [29], according to the formula (3), the concentration of Ca^{2+} ions in the saturated $\text{Ca}(\text{OH})_2$ solution is calculated about $1.12 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$.

$$c_{\text{Ca}^{2+}} = \sqrt[3]{\frac{K_{\text{spCa}(\text{OH})_2}}{4}} = \sqrt[3]{\frac{5.5 \times 10^{-6}}{4}} = 1.12 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \quad (3)$$

Thus, the formation of CaMoO_4 nucleus can be determined according to The Rule of Solubility Product, i.e. the relation of Q and K_{spCaMoO_4} .

Where $Q = c_{\text{Ca}^{2+}} \cdot c_{\text{MoO}_4^{2-}}$, which is the ionic product of Ca^{2+} ions and MoO_4^{2-} ions, $c_{\text{Ca}^{2+}}$ and $c_{\text{MoO}_4^{2-}}$ represent the concentration of Ca^{2+} ions and MoO_4^{2-} ions in the solution, respectively.

While $K_{\text{spCaMoO}_4} = [\text{Ca}^{2+}] \cdot [\text{MoO}_4^{2-}]$, which is the solubility product of CaMoO_4 and its value is 1.46×10^{-8} at room temperature [29]. Where $[\text{Ca}^{2+}]$ and $[\text{MoO}_4^{2-}]$ represent the equilibrium concentration of Ca^{2+} ions and MoO_4^{2-} ions in the saturated solution, respectively.

When $Q > K_{\text{spCaMoO}_4}$, the solution is an oversaturated, and there are CaMoO_4 grains produced. Whereas $Q = K_{\text{spCaMoO}_4}$ and $Q < K_{\text{spCaMoO}_4}$, there is no CaMoO_4 grain formed in both conditions. The former is a saturated solution, and it is a solid solution equilibrium system, while the latter is an unsaturated solution.

At the early stage of the galvanic cell reaction, the concentration of Ca^{2+} ions $c_{\text{Ca}^{2+}}$ is about $1.12 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. Only when the concentration of MoO_4^{2-} ions $c_{\text{MoO}_4^{2-}}$ exceeds $1.30 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ (calculated according to the formula $Q > K_{\text{spCaMoO}_4} = 1.46 \times 10^{-8}$), the solution is oversaturated, Ca^{2+} ions can combine with MoO_4^{2-} ions to form CaMoO_4 crystal nucleus, and then gradually grow into dense CaMoO_4 films.

At room temperature, $c_{\text{Ca}^{2+}}$ of the saturated $\text{Ca}(\text{OH})_2$ solution is lower, so the formation of CaMoO_4 needs more MoO_4^{2-} ions. Whereas the difference of the standard electrode potential between molybdenum electrode and nickel electrode is relatively lower (about 0.33 V), in other words, the driving force of the anode oxidation (i.e. the dissolution–oxidation reaction of molybdenum metal) is relative weak, and it results in the slow formation of MoO_4^{2-} . Hence, it is hard to obtain stable CaMoO_4 grains in this case. After adding some oxidant (such as NaClO and H_2O_2), the dissolution–oxidation reaction of molybdenum substrate has been promoted with an assistance of oxidant, and then the production of MoO_4^{2-} ions becomes easier in alkaline solution. Therefore, by adding adequate oxidant such as NaClO and H_2O_2 , the growth of CaMoO_4 thin film can be promoted accordingly.

Fig. 2 gives the XRD patterns of the prepared CaMoO_4 thin film samples. One can see that the d -space, relative intensity as well as diffraction angle of sample CM3 and sample CM4 are in agreement with JCPDS card (No.85-1267) [30], especially several strong peaks

Table 1
Preparing conditions of CaMoO_4 films via an irreversible galvanic cell method.

Sample number	Volume of added saturated $\text{Ca}(\text{OH})_2$ solution (ml)	Volume of added sodium hypochlorite (NaClO) solution or hydrogen peroxide (H_2O_2) (ml)	Reaction time (h)	Reaction temperature ($^\circ\text{C}$)
CM1	150	–	280	25
CM2	150	–	500	25
CM3	150	3 ml 3 wt.% NaClO solution	300	25
CM4	150	20 ml 30 wt.% H_2O_2 solution	120	25

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