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Mechanisms and applications of cell electrochemical technique to prepare luminescent $SrMoO_4$ thin films

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Abstract

Cell electrochemical technique is a novel film deposition method. With the improved cell device, the rate determining step, utilization ratio of molybdenum, and applications to deposit $SrMoO_4$ thin films have been investigated. Researches on the relation between the overpotentials of electrodes and the currents in the circuit reveal that the rate determining step is the reduction of water during the deposition of $SrMoO_4$ thin films. The rates of electrode reactions can be tailored by controlling the electrolyte temperature. The utilization ratio of molybdenum is up to 90%, while it is nearly 60% for constant current method. In addition, X-ray diffraction analyses show that the as-grown $SrMoO_4$ thin films are well crystalline and have a scheelite structure; scanning electron microscopy examinations reveal that $SrMoO_4$ crystals grow well in tetragonal tapers. These thin films show a broad emission band centered at 520 nm using an excitation wave of 230 nm at room temperature.

Keywords: Cell electrochemical technique; $SrMoO_4$; Thin film

1. Introduction

Scheelite-structured tungstates and molybdates are good laser host materials [1–4], particularly for pulsed lasers [5]. They are also important materials in the field of electrooptics [6,7]. They remain a tetragonal structure within a wide range of temperatures [3] and pressures [8]. So under some extreme environments they may become the first-chosen materials.

Various methods, such as sputtering [9], vacuum evaporation [10], pulsed-laser deposition [11] and spray pyrolysis [12], have been adopted to prepare AMO_4 (A = Ca, Sr, Ba; M = Mo, W) thin films. But such films prepared by above methods generally show no luminescence [9,12] because of poor crystallization. In order to obtain high quality films, heat treatments (500–1100 °C) are necessary. This not only consumes a huge amount of energy but also can result in impure phases [9]; besides this, it also leads to poor adhesion due to the thermal stresses associated with the thermal treatment. Therefore, it is urgent to develop low temperature techniques in order to synthesize crystalline luminescent molybdate thin films.

Electrochemical techniques, such as galvanostatic or potentiostatic methods, have been widely used to prepare AMO_4 (A = Ca, Sr, Ba; M = Mo, W) films [13–17]. The advantages of electrochemical coating techniques over conventional techniques have been summarized by Switzer [18]. The following ones seem especially attractive. Firstly, the thickness and morphology of the deposit can be controlled by the electrochemical parameters; secondly, relatively uniform deposits can be obtained on complex shapes; thirdly, the deposit rate is higher than for most other methods and lower cost is needed for the equipment [19].

It is well known that different metals generally have different potentials when dipped in an electrolyte. While connected by wires or conductors, they constitute a cell so that electrons can transfer from one metal to the other efficiently. The method based on cell and metal's spontaneous corrosion is called cell electrochemical technique.

Scheelite-typed crystalline AMO_4 (A = Ca, Sr, Ba; M = Mo, W) thin films have been successfully prepared by using cell electrochemical method in our group [20]. Some of them can be prepared within 1 h [21], which is as quick as those prepared at current density of several mA/cm^2.

So far, dynamics and mechanisms of electro-deposition of oxide thin films have been scarcely investigated, especially

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in situ investigations. However, they are of great importance to optimize experimental routines and parameters. In this paper, some mechanism problems and applications to electrodeposit $SrMoO_4$ thin films have been investigated. In order to study the phase, surface morphology and fluorescence of these $SrMoO_4$ thin films, X-ray diffraction, scanning electron mircoscopy and photoluminescence examinations have been done, respectively.

2. Device and experimental procedure

2.1. Cell device

In the normal two or three-electrode-system, the anode and cathode are directly connected with a metal wire. The potential of anode or cathode is not the correspondingly real potential. Neither can the current be measured. But they are vital to supervise the film deposition process. Hence, it is necessary to improve the cell device.

Fig. 1 shows the schematic illustration of cell device we have improved. In Fig. 1 a constant resistor is used to combine the anode and cathode instead of a metal wire. And a data collector is used to collect the real-time data of potentials and currents measured in the circuit. Therefore, it is possible to in situ supervise electrode reactions and to study some dynamic problems.

2.2. Experimental procedure

All experiments were accomplished in the cell device as shown in Fig. 1. The molybdenum (30 mm × 15 mm × 0.1 mm, with purity of 99.5%) and platinum plates were used as the anode and cathode respectively. An Ag/AgCl (sat. KCl) standard electrode was used as reference electrode.

After being polished mechanically, the molybdenum plates were pretreated with degreasing and ultrasonic cleaning. The electrolyte was prepared from $SrCl_2{\cdot}6H_2O$ (with purity of 99.5%), NaOH (with purity of 96%), and redistilled water. The concentration of Sr^{2+} ions was 0.4 mol/l. Before experiments, the solution was purged with N_2 gas for 10 min. In our researches, a VOLTLAB (PST050 VOLTMASTER, made in France) was used to measure potentials and a personnel computer was used to save the data (except sample SM-1). The span of measurements was two seconds per point. As to experiments assisted by hydrothermal treatment, the sealed cell was put in a container and the water temperature was controlled by a heater. Following the electrochemical treatments, the samples were washed with deionized water, then dried. The treatment parameters were listed in Table 1.

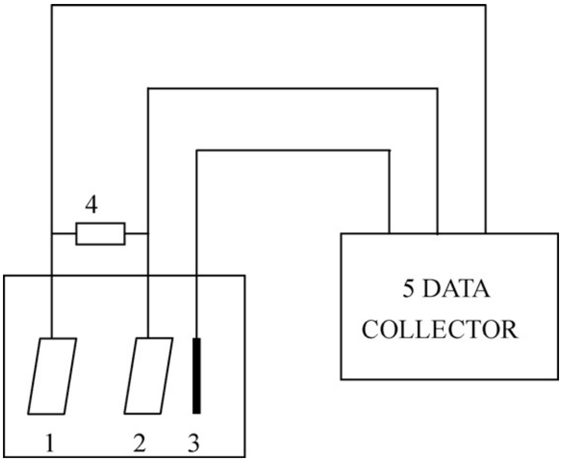

Fig. 1. Schematic illustration of the improved cell device—1: anode; 2: cathode; 3: reference electrode; 4: resistor; 5: data collector.

Table 1
Treatment parameters of $SrMoO_4$ thin films

Sample	Temperature (K)	Span (s per point)	Time (s)
SM-20	286	2	12,7800
SM-17	308	2	28,800
SM-19	323	2	19,260
SM-16	338	2	7,800
SM-1	298	–	14,4000

The films were characterized by X-ray diffraction (X'Pert PRO MPD, made in Netherlands). It was used with Cu Kα radiation at 40 KV and 40 mA and a scan rate of 0.02°/s from 10° to 90° 2θ. Morphologies and microstructures of films were investigated by scanning electron microscopy (JSM-5000, JEOL, Tokyo, Japan). Luminescence was examined by Spectrofluorometer (M-850, Hitachi, Japan).

3. Results and discussions

3.1. Investigations on the rate determining step of electro-deposition of $SrMoO_4$ thin films

Several reactions occur simultaneously during the deposition of $SrMoO_4$ thin films. They associate with several phases, interfaces, and processes (such as dissolution, diffusion, crystallization). The reaction with lowest rate will be the rate determining step. To the present, no in situ investigations on the rate determining step of the deposition of oxide films by electrochemical methods have ever been reported, especially by cell electrochemical methods.

The following list some main reactions:

$$\mathrm{Mo} + 8\mathrm{OH}^- \rightarrow \mathrm{MoO_4}^{2-} + 4\mathrm{H_2O} + 6\mathrm{e} \tag{1}$$

$$\mathrm{H_2O} + \mathrm{e} \rightarrow \mathrm{H}_{\mathrm{adorption}} + \mathrm{OH}^- \tag{2}$$

$$2\mathrm{H_2O} + 2\mathrm{e} \rightarrow \mathrm{H_2} + 2\mathrm{OH}^- \tag{3}$$

$$\mathrm{Sr}^{2+} + \mathrm{MoO_4}^{2-} \longleftrightarrow \mathrm{SrMoO_4} \tag{4}$$

The number of transfer electron is six, one, two and zero for formulas (1)–(4), respectively.

The correlation between the overpotentials (they are calculated according to formula (5)) of anode and the logarithms of currents abides by Tafel law. While the relation of the number of transfer electron to Tafel coefficient b [22] can be described

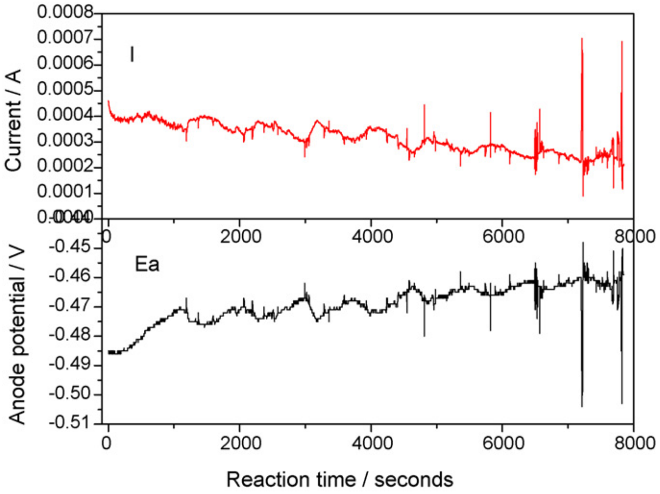

Fig. 2. Curves of anode potentials and currents with the reaction time. These data were collected by a VOLTLAB and computer during the preparation of SM-16 thin film at 338 K for 130 min. The measurement span was 2 s per point.

as formula (6):

$$\eta = E + 0.21 + \frac{2.303 \times 8RT}{6F}(\mathrm{pH} - 14) \qquad (5)$$

$$b = \frac{2.303RT}{\beta nF} \qquad (6)$$

where η stands for the overpotential of anode; E stands for the measured potential of anode; pH refers to the pH value of solutions (equaling 12 in our experiments); T means the temperature (K); $R = 8.314\ \mathrm{J\,K^{-1}}$; F stands for Faraday constant (equaling 96486.7 °C); n stands for the number of transfer electron in rate determining step; and β stands for transfer coefficient (generally equaling 0.5).

By calculating the number of transfer electron from Tafel coefficient, it is clear that which reaction determines the deposition rate. Therefore, it becomes explicit that how to tailor the deposition rate.

Fig. 2 illustrates the curves of currents and anode potentials with the reaction time. It shows that the current and potential change reversely as a whole, which is due to the electric insulation of $SrMoO_4$ thin film. From Fig. 2 one can see that the film becomes thicker and denser with time passing by.

Fig. 3 shows the relationship between the overpotentials and the logarithms of currents. It reveals that the overpotentials almost change linearly with the logarithms of currents. At other temperatures, such investigation has also been done and the linear fitting parameters are listed in Table 2. It can be seen that at proper temperatures the overpotentials still change linearly with the logarithms of currents. In addition, from Table 2 it can be inferred that the rate determining reaction during the deposition of $SrMoO_4$ thin films should be a faradic process. Otherwise the linear coefficient B will be up to infinite and the correlation coefficient will be far from 100%.

By replacing T and b with the corresponding temperature and Tafel coefficient, respectively, in formula (6), the number of transfer electron in the rate determining reaction can be worked out. Its value is presented in Table 2. Interestingly, the absolute value of each calculated number of transfer electron is right in the range between 0 and 2. Since all the data were measured and collected by a VOLTLAB and computer, and the measurement span was two seconds per point, it is convinced that the rate determining reaction should be reactions (2) or (3) during the deposition of $SrMoO_4$ thin films. Therefore, the rate of deposition of $SrMoO_4$ thin films can be controlled by adjusting the reduction of water.

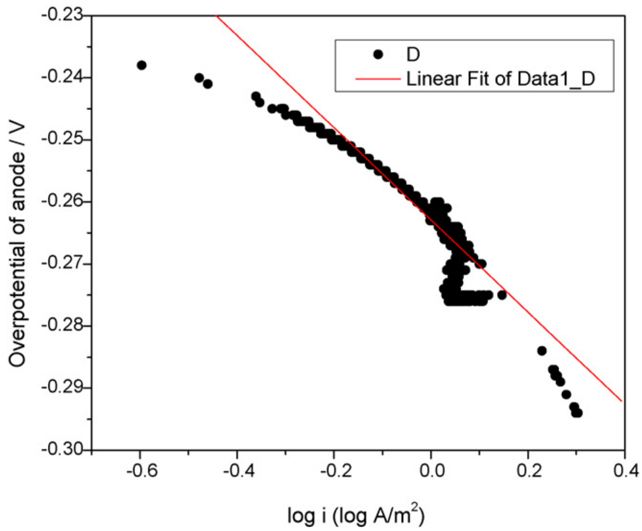

Fig. 3. Dependence of the overpotentials on the logarithms of currents and its linear fitting ($Y = A + BX$). The calculation of overpotential was according to formula (5) with the data shown in Fig. 2. The temperature was 338 K and pH value was 12.

Table 2
Linear fitting parameters of the dependence of the overpotentials on the logarithms of currents and the calculated numbers of transfer electron in the rate determining step for each sample

Sample	Temperature (K)	Correlation coefficient, R	Fitting parameter, B	n
SM-20	286	−0.9158	−0.12283	−0.92
SM-17	308	−0.9226	−0.295	−0.41
SM-19	323	−0.9528	−0.06714	−1.91
SM-16	338	−0.9328	−0.07425	−1.81

3.2. *Hydrothermal influences*

Table 3 presents the effect of temperature on cell electro-deposition of $SrMoO_4$ thin films.

Table 3
Effect of temperature on cell electro-deposition of $SrMoO_4$ thin films

Sample	Temperature (K)	Time (s)	Current density (mA/cm^2)
SM-20	286	12,7800	0.0145[a]
SM-17	308	28,800	0.0830[a]
SM-19	323	19,260	0.0861[a]
SM-16	338	7,800	0.0913[a]

[a] Average current density during the electrochemical treatment.

During the electro-deposition of films, current density varies with the rate of electrode reaction. From Table 3 it can be seen that the reaction rate of sample SM-17 is about six times of that of sample SM-20. It indicates that the rate of cell electro-deposition is able to be controlled by altering the hydrothermal temperature, which is in good agreement with other researches [21].

The reasons may lie in the following.

On one hand, it is regarded that hydrothermal treatment has accelerated hydrogen desorption. As discussed above, the rate determining step is the reduction of water. Hydrogen often adsorbs on cathode and is very difficult to desorb. Assisted by hydrothermal treatment, the adsorbed hydrogen atom moves more tempestuously, which makes it easier to desorb. Hence, the reaction (formulas (2) or (3)) shifts towards the generation of hydrogen. So the current density becomes larger.

On the other hand, the rate of electrode reactions must have been sped up by increasing temperature. Because the reaction rate and temperature obeys the Arrhenius equation. Of course, the increase of reduction will accelerate the film deposition.

3.3. Utilization ratio of molybdenum

It is not only economical but also technically necessary in some cases to make reactants efficiently convert to desired substances. To know about the deposition efficiency, utilization ratio has been studied.

It is assumed that all impurities, such as carbonates and hydrates, can be dissolved by post-treatment. And molybdenum oxides except $SrMoO_4$ can be ignored. So that it can be presumed that only the dissolution of molybdenum and the deposition of $SrMoO_4$ thin film will account for the weight loss of substrate.

The dissolved molybdenum exists in two places, the film and the bulk solution. The quantity of dissolved molybdenum can be calculated by Faraday law. The quantity of molybdenum in the film can be worked out according to the conservation of mass. The utilization ratio is calculated by the following formulas:

$$Q = \int_{t1}^{t2} I \, dt \qquad (7)$$

$$n = \frac{Q}{6F} \qquad (8)$$

$$\Delta m = M_{\text{film}} n_{\text{film}} - M_{\text{MO}} n \qquad (9)$$

$$\theta = \frac{n_{\text{film}}}{n} \times 100\% \qquad (10)$$

where Q refers to quantity of charge (C); I refers to current (A); t stands for time (s); n means the quantity of dissolved molybdenum (mol); n_{film} means the quantity of film (mol); Δm stands for the weight loss of substance (g); M means molecular weight (g mol^{-1}). It is 247.54 and 95.94 g mol^{-1} for $SrMoO_4$ film and Mo, respectively. θ denotes the utilization ratio of molybdenum.

Table 4 shows the utilization ratio of molybdenum for synthesis of crystallized $SrMoO_4$ films of electrochemical metal dissolution. It shows that the utilization ratio of molybdenum for cell method is much higher than that for constant current method. It suggests that it is more efficient to deposit $SrMoO_4$ thin films by cell electrochemical techniques.

Table 4
Utilization ratio of molybdenum for electro-deposition of $SrMoO_4$ thin films

Sample	n (mol)	n_{film} (mol)	θ (%)	Method
1#	0.00002075	0.00001289	62.12	Constant current
2#	0.00006275	0.00003604	57.43	Constant current
SM-20	0.00001124	0.00001110	98.80	Cell
SM-17	0.00001446	0.00001106	76.48	Cell
SM-19	0.00001002	0.0000833	83.09	Cell

3.4. Characterizations of $SrMO_4$ thin films

3.4.1. X-ray diffraction analyses

Fig. 4 gives the XRD patterns of $SrMoO_4$ thin films prepared by cell electrochemical method. Since the film was deposited on molybdenum, several peaks corresponding to the molybdenum substrate can also be observed. All the other peaks are well consistent with the JCPDS card [23]. From Fig. 4 it can be concluded that the $SrMoO_4$ thin films prepared by cell electrochemical methods are well crystallized with scheelite-typed structure.

3.4.2. Microstructure

The microstructure of $SrMoO_4$ thin films prepared by cell electrochemical method is shown in Fig. 5. It indicates that the film is dense and homogeneous. And $SrMoO_4$ crystals grow well in the shape of tetragonal tapers.

3.4.3. Photoluminescence

Fig. 6 presents the photoluminescence property of $SrMoO_4$ thin films prepared by cell electrochemical methods. These $SrMoO_4$ films show a broad emission band centered at 520 nm with the excitation of 230 nm at room temperature, which is in well agreement with literature [13]. Such green emission is widely regarded as the intrinsic luminescent behavior of MoO_4^{2-} group [24,25]. The widely accepted transition of the

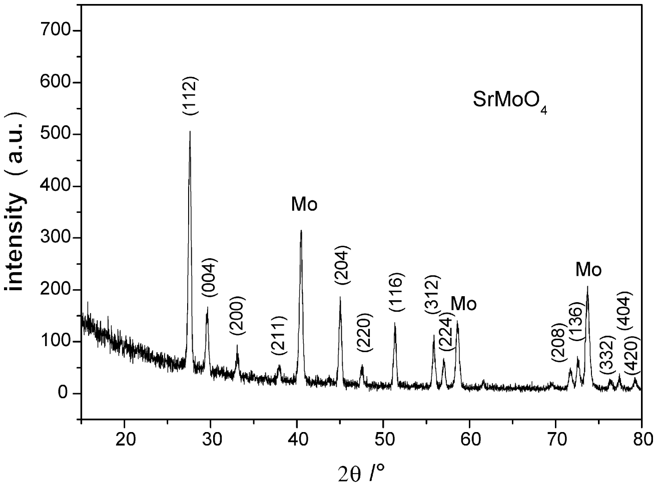

Fig. 4. XRD patterns of $SrMoO_4$ thin films prepared by cell electrochemical method (T = 323 K, t = 19260 s).

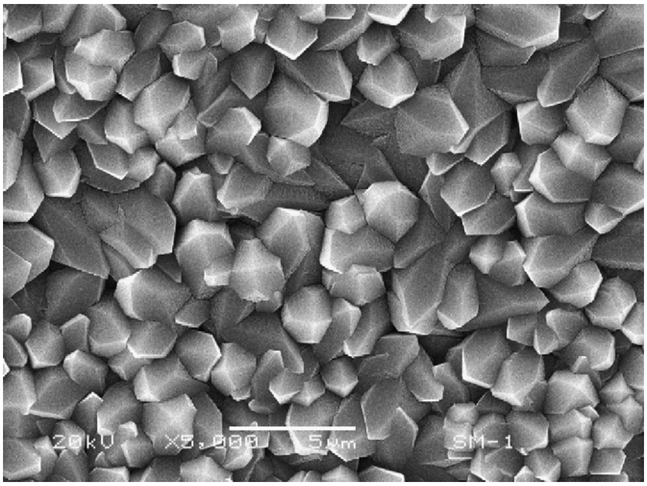

Fig. 5. SEM image of $SrMoO_4$ thin film prepared by cell electrochemical method at 298 K for 40 h.

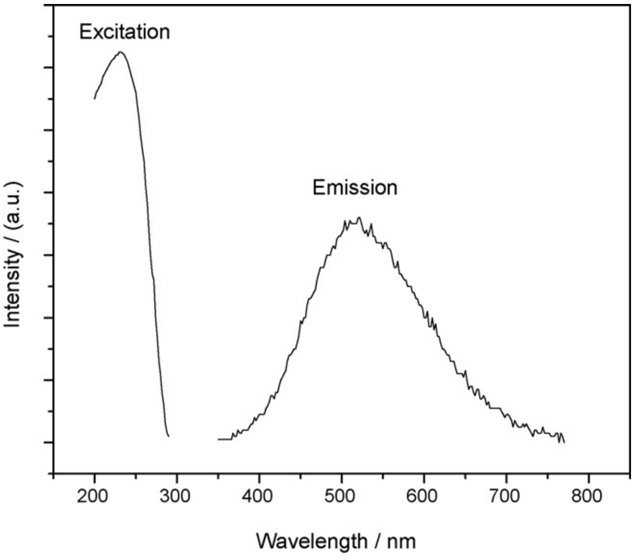

Fig. 6. Photoluminescence of $SrMoO_4$ thin films prepared by cell electrochemical methods.

green luminescence is the $^3T_1, {}^3T_2 \rightarrow {}^1A_1$ transition in the tetrahedral molybdate group. Such a transition contains a forbidden and an allowed component [24]. It is well-known that a single energy level will be broadened to a band in compounds. Hence, the emission spectrum of $SrMoO_4$ thin films becomes lying from 400 to 700 nm.

4. Conclusions

Using the real-time data collected by a VOLTLAB and computer, the relation between the potentials and currents in the circuit has been investigated. Studies show that the number of transfer electron in the rate determining step is in the range between 0 and 2 during the deposition of $SrMoO_4$ thin films by cell method. It can be deduced that the rate determining step is the reduction of water during the fabrication of $SrMoO_4$ thin films by cell method. Further investigations reveal that the deposition rate can be tailored by controlling the temperature of solutions. It is considered that the temperature deeply impacts the rate of hydrogen desorption and electrode reactions.

The utilization ratio of molybdenum is up to 90% during the synthesis of $SrMoO_4$ thin films by using cell electrochemical technique, which suggests that cell method is an efficient way to fabricate crystalline molybdate thin films directly.

Besides, the XRD analyses of the films show that the films are good crystalline with single scheelite structure; the SEM examinations appear that $SrMoO_4$ crystals grow well in the shape of tapers; at room temperature these $SrMoO_4$ thin films exhibit a broad emission band centered at 520 nm under the excitation of UV.

Researches also suggest that cell electrochemical method is a new and promising way to synthesize functional films.

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