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Analysis of galvanic cell deposition process in preparation of $BaMoO_4$ films

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Abstract The galvanic cell method has been used for the synthesis of $BaMoO_4$ double oxide film in barium hydroxide aqueous solutions. This method could resolve the repulsion of the electric field on the anode and favor the mass transfer of cations. The crystal growth in the solution is easier compared with the traditional electrochemical deposition with applied power. The deposition process of the galvanic cell technique has been investigated by deposition time, pH, and ion concentration, and the basic features of this method are discussed.

Introduction

Galvanic corrosion is quite an old and common phenomenon in nature, and it is a troublesome problem for steel corrosion in world due to its inherent disgusting character. However, it could be finitely used as test method [1, 2], solid-state galvanic cells [3–5], synthesis technique [6, 7], and so on. As we know, some oxide films were formed in the natural environment by a long period of galvanic corrosion, such as Fe_2O_3 films, ZnO films, etc. Thus we have heard reasons to believe that the double molybdate and/or tungstate oxide films can be formed in special conditions.

Molybdate, tungstate ABO_4 (A = Ca, Sr, Ba; B = W, Mo), and their solid solutions with a scheelite-type structure are important luminescent materials, which have attracted a lot of interest because of its potential applications, such as electro-optical, laser host materials, and acousto-optic filter [8–10]. In the present study, our group developed a galvanic cell method to prepare these double oxide films on metal substrates in alkaline aqueous solution containing cations at room temperature [11, 12]. However, the deposition process of $BaMoO_4$ films are still unclear, especially the galvanic cell dynamic reaction process should be discussed, which may provide a reference for the synthesis of other oxide films. Therefore, the whole deposition process is discussed by comparing differences with electrochemical technique [13] to obtain perspective picture of this kind of preparation technology.

Experimental

Molybdenum metal substrates with 99.9 wt.% purity and dimensions of $15 \times 30 \times 0.1\ mm^3$ were used as reaction substrates [12]. The counter electrodes (cathode) were nickel, $15 \times 30\ mm^2$ plates. After mechanical polishing and mixed strong-acid treatment, the molybdenum substrates were cleaned with an ultrasonic cleaner in deionized water solution, and finally dried and weighed. Polytetrafluoroethylene (PTFE) containers were used as the reaction vessels. Except for working electrodes and nickel cathodes, all naked surfaces in contact with the electrolyte solution were covered with PTFE. The distance from cathode to anode was 1.5 cm. The electrolyte solutions prepared with high-purity $Ba(OH)_2 \cdot 8H_2O$ purged free of CO_2 with N_2 gas for 20 min by bubbling through the solution. All the experiments were performed under different concentrations (0.0067–0.48 mol L^{-1}), time (20–230 h), and pH values (10.36–13.18). The samples were immersed in tepid

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deionized water solution for 5 min, and then dried at room temperature and weighed.

The grain size, morphology, and microstructure were observed by SEM (JSM-5900, JEOL, Japan). The resultant phase of the as-grown films was analyzed by XRD (XD-2, Puxi, Beijing, China). The X-ray diffraction studies were carried out in the range of scanning angle 20–85° using X-ray diffractometer with Cu Kα radiation of wavelength 1.54056 Å at 40 kV and 30 mA.

Results and discussion

The scanning electron micrograph of the surface of $BaMoO_4$ film prepared by the galvanic cell method on molybdenum substrate in barium hydroxide solutions is shown in Fig. 1. It shows that the crystallites with a tetragonal structure first formed less than 40 h, but after that time the presence of several grains is obvious on the substrate. In order to obtain the desired films, we will demonstrate the whole deposition process and discuss the advantages of this method. During anodization the molybdenum substrate in alkaline solutions oxidizes according to the following reaction:

$$\mathrm{Mo} + 8\mathrm{OH}^- \rightarrow \mathrm{MoO}_4^{2-} + 4\mathrm{H}_2\mathrm{O} + 6\mathrm{e}^- \quad (1)$$

Then, the $MoO_4{}^{2-}$ species react with Ba^{2+} ions in the solution to form $BaMoO_4$ according to:

$$\mathrm{MoO}_4^{2-} + \mathrm{Ba}^{2+} \rightarrow \mathrm{BaMoO}_4 \quad (2)$$

Finally, the $BaMoO_4$ crystals nucleate at molybdenum substrate and then grow to form $BaMoO_4$ film. From reactions (1) and (2), we can see that the whole deposition process includes both the oxidation–dissolution reaction (1) and precipitation reaction (2), which are similar with electrochemical deposition [13] except that the precipitation reaction takes place in the double-layer region. Here the two processes should be associated with each other. As we know in electrochemical deposition higher current density makes the dissolution rate become faster and can provide a greater amount of $MoO_4{}^{2-}$ but the diffusion of Ba^{2+} ions may not follow the dissolution, thus the micro-current is expected for us.

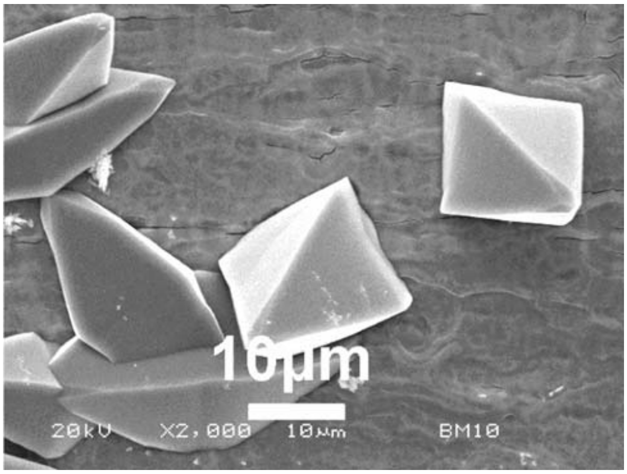

Fig. 1 SEM micrograph of the surface of the $BaMoO_4$ film prepared by a galvanic cell method under treatment time of 40 h, at pH value of 12.84, and with concentration of 0.04

Figure 2a demonstrates the variation of weight of $BaMoO_4$ films under different treatment times. In this figure the weight change M for vertical coordinates is the difference value of film weight between as-prepared film

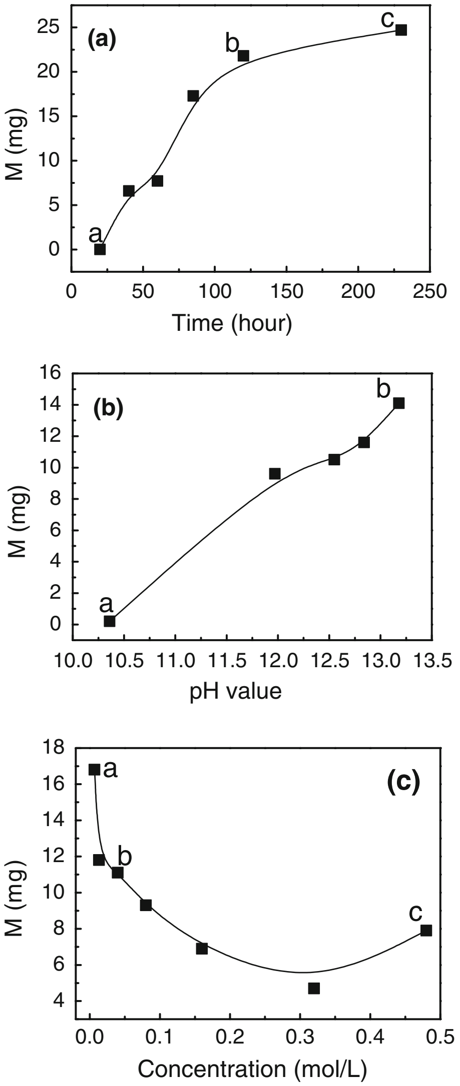

Fig. 2 The difference values (M) of weight of $BaMoO_4$ films between as-prepared film and molybdenum substrate in barium hydroxide aqueous solution: **a** under treatment times of 20, 40, 60, 85, 120, 230 h; **b** at pH values of 10.36, 11.97, 12.55, 12.84, 13.18; **c** with increased concentrations of 0.0067, 0.0133, 0.04, 0.08, 0.16, 0.32, 0.48 mol L^{-1}

and molybdenum substrate. This change in weight was used to estimate the film growth by assuming that the quality of molybdenum substrate dissolved into solution was the same when the crystalline grains were formed firstly. From the Fig. 2a, we can see that the curve ab represents growth process which takes the dominant position in the course. Actually, the crystal nucleus began to build gradually within 20–40 h because the partial solutions for MoO_4^{2-} and Ba^{2+} around the electrode already tend to saturation as a result of the electric adsorption of MoO_4^{2-} ions and inherent limited Ba^{2+} concentration which have been affected by the repulsion of the electric field on the anode. However, this method involves the use of an electrode with relative higher electric potential, such as nickel, platinum, NaClO [14], O_2 etc., which eliminates the need of a power supply. Instead it provides a potential difference with respect to the molybdenum working electrode due to the different electrode materials to maintain micro-current for the oxidation–dissolution process. Thus, the repulsion of the electric field on the anode is even quite feeble. On the other hand, due to the week repulsion, the mass transfer of Ba^{2+} may be facilitated favoring the formation of $BaMoO_4$ films. Moreover, the potential difference just supply micro-current for the oxidation–dissolution of molybdenum substrate which is big enough for active metal molybdenum in alkaline solution to form MoO_4^{2-} ions, so the crystal growth in such solution is freer. As shown in Fig. 2a within the curve ab the weight (*M*) of $BaMoO_4$ film increased rapidly. Within this treatment time it implies that the grain growth is vigorous, the grain size and film thickness are increased obviously. The grain size and film thickness will continuously increase with the time process, but the increase is not eternal. The molybdenum electrode and nickel electrode can keep a certain electrode potential difference to drive the sustainable electrode reaction. However, the as-grown $BaMoO_4$ grains adhered to the surface of molybdenum substrate that can lower the conductivity, and strengthen the dielectric constant between the molybdenum substrate and the alkaline solution. Therefore, when the treatment time was increased to more than 120 h, the electrode reaction will slow down, which was in agreement with the curve cd exhibited.

From expression (1), we can see that pH value has great impact on the formation of MoO_4^{2-} ions. Yoshimura and coworker [13] obtained the $BaMoO_4$ films by electrochemical dissolution of molybdenum substrate. The film grows in the direction that its *c* axis is perpendicular to the surface of the substrate. Crystal grains grew like a "dendritic" deposition toward higher concentration due to the very low concentration of discharge ions nearby electrodes. So the current density is one of the major factors affecting the surface morphology and the degree of order. Although both the higher pH value and higher current density can accelerate the dissolution rate of molybdenum substrate, they may not be better conditions to form unique film if the mass transfer and free solution process were considered. On the other hand, it is obvious that the dissolution in higher pH is easy, but the diffusion with lower concentration of Ba^{2+} may be difficult. Moreover, it is impossible for coexisting of both the high concentration of Ba^{2+} ions and the high pH because of the inherent voluminosity constant of $Ba(OH)_2$ solution. It proved once again that the micro-current is necessary for the oxidation–dissolution of active metal, although molybdenum metal has a tendency to dissolve and form MoO_4^{2-} ions in alkaline solution. Therefore, regardless of direct chemical reaction [14], galvanic cell method or oxidant-assistant galvanic cell method [15], they just provide stronger driving force than that of just alkaline $Ba(OH)_2$ solution. As shown in Fig. 2b, the *M* value increases with the increase of pH value. If we want to accelerate the oxidation–dissolution process, adding oxidant was feasible. When oxidant is added the electrode reaction may be accelerated but it does not make nickel electrode lose its original function. Here, the oxidant can be reduced on nickel electrode, so galvanic cell system still keeps working and the repulsion of the electric field may not be increased more.

Except for the main problems of driving force, the concentration of Ba^{2+} ions is also an important factor for film formation. As shown in Fig. 2c, where the abscissa represents the concentration of Ba^{2+} ions, the curve abc represents the quality change (*M*) when the treatment concentration was increased. It is obvious that the change of quality is not a simple increase or decrease but showed a U-type change. In the solution process, simple changes of treatment conditions may lend to some unpredictable variation. At lower and higher Ba^{2+} ions concentration the variation of weight is higher than that within the range of 0.2–0.4. It implies that the deposition pattern of grains may be changed when we change the Ba^{2+} ions concentration from lower to higher. X-ray diffraction patterns of $BaMoO_4$ film prepared by a galvanic cell method at lower concentration of Ba^{2+} ions are shown in Fig. 3a–c. This figure indicates the presence of crystalline tetragonal $BaMoO_4$ when the concentration of Ba^{2+} ions is lowered. The morphologies of the $BaMoO_4$ films with high treatment concentration are not uniform in Fig. 3d, and when the treatment concentration increased to 0.48 mol L^{-1} in Fig. 3e, the obvious grain boundary, uniform surfaces, and tetragonal grains disappeared. These results are in agreement with the tendency characterized by XRD and the weight variation. Therefore, if the Ba^{2+} ions concentration becomes much higher, there may be great changes on the morphology and crystal phase structure.

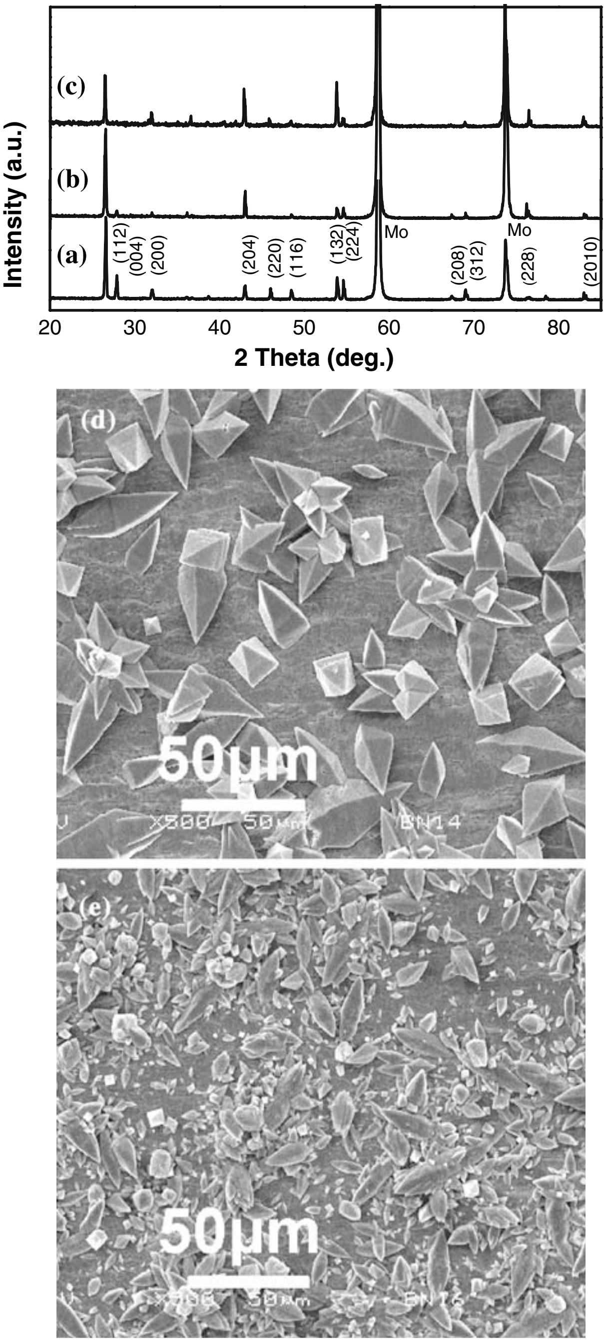

Fig. 3 X-ray diffraction patterns (a–c) and SEM micrographs (**d–e**) of the $BaMoO_4$ films prepared on molybdenum substrates in barium hydroxide aqueous solution by a galvanic cell method at room temperature under different treatment concentrations: a = 0.0067 mol L^{-1}, b = 0.0133 mol L^{-1}, c = 0.04 mol L^{-1}, **d** = 0.16 mol L^{-1}, and **e** = 0.48 mol L^{-1}, respectively

Conclusions

The galvanic cell method has been successfully used to prepare $BaMoO_4$ double oxide film at room temperature. The whole deposition process has been discussed qualitatively through investigating the variation of weight of $BaMoO_4$ films between as-prepared film and molybdenum substrate. Based on our recent study, we hope that the advantages of galvanic cell method can be fully demonstrated and this work could provide a framework to design other molybdate oxide films.

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References

1. Sawa G, Inayoshi T, Nishio Y et al (1977) J Appl Phys 48:2414
2. Gopalan S, Virkar AV (1993) J Electrochem Soc 140:1060
3. Kennedy JH, Hunter JC (1976) J Electrochem Soc 123:10
4. Schoonman J, Wapenaar KED, Oversluizen G et al (1979) J Electrochem Soc 126:709
5. Schoonman J (1976) J Electrochem Soc 123:1772
6. Song YY, Gao ZD, Kelly JJ et al (2005) Electrochem Solid-State Lett 8:C148
7. Watanabe H, Kitamura T, Hoshino K (2003) Electrochem Solid-State Lett 6:D1
8. Lam RUE, Blasse G (1979) J Chem Phys 71:3549
9. Šulc J, Jelínková H, Basiev TT et al (2006) Proc SPIE 6100:61000Z.1
10. Rosa ILV, Marques APA, Tanaka MTS et al (2008) J Fluoresc 18:239
11. Cui C, Bi J, Wu C et al (2008) Mater Res Bull 43:1160
12. Bi J, Cui CH, Lai X et al (2008) Mater Res Bull 43:743
13. Cho WS, Yoshimura M (1997) Solid State Ion 100:143
14. Cui C, Bi J, Shi F et al (2007) Mater Lett 61:4525
15. Cui C, Bi J, Gao D (2008) J Cryst Growth 310:4385