Molybdenum Oxide Thin Solid Films Prepared With a New Chemical Bath Deposition Method

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Thin solid films of molybdenum oxide were prepared with chemical bath deposition method. The films have been prepared from acidic, aqueous bath containing solution of ammonia molibdate and diethyl sulfate on glass substrates coated with fluorine doped SnO_2 thin film. The films were characterized by studying their structural and electrochemical properties. It was found that the thickness of the prepared films from one chemical bath is approximately 62 nm. Electrochromic properties of thin films were examined by changing polarity of the voltage into aqueous 0.1 mol/dm^3 solution of $LiClO_4$.

Key words: Electrochromism, molybdenum oxide films, chemical bath deposition

Introduction

Electrochromism can be broadly defined as a persistent and reversible colour change induced in a material by an applied electric field or an electric current [1]. Molybdenum oxide MoO_3, is one of transition-metal oxides constituting a very interesting group of semiconducting material that is based on cathodic colouration.. It's thin solid films derived materials have received increasing attention in recent years. Regarding the MoO_3 used in electrochromic display applications [2,4], in the field of microelectronics [5], electrochemical devices [6], charge–density wave conductors [7], optical materials [8] there is an increase interest to fabricate these films. In addition to electrochromic properties, this material also demonstrates photochromic and thermochromic properties, due to the formation of color centers by light irradiation and temperature effects, respectively [9].

Recently, soft solution processing (SSP) has raised considerable attention, as it is a one-step, environment-friendly and low-energy consumption process among existing methods of preparing thin films [10]. As a branch of SSP, chemical bath deposition (CBD) has been well developed to fabricate the large-area semiconductor thin films in view of many advantages: it does not require sophisticated instruments-like vacuum system and other expensive equipments and the starting chemicals are commonly available and cheap; the low-temperature deposition avoids oxidation and corrosion of metallic substrates and various substrates including insulators, semiconductors or metals can be used; the preparation parameters are easily controlled [11-13]. The chemical bath deposition technique uses a controlled chemical reaction in the liquid phase to effect the deposition of a thin film. In this method, substrates are immersed in appropriate solution containing the appropriate anion source and the metal ions. Usually, a chelating agent is used to limit the concentration of the one ion types (the metal ion or anion) and provide some stability to the bath, which would otherwise suffer quick precipitation.

There is variety of methods for preparation of thin electrochromic molybdenum oxide films. Usually they are prepared by vacuum evaporation [14-16], electron beam evaporation technique [17], sputerring [18,19], chemical vapour deposition [20-22] plasma-enhanced chemical vapour deposition [23] and electrodeposition [24]. Films prepared by one of these methods shows colouration phenomenon that is similar to those observed in tungsten oxide films [25].

To the best of our knowledge, up to now, there is no report on chemical bath deposition method of the MoO_3 thin films.

This paper presents a new economical and simple method for deposition of electrochromic molybdenum oxide thin films.

2. Experimental details

2.1. Preparation of the deposition solution

Preparation of the 0.01 mol/dm^3 aqueous solution of $(NH_4)_6Mo_7O_{24}$ was performed by weighting 0.62 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and it's dissolving in a beaker in 50 cm^3 deionized water. In addition 40 cm^3 of H_2O and 3 cm^3 of $(C_2H_5)_2SO_4$ were added. This was the solution used as chemical bath.

2.2. The deposition of the molybdenum oxide thin solid films

The composition of the chemical bath for deposition of molybdenum oxide thin film was optimized by varying the volume of $(C_2H_5)_2SO_4$ and concentration of $(NH_4)_6Mo_7O_{24}$. The optimized composition is given in the previous section.

Molybdenum oxide thin films were deposited onto glass substrates coated with fluorine doped SnO_2. Immersing the substrates into the chemical bath and with slow increase of temperature, follow by stirring, due to new conditions $(C_2H_5)_2SO_4$ becomes more soluble. At

temperature of 85 °C, $(C_2H_5)_2SO_4$ is completely dissolved. With increase of temperature, as a result of $(C_2H_5)_2SO_4$ hydrolysis the pH value of the solution i.e. the chemical bath is getting lower. The deposition process of molybdenum oxide thin film starts at 95 °C. The deposition starting time depends primarily on the temperature and concentration of the solution, while the films thickness is a function of the deposition time. The duration of the deposition process can vary from 5 to 20 min depending on the desired film thickness. At higher temperature and higher concentration, deposition starts earlier. The minimum amount of $(C_2H_5)_2SO_4$ needed for successful deposition of molybdenum oxide thin films was optimized for two solutions of $(NH_4)_6Mo_7O_{24}$ with different concentrations: solution I (c = 0.01 mol/dm^3) and solution II (c = 0.02 mol/dm^3). It was found that in case of more concentrated solution deposition starts at lowest pH. Due to that the minimum amount of $(C_2H_5)_2SO_4$ for more concentrated solutions is higher.

2.3. Characterization of the films

The identification of thin films was performed by a Bruker D8 Advance X-ray diffractometer and SEM analysis. The electrochemical properties were characterized by cyclic voltammetry measurements. Cyclic voltammograms were recorded by using MicroAUTOLAB II equipment (Eco-Chemie, Utrecht, Netherlands). A KCl-saturated Ag/AgCl electrode was used as a reference electrode, and a platinum wire as an auxiliary electrode. Aqueous solution of $LiClO_4$ with concentration 0.1mol/L was used. Also the thickness of the films was measured using a Surftest SV-500 Mitutoyo Co. profilometer.

3. Results and discussion

3.1. Structural properties and identification

Diffractograms recorded with a Bruker D8 Advance X-ray diffractometer show that the thin films possessed crystalline structure. The determinated *d*-values for the deposited material show that the deposited material is not stoichiometric MoO_3 and the exact ratio between molybdenum and oxygen atoms is not known yet. Due to that the thin films in the further text will be denoted as MoO_x. The comparison of experimental and literature *d*-values is given in the table 1. The marked experimental *d*-values are identical with those given in the literature.

2.7	1.85	2.31	6.93	2.66	3.46	3.81	3.26	MoO_3
2.81	3.34	6.04	2.67	2.72	3.92	3.39	3.6	MoO_3
1.95	1.72	1.99	4.56	2.53	3.04	9.12	3.45	MoO_3
1.95	2.65	3.67	3.77	3.45	3.31	6.9	3.24	$MoO_3{\cdot}2H_2O$
2.14	2.17	1.91	8.4	3.75	4.41	5.2	3.3	MoO
1.99	2.6	4.03	7.21	1.87	3.37	3.58	3.27	Mo_9O_{26}
5.41	7.26	10.3	11.5	2.85	3.83	3.94	3.59	$MoO_{2.8}$
3.63	2.1	2.23	2.89	3.17	5.77	6.7	3.34	$MoO_3{\cdot}H_2O$
3.14	1.93	2.22	2.44	2.72	1.64	4.23	3.36	$Mo_3O_8{\cdot}nH_2O$
2.41	1.4	2.4	2.43	1.72	1.7	2.42	3.41	MoO_2
2.08	2	1.74	1.86	2.3	6.65	7.3	3.56	$Mo_5O_7(OH)_8$
1.1	1.32	1.35	1.38	2.55	1.89	7.33	3.68	$Mo_5O_8(OH)_8$
2.33	2.34	3.52	7.05	1.87	2.64	3.3	3.75	$MoO_{2.5}(OH)_{0.5}$
1.76	1.28	1.36	1.95	2.73	2.03	2.26	3.69	$MoO(OH)_2$
2.79	2.72	3.95	1.65	2.66	3.75	4	3.48	$(Mo_4O_{11})O$
2.68	3.47	1.66	1.85	3.26	3.44	3.9	4.03	$(Mo_9O_{26})M$
1.87	2.7	3.96	4.47	1.94	3.47	3.42	4.05	$(Mo_8O_{23})M$

Table 1. Literature *d* values for various molybdenum oxides. The values that are identical with experimental *d* values for the deposited material are marked with gray background.

The Scanning Electron Microscopy (SEM) photomicrograph shown on Fig. 1 illustrates the crystal form (hexagonal prisms) of the monocrystals of the molybdenum oxide deposited at the temperature of 95 °C. We can clearly see that the films monocrystals are 5-10 μm long and 1.5-2 μm thick.

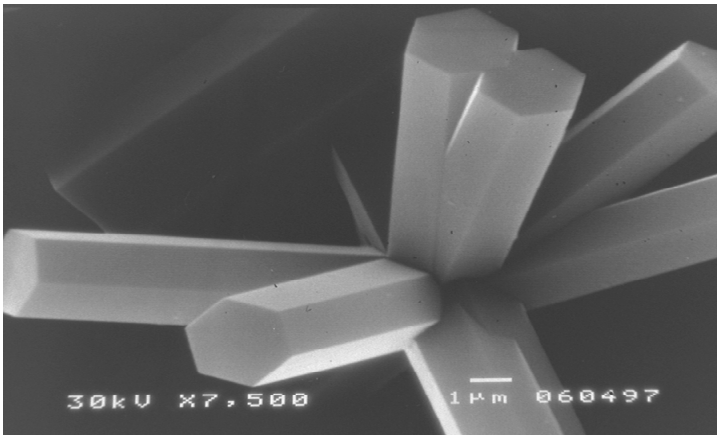

Figure 1. SEM photomicrograph illustrating a partial view of the deposit.

3.2 Electrochemical properties

Electrochemical properties of molybdenum oxide thin films were investigated by cyclic voltammetry measurements. Cyclic voltammograms (CV) of two samples (1 and 2) with different thickness are shown in Fig. 2a and Fig. 2b. Sample 1 (Fig. 2a) has thin film which is deposited for 5 min while sample 2 (Fig. 2b) has 10 min deposition time. Both voltammograms were recorded at scan rate of 10mV/s and it can be seen that they have similar shape. Voltammograms show very well defined peaks that occur in the process during intercalation or deintercalation of Li^+ ions (which are from the electrolyte 0.1 mol/L $LiClO_4$). The peaks, one oxidation and one reduction, have, a different position in their maximum in each case. The difference in the maximum of oxidation and reduction peak in Fig.2a and Fig 2b. is directly correlated with amount of intercalated and deintercalated lithium ions. The presence of only one oxidation and one reduction peak means that the system is composed from only one redox couple and this couple is very stable for at least 5 cycles.

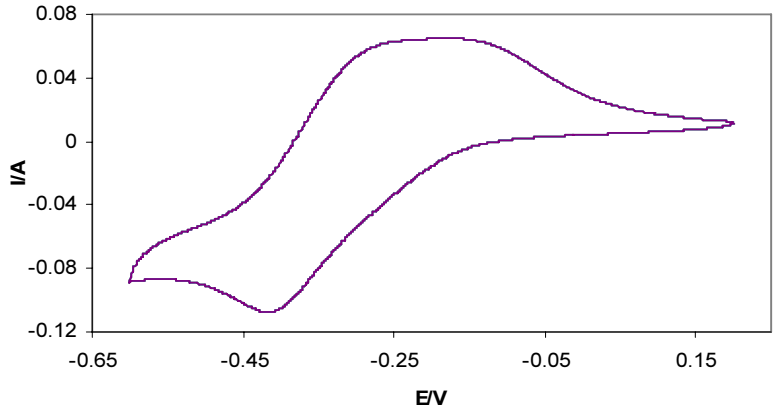

Fig.2a. Cyclic voltammogram of sample with 5 min deposition time, recorded at scan rate 10 mV/s.

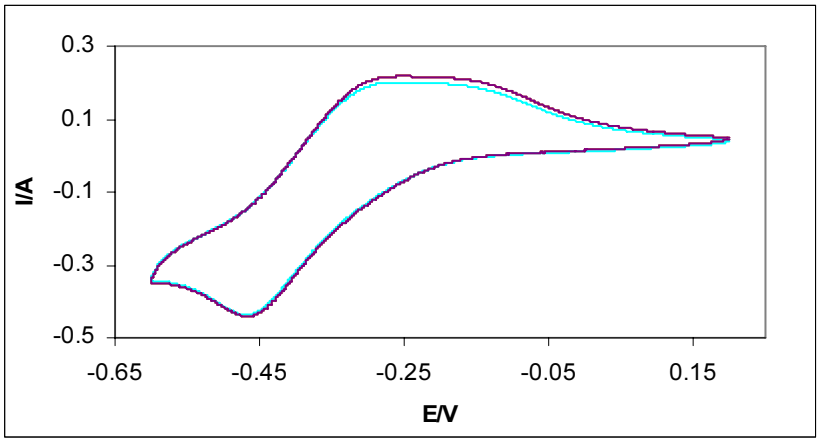

Fig.2b. Cyclic voltammogram of sample with 10 min deposition time, recorded at scan rate 10 mV/s.

5. Conclusion

Molybdenum oxide thin films prepared by the proposed chemical bath deposition method show good performance for electrochromic applications in electronic devices. Diffractograms show that the films comprise non-stoichiometric MoO_x crystalline material. The analysis of recorded cyclic voltammograms proved that the films, from the electrochemical point of view, are very stable and consisted of one redox couple. The proposed method is simple, economical and provides deposition on odd-shape substrates.

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