

**Chemical Deposition Of Molybdenum Oxide Thin Films
From Dimethyl Sulfate Bath**

Toni Todorovski^a, Metodija Najdoski^{a*}, Julijana Velevska^b

^aInstitute of Chemistry, Faculty of Natural Sciences and Mathematics
The “Sv. Kiril and Metodij” University, PO Box 162, 1000 Skopje,
Republic of Macedonia

^bInstitute of Physics, Faculty of Natural Sciences and Mathematics
The “Sv. Kiril and Metodij” University, PO Box 162, 1000 Skopje
Republic of Macedonia

New chemical bath deposition method for preparation of molybdenum oxide thin films is described. The films have been prepared from acidic aqueous solution of dimethyl sulfate and ammonium heptamolybdate. The deposition was performed on glass substrates coated with thin, transparent and conductive, fluorine doped SnO₂ film. Structural and electrochemical properties of molybdenum oxide thin films have been studied. It was found that the thickness of the prepared films from one chemical bath is approximately several micrometers. The analysis of recorded cyclic voltammograms proved that the films, from the electrochemical point of view, are very stable and consisted of redox couple.

Key words: Thin Films, Chemical Bath Deposition, Electronic Materials, Crystal Structure

Introduction

Chromism is a reversible change in a substance's colour resulting from a process caused by some form of stimulus (1). Many materials are chromic, including inorganic and organic compounds and the property is a result of many different mechanisms (1). There are several types of chromism, and consequently, several types of chromic substances: thermochromic, photochromic and electrochromic.

Electrochromism is a unique property of thin films or thin film systems to change colour, due to an applied potential, and change back to the original state by a potential reversal (2). Electrochromic materials have been known since 1967 (3). Numerous materials, inorganic and organic, liquids and solids, exhibit electrochromic behavior.

Electrochromic substances can be divided into two classes (4-6):

- cathodically colouring electrochromic materials;
- anodically colouring electrochromic materials.

Cathodically colouring substances possess a reduced coloured state, while anodically colouring substances are those with an oxidized coloured state.

Molybdenum oxide films are one of the most significant electrochromic materials which are based on cathodic colouration. There is variety of methods for preparation of these molybdenum oxide films. Usually they are prepared by evaporation (3), sputtering (7), chemical vapour deposition (8) and plasma-enhanced chemical vapour deposition (9). Films prepared by one of these methods shows colouration phenomenon that is similar to those observed in tungsten oxide films (2).

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, 12]. This technique involves deposition of semiconductor thin films on substrates that are immersed in dilute solutions. It is well known that there are two distinct mechanisms or models leading to the formation of CBD films, notably:

- adsorption and coagulation of colloids pre-formed in solution by homogeneous reaction (as usually called cluster-by-cluster process;
- ion-by-ion condensation at the surface of the substrate by heterogeneous reaction [13].

In practice, both processes may occur and/or interact in the growing films. Key parameters include the degree of supersaturation of the solution and the catalytic activity of the surface of the substrate [14]. Generally, the ion-by-ion process favors the formation of dense, adherent, mirror-like films, while the cluster-by-cluster process leads to opaque, non-uniform and poorly adherent films [15].

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

Experimental

Preparation of the deposition solution

A mass of 0.62 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ is weighted. The substance is placed in a beaker with 50 cm³ deionized water and the mixture is stirred. The prepared solution is 0.01 mol dm⁻³ aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. In addition 40 cm³ of H₂O and 3 cm³ of $(\text{CH}_3)_2\text{SO}_4$ are added in this solution.

The deposition of the thin films

Molybdenum oxide thin films were deposited onto glass substrates. By immersing the substrates into previously prepared solution and progressive increase of temperature, followed by stirring, $(\text{CH}_3)_2\text{SO}_4$ becomes more soluble that results in its complete dissolution. At temperature of 75 °C, $(\text{CH}_3)_2\text{SO}_4$ hydrolyzed and the solution becomes acidic. By further increase of the temperature to a maximum of 90 °C, after a couple of minutes, molybdenum oxide starts to deposit on the glass substrates. The starting time of the deposition depends primarily on the temperature and concentration of the solution while the films thickness is a function of the deposition time. Naturally longer deposition time will produce thicker film and *vice versa* shorter deposition time produces thinner film. The duration of the deposition process can vary from 5 to 20 min depending on the desired film thickness.

The minimum amount of $(\text{CH}_3)_2\text{SO}_4$ needed for successful deposition of molybdenum oxide thin films was determined for two solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ with different concentrations: Solution 1 ($c = 0.01 \text{ mol dm}^{-3}$) and solution 2

($c = 0.02 \text{ mol dm}^{-3}$). It was found that in case of more concentrated solution deposition starts at lower pH. Due to that the minimum amount of $(\text{CH}_3)_2\text{SO}_4$ for more concentrated solutions is higher.

Results and discussion

Structural properties and identification

The X-ray analysis shows that the thin films have crystalline structure. The determined 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 Mo_xO_y . In the Table 1 the marked experimental d -values are identical with those given in the literature.

The Scanning Electron Microscopy (SEM) photomicrograph shown on Fig. 1 illustrates the crystal form (hexagonal prisms) of the monocrystals of the molybdenum oxide films deposited at the temperature of $85 \text{ }^\circ\text{C}$. We can clearly see that the films monocrystals are $5\text{-}10 \text{ }\mu\text{m}$ long and $1.5\text{-}2 \text{ }\mu\text{m}$ thick.

The comparison of the infrared spectroscopy results of the commercially available MoO_3 and the precipitate from the chemical bath shows no significant difference, which points to the similar - equal chemical composition.

Electrochemical properties

Electrochemical properties of molybdenum oxide thin films were investigated by cyclic voltammetry measurements. Cyclic voltammograms were recorded 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. The electrolyte was a 0.1 mol/L LiClO₄ aqueous solution. Cyclic voltammograms (CV) of two samples (1 and 2) with different thickness are shown in Fig. 2. The deposition time for Sample 1 (Fig. 2a) is 5 min while the deposition time for sample 2 (Fig. 2b) is 15 min. Both voltammograms were recorded at scan rate of 10 mV/s and it can be seen that they have similar shape. Due to the process of intercalation/deintercalation of Li⁺ ions (which are from the electrolyte 0.1 mol/L LiClO₄), voltammograms show very well defined peaks, one oxidation and one reduction, which 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.

Conclusion

Molybdenum oxide thin film monocrystals have average grain size of 1.5-2 μm. Diffractograms show that the films comprise non-stoichiometric MoO₃ crystalline material. The analysis of recorded cyclic voltammograms proved that the films, from the electrochemical point of view, are very stable and consisted of redox couple. All this makes these thin films very promising material for electrochromic applications in electronic devices that can be prepared by simple and economical method.

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Figure Captions

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

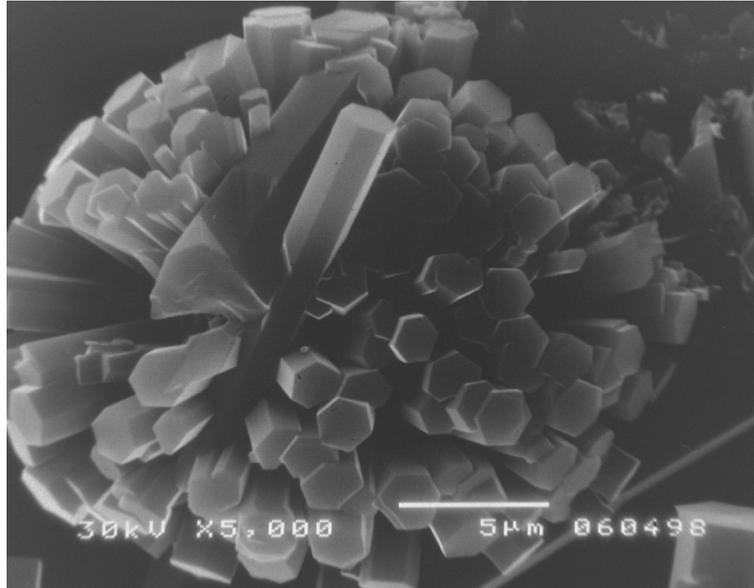


Fig.2a. Cyclic voltammogram of sample with 5 min deposition time, recorded at scan rate 10 mV/s.

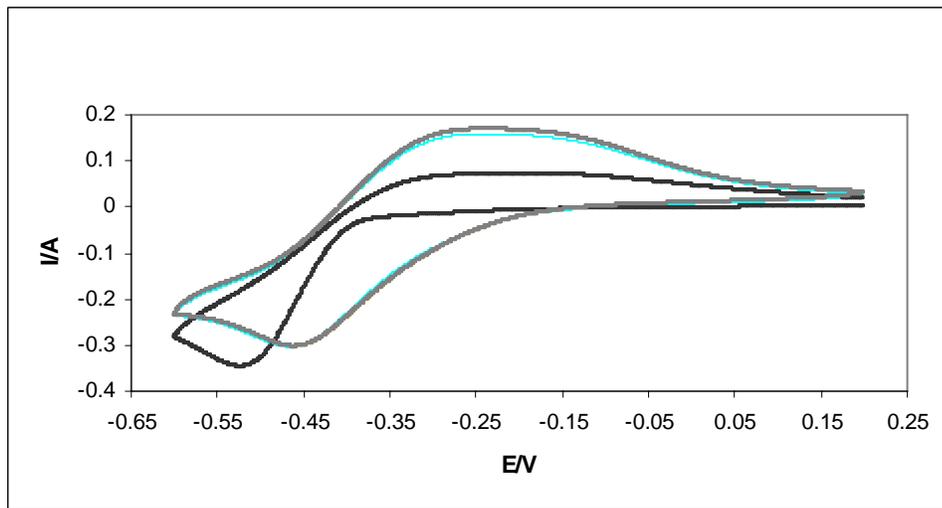


Fig.2b. Cyclic voltammogram of sample with 15 min deposition timem, recorded at scan rate 10 mV/s.

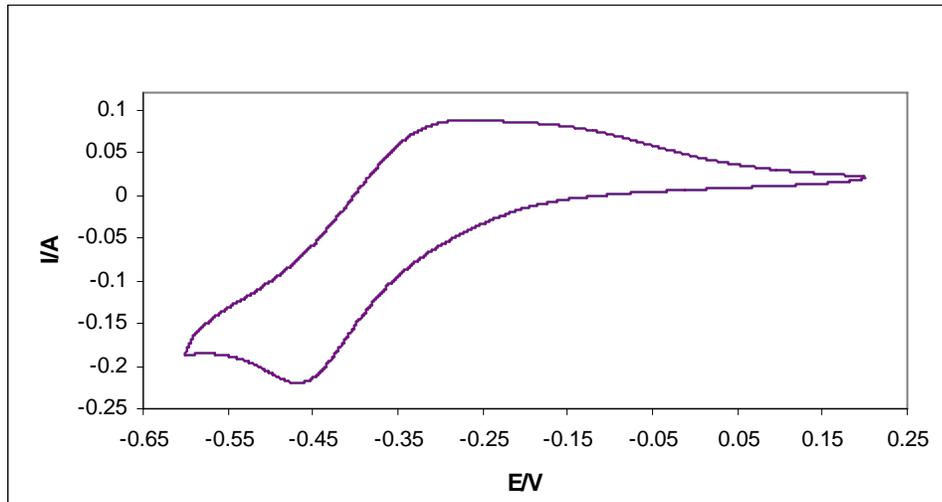


Table captions

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.

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 ·2H ₂ O
2.14	2.17	1.91	8.4	3.75	4.41	5.2	3.3	Mo-O
1.99	2.6	4.03	7.21	1.87	3.37	3.58	3.27	Mo ₉ O 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 ·H ₂ O
3.14	1.93	2.22	2.44	2.72	1.64	4.23	3.36	Mo ₃ O ₈ ·nH ₂ O
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 ₅ O ₇ (OH) ₈
1.1	1.32	1.35	1.38	2.55	1.89	7.33	3.68	Mo ₅ O 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 ₄ O ₁₁)O
2.68	3.47	1.66	1.85	3.26	3.44	3.9	4.03	(Mo ₉ O ₂₆)M
1.87	2.7	3.96	4.47	1.94	3.47	3.42	4.05	(Mo ₈ O ₂₃)M
1.84	2.64	2.67	2.72	2.81	3.4	3.6	3.93	(Mo ₄ O ₁₁) ₆₀ M
3.08	3.19	4.22	14.6	3.15	3.63	3.95	2.67	(Mo ₁₇ O ₄₇) ₁₂₈ O