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Crystallization of chemically vapor deposited molybdenum and mixed tungsten/molybdenum oxide films for electrochromic application

K.A. Gesheva [a], A. Cziraki [b], T. Ivanova [a], A. Szekeres [c,*]

[a] Central Laboratory for Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
[b] Eotvos Lorand University, Faculty of Solid State Physics, 1 Pazmany Peter setany, 1117 Budapest, Hungary
[c] Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria

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Abstract

The paper deals with investigation of Mo oxide and mixed W/Mo oxide films showing high electrochromic performance. Films are deposited on Si and conductive glass substrates using pyrolytical decomposition at 200 °C of Mo and W hexacarbonyls in Ar/O_2 atmosphere. The study is focused on structural transformation of the films in dependence on deposition and annealing process parameters. In case of conductive glass substrate (typical for electrochromic devices), the crystallization process in Mo oxide films is almost completed at 400 °C forming triclinic $MoO_{2.89}$ and orthorhombic MoO_3 crystalline phases. The structure of mixed W/Mo oxide films is triclinic crystalline phase of tungsten oxide matrix with Mo atoms as substitutes. Discussed are, as well, differences in the crystallization process for the same films, when the substrate is Si. All the films show electrochromic effect, the mixed W/Mo oxide films expressing stronger electrochromic effect with superior color efficiency and optical modulation.

Keywords: Chemical vapor deposition; Metal oxide films; Crystallization; X-ray diffraction; Electrochromic effect

1. Introduction

The investigations of the transition metal oxide thin films are connected with their application as active layers in electrochromic devices, mainly smart windows [1]. For an electrochromic device, a high optical transmittance of the active metal oxide layer is very important. The optical properties are defined by the film's specific structure, which should permit easy intercalation of ions. Molybdenum trioxide, compared to tungsten trioxide, shows lower color efficiency. However, the closer position of its optical absorption peak to the human eye sensitivity peak makes this material very attractive as electrochromic material [2,3]. Mixed films based on W and Mo oxides are expected to exhibit an enlarged optical absorption band. This could originate from increased electron transitions between two types of metallic sites in the two-component material [4]. Nevertheless the absorption band of MoO_3 is close to the maximum of the spectrum of human eye sensitivity, this material is still not used as active electrochromic layer due to its instability in acid and base media. That's why mixed oxides, based on tungsten with molybdenum trioxides system with general formula of $Mo_xW_{1-x}O_3$, are studied with aim to improve the electrochromic properties. Mixed oxide films as electrochromic materials, have been reviewed by Grangvist [5] and Monk [6]. It has been shown that bulk $Mo_xW_{1-x}O_3$ crystals have different structures depending on the composite content and the deposition method [5]. Therefore, similar behaviour can be expected for thin films of mixed oxides.

Electrochromic cells (EC) consist of multilayer stack embedded between two conductive glass substrates. In the device, the metal oxide films have a function of working electrodes and it is expected that the working characteristics of the cells will be improved by using of mixed W/Mo oxide films. Comparison of the working characteristics of experimental EC cells with electrodes of WO_3, MoO_3 and W/Mo oxide films prepared by vacuum evaporation [7] supports this expectation. It has been shown that these devices exhibit good optical

* Corresponding author.
E-mail address: szekeres@issp.bas.bg (A. Szekeres).

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properties with very low luminous transmittance values in the colored state, which make them suitable for large-area window applications [7]. For application as electrochromic devices, smart windows, the films are deposited on conductive glass assuring in unactive mode transparency of the window. Films on Si substrates are also studied, since the same films are very good gas sensors.

The goal of this paper is by XRD study to characterize the crystallization of the films (Mo oxide and mixed W/Mo oxide films) in dependence on the deposition and annealing temperature and the type of substrate. More specific, the influence of films crystallization on their electrochromic behaviour will be also studied.

2. Experimental details

Films of Mo oxide and mixed W/Mo oxide films were deposited on (100)Si substrates and conductive glass (Donnelly type SnO_2:Sb) by atmospheric pressure pyrolytical decomposition of the corresponding hexacarbonyls, $Mo(CO)_6$ and $W(CO)_6$. The sublimator temperature of 90 °C was controlled with an accuracy of ±1 °C. The CVD mixed oxide films deposition was done by the following steps: mixing the two precursor powders in a certain ratio ($Mo(CO)_6$:$W(CO)_6$ = 1:4) and heating the mixture at temperature of 90 °C. The selected flow rate of argon through the sublimator assured a constant supply of precursor vapor. Oxygen entered separately the reactor. The chosen ratio of flow rates of argon to oxygen was 1/32. The deposition temperature was 200 °C. This was a cross-point of the deposition temperatures for the molybdenum and tungsten metal oxide film [8]. The deposition time was kept constant (40 min) and because of the different growth rates the film thickness was 400 nm for MoO_3 and 300 nm for mixed W/Mo oxide films. Some of the samples were additionally annealed at 400 and 500 °C for 1 h in air.

The development of crystalline phases in the CVD metal oxide films due to thermal annealing was analyzed by Philips X'Pert diffractometer employing Cu radiation (λ = 0.154056 nm). The crystalline phases were identified using data from the ASTM system [9]. The X-ray diffraction (XRD) patterns are measured in the whole angle range, but the XRD patterns are presented here only in the main angle range (20–40°), where most of the characteristics peaks for the metal oxides are situated.

The electrochromic behaviour is studied by cyclic voltammetry measuring the current density versus applied voltage. The characterization of the films deposited on conductive glass was performed in electrochemical cell with standard three-electrode arrangement. In the cell the metal oxide film served as working electrode, for electrolyte — propylene carbonate (PC) with Li $(ClO)_4$ was used. This electrolyte is chosen because of its stability to high currents. Platinum was used as a counter electrode and the reference electrode was a saturated calomel electrode (SCE). The electrochemical set-up allows measuring the current, passing charge and light transmittance as a function of the applied voltage. When the films are good, the dependence of charge versus applied voltage is a closed curve and from its area the charge can be determined. The estimated values of intercalated and deintercalated charge are the values for $Q_{inserted}$ and $Q_{extracted}$, respectively.

The transmittance spectra were measured on a double-beam spectrophotometer Shimadzu UV-190.

3. Results and discussion

The broad XRD peak observed in deposited on (100)Si and annealed at 400 °C Mo oxide film (see Fig. 1a) reveals that the film structure is "XRD amorphous", which means that if there are crystallites their size and/or amount are rather small and, therefore, they are beyond the measurement sensitivity. We note that from the earlier derived Raman results, showing that the film is polycrystalline [10]. This seems to be a contradictory with these XRD results, but since the two techniques are different and moreover, XRD is in a strong dependence on the size and amount of crystallites, the obtained XRD results are reasonable and can be explained by the presence of small within a few nanometers crystallites in the grown films. After annealing at 500 °C, the Mo oxide films exhibit higher degree

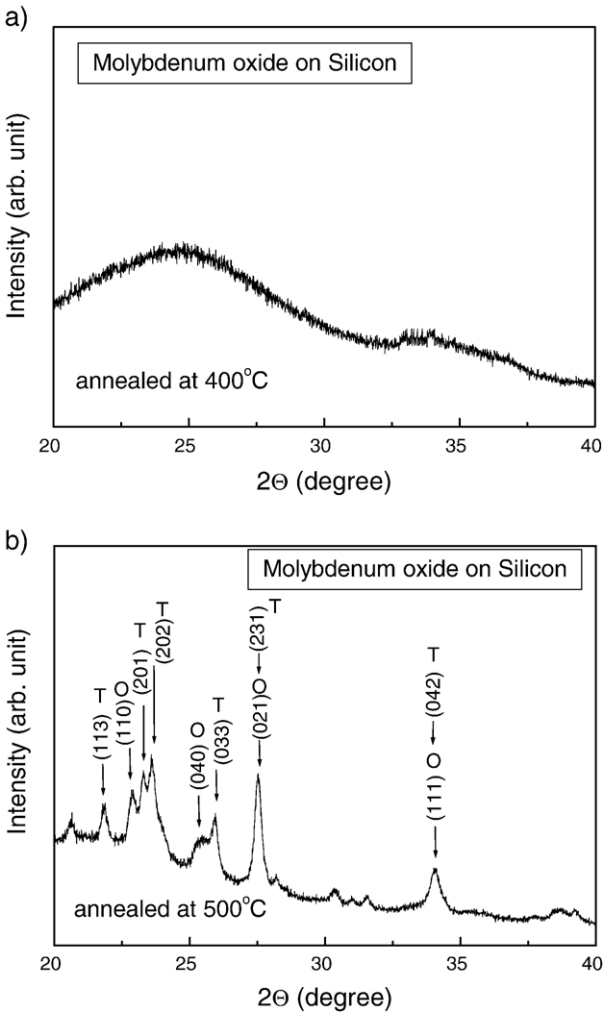

Fig. 1. XRD spectra of Mo oxide films annealed at 400 (a) and 500 °C (b). The films were deposited on silicon substrate at 200 °C and at a gas ration of 1/32. The inserted T and O letters label the triclinic and orthorhombic phases, respectively.