OPTICAL THIN FILM COATINGS OF CVD MOLYBDENUM OXIDES AND INVESTIGATIONS OF THEIR ELECTROCHROMIC PROPERTIES

T.Ivanova[1], K.A.Gesheva[2]
Central Laboratory of Solar Energy and New Energy Sources, Blvd. "Tzarigradsko chaussee"72, 1784 Sofia, Bulgaria

Electrochromic materials have the ability to modify their optical properties reversibly under the action of a small voltage. This characteristic is very important and interesting for "smart windows" and display applications (1, 2). The MoO_3 films are almost transparent, but when small alkali ions and electrons are electrochemically injected into these films, there is an observed color change to dark blue (3, 4). The color change is supposed to be directly related to the double intercalation/deintercalation of electrons and ions in the films, what can be written as:

$$xM^+ + xe^- + MoO_3 \leftrightarrow M_xMoO_3 \qquad (1)$$

where M^+ is a small alkali ion.

In this work, we present preparation and structural investigation of CVD deposited MoO_3 thin films. Electrochromic effect is studied at a single working electrode (MoO_3 film) under potentiostatic control using three-electrode configuration - a cyclic voltammetric technique.

Molybdenum oxide films were deposited by pyrolytical decomposition of $Mo(CO)_6$ in an argon-oxygen ambient at atmospheric pressure (APCVD process). The precursor placed in a sublimator immersed in a silicon oil bath is heated at 90°C. The flow rate of Ar through it assures an amount of precursors vapor. Through a separate line O_2 enters the reactor. In the present study the ratio of flow rates of argon to oxygen is varied from 1/12 to 1:40.

The deposition temperatures were 150 and 200°C. The film thickness was in the range of 120-240 nm for the low-temperature set of samples and 320-400 nm for the 200°C-set of samples. The deposition time was kept constant (40 min). For improving the film structure and the optical transparency, post-deposition annealing was applied in the temperature range of 200-500°C.

There are two basic polymorphs of MoO_3: a layered structure referred to as α - phase and distorted ReO_3 - like structure (β - MoO_3). These two phases are observed in the CVD films depending on the deposition parameters. The intense peak at 520 cm^{-1}, corresponds to the vibrations of the optical phonons of silicon. Comparing the spectra for samples at 1/40 gas ratio for the two set of films (two deposition temperatures) can be seen from fig.1 that the 150°C MoO_3 ones show sharper Raman peaks at 772, 843 cm^{-1} and a broader at 950 cm^{-1}. Can also be concluded that the 200°C film exhibits Raman bands only of the orthorhombic crystalline modification, while the MoO_3 film obtained at the lower temperature has structure, which is obviously α + β phase mixture.

The electrochemical measurements were carried out for the thin films, deposited on conductive glass substrates. All the films show electrochromic effect. Coloration as a result of Li intercalation is observed for the studied films. After 5 cycles it was also found that the molybdenum oxide films are reversible electrochemically and optically. The differences between the two main sets of samples are clearly seen. For all the samples, it is observed higher current densities for lower deposition temperature set. Fig. 2 presents the as deposited MoO_3 films for the 150 and 200°C deposition temperature. The curves have no significant features and peaks, which is an indication for amorphous disordered structure of the film. The main peak due to the injection of Li^+ ions appears around -1.37 V and the corresponding peak caused by ion extraction is at -1.14 V.

In conclusion, we state that MoO_3 thin films can be successfully obtained by atmospheric pressure chemical vapor deposition. These films are transparent, exhibiting different vibrational properties in dependence of CVD process parameters. In as deposited state all the thin films are amorphous - like and a crystallization starts after post deposition annealing. They showed reversible color change upon Li ion intercalation. In general, MoO_3 thin films show properties and quantities, which are useful for electrochromic applications.

Acknowledgements
The authors want to acknowledge the help of Dr.G.Popkirov group, where the electrochromic effect measurements were performed.

References

1. C.G.Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, New York, (1995)
2. A. Antonaia, T. Polichetti, M. L. Addonizio, S. Aprea, C. Minarini, A. Rubino, *Thin Solid Films*, **354**, 73, (1999)
3. S.H.Lee, M.J.Seong, C.E.Tracy, A. Mascarenhas, J.P. Pitts, S.K. Deb, *Solid State Ionics*, **147**, 129, (2002)
4. O. Zelaya-Angel, C. Menezes, F. Sanchez - Sinencio, G. F. l. Ferreira, *J. Appl. Phys.*, **51,** 6022, (1980)

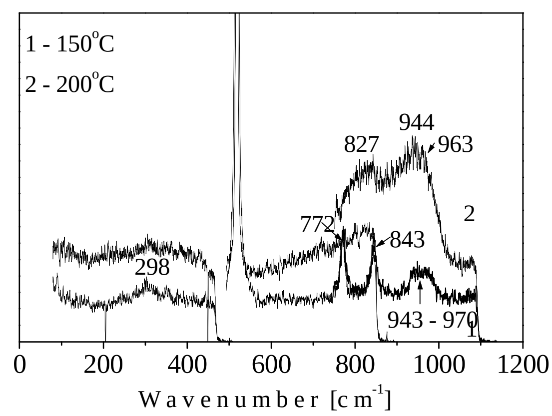

Fig. 1. Raman spectra of MoO_3 films, deposited at 150 and 200°C and additionally annealed at 400°C in air.

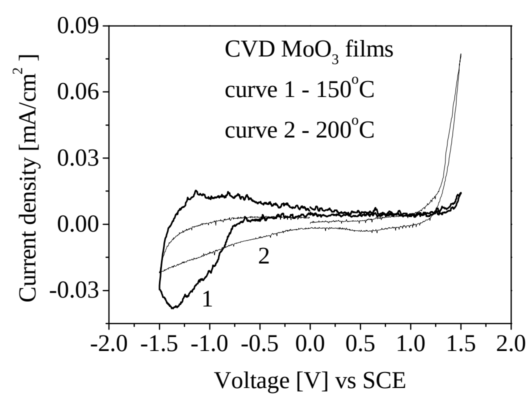

Fig. 2. CV curves of CVD MoO_3 films, deposited at deposition temperatures of 150°C and 200°C.