ELECTROCHROMIC CHARACTERIZATION OF Mo - W MIXED OXIDES AND MoO_3 THIN FILMS

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An electrochromic material is the one that changes colour in a persistent and reversible manner by an electrochemical reaction and the phenomenon is called electrochromism (1, 2). Mixed metal oxides have been investigated for their potential to possess improved electrochromic (EC) effect. We have tried previuosly with physical mixture of Mo and W hexacarbonyls and we obtained thin films with good optical behavior.

MoO_3-WO_3 films were deposited by pyrolytical decomposition of $W(CO)_6$ and $Mo(CO)_6$ in argon-oxygen at atmospheric pressure (APCVD process). The ratio of flow rates of Ar to O_2 is 1:16. The deposition temperature was 200^{o}C for 40 min. Cyclic voltammetry experiments were performed in a standard three-electrode arrangement. The electrodes were immersed in an electrolyte of 1 mol/l $LiClO_4$ in (PC).

FTIR spectrum of 300^{o}C annealed films (fig. 1, curve 1) exhibits very strong and broad band, centered at 668 cm^{-1}, but there is obviously an overlapping of more IR bands. The 668 cm^{-1} band is associated to the Mo - O - Mo bending vibration of MoO_3 (3). The weak shoulder at 796 cm^{-1} could either be associated to MoO_3 or to WO_3 vibrations. Interesting features appeared in the spectral range 930 - 1066 cm^{-1} - there are stretching modes of terminal double bonds of Mo = O and W = O (4). The main absorption band of the 400^{o}C annealed MoO_3 - WO_3 film is shifted towards 703 cm^{-1}, which might be due to vibrations of OMo_2 units . The weak bands at 932 and 998 cm^{-1} are due to terminal bonds of the both oxides. The 500^{o}C annealed film spectrum reveals two separate peaks at 724 and 803 cm^{-1}, superimposed over a broad and very strong absorption band, centered at 750 cm^{-1}. The two separate peaks are mostly reported as related to W - O stretching vibrations of crystalline WO_3 films (5). The lowest temperature annealed sample has IR peak centered at 717 cm^{-1}, and after annealing the center position is moved to 736 and 770 cm^{-1} for 400^{o}C and 500^{o}C annealed films, respectively. This shifting can be associated with crystallization in the film structure.

AFM images show surface morphology consisting of cluster - like grains with average size of 153 nm..

The CVD films of molybdenum oxide are coloured brownish after deposition and annealing, while the mixed oxide thin film have blue colour. This blue colour can be related to the influence of the tungsten oxide component and/or may be the presence of oxygen vacancies, which promote a reduction of the metallic atoms in the oxide structure.

All the investigated films are deposited on glass covered by film of SnO_2:Sb. Transmittance of the bare substrate is around 82% at 600 nm. The pure MoO_3 films are considerably more transparent than the mixed films. Their optical properties are improved after temperature treatment. The mixed oxide films show slightly decreasing of the transmittance after annealing.

All the films show an electrochromic effect. Colouration as a result of Li intercalation is observed for the films. The mixed oxide films exhibit the shape of the curves, which are considerably different than for pure metal oxide films. The CV curves of mixed oxide films have no pronounced peaks, the structure may be almost amorphous. The transmittance of mixed oxide films decreases rapidly after intercalation of Li ions into the film structure. They are coloured deep brown - bluish and the transmittance values decreased with about 30% at λ = 600 nm.

In conclusion, CVD mixed oxide thin films on the basis of Mo and W can be prepared with good electrochromic behavior. Colouration as a result of Li intercalation is observed for the films.

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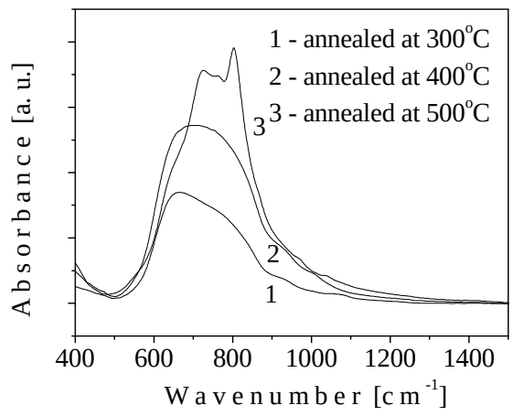

Fig. 1. FTIR spectra of CVD MoO_3 - WO_3 films, annealed at different temperatures for 1 h in air.

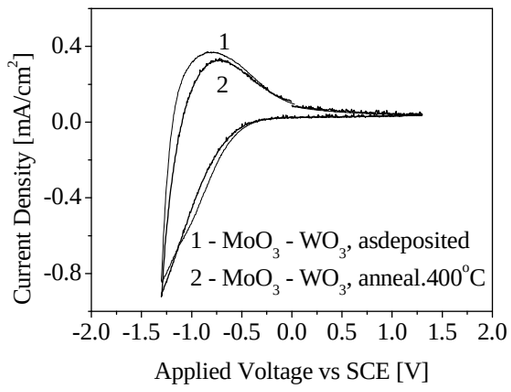

Fig. 2. CV curves of MoO_3 - WO_3 films, deposited at 200^{o}C in as deposited state and annealed at 400^{o}C for 1 h.