

OPTOELECTRONIC PROPERTIES OF CVD MoO₃ AND MoO₃-WO₃ FILMS AND THEIR APPLICATIONS IN ELECTROCHROMIC CELLS

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Thin films of MoO₃ and mixed Mo/W oxides were obtained by atmospheric pressure CVD, implying pyrolytic decomposition of metal hexacarbonyls. The optical transmittance was measured for the films. When deposited on typical glass substrates, the films showed about 80% transmittance in the visible. On conductive glass, this value dropped to around 60%. The electrochromic properties of MoO₃ and the mixed Mo/W oxide films were investigated by cyclic voltammetry, performed in a standard three-electrode arrangement. The cyclic change of current and transmittance as a function of the applied voltage for different wavelengths was measured. Over the voltage range studied, coloring appears in the cathodic EC film – MoO₃, WO₃ or mixed film, which at negative voltage suddenly colors to deep blue. Correspondingly, at that moment, there is a minimum in the transmittance curve. Going towards positive applied voltages, the EC film begins bleaching (for about 3 minutes) and the cell regains its initial transparency. With the help of a monochromator, the experimental set-up allowed to study the change in the colour efficiency, as a function of different wavelengths in the spectral range of 400-800 nm.

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1. Introduction

Transition metal oxides are largely studied because of their electrochromic properties, for applications as smart windows and display devices. Tungsten oxide is the most studied material, in terms of its technology, structure and optical properties [1-6]. Similarly to tungsten oxide, the molybdenum trioxide thin films, which also exhibit electrochromism, are easily produced by different techniques, including chemical vapor deposition (CVD). Although molybdenum trioxide has a comparatively lower coloration efficiency for a given inserted electrical charge, the closer position of its optical absorption peak to the human eye sensitivity peak makes this material very attractive for many applications [7-12]. At low temperatures, the CVD carbonyl process is suitable for deposition of these materials - $T_{\text{dep.}} = 150\text{ }^{\circ}\text{C}$ or $200\text{ }^{\circ}\text{C}$ - one of the lowest reported CVD temperatures for obtaining MoO₃ films at atmospheric pressure [12]. A temperature of $200\text{ }^{\circ}\text{C}$ is a crossing point, the only temperature at which the two pure precursors can be vaporized together. This was the substrate temperature for obtaining the mixed films. Mixed films are expected to exhibit an enlarged optical absorption band. This could originate from the larger amount of defects in the two-component material. A higher coloration efficiency is expected, due to increased electron transitions between two kinds of metal sites with different valences (W^{6+} , W^{5+} , W^{4+} , Mo^{6+} , Mo^{5+} , Mo^{4+}).

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The two basic crystal phases are the unique layered structure (α - MoO₃ with orthorhombic symmetry) [13] and metastable monoclinic β MoO₃ [14]. These phases differ in their vibrational and optical properties. Detailed studies of the structural, vibrational and optical properties of the APCVD films of MoO₃ and mixed oxide films have been published in the last few years [15,16]. The purpose of this work was to study in greater detail the electrochromic properties, and to relate the results to Raman, spectrophotometric and ellipsometric data.

2. Experimental details

The structure and properties of the deposited films are strongly influenced by technological parameters such as the deposition temperature ($T_{\text{dep.}}$), the sublimator temperature ($T_{\text{subl.}}$) and the vapor/gas ratio (Mo(CO)₆/Ar). MoO₃ films are successfully obtained in the temperature range 150-200 °C. Experiments with deposition temperatures above 200 °C (300 and 400 °C) showed that there was no film deposit on the substrate, but powder and deposits were observed on the reactor walls. This is a sign that the CVD process for MoO₃ film deposition requires a lower $T_{\text{dep.}}$, compared with the similar process for WO₃ films, which were successfully deposited in the temperature range from 200 to 400 °C [6]. The film thickness obtained was in the range 120-240 nm, for MoO₃ films deposited at 200°C. Remarkably, deposition at a lower temperature (150°C), resulted in a higher deposition rate (10 nm/min compared to 6 nm/min for films deposited at 200°C), and thicker films. Lower temperatures obviously favor higher deposition rates for the Mo carbonyl CVD-process, possibly due to thermal decomposition of the molybdenum hexacarbonyl in the vapor phase at higher temperatures. Our first experiments of CVD mixed oxide preparation were performed following the following method: i) the two precursor powders were physically mixed in the ratio Mo(CO)₆:W(CO)₆=1:4; ii) the mixture was heated in a silicon bath at a temperature of 90°C; iii) the obtained films were subjected to post-deposition annealing at 200-500°C, to improve their structures and optical properties. Due to the differences in the vapor pressures of the two carbonyls, the ratio of their partial pressure could not be kept constant, and therefore the control of the film composition was very difficult.

The Raman scattering spectra were measured by a Dilor XY triple monochromator, with a multichannel optical detector. During recording of Raman spectra in the range 100-1100 cm⁻¹, the intensity of He-Ne laser (λ =632.8 nm) excitation was controlled with an accuracy of 1%. The excitation power on the sample surface was 0.5 mW, and the excitation spot diameter was 3 μ m. The films were deposited on silicon substrates for these measurements. The Auger equipment was constructed at Bielefeld University, operating with an electron energy of 3 keV.

The transmittance and reflectance spectra of the films were registered in the range 300-900 nm with a Shimadzu UV-190 double-beam spectrophotometer. The measurements of the full reflectance (diffusive plus normal) were carried out in a 100-mm integrating sphere. As a reference, the 100 % response of the magnesium oxide reflectance was taken. The films were deposited onto double-sided polished silicon substrates for the IR-spectra, and onto glass substrates for the UV-VIS spectra. The ellipsometric measurements were performed on a Rudolph Research ellipsometer, in the spectral region 300-820 nm at an angle of incidence of 50°. The accuracy of the angles of the polarizer, analyzer and light incidence were within $\pm 0.01^\circ$. Cyclic voltammetry experiments were performed in a standard three-electrode arrangement. The cell adopted had Pt as a counter electrode, and a saturated calomel (SCE) reference electrode. The sweeping potentials were provided by a Bank - elektronik Potentiostat, under computer control. The electrodes were immersed in an electrolyte of 1 mol/l LiClO₄ in propylene carbonate (PC) or 1 M H₂SO₄+ 50% glycerine. The current density vs. electrode potential curves were registered at a scanning rate of 20 mV/s. To change the wavelength, a monochromator was installed in the system, permitting the color efficiency to be estimated over a large spectral range (400-800 nm).

3. Results and discussion

3.1. Raman spectra

The shape of the Raman spectra of mixed oxide films suggests that the film structure remains amorphous-like, even after high temperature annealing at 400-500 °C. Annealing at 500 °C contributes crystallization (see Fig. 1), but the WO₃ and Mo_xW_{1-x}O₃ films still stay amorphous-like.

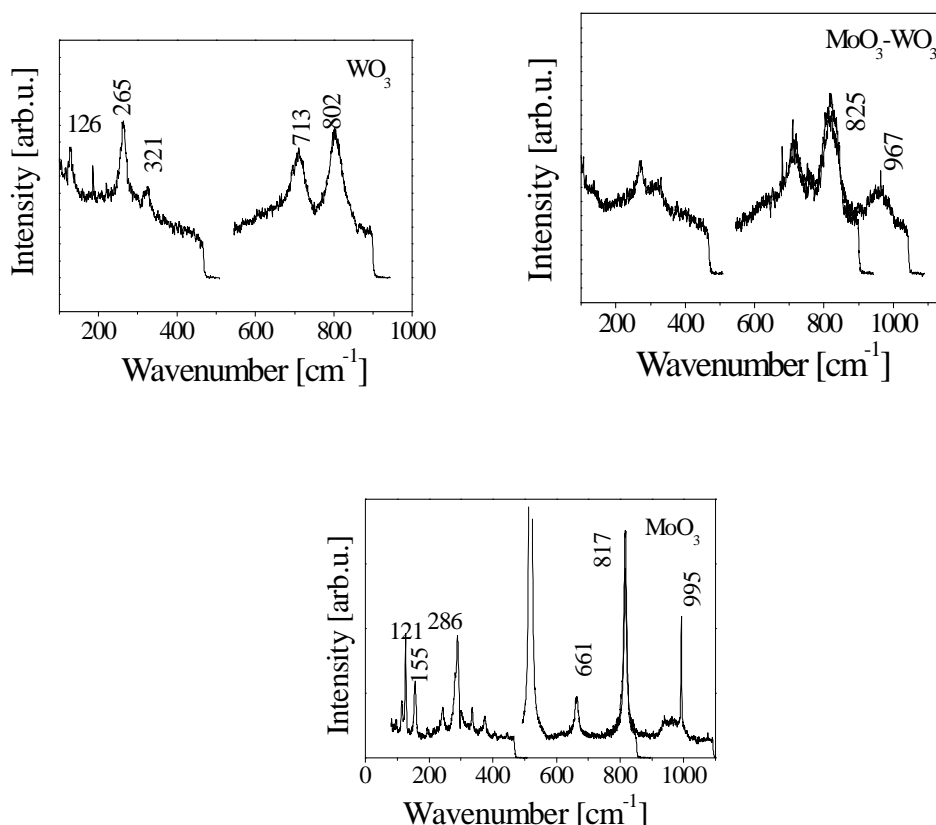


Fig. 1. Raman spectra of the WO₃, Mo_{1-x}W_xO₃ and MoO₃ films, annealed at 500 °C.

The main Raman lines at 661, 817 and 995 cm⁻¹ are related to the stretching vibrations, and can be connected with the α phase of MoO₃. The most pronounced Raman peaks for CVD WO₃ films are at 265, 713 and 802 cm⁻¹. The mixed oxide spectrum reveals Raman lines at 718 and 825 cm⁻¹, as well as a broad band at 967 cm⁻¹. From the Raman study, it can be concluded that the MoO₃ film deposited under the process conditions crystallized in a unique layered structure. Therefore, the peaks in the Raman spectra are an indication of the presence of crystalline MoO₃ phases in an amorphous WO₃ framework, and the MoO₃ structure is predominantly the α - phase.

The dN(E)/dE Auger spectrum as a function of kinetic energy has shown that Mo, W, C and O are present in the film. In order to take the distribution of the concentrations of the elements, the Mo-W oxide film was sputtered in Ar and the Auger signal was detected as a function of the sputtering time. The atomic concentration of a certain chemical element is estimated with sensitivity factors, which depend on the beam energy. For our case, the factors were: for Mo - 0.35, for W - 0.15, for C - 0.2 and for O - 0.5 [17].

Fig. 2 represents the estimated % atomic concentrations of the elements through the film thickness (as a function of sputtering time). It is observed that there is a uniform distribution of the elements. The presence of carbon is due to the chosen precursors, but this impurity does not appear

to affect the optical properties of these films. The Mo content is small, considering the average values of element concentrations. The CVD mixed film composition can be written as $\text{Mo}_{0.07}\text{WO}_{0.93}\text{O}_3$. This result is in good agreement with Raman data, showing that tungsten oxide is predominantly present.

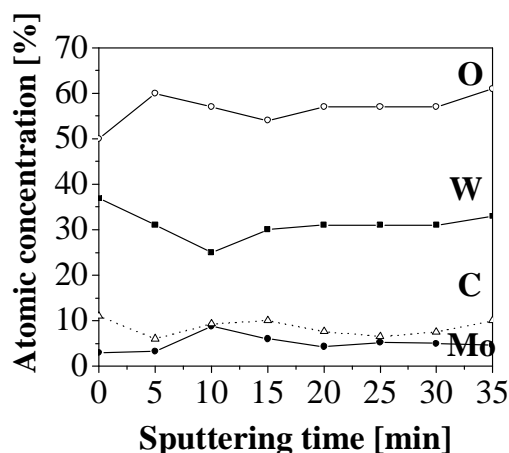


Fig. 2. The atomic concentration in the CVD Mo-W oxide film as a function of the sputtering time.

3.2 Electrochromic properties

In order to estimate the colour change, the cyclic voltammetry equipment was additionally supplied with an optical system: a chopped light source and a lock-in amplifier. The light passed through a monochromator, and then through a quartz cuvette, in which the three electrodes were immersed in the electrolyte.

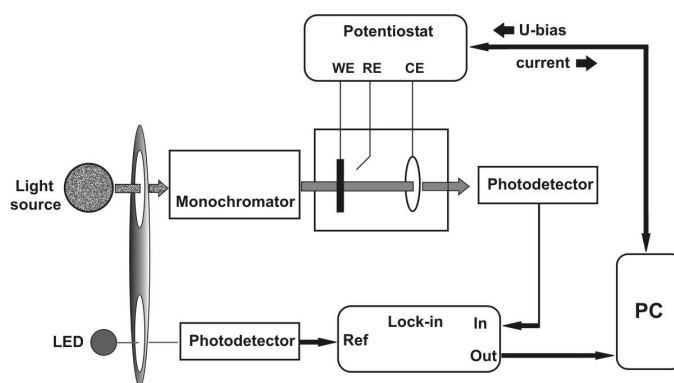


Fig. 3. Experimental set-up for electrochromic effect measurements.

The signal was measured automatically as a function of the applied voltage. A reference IR signal was also available. The signal change was monitored by an oscilloscope. This equipment allowed simultaneous measurement of the current, the charge and the transmittance, as functions of the applied voltage. The schematic diagram of the experimental set up is given in Fig. 3.

CVD mixed $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ thin films were electrochemically characterized, and were compared with pure oxides. All the films showed coloration as a result of Li^+ intercalation. The reaction which is expected to have taken place was:



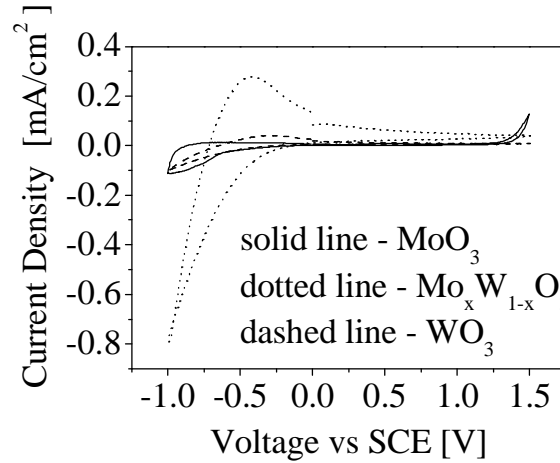


Fig. 4. Cyclic voltammetric curves of CVD MoO₃, WO₃ and mixed MoO₃-WO₃ films after annealing at 400 °C for one hour.

The most interesting feature is the rapid increase in the charge for the mixed oxide films. We note that these are the first APCVD mixed W/Mo oxide films made "in situ" with well defined electrochromic behaviours. After changing the voltage polarity (Li⁺ extracting), the films bleached and became transparent.

The diffusion coefficient D of the Li ions is of particular interest, and was determined from the formula:

$$i_p = 2.72 \times 10^5 n^{3/2} D^{1/2} C_o v^{1/2} \quad (2)$$

where D is measured in [cm²/s], the Li⁺ concentration is C_o - [mol/cm³], the sweep rate is v [V/s], the number of electrons, n , is assumed to be a unity, and the current density peak is i_p - [A/cm²].

Table 2. Values of diffusion coefficient for Li⁺ ions inserted in MoO₃, WO₃ and Mo_xW_{1-x}O₃ films.

Material	$T_{\text{anneal.}}/\text{time ann.}$	D [cm ² /s]
MoO ₃	As-deposited	6.76×10^{-12}
	400°C/one hour	5.3×10^{-12}
WO ₃	As-deposited	9.6×10^{-11}
	400°C/ one hour	2.25×10^{-11}
Mo _x W _{1-x} O ₃	As-deposited	4.41×10^{-10}
	400°C/ one hour	1.4×10^{-11}

Experimentally, the colour efficiency (CE) qualifies the modulation of the optical properties. This quantity was strongly dependent on wavelength and changes in the optical density (ΔOD). It can be determined by the equation:

$$CE = \Delta OD/Q, \quad (3)$$

where ΔOD represents the change in a single-pass of the optical density at the wavelength of interest, λ , caused by the transfer of charge Q .

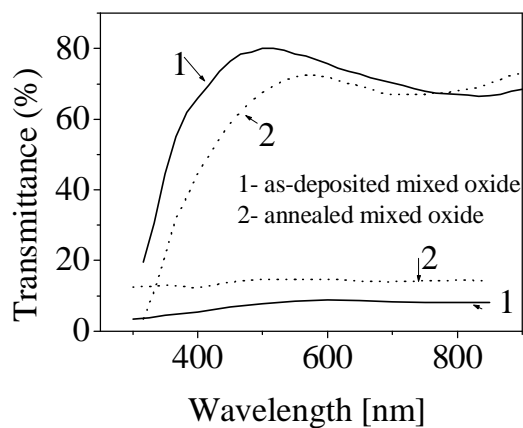


Fig. 5. Spectral transmittance of CVD mixed oxide films before and after Li intercalation.

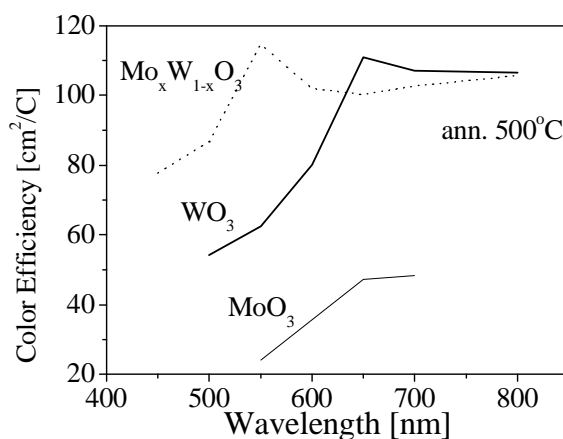


Fig. 6. *CE* values for MoO_3 , WO_3 and $\text{MoO}_3\text{-WO}_3$ films, annealed at 500 °C in air for one hour.

The transmittance of the mixed $\text{MoO}_3\text{-WO}_3$ films decreased rapidly after intercalation of Li^+ ions. The films were coloured deep bluish, and the transmittance values were under 10% .The modulation was 60-70% (see Fig. 5)

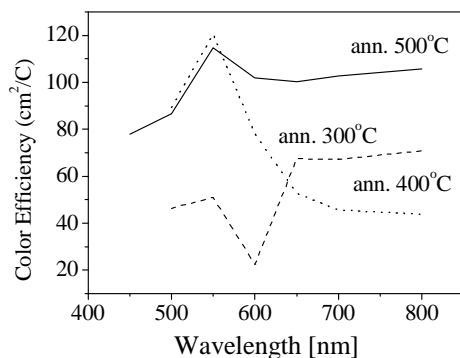


Fig. 7. Colour efficiency of CVD $\text{MoO}_3\text{-WO}_3$ films, annealed at 300, 400 and 500 °C.

Two types of cell were prepared: the first with a working electrode–mixed film as-deposited, and the second with an annealed mixed film. The construction of the cell was:



where PVA = polyvinyl alcohol, and PC = propylene carbonate. Two CVD mixed films were used: in the as-deposited state and after annealing at 500°C for one hour. The electrolyte was solid polymeric. Although not optimal (see the figures for the colour efficiency values of mixed films), the results for the cell colour efficiency at 600 nm are given in Table 4.

Table 4. Transmittance values at $\lambda=600$ nm of EC cells before and after Li⁺ intercalation.

Cell construction	Transmittance before intercalation / %	Transmittance after intercalation / %
Mo _x W _{1-x} O ₃ (ann. 500°C)/el./SnO ₂ : Sb	48.44	17.36
Mo _x W _{1-x} O ₃ (as deposited)/el./SnO ₂ : Sb	46	29

4. Conclusions

A low temperature CVD technological process has been developed for deposition of thin films of transition metal oxides. All the films were highly transparent. If deposited on conductive glass, the integral transmittance was about 60%. All the films showed the electrochromic effect. The films exhibited good reversibility of cycles between the coloured and the bleached state, and good colour efficiencies. The results of these investigations confirm that these CVD MoO₃ and Mo_xW_{1-x}O₃ thin films possess optical and electrochromic characteristics suitable for application in EC devices.

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