Optical and vibrational spectra analysis of CVD - mixed oxide films: optimization of the films electrochromic performance

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Abstract. Mixed oxide films based on Mo and W were successfully prepared by atmospheric pressure CVD at the low substrate temperature of 200°C. High amount of oxygen was used to ensure a high degree of oxidation resulting in more stoichiometric oxide films. The structural transformations under different thermal treatments were studied by Raman spectroscopy and FTIR spectroscopy analysis. The films were characterized electrochemically by cyclic voltammetry using different electrolytes, scan rates, etc. The mixed oxide films exhibited a strong electrochromic (EC) effect.

1. Introduction
Electrochromic materials have been studied intensively due to their ability to change reversibly their optical transmittance upon application of a voltage [1, 2]. WO₃ has been the most widely investigated material due to its superior electrochromic characteristics. It has also been studied in view of applications as gas sensors and photosensitive electrodes [3, 4]. Mixed W/Mo based oxide systems are interesting due to the possibility to combine the advantages of the single components’ properties. Electrochromic MoO₃ has an absorption band close to the maximum of human eye sensitivity. Various technologies have been reported for their preparation, such as vacuum evaporation, sol-gel and CVD techniques [5,6]. Due to the presence of electronic W⁵⁺, W⁶⁺ states, and the corresponding lower energy states of Mo, W/Mo based oxide systems exhibit stronger optical absorption. Electrochromic films are functional element in “smart windows” envisaged as energy control windows in buildings and automobiles. They control the energy of the solar flux entering the building, thus saving air-conditioning cost in summer and heating cost in winter [7].

This paper presents the investigation of low-temperature chemical-vapor growth of W/Mo oxide films. Their structure and chemical bonding are studied by Raman and FTIR spectroscopy. The optical transmittance is investigated by UV-VIS spectrophotometry. The optical modulation and color efficiency are determined from cyclic voltammetry data.

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2. Experimental
Mixed oxide films based on Mo and W were successfully prepared by means of an atmospheric pressure CVD method and CVD equipment that were described previously [8]. The substrates were heated to 200 °C. The precursor used was a physical mixture of Mo(CO)$_6$ and W(CO)$_6$ in a ratio 1:6 in favor of W(CO)$_6$; the sublimation temperature was 90 °C. The carbonyls vapors were carried by an Ar flow from the sublimator to the reactor. This Ar flow rate is related to the oxygen flow rate (reactive gas) at a given ratio, which is a measure for the oxygen amount. The ratios studied were 1/16 and 1/32. The samples were annealed at 500°C for 1 hour. The film thickness was 280 nm for WO$_3$-MoO$_3$ films prepared at a gas flow rate of 1/32, and 200 nm, for films at flow rate of 1/16. The IR measurements were carried out on Shimadzu FTIR Prestige-21 equipment. The Raman study was performed using a SPEX 1403 Raman spectrometer, Ar⁺ laser line 488 nm, laser power 54 mW. The optical transmission and reflection were measured by a Cary 5E Spectrophotometer at normal incidence in the range 350 - 2500 nm. The cyclic voltammetry experiments were performed in a standard three-electrode cell arrangement.

3. Results and discussions
The Raman spectra were recorded in the spectral range 100 – 1200 cm$^{-1}$. The peak located at 520 cm$^{-1}$ and the broad band at 960 cm$^{-1}$ are due to vibration modes of the Si substrates. The Raman spectra of as deposited MoO$_3$-WO$_3$ films (figure 1) reveal crystallized film produced at a higher oxygen amount (gas flow ratio of 1/32). The well-defined Raman lines are evidence of crystallization. Our previous studies [8] of MoO$_3$-WO$_3$ films deposited from different precursor mixture 1:4 showed that the films remain amorphous after annealing at 400 °C. The Raman spectrum of an as deposited film obtained at a lower oxygen amount (figure 1a, curve 1) is typical for an amorphous sample, the weak broad band at 783 cm$^{-1}$ being attributed to the stretching mode of monoclinic MoO$_3$ [9]. The spectrum of the film deposited at a higher amount of oxygen (1/32) contains four Raman lines at 261, 326, 711 and 809 cm$^{-1}$. These lines are assigned to crystalline monoclinic WO$_3$ as they match well the fundamental W-O-W bands of monoclinic WO$_3$ (273, 327, 715, 804 cm$^{-1}$) [10].

![Figure 1](image_url)

**Figure 1.** Raman spectra of MoO$_3$-WO$_3$ films in as-deposited a) and annealed states b): curves 1) presents spectra of films produced at the lower gas ratio 1/16 and curve 2) at ratio 1/32, i.e., a higher amount of oxygen.

The broad Raman bands are an indication for the presence of an amorphous fraction into the crystallized film. A possible explanation of the crystallization in the as-deposited film is its bigger thickness (280 nm) compared to the other film (200 nm). Thicker films crystallize during the film growth. Another contribution could be the faster growth-rate of WO$_3$ component in the presence of Mo precursor. We obtained similar results in some of our previous studies of MoO$_3$-WO$_3$ films [8].
Annealing of MoO$_3$-WO$_3$ at 500 °C in air for 1 hour (figure 1b) leads to full crystallization of the films, and stronger Raman lines are observed for the film deposited at a higher oxygen content. Intense Raman lines at 237.7, 325, 716.4 and 807.4 cm$^{-1}$ are seen; are assigned to monoclinic WO$_3$. In the spectrum of the MoO$_3$-WO$_3$ film deposited at the higher oxygen amount, a stronger peak at 133 cm$^{-1}$ and weak peaks at 170 and 190 cm$^{-1}$ are present. The weak lines are related to deformation modes of monoclinic $\beta$-MoO$_3$ and the peak at 237 cm$^{-1}$ is also assigned to MoO$_3$. This analysis leads to the conclusion that the CVD MoO$_3$-WO$_3$ films crystallize in monoclinic WO$_3$ with small inclusions of MoO$_3$.

The FTIR spectra presented in figure 2 were recorded for CVD Mo-W oxide films prepared at the two gas flow ratios, 1/16 and 1/32. The as-deposited samples reveal broad absorption bands at different locations. For the lower oxygen content (1/16), the band covers the spectral range 600-800 cm$^{-1}$ centered at 705 cm$^{-1}$; for the film prepared with higher oxygen content (1/32), the band is centered at 653.7 cm$^{-1}$. Weak IR bands are observed at 359, 418 cm$^{-1}$ for 1/16, and at 453 cm$^{-1}$ for 1/32. Our IR study of CVD MoO$_3$ and WO$_3$ films [8] showed main bands at 790 cm$^{-1}$ for MoO$_3$ and at 690 cm$^{-1}$ for WO$_3$ for as-deposited samples. A shift of the bands is observed due to vibration modes characteristic for MoO$_3$ and WO$_3$. The broad absorption band at 705 cm$^{-1}$ is assigned to W-O-W bridging modes and Mo-O vibrations [11]. The IR bands at 653.7 cm$^{-1}$ is attributed to stretching W-O vibrations of monoclinic WO$_3$.

![Figure 2. FTIR spectra of MoO$_3$-WO$_3$ films, a) as deposited and b) annealed at 500°C: curve 1 - for the lower oxygen amount 1/16, curve 2 - for 1/32.](image)

After annealing at 500 °C, the spectrum of the MoO$_3$-WO$_3$ film prepared at 1/16 shows bands at 357, 374 (weak), 418.5, 475, 802 and a strong band at 723 cm$^{-1}$. The IR spectrum of the 1/32-film is similar, with weak bands at 395.6 and 639.9 cm$^{-1}$, a sharp line at 801.9 cm$^{-1}$, and a strong one at 723 cm$^{-1}$. The maxima at 723 cm$^{-1}$ and 801.9 cm$^{-1}$ belong to monoclinic WO$_3$ [12]. The line at 723 cm$^{-1}$ is shifted compared to that at 706 cm$^{-1}$, this shift being related to the presence of Mo (VI) species [13]. The FTIR study confirms the presence of monoclinic WO$_3$ and reveal the influence of the MoO$_3$ fraction on the spectra.

The UV-VIS spectra of as-deposited MoO$_3$-WO$_3$ films on glass substrates show transparency, as high as 80% for films deposited at higher amount of oxygen, and 70% for the lower oxygen content samples.

The higher transmittance is related to an oxidized film grown in the presence of a high amount of oxygen. The optical transmittance of MoO$_3$-WO$_3$ films decreases by 20%, when conductive glass is used as a substrate (figure 3). An unexpected tendency is observed for the films prepared at the lower oxygen content (1/16), namely, the transmittance decreases after annealing. We observed such behavior in CVD MoO$_3$-WO$_3$ films deposited at similar process parameters with precursor mixture.
Mo(CO)$_6$·W(CO)$_6$ = 1:4 [14]. A possible explanation is a mass transfer process that would lead to structural rearrangement, but is not completed as it needs a longer time.

![Graph](image1.png)

**Figure 3.** Transmittance of CVD annealed MoO$_3$-WO$_3$ films obtained at the two gas flow rates ratios, a) 1/16 and b) 1/32. The substrates are conductive glass.

Films prepared at higher amount of oxygen (1/32) increase their transmittance after annealing. The same was observed for the single oxide components. The MoO$_3$-WO$_3$ films show coloring in 1 M LiClO$_4$ + PC and a good reversibility. The optical modulation and color efficiency were determined from voltametric data. Figure 4 presents the values obtained for as-deposited films. The optical modulation is 30 - 40 % for MoO$_3$-WO$_3$ films produced at the lower oxygen amount (1/16) with a maximum at $\lambda = 550$ nm. MoO$_3$-WO$_3$ films prepared at 1/32 show higher values of the color efficiency, namely, CE = 140.8 cm$^2$/C (550 nm). Our earlier study of CVD MoO$_3$-WO$_3$ films deposited from precursor Mo(CO)$_6$·W(CO)$_6$ = 1:4 showed $\Delta T$ = 45.2 % (550 nm) and CE = 196.5 cm$^2$/C (550 nm) for as-deposited samples [15]. These superior films were amorphous in structure. The results show that CE and $\Delta T$ are influenced by the Mo component in the mixed oxide structure.

![Graph](image2.png)

**Figure 4.** Color efficiency a) and optical modulation b) of CVD MoO$_3$-WO$_3$ films in as deposited state. The electrolyte used is 1 M LiClO$_4$ + PC.

Annealing at 500 °C leads to lower values of the optical modulation and color efficiency, namely, the films prepared at 1/16 showed $\Delta T$ = 28 - 43 % and CE values of 40 - 100 cm$^2$/C. We assume that this is due to crystallization of the films, as it is known that amorphous structures favor the electrochromic effect.
4. Conclusions
The structure of CVD MoO$_3$-WO$_3$ films is found to be strongly influenced by the oxygen content. WO$_3$ is the predominant crystalline phase in the mixed films structure. The transmittance is 80% when the films are deposited on glass substrates. The as-deposited at higher amount of oxygen mixed Mo/W based oxide films exhibit higher values of color efficiency and optical modulation.

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