APCVD Transition Metal Oxides - Functional Layers in “Smart windows”

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Abstract. Transition metal oxides (TMO) exhibit electrochromic effect. Under a small voltage they change their optical transmittance from transparent to colored (absorbing) state. The individual material can manifest its electrochromic properties only when it is part of electrochromic (EC) multilayer system. Smart window is controlling the energy of solar flux entering the building or car and makes the interiors comfortable and energy utilization more effective. Recently the efforts of material researchers in this field are directed to price decreasing. APCVD technology is considered as promising as this process permits flow-through large-scale production process. The paper presents results on device optimization based on WO₃-MoO₃ working electrode. Extensive research reveals that WO₃-MoO₃ structure combines positive features of single oxides: excellent electrochromic performance of WO₃ and better kinetic properties of MoO₃ deposition. The achieved color efficiency of APCVD WO₃-MoO₃ films is 200cm²/C and optical modulation of 65-70% are practically favorable electrochromic characteristics. To respond to low cost requirement, the expensive hexacarbonyl can be replaced with acetylacetonate. We have started with this precursor to fabricate mixed WₓV₁₋ₓO₃ films. The films possess excellent surface coverage and high growth-rate. CVD deposition of VO₂, a promising thermochromic thin film material is also presented.

1. Introduction
Recently, the necessity for global environmental conservation and the reduced use of electrical energy and decrease of CO₂ have led to the development of energy-saving systems. Electrochromic devices (ECDs) and especially “Smart windows” as energy efficiency-related have recently attracted considerable attention because of their low switching voltage, the ability to display various colors, high reflective contrast ratio, large viewing angle, memory effect and long-term functioning. The properties of transition metal oxides, serving as functional layers in ECD are mainly determined by their specific band structure and electron distribution. They possess d-electrons, which create d-band partially overlapping s-band. The d-band provokes the interesting chemical, physical and optical properties of transition metal oxides. Electrochromism is defined as effect of color change caused by applied voltage and has been found in several different metal oxides, the metals belonging to transition series. This experimental fact suggests close relation between electrochromic properties and electronic structure of the functional material.

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Major challenges in the development of smart windows involve the low cost fabrication of large-area devices with high optical quality. The electrochromic phenomenon was first discovered in tungsten oxide (WO$_3$) [1], which is still considered to be one of the best choices for the primary working electrode in EC devices [2] and remains the most promising candidate for large-scale EC devices [3]. EC effect occurs in the intercalated thin films of the smart window (WO$_3$) by dual injection (cathodic) or ejection (anodic) of ions and electrons. A typical reaction for a cathodic colouring material using lithium ions is [4]:

$$\text{WO}_3 \text{ (colorless)} + y\text{Li}^+ + ye^- \leftrightarrow \text{Li}_y\text{WO}_3 \text{ (blue)}$$

To assure this process a multilayer system is needed, functional electrode, counter electrode, and electrolyte between assuring ions in the system. Electrochromic films as working electrodes must be conductive for ions and electrons and after ions insertion from electrolyte or from an adjacent ion conductor there will be a charge-balancing counter flow of electrons from the transparent conductors. These electrons will evoke the modulation of optical properties and will remain in the EC film as long as the ions stay there. Ion conductor (electrolyte) can be a thin film or a bulk-like polymeric material or a liquid. Its role is to let a quick transport of ions between the EC film and the counter electrode without electrons passing through. The ion conductor should have high ion conductivity and negligible electronic conductivity, and it must be transparent in the range $0.35 \mu m \leq \lambda \leq 1.5 \mu m$ if the device is for architecture applications. Counter electrode is an important part of the EC device. It must be conductive for ions, as well as electrons. In order to have efficient counter electrode, it must meet some requirements: necessity of reversible preservation of charge under the form of injected ions and serve as ion storage; to be transparent in the spectral range of the device application; under the influence of ion injection to be optically passive or to exhibit electrochromism in a sense opposite to that of working EC electrode and to be long-term stable when cycling.

The basic characteristics of electrochromic device “Smart windows” as practical window are contrast ratio (CR) at least 4:1; coloring and bleaching times (switching speed) of a few minutes; operating glass surface temperatures of 20°C to 80°C; switching with applied voltage of 1-5 V; open circuit memory of a few hours (maintains a fixed state of transmission without corrective voltage pulses); acceptable neutral color; large area with excellent optical clarity; sustained performance over 20-30 yr; acceptable cost ($100/m^2$).

Major challenges in the development of smart windows involve the low cost fabrication of large-area devices with high optical quality. One important part of the EC price is due to the expensive transparent conductive coating. Polymeric flexible substrate materials are under development to replace the conductive glass [5]. Recent results [6] are related to a new transparent conducting layer namely ZnO doped with gallium (GZO) and other doped ZnO films.

WO$_3$ was studied in details in our group [7, 8] and it shows excellent electrochromic characteristics. The problem with APCVD WO$_3$ is that the growth-rate is too small at low temperatures. We accepted 200-300°C deposition temperature, because at higher temperatures, the alkali elements in the glass substrates diffuse, and if temperature gets over 400°C the glass starts “softening”. Keeping low temperatures when glass is involved is very important. We started to investigate APCVD MoO$_3$ expecting to grow faster at lower temperature. MoO$_3$ exists in many polymorph phases, one of which, the thermodynamically stable layered structure phase of MoO$_3$, often marked as $\alpha$ – phase is with an orthorhombic symmetry. The internal interaction among atoms is dominated by ionic and covalent forces, the sub layers pair interact by the weak van der Vaals forces [9]. Molybdenum oxide is known as a cathodic electrochromic material since long ago [10].

Molybdenum oxide films were obtained by atmospheric pressure chemical vapor deposition (APCVD) method, using the molybdenum carbonyl as a vapor precursor in an oxygen rich ambient. Molybdenum hexacarbonyl is a white powder which at room temperature does not react with air, with very low temperatures of sublimation and its powder density is Mo(CO)$_6$ = 1.96 g/cm$^3$. V. Syijrkin [11] presents a formula for determination of vapor pressure at a given temperature:
The vapor pressure ($p$) can be calculated using the equation:

$$
\log p = A - \frac{B}{T}
$$

where $p$ – vapor pressure is in units kPa, and $A$ and $B$ are constants.

Most probably the chemical reaction that takes place in the CVD reactor can be schematized as:

$$\text{Mo(CO)}_6 + \text{O}_2 \rightarrow \text{MoO}_3 + \text{CO}_2 \uparrow$$

We have experimented on different types of substrates and varying technological conditions [12-13]. The structure and film properties are strongly influenced by the technological process parameters, a large number of experiments were done for obtaining the films with optimal optical quality. The experimental approach is fixing one parameter and varying the others. The altered technological parameters of APCVD process are the substrate temperature ($T_{\text{deposition}}$), the sublimator temperature ($T_{\text{sublimator}}$) and the gas ratio (Mo(CO)$_6$/Ar). It has been established that MoO$_3$ films are successfully obtained in the temperature range of 150-200ºC with MoO$_3$ film thicknesses ranging 320-400 nm for the 150ºC set of samples and 120-240 nm for the 200ºC-set of samples [14]. The two sets were grown for one and the same deposition time. The lower-temperature set process was proceeding with higher deposition rate of 10 nm/min compared to 6 nm/min for the higher temperature samples, resulting in thicker films. This behavior is associated with thermal decomposition in the vapor phase.

Experiments with increasing the deposition temperatures above 200ºC (300 and 400ºC) showed that there was no film deposits nevertheless there were enough precursors vapors in the reactor, because powder deposits on the reactor walls were registered. This was a sign that this particular CVD process and the chosen construction of CVD equipment for MoO$_3$ film deposition requires lower substrate temperatures in comparison with the analogical process for WO$_3$ films, which were successfully deposited in the temperature range from 200 to 400ºC [11, 15, 16] Previous CVD research has focused primarily on producing molybdenum oxide films from chlorides, fluorides and carbonyls as vapor precursors. Lander and Germer [17] first deposited MoO$_3$ by low pressure CVD (LPCVD) by using Mo(CO)$_6$. Thin films of polycrystalline orthorhombic MoO$_3$ films were prepared and studied by double-step CVD at atmospheric pressure [18]. J. S. Cross et al [19] proceeded a thermodynamical study of low pressure chemical vapor deposition (LPCVD) of MoO$_3$, where the precursor used is Mo (CO)$_6$. The substrate temperature is varied in the range of 300-450ºC. Solid orthorhombic $\alpha$-MoO$_3$ is the most stable phase over these ranges of the temperatures. T. Maryama et al. [20] proposed APCVD method using Mo(CO)$_6$ with substrate temperature varied 150 to 400ºC and they obtained polycrystalline MoO$_3$ at 350ºC. The authors [20] found that the deposition rate increased with temperature to 250ºC with exhibited peak at 300ºC, then a decrease for substrate temperatures above 300ºC. They determined color efficiency 25.8 cm$^2$C$^{-1}$ at $\lambda=550$ nm.

2. Experimental

Using our experiences in WO$_3$ and MoO$_3$ film depositions, mixed films on their basis were deposited. The precursors are the corresponding hexacarbonyls. The hexacarbonyl precursors (W(CO)$_6$, Mo(CO)$_6$) were mixed in a ratio Mo(CO)$_6$:W(CO)$_6$=1:4. The deposition proceeded in argon-oxygen rich ambient at atmospheric pressure (APCVD process) in a horizontal cold walls CVD reactor. The precursor powder placed in a sublimator immersed in silicon oil bath has been heated at temperature of 90ºC and has been controlled with an accuracy of ±1ºC. This sublimator temperature provides a sufficient vapor pressure of the hexacarbonyls. The gas lines ("Galtek" type Teflon) were heated up to the sublimator temperature in order to assure successful transport of the vapors to CVD reactor. Argon (99.995%) flow carries the precursor vapors to the reactor. The selected flow rate of Ar through the sublimator assures a constant amount of the precursors vapor. Through a separate line, oxygen (99.95%) enters the reactor. In the present study the ratio of flow rates of Ar/O$_2$ is 1:32 [21-24].
For comparative study the deposition temperature was kept at 200°C because only at that temperature it was possible for the three kinds of the metal oxide films to be obtained. WO₃ can be prepared at higher temperatures (up to 400°C) and the growth rate increases with increasing temperature. The growth rate of MoO₃ decreases with increasing temperature due to the gas phase reaction [25, 12]. From this point of view, the temperature of 200°C is a cross point for the deposition of the mixed oxide films. The deposition time duration was kept constant (40 min).

The characterization methods applied are: UV - VIS Spectrophotometry characterizing transmittance and reflectance of CVD films, estimation of optical band gap energy (Eg). Auger Electron Spectroscopy (AES) for determination of chemical composition. FTIR Spectroscopy was employed for the investigation of vibrational properties and the chemical bonds; Raman Spectroscopy for determination of crystallization degree, phases and chemical bonds. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM), field emission scanning electron microscopy (FESEM) – all techniques for study of film morphology; Spectral Ellipsometry (SE) - study of the spectral dependences of optical constants (refractive index and extinction coefficient), analysis of dispersion curves of optical absorption. Cyclic Voltammetry - for investigation of electrochemical behavior of thin films under applied voltage and reversibility of electrochromic effect.

3. Results and Discussions
Optical transmittance was measured for the single oxides and the mixed oxide films. The results are shown on figure 1. It is seen that after annealing the transmittance of single oxides increases, while for the mixed WO₃-MO₃ it decreases. A possible explanation is mass transfer starting during annealing at elevated temperatures, but the process is not accomplished (annealing time was accepted to be one hour), the structure gets disordered, amorphous-like and the transmittance drops down.

![Figure 1. UV-VIS spectra of single oxides and mixed in as-deposited (1) and annealed (2) at 400°C. See the lower transmittance of mixed films after annealing](image-url)
The IR spectra recorded for the three types of films after 500°C annealing, have presented the different behavior once again of MoO$_3$ and the main band located at 834 cm$^{-1}$ (figure 2). This absorption band is related to Mo - O - Mo vibrations. The IR bands of W$_x$Mo$_{1-x}$O$_3$ and WO$_3$ are broad with greater overlapping of the two spectra with three maxima observed at 810, 717 and 640 cm$^{-1}$. The bands at 810 and 640 cm$^{-1}$ can be assigned to stretching W-O vibrations of crystalline monoclinic WO$_3$ and the absorption line at 717 cm$^{-1}$ is due to bending W=O vibrations. The IR spectra reveal that in the structure of Mo$_x$W$_{1-x}$O$_3$ films prevails the tungsten oxide fraction. The shifting of the main absorption band for the mixed film is another evidence for the presence of a new phase.

![Figure 2. IR spectra of the 500°C annealed films of MoO$_3$, WO$_3$ and MoO$_3$-WO$_3$.](image)

Figure 3. XRD spectra of MoO$_3$, WO$_3$ and MoO$_3$-WO$_3$ films, deposited on conductive glass substrates at the deposition temperature of 200°C and annealed at 400°C.
XRD patterns of MoO$_3$, WO$_3$ and MoO$_3$-WO$_3$ films, deposited on conductive glass substrates are presented on figure 3. Most of the XRD lines found can be assigned to the corresponding oxides. MoO$_3$ film consists of orthorhombic Mo trioxide and a small fraction of sub-oxide. The triclinic WO$_3$ phase is prevailed in the tungsten oxide film with W$_{20}$O$_{58}$ sub-oxide. The XRD spectrum of the mixed oxide film is very similar in shape to that of WO$_3$. Similar effect is observed for IR spectra. The XRD peak positions are the same with enhanced intensity, which leads to suggestion that W atoms are partly substituted by Mo atoms.

Figure 4 presents high resolution TEM micrograph of CVD as-deposited MoO$_3$-WO$_3$ film, grown at gas flow ratio 1/32. The columnar structure of the film is clearly observed, it is typical for the CVD grown films at temperatures below the melting point of the film material. These columns form grain boundaries which facilitate the ions intercalation.

AFM study reveals grained structure of CVD grown films. As seen from figure 5, there is a contrast change over a grain, which is evidence for clusterization in the film structure. These grains also facilitates the ions interaction, the coefficient of diffusion is bigger. The average surface roughness for MoO$_3$ is 31,4 nm, for WO$_3$ is 24,8 nm and for mixed oxide film is 45,7 nm, respectively. It must be noted that the film thickness is different, although the deposition parameters are the same.

Cyclic voltammetry is used as method to study insertion reactions and to receive information about the electrochemical effects. Cyclic voltammetric experiments were performed in a standard three-electrode arrangement. The electrodes were immersed in electrolytes of 1 mol/l LiClO$_4$ in propylene carbonate (PC). Current density vs. voltage voltammograms were registered between -1 V and +1.5 V. The cyclic voltammetric (CV) curves manifest that the as-deposited and annealed MoO$_3$-WO$_3$ films...
showed considerably a larger current density compared to the those of the single metal oxide (MoO$_3$, WO$_3$) films (see figure 6).

There is an improvement in the electrochromic properties with annealing. However, the most interesting feature is the rapid increase in the electrical charge (see table 1) for the mixed oxide films, proving its suitability and quality for applying in EC devices. The inserted and extracted charge density had been estimated from CV curves and they showed that the exchanged charges for WO$_3$-MoO$_3$ are much higher than those for single oxides.

![Figure 6. Cyclovoltametric curves of CVD MoO$_3$, WO$_3$ and MoO$_3$-WO$_3$ films, annealed at 400°C for 1 hour.](image)

Table 1. Inserted and extracted charge density determined from CV data.

| CVD Films       | $Q_{\text{inserted}}$ [mC/cm$^2$] | $Q_{\text{extracted}}$ [mC/cm$^2$] |
|-----------------|----------------------------------|-----------------------------------|
| MoO$_3$ As deposited | 31.57                            | 30.36                             |
| Ann. 400°C      | 16.62                            | 41.18                             |
| WO$_3$ As deposited | 23.56                            | 20.53                             |
| Ann. 400°C      | 30.20                            | 31.40                             |
| MoO$_3$-WO$_3$  As deposited | 116.3                            | 170.9                             |
| Ann. 400°C      | 195.59                           | 204.5                             |

Electrochromic characteristics were determined from the voltamograms. Color efficiency can be determined from:

$$CE = \frac{\Delta(OD)}{\Delta Q_{\text{ins}}}$$

where the optical density (OD) is related to extinction and film thickness:

$$OD = \frac{4\pi}{\lambda}kd$$

Experimentally, the change of optical density $\Delta(OD)$ can be determined from the relation:

$$\Delta(OD) = -\log 10\left(\frac{T_{\text{colored}}}{T_{\text{bleached}}}\right)$$
where $T_{\text{colored}}$ is the transmittance measured after ion injection and $T_{\text{bleached}}$ – transmittance of bleached film (extraction of alkali ions).

Color efficiency values for the three kinds of films, annealed at 500°C have been calculated and the results for different wavelengths are shown on figure 7. The color efficiency (CE) strongly depends on the wavelength and the changes of the optical density $\Delta OD$. The CE values in the visible range for MoO$_3$-WO$_3$ films are better than those for WO$_3$ films.

![Figure 7. Color efficiency values of CVD MoO$_3$, WO$_3$ and MoO$_3$-WO$_3$ films after annealing at 500°C for 1 hour in air](image)

Table 2 presents the estimated values of color efficiency and optical modulation of Mo-W oxides, depending on the scan-rate of the potential applied. Optimization is made related to the scan-rate of the applied potential by changing it as follows: 2, 5, 10, 20 and 50 mV/s.

| Scan rate [mV/s] | $I_{\text{anodic}}$ [mA] | $I_{\text{cathodic}}$ [mA] | $\Delta Q$ [mC] | $\Delta T$ (550 nm) | CE [cm$^2$/C] (550 nm) |
|-----------------|--------------------------|-----------------------------|----------------|-------------------|-----------------------|
| 50              | 1.22                     | -1.68                       | 19.18          | 21.10             | 43.49                 |
| 20              | 0.64                     | -0.76                       | 20.91          | 29.96             | 53.97                 |
| 10              | 0.36                     | -1.08                       | 30.64          | 45.21             | 196.46                |
| 5               | 0.09                     | -0.63                       | 33.54          | 49.59             | 88.69                 |
| 2               | 0.08                     | -0.39                       | 65.90          | 21.20             | 43.49                 |

Optimization is made related to the scan-rate of the applied potential by changing it as follows: 2, 5, 10, 20 and 50 mV/s. Table 2 presents the estimated values of color efficiency and optical modulation of mixed Mo-W oxide films depending on the scan-rate of the potential applied.

The high values of the color efficiency are obtained for mixed WO$_3$-MoO$_3$ films and after optimization it had been found that the optimal potential scan-rate is 10mV/s. The optical modulation, namely the difference between the transmittance in colored and bleach states was also estimated, and the results are seen in table 2. The best values (estimated for 550 nm, maximum of the solar spectrum) at the optimal potential scan-rate is 45%.

Two kinds of EC devices were prepared, integrated mixed WO$_3$-MoO$_3$ films in as-deposited state and after 500°C annealing. The solid electrolyte was prepared with 1 mol/l LiClO$_4$ in PC and adding polyvinyl alcohol: WO$_3$-MoO$_3$ /LiClO$_4$+PC+PVA/SnO$_2$: Sb. Table 3 shows that EC device involving
as deposited mixed oxide films showed lower transmittance after intercalation of Li ions, better electrochromic effect.

| Table 3. Transmittance values before and after ion intercalation. |
|---------------------------------------------------------------|
|                   | Initial Transmittance | Transmittance after Li injection |
| WO₃-MoO₃,         | 48.5 %                | 17.4%                            |
| As deposited      |                       |                                  |
| WO₃-MoO₃, 500°C annealed | 46.0%                | 29.0%                            |

Other interesting electrochromic materials are vanadium oxide and mixed W-V-O films. VO₂ undergoes a phase change across a critical temperature of 68°C. It is a promising thermochromic material for energy efficient fenestration [25]. Vanadium dioxide is largely studied and we try to add to the common knowledge results on APCVD carbonyl process deposited VO₂ films. Recently, we deposited thin films employing a mixed precursor of W(CO)₆ and V(CO)₆ [26]. However utilizing V(CO)₆ is not reasonable as it is too expensive. Thus, we adopted the cheaper vanadyl acetylacetonate as possible vanadium precursor. The tungsten hexacarboxyl has lower sublimation temperature, it would supply more vapors at higher temperature compare to acetylacetonate. To avoid two separate vapor source installations, we succeeded to obtain mixed oxide films employing one vapor source approach. We started with CVD deposition of vanadium oxide films first to establish the lowest possible deposition temperature, and vapor source temperature [27, 28].

The thickness of pure VO₂ films deposited at 400°C and vapor source temperature of 170°C (first set of samples) is 349 nm; refractive index 1.53. After annealing at 500°C for 1 hour, the thickness remained the same, 350 nm close to as deposited VO₂ film. VO₂ films deposited at 400°C substrate temperature, and 140°C vapor source temperature (second set of samples) has thickness of 316 nm.

FTIR spectra, shown on figure 7 of the two sets of samples revealed the following: from 400 to 750 cm⁻¹ the bands are mainly attributed to the stretching modes of doubly coordinated oxygen (V₂–O) and triply coordinated oxygen (V₃–O) bonds. The peak at 414 cm⁻¹ is attributed to stretching V-O vibrations [29]. The peak at 538 cm⁻¹ is attributed to the bridged V–O–V stretching vibrations (longer V–O bonds). The peak at 554 cm⁻¹ corresponds to the stretching vibrations of the (V-O-V) bridging bonds. The peaks at 697, 809 and 812 cm⁻¹ are due to the lattice vibrations in vanadium oxide network [30]. The peaks at 865 and 907 cm⁻¹ are attributed to VO₂ (B) IR bands [30].

**Figure 7.** FTIR spectra of the two VO₂ samples (as-deposited and annealed at 500°C).
Raman spectra shown in figure 8 reveal the existence of two phases – amorphous-like and polycrystalline. Very strong and clear peak is observed at 122.5 cm\(^{-1}\), which is assigned to the stretching mode of (V\(_2\)O\(_2\))\(_n\), which in turn corresponds to the chain translation [30]. The weak low frequency Raman peak at 198.5 cm\(^{-1}\) is due to VO\(_2\), corresponding to lattice vibrations. This peak is strongly associated with the layered structure [31]. The peaks centered at 293.9, 411.9, 526.7 cm\(^{-1}\) are related to stretching and bending modes of V\(_2\)O\(_5\). The weak peak at 816.2 cm\(^{-1}\) is assigned to the B\(_g\) modes of VO\(_2\) [30].

VO\(_2\) films deposited at substrate temperature of 400ºC are thick, well adhered and with two separate phases observed on film surface: well oriented in one direction crystals and amorphous phase. It can be due to the chemical reaction nature. The high mobility necessary for stronger orientation at lower deposition temperatures most probably is ensured by the enthalpy of the ongoing chemical processes on the films surface.

The structure and optical properties of CVD-mixed oxides, deposited from precursors mixture W(CO)\(_6\) : V(CO)\(_6\) = 10:1 are also studied. The thickness of W-V-O film deposited at 550ºC and vapor source temperature of 140ºC is 198 nm and refractive index is 1.96. Thickness decreases at higher deposition temperature (550ºC), which is a sign that mixed vapors are seeking lower deposition temperature. The mixed W-V-O films looked like porous, visually separate islands-like-shapes were seen as randomly distributed through the film surface (see figure 9). There is a predominant fraction of amorphous phase. The strongest peak at 520 cm\(^{-1}\) is related to Si substrate and it is sharp and high. The peak at 104 cm\(^{-1}\) is due to lattice vibration. Raman peaks at 145 and 197 cm\(^{-1}\) are associated with layered structure of vanadium oxide [33]. In our case this peak is shifted towards 152 cm\(^{-1}\). The weak
peak at 234 cm\(^{-1}\) is related to \(\delta(O-W-O)\) bonds. The band at 304 cm\(^{-1}\) is attributed to bending vibrations of crystalline WO\(_3\). The strong peak around 525 cm\(^{-1}\) is related to the Si substrate. The peak at 669 cm\(^{-1}\) is related to double coordinated oxygen V\(^{2+}\)-O stretching mode or monoclinic WO\(_3\). The broad band at 852 cm\(^{-1}\) and the peak at 942 cm\(^{-1}\) are related to V\(^{4+}\)-O bonds and W=O. The results are cross-proved by FTIR measurements, which are not included here. On the films surface from the same set of mixed W-V-O oxide films deposited on glass substrate well seen are spherical “droplets-like” particles evenly distributed over the surface area of the glass.

On figure 10 the voltamograms for as-deposited and annealed W-V-O films are presented. No significant change is observed in the behaviour of the switching functional film after annealing at 500°C. Table 4 contains data for the colour efficiency (CE) and the optical modulation. The transmittance after annealing at 500°C W-V-O films is higher than for the as-deposited films (data not shown here). Nevertheless, the calculated value for the colour efficiency is lower, which means that the intercalated electrical charge is changed in a way that the resulting value for the CE is decreased.

![Figure 10. CV curves for as-deposited and annealed at 500°C W-V-O films.](image)

| WO\(_3\)-V\(_2\)O\(_5\) Precursor 10:1; Ar/O\(_2\)=1/32 | CE [cm\(^2\)/C] | Optical modulation [%] |
|-----------------------------------------------|-----------------|-------------------------|
| | As dep. | Ann. 500°C | As dep. | Ann. 500°C |
| WO\(_3\)-V\(_2\)O\(_5\) Precursor 10:1; Ar/O\(_2\)=1/32 | 20.11 | 11.04 | 65.2 | 73.5 |

At the same time, the value of the optical modulation, namely the difference between the transmittance in colored and bleached state is increased from 65% up to 73-74%. Depending on the application envisaged, where either the CE or optical modulation is more important, the stage of film annealing can either be kept or removed from the overall technology of W-V-O electrochromic films.

4. Conclusions

The APCVD technology is a suitable deposition method for preparation of transition metal oxide thin films to serve as successful functional layers in electrochromic devices. The mixed WO\(_3\)/MO\(_3\) films are found to combine the desirable good properties of the molybdenum and tungsten oxides. Mo/W oxide films express high color efficiencies and optical modulation approaching the electrochromic properties of the most studied EC material – WO\(_3\). Mixed oxide films produced by APCVD method grow faster comparing to single APCVD WO\(_3\) films.

The results from the tested electrochromic cells of transition metal oxides based on tungsten, molybdenum and vanadium are a proof for applicability of the APCVD films as functional electrodes in electrochromic devices for smart windows and displays.
Acknowledgements
This paper was presented at INERA Workshop “Transition Metal Oxide Thin Films: Functional Layers in “Smart windows” and “Water Splitting devices”, September 4-6th, 2014, Varna, Bulgaria. The Workshop is part of the Program of INERA REGPOT Project of Institute of Solid State Physics, Bulgarian Academy of Sciences.

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