Study of electrochromic APCVD WO$_3$-V$_2$O$_5$ films

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Abstract. WO$_3$-V$_2$O$_5$ thin films were deposited by atmospheric pressure chemical vapour deposition (APCVD). WO$_3$-V$_2$O$_5$ thin films are investigated related to their potential use as primary electrochromic layers (working electrodes) in Electrochromic Devices. A typical EC Device is a sandwich like structure with two conductive glasses and an electrolyte with working electrodes that possess electrochromic properties. APCVD has the advantages of scalability to large areas with uniform thickness and potentially low cost.

1. Introduction
An electrochromic device (ECD) is an optical system, consisting of two conductive glasses, over one of which the functional layer, the electrochromic (EC) material, is deposited. The second conductive glass could be either bare, or an “ion storage” film could be deposited on it, forming together the counter electrode. An electrolyte is deposited between the two electrodes. In the present work, WO$_3$-V$_2$O$_5$ thin films are investigated related to their use as working electrodes for such an EC Device.

If a small voltage pulse is applied to the device (contacts are made at the conductive glasses, on bare places left), electrons from the conductive glass get injected into the functional layer. For an electro neutrality of the circuit, ions from the electrolyte intercalate into the film, and in result the newly made film structure becomes absorptive, absorbs part of the solar light, and what we see is the complementary color. If WO$_3$-V$_2$O$_5$ is the functional layer, the color we see is dark blue, since the concentration of WO$_3$ dominates and this material absorbs in the near IR. In the area of the EC materials and devices, numerous publications are made, following the first publications of the discovering of the effect in that material by Satyen Deb [1]. Many publications related to the electrochromic effect in different thin film materials let to a handbook and many books [2-4]. The electrochromic materials gain great scientific interest as they find applications in automobiles, sunroof of buildings, display devices, light regulation and architectural glazing [2].

The advantages of the chemical vapor deposition at atmospheric pressure is related to the fact, that in a large-scale production a flow-through process is possible when the deposition goes at atmospheric pressure. CVD MoO$_3$, WO$_3$ and mixed films based on them are studied in details [5]. Among those transition metal oxides, tungsten trioxide appears to be the best electrochromic compound [2]. Its advantages are high coloration efficiency, good stability, and relatively low cost. However a major disadvantage of the APCVD process for WO$_3$ deposition is the very slow growth rate. Mixing of tungsten oxide with other transition metal oxide led to considerable increasing of the growth rate, improvement of layer properties especially in optical and electrochromic aspects [5]. We relate the
role of vanadium oxide in the growth-rate increase with its lower-temperature CVD behavior. It vaporizes easier and forms growth centers, so the vapors could easily start growing. Films are much thicker at the same technological conditions as for the single WO$_3$ oxide films.

In this work, we present preparation and investigation of mixed WO$_3$-V$_2$O$_5$ films, deposited on glass and conductive glass substrates by APCVD method. Structural properties are studied by Raman and FTIR spectroscopies. Optical characterization is performed.

2. Experimental details

WO$_3$-V$_2$O$_5$ thin films were obtained by atmospheric pressure CVD in oxygen ambient. The precursor used was a physical mixture of W(CO)$_6$ and V(CO)$_6$ in ratio W(CO)$_6$ : V(CO)$_6$ = 10:1. The substrate temperature was kept at 200°C. The sublimator temperature was chosen to be 70°C. The other important technological parameter is the ratio of the flow-rates of the carrying carbonyl vapors, namely the Ar flow, and the flow-rate of a reactive gas, oxygen (O$_2$). In this study, the gas flow-rates ratio was Ar$_{carbonyl}$/O$_2$ = 1/32. Depositions were performed by using substrates of bare glass and substrates covered with conductive films of ITO (Donelly type). The observed low value of the thickness of the films on the bare glasses is related to the absence of “initially formed centers of growth”. However, the thickness of the films deposited on the substrates covered with conductive layers of ITO, is relevantly high, due to the “centers of growth” of the ITO films themselves.

FTIR measurements were performed in the spectral range of 350- 4000 cm$^{-1}$ by Shimadzu FTIR Spectrophotometer IRPrestige-21. The studied samples were also deposited on Si substrates and bare Si wafer (p-Si, with orientation <100>) was used as background. Raman spectra were also investigated. The Raman spectra were obtained using LabRAM HR Visible micro-Raman spectrometer. The 633 nm line of a He-Ne laser were used for excitation. An X100 objective was used both to focus the incident beam and to collect the scattered light in backscattering configuration. To prevent the samples by local laser overheating a low laser power (0.70 mW) was used. The range was 100-1280 cm$^{-1}$, with accumulation time – 60s X 5. UV-VIS spectrophotometric study was made by UV 3600 Shimadzu spectrometer in the spectral range of 300-1000 nm.

The surface morphology of the studied metal oxide films has been investigated by AFM (Atomic Force Microscope) DiMultimode V model (Veeco) in tapping mode. Scan rate was 1.5-2 Hz, the images resolution was 512samples/line. The samples were scanned at least two places. Silicon cantilevers (1-100hm-cm Phosphorus (n) doped Si) with a resonance frequency of 250-308 kHz, force constant 20-80 N/m, tip radius < 10 nm,50+/−10nm Al coating on the back side (MPP-11120-10, Veecoprobe) were used in the dynamic AFM experiments. Image processing was performed by means of Nanoscope 7.30.

3. Results and Discussions

Two of the films deposited on conductive glasses were measured in transmittance and reflectance modes in the visible and infrared regions. To study the structural transformation of as deposited films, one of them was annealed at 500 °C and the other at 400 °C.

APCVD WO$_3$-V$_2$O$_5$ films obtained on conductive glass show (figure 1) transparency above 65% in as deposited state and after thermal treatment at higher temperature (400 – 500 °C), the transmittance reaches up to 75 - 80% at 600 -700 nm. As it is seen from the figure, the reflectance after annealing decreases (around 10%), thus the overall optical behavior is improved. Usually the as deposited APCVD mixed oxide films possess amorphous like structure [2]. After annealing at elevated temperatures, the films undergo recrystallization, leading to higher degree of optical transparency.
WO₃-V₂O₅ films were also investigated by FTIR Spectroscopy in as deposited state (figure 2, top) and after annealing at 400 and 500 °C in air for 1 hour (figure 2, bottom).

FTIR study shows that the spectra of WO₃ – V₂O₅ films are very similar in shapes to the corresponding spectra of pure tungsten oxide films [4], but the revealed absorption bands are with lower intensity. Several weak absorption bands have been detected that can be attributed to the vanadium oxide component.

In the as deposited films the characteristic absorption band for the single WO₃ is centred at 670 cm⁻¹, the band covers the spectral range 620 – 730 cm⁻¹. There can be found a contribution from several deformations, and stretching modes of WO₃ [5]. After thermal treatment at 400 °C and 500 °C, the broad band is not observed. Instead, the weak bands due to the stretching and bending vibrations of V-O bonding appeared in spectral range 400 – 550 cm⁻¹ [6].

Figure 1. Transmittance and reflectance spectra of CVD WO₃-V₂O₅ films deposited on conductive glass substrates.
In the range around 830 cm\(^{-1}\) some IR band assigned to asymmetrical stretching mode of V-O-V vibrations can be seen. The FTIR study clearly indicates that although the small amount of vanadium carbonyl in the precursor mixture, the vanadium oxide is present into the films structure and affects their properties.

The APCVD WO\(_3\)-V\(_2\)O\(_5\) films grown at these technological conditions also remain amorphous-like even after high temperature annealing at 500\(^{\circ}\)C.

The Raman band at 248 cm\(^{-1}\) is due to the deformation modes of the two metal oxides. The band at 335 cm\(^{-1}\) is attributed to the bending vibrations of crystalline WO\(_3\), which appears in the spectra of the as-deposited and annealed films. The bands at 682 and 840 cm\(^{-1}\) are related to the two different types of bridging oxygen of \(\nu(O-W-O)\) vibrations\([7]\). The line at 985 cm\(^{-1}\) is assigned to terminal double bonds W=O or/and V=O bonds. The vanadium oxide component is represented by two weak Raman lines at 396 and 483 cm\(^{-1}\), which can be assigned to the bending vibrations of V-O-V and to stretching V-O bonds of orthorhombic V\(_2\)O\(_5\)\([8]\). The Raman peak at 483 cm\(^{-1}\) is observed also in the spectrum of the annealed film.

Figure 2. FTIR spectra of APCVD WO\(_3\)-V\(_2\)O\(_5\) films as deposited (top) and annealed at 400 - 500\(^{\circ}\)C (bottom).

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As it is seen from figure 3 (bottom), a new larger Raman band appears centred at 600 cm\(^{-1}\), which we consider as evidence for vanadium oxygen bonds. Studying thermochromic properties of vanadium oxide doped with tungsten, the authors of [9] observed a Raman peak around 600 cm\(^{-1}\). The strong Raman peak at 895 cm\(^{-1}\) could be related to vanadium oxide crystalline phase. Surface observations during the Raman spectra measurements show existence of separate crystals immersed in a homogenous surface material, not exhibiting Raman features. Raman study of APCVD WO\(_3\)-V\(_2\)O\(_5\) films reveals that the film structure is predominantly amorphous as the Raman bands are broad and with low intensity.

Having in mind the Raman results the separate crystals found in the AFM micrographs (figure 4, left), here we relate with the vanadium oxide phase, since our previous study of single WO\(_3\) has shown that this material stays predominantly amorphous even after 500 °C [10]. When heated at 500 °C the films have the typical for the mixed transition metal oxides surface, namely cluster formation (figure 4, right). This would result in improved electrochromic performance, because of the increased area of the grain boundaries where ions can easier intercalate. The separate crystals are seen above the typical clustered surface.

Figure 3. Raman spectra of APCVD WO\(_3\)-V\(_2\)O\(_5\) films in as-deposited state (left) and after annealing at 500 °C (right).
WO$_3$ – V$_2$O$_5$ thin films of the same type as the presented here samples, but obtained at higher sublimation temperature (80 °C) have shown well expressed electrochromic behaviour demonstrated in a three electrode configuration. The W-V-O film on conductive glass served as functional electrode, electrochemically derived NiO on conductive glass was used as a counter electrode, and a Calomel Electrode, as reference electrode. The electrolyte was a 0.6 M LiClO$_4$ in Propylene carbonate (PC), placed in a quartz cuvette. Film coloration was observed under voltage applied in the range -1 - +4 volts.

Further study will be related to detailed voltammetric measurements to determine the colour efficiency and optical modulation.

4. Conclusions
Atmospheric pressure chemical vapour deposition is employed to produce mixed WO$_3$ – V$_2$O$_5$ films. Their optical transmittance and reflectance are measured for the as-deposited and annealed states. Infrared and Raman vibrational spectra are also measured. Films are predominantly amorphous, not only in as-deposited state but also after annealing at elevated temperatures. The lower temperature vanadium oxide undergo crystallization after annealing, forming separate crystals seen as immersed in amorphous – like homogenous film surface. Films have shown electrochromic effect when a small voltage of couple of volts is applied across them.

5. References
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