Optical characterization of WO$_3$-VO$_x$ thin films for application in electrochromic devices - “smart windows”

G Bodurov$^1$, T Ivanova$^1$, M Aleksandrova$^2$ and K A Gesheva$^{1,3}$

$^1$Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria

$^2$Technical University of Sofia, Faculty of Microelectronics, 8 Kliment Ohridski Blvd., 1000 Sofia, Bulgaria

E-mail: kagesh@phys.bas.bg

Abstract. WO$_3$-VO$_x$ thin films were deposited by atmospheric pressure chemical vapor deposition (APCVD). A typical electrochromic device is a sandwichlike structure with two conductive glasses and an electrolyte layer. An electrochromic transition metal oxide film is deposited over one of the glass substrates thus forming the working electrode. The counter electrodes in the devices are bare conductive glasses, and the polymeric electrolyte is used to laminate the two glass substrates and to supply the devices with Li ions. The working electrode material is investigated related to its initial transmittance, vibrational properties, and structure.

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 may be deposited to form the counter electrode. The two glasses are laminated by a polymeric electrolyte, in which in advance small alkali ions are introduced. The device elements are three: a working electrode (conductive glass covered by EC film); a counter electrode, and a polymeric layer laminating the two device electrodes. If a small voltage pulse is applied to the device, electrons from the conductive glass are injected into the film, ions from the polymeric electrolyte intercalate as well in the film structure, and, as a result, the newly formed film structure becomes absorptive. This film absorbs part of the solar light so that what we see is the complementary color. Following the first publication for the effect discovered in WO$_3$ by Satyen Deb [1], a large number of studies have been published in the area of EC materials and devices. The intensive work worldwide has resulted in many books on the topic [2-5]. Among transition metal oxides, tungsten trioxide appears to be the best electrochromic compound [2]. Its advantages are the high coloration efficiency, good stability, and relatively low cost. However, mixing tungsten oxide with other transition metal oxide can lead to improvement of their properties especially, in optical and electrochromic aspects. Moreover, our previous experience with the W-Mo oxide films obtained by atmospheric pressure chemical vapor deposition (a carbonyl process) resulted in a higher growth-rate as compared to the single APCVD WO$_3$ films [5]. This aspect is important in view of a production process.

$^3$ To whom any correspondence should be addressed.
In this work, we present the preparation and investigation of mixed APCVD-WO$_3$-VO$_x$ films, deposited on glass and conductive glass substrates. The vibrational properties are studied by Raman and FTIR spectroscopy. Only FTIR results are presented here, together with UV-VIS transmittance spectra.

2. Experimental details

WO$_3$-VO$_x$ thin films were obtained by atmospheric pressure CVD in oxygen ambient. The corresponding carbonyl mixture is W(CO)$_6$:V(CO)$_6 = 10$:1. The substrate temperature was kept at 200$^\circ$C. A sublimator temperature of 60$^\circ$C for WO$_3$-VO$_x$ films was used. The ratio of the flow-rates of the carrying carbonyl vapors Ar flow and the flow-rate of the reactive oxygen gas was $\text{Ar}_{\text{carbonyl}}/\text{O}_2 = 1/32$. The deposition time was 40 min. The thickness of th MoO$_3$-VO$_x$ thin films is 110 nm.

FTIR measurements were performed in the spectral range of 350 - 1200 cm$^{-1}$ by a Shimadzu FTIR Spectrophotometer (IR Prestige – 21). The samples studied were deposited on Si substrates and a bare Si wafer (p-Si, with orientation $<100>$) was used as a reference sample. The UV-VIS measurements were carried out by a UV 3600 Shimadzu spectrophotometer in the spectral range of 300 - 1000 nm.

3. Results and discussions

The WO$_3$-VO$_x$ films were investigated by FTIR spectroscopy in as-deposited state and after annealing at 300, 400 and 500$^\circ$C in air for 1 hour (figure 1). Single WO$_3$ films are also given as a comparison in figure 2. The WO$_3$ films were obtained at similar CVD process conditions. Table 1 presents the results.

![Figure 1. FTIR spectra of APCVD WO$_3$, films as deposited and annealed at 400 and 500$^\circ$C.](image1)

![Figure 2. FTIR spectra of APCVD WO$_3$-V$_2$O$_5$ films, as deposited and annealed at 300, 400 and 500$^\circ$C.](image2)

The FTIR study shows that the spectra of mixed oxide films are very similar in shapes to the FTIR spectra of pure tungsten oxide films, but have lower intensity. On the other hand, several weak absorption bands appeared which are clearly assigned to the vanadium oxide component.

The FTIR spectra of pure tungsten oxide films (figure 1) reveal broad absorption bands. In as-deposited state, there is band spreading in the spectral range 600-731 cm$^{-1}$, where contributions from several deformation and stretching modes of WO$_3$ can be present [6]. After annealing at 400 and 500$^\circ$C, the broad band splits into two strong lines at 724 and 802 cm$^{-1}$; this splitting can be observed in the spectra of the annealed mixed oxide samples. These two IR maxima are the most characteristic for the presence of monoclinic crystalline WO$_3$ [7]. As can be seen, the weak bands due to the stretching and bending vibrations of V-O bonds appear in the spectral range 400 – 470 cm$^{-1}$ [8] in all spectra of WO$_3$-V$_2$O$_5$ films. In the range above 750 cm$^{-1}$, IR bands assigned to asymmetric stretching mode of V-O-V vibrations can be found [9]. The FTIR study clearly indicates that in spite of the small amount of
vanadium carbonyl in the precursor mixture, vanadium oxide is present into the films structure and influences their properties.

Table 1. FTIR data for APCVD WO$_3$-V$_2$O$_5$ and pure WO$_3$ films, deposited at similar technological parameters and additionally annealed at different temperatures.

| Annealing temperature | WO$_3$ films | WO$_3$-V$_2$O$_5$ films | Assigned to |
|-----------------------|--------------|--------------------------|-------------|
| As deposited          | 370.0 very weak | 623-800 broad center 682.1 | W-O bonds |
|                       | 439.6 and 468.8 | ~ 717, 803 cm$^{-1}$ crystalline monoclinic WO$_3$ | bending V-O-V vibrations |
| 600.6-731.5 broad     | 401.8 and 421.7 | - 717, 803 cm$^{-1}$ crystalline monoclinic WO$_3$ | stretching V-O bonds |
| center 658.8          | 458.3         | - out of plane W-O-W deformation mode ~ 700 cm$^{-1}$ | stretching V-O-V vibrations |
| 809.2 sh              | 627.8 clear   | ~ 796 cm$^{-1}$ stretching V-O-V bonds | W-O bonds |
|                       | 400.3 and 420 | ~ 796 cm$^{-1}$ stretching V-O-V bonds | stretching vibrations of W-O bonds in the crystalline monoclinic WO$_3$ |
| 300°C                 | 372.7 weak    | 623-800 broad center 682.1 | W-O bonds |
|                       | 400.3 and 420 | ~ 717, 803 cm$^{-1}$ crystalline monoclinic WO$_3$ | W-O bonds |
|                       | 458.3         | - out of plane W-O-W deformation mode ~ 700 cm$^{-1}$ | bending V-O-V vibrations |
|                       | 725.5 strong  | ~ 796 cm$^{-1}$ stretching V-O-V bonds | stretching W-O in disordered W-O framework or W---O---W bridging stretching band |
|                       | 804.9 strong  | W-O stretching vibrations in the crystalline monoclinic WO$_3$ | W-O stretching vibrations in the crystalline monoclinic WO$_3$ |
|                       | 1049.3 sh     | W-O stretching vibrations in the crystalline monoclinic WO$_3$ | Si-O bonds due to Si substrate |
| 400°C                 | 372.7 v. weak | 630.8 clear              | W-O bonds |
|                       | 390.0 weak    | stretching W-O in disordered W-O framework or W---O---W bridging stretching band | stretching V-O bonds |
|                       | 441.5 and 470.5 | W-O stretching vibrations in the crystalline monoclinic WO$_3$ | bending V-O-V vibrations |
|                       | 724.0 strong  | 801.9 strong             | W-O stretching vibrations in the crystalline monoclinic WO$_3$ |
|                       | 728.6 strong  | 801.9 strong             | W-O stretching mode, monoclinic WO$_3$ |
|                       | 1070.6 clear  | 801.9 strong             | W-O stretching mode, monoclinic WO$_3$ |
|                       |              |                          | Si-O bonds due to Si substrate |
| 500°C                 | 371.2 weak    | 627.8 clear              | W-O bonds |
|                       | 390.0 weak    | stretching W-O bonds      | stretching V-O bonds |
|                       | 441.5 and 470.5 | bending V-O-V vibrations | W-O bonds |
|                       | 724.0 strong  | 801.9 strong             | W-O stretching mode, monoclinic WO$_3$ |
|                       | 728.6 strong  | 801.9 strong             | W-O stretching mode, monoclinic WO$_3$ |
|                       | 1070.6 clear  | 801.9 strong             | W-O stretching mode, monoclinic WO$_3$ |

The optical behavior of the APCVD WO$_3$-V$_2$O$_5$ films as a function of the annealing temperature is shown in figure 3 and figure 4. Figure 3 presents the optical transmittance of films deposited on ordinary glass, while in figure 4, the substrate is a conductive glass (glass covered by SnO$_2$:Sb, a very thin conducting layer). The initial transmittance of WO$_3$-V$_2$O$_5$ film on glass is 78%; it then increases
with the annealing temperature up to 88% at 400°C, and drops significantly to 67% after annealing at
500°C (at 550 nm). The decrease of the optical transmittance after high temperature treatment was
observed for MoO₃-WO₃ films [5].

![Image of UV-VIS spectra of APCVD WO₃-V₂O₅ films annealed at different temperatures. The substrate used is ordinary glass.](image1)

![Image of UV-VIS spectra of APCVD WO₃-V₂O₅ films annealed at different temperatures. The substrate used is conductive glass.](image2)

**Figure 3.** UV-VIS spectra of APCVD WO₃-V₂O₅ films annealed at different temperatures. The substrate used is ordinary glass.

**Figure 4.** UV-VIS spectra of APCVD WO₃-V₂O₅ films annealed at different temperatures. The substrate used is conductive glass.

The films deposited on conductive glass exhibit lower transparency which is due to the substrate.
The annealing at 400°C and 500°C resulted in spectra with transmittance of 74 and 76%, respectively,
at 550 nm. The transmittance for as deposited film was 56%, and for the ones annealed 300°C, 69%.

Further experiments will use the W-V oxide films as working electrode in a three electrode
configuration cell to perform voltametric measurements (current density vs voltage dependence). From
the voltamograms obtained, the color efficiency and optical modulation will be determined.

**Conclusions**
The proposed APCVD technology is found to be suitable for deposition of mixed W-V oxide films.
The WO₃-VOₓ thin films are highly transparent. The films are expected to serve as successful working
electrodes in electrochromic devices.

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