JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 11, No. 10, October 2009, p. 1513 - 1516

Electrochromic mixed films based on WO_3 and MoO_3, obtained by an APCVD method♣

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Electrochromism is a reversible effect, for which the transmittance (colour) modulation is induced by an applied external voltage. By changing the polarity, the film returns to its initial state. The low temperature chemical vapour growth processing of thin films of mixed W and Mo oxides is presented. The investigation is related to optimization of the film structure and the related optoelectronic properties as a function of the CVD process parameters. The morphology of the films is determined by SEM microscopy and EDX analysis reveals their compositions. The vibrational properties of the films are investigated by FTIR and Raman spectroscopy. Electrochromic behavior was examined by cyclic voltammetric experiments, performed in a standard three-electrode arrangement. From the cyclic voltammetry data, the optical modulation and colour efficiency (CE) values were estimated. The estimated CE values for a wavelength of 550 nm (the maximum of the solar energy spectrum) are one of the best reported in the literature.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: CVD, Thin films, Morphology, Electrochromic properties

1. Introduction

Electrochromism has attracted the interest of many researchers for prospective applications such as automobile and building glazing, energy conservation, etc. [1, 2]. Transition metal oxides are inorganic compounds that are extensively studied as electrochromic materials, and WO_3 is reported to exhibit the best properties. MoO_3 films also show well pronounced electrochromism [3]

Mixed oxide films of transition metals gather considerable attention due to their interesting optoelectronic properties. They offer the opportunity to combine the desirable properties of the individual compounds. In the case of films based on MoO_3 and WO_3, the aim is to reach the high colour efficiency of WO_3 and to approach the more uniform colouring and higher open circuit memory properties characteristic of Mo oxide. [4].

The paper presents the low temperature chemical vapour growth of mixed films of W and Mo oxides. The film structures and chemical bonding were studied by FTIR and Raman spectroscopy, and the electrochromic behaviour was monitored by cyclic voltammetry.

2. Experimental

Mixed oxide films based on Mo and W were fabricated by an atmospheric pressure CVD method [5]. The CVD equipment consisted of a horizontal quartz reactor with cold walls and the substrates were heated by a high frequency generator (HFG) to a substrate temperature of 200°C. The precursors used were physical mixtures of the two carbonyls in ratios of 1:4 and 1:6 in favour of $W(CO)_6$. The precursor powder was placed in a sublimator heated to 90°C. The carbonyl vapours were carried by an Ar flow from the sublimator to the CVD reactor. This Ar flow rate is related to the flow rate of O_2 (the reactive gas, entering the reactor from a separate line) in a specific gas flow ratio referring to the definition of the oxygen content mentioning in the text. The ratios studied were 1/16 and

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

1/32. The substrates used were Si wafers, glass and conductive glass substrates.

FTIR measurements were performed using a Shimadzu FTIR Spectrophotometer IRPrestige-21 and a bare Si wafer was used as a background. The Raman study was performed with a SPEX 1403 Raman spectrometer with a laser line - Ar^+ 488 nm, the laser power was 54 mW.

Cyclic voltammetry experiments were performed in a standard three-electrode cell arrangement. In order to estimate the colour change, the cyclic voltammetry equipment was upgraded with an optical system, a chopped light source and a lock-in amplifier. The electrodes were immersed in an electrolyte of 1 mol/l LiClO4 in propylene carbonate (PC).

3. Results and discussion

The first set of films, obtained from the precursor mixture 1:4 and gas flow ratio 1/32, had a film thickness of 300 nm. The MoO_3-WO_3 films deposited by a precursor, containing the higher amount of $W(CO)_6$, showed film thicknesses of 280 nm and 200 nm at gas flow rates of 1/32 and 1/16, respectively.

Morphology studies were performed using a SEM microscope with an attached EDX accessory for chemical composition determination. Fig. 1 presents a SEM micrograph of an as-deposited MoO_3-WO_3 film from the first set.

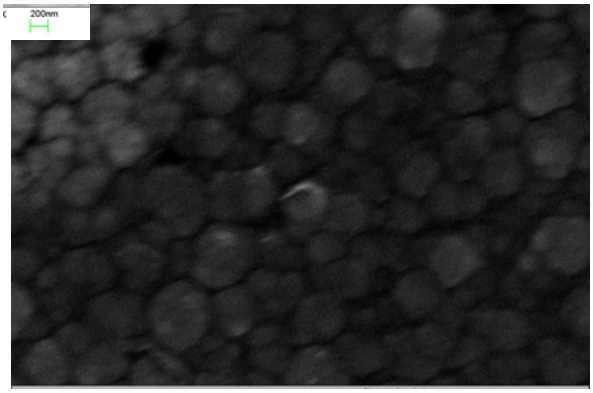

Fig. 1. SEM micrograph of a CVD as-deposited MoO_3-WO_3 film, obtained from the precursor mixture of 1:4 and a gas flow rate of 1:32.

The film surface structure consisted of randomly distributed grains with different sizes.

Figs. 2 and 3 present SEM images of mixed oxide films from the second set, with a precursor mixture 1:6 and gas flow ratios of 1:16 and 1/32, respectively. It can be observed that the as-deposited film at lower oxygen content possessed a fine grain structure of the surface with grain sizes much smaller than those in Fig. 1. After high temperature annealing, the surface significantly changed.

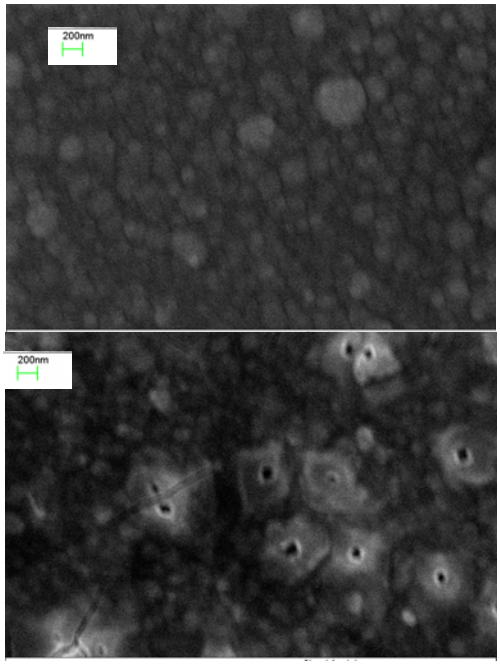

Fig. 2. SEM images of mixed films, obtained from precursor 1:6 and oxygen 1/16, before and after annealing.

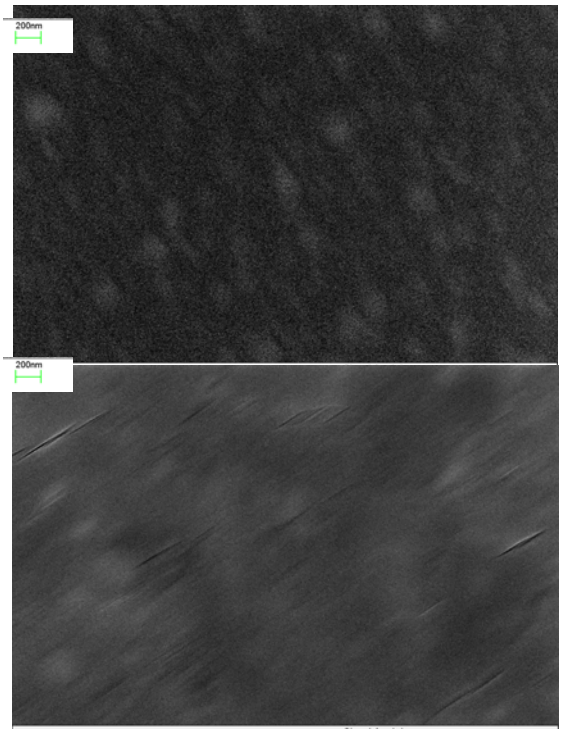

Fig. 3. SEM micrographs of MoO_3-WO_3 films obtained from a precursor 1:6 and oxygen 1/32 in the as-deposited state and after annealing at 500°C.

The SEM image of the MoO_3-WO_3 film at 1/16 and annealed at 500°C shows that an irregular agglomeration takes place or, based on the contrast differences (as seen from the lighter contrast of the bigger spots), it can be considered as the presence of a new oxide phase. The as-deposited film with high oxygen content (1/32) exhibits a very smooth and uniform morphology with decreasing grain density, compared with the as-deposited at 1/16 MoO_3-WO_3 film. The high temperature annealing leads to a very homogenous morphology, there is an extremely smooth surface and no grain structure was observed. This particular set of samples will need further investigation with more precise and sensitive microscopic techniques.

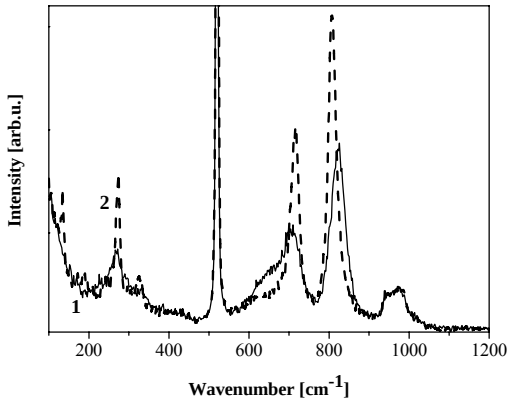

Fig. 4. Raman spectra of MoO_3-WO_3 films, obtained by precursor 1:4 (curve 1) and 1:6 (curve 2) and gas flow rate 1:32 after annealing at 500°C.

Raman spectra of annealed MoO_3-WO_3 films, obtained from the two precursor mixtures (1:4 and 1:6) and a gas flow ratio 1/32 are presented in Fig. 4. The Raman bands at 520 cm^{-1} and 960 cm^{-1} are due to the vibrational modes of the Si substrate. The Raman line positions and their assignments are summarized in Table 1.

The first set of samples is amorphous with almost featureless Raman spectra. The films deposited from $Mo(CO)_6$:$W(CO)_6$ = 1:6 reveal differences: MoO_3-WO_3 films deposited at a low oxygen content (1/16) are amorphous, but the higher oxygen samples show clear Raman lines, a sign of a certain degree of crystallization. The Raman bands are related to crystalline monoclinic WO_3 [6]. Annealing at 500°C leads to crystallization, with the strongest Raman lines being for the annealed MoO_3-WO_3 films (Mo $(CO)_6$:$W(CO)_6$=1:6; Ar/O_2=1/32). Other Raman spectra exhibit broad bands, suggesting the presence of an amorphous fraction.

In the Raman spectrum of the annealed film from the first set (1:4), bands attributed to Mo oxide, namely at 220, 268.7, 647.8 and 826 cm^{-1}, were detected [6].

Table1. Raman analysis data for the CVD MoO_3-WO_3 films.

Mo/W (1:4)	Mo/W (1:6)	Assigned to
	133.8 168.4 190.3	Lattice modes of WO_3 and MoO_3
220	230.9	δOMo_2, monoclinic MoO_3
268.7 cl.	274.8 str.	δ(O-Mo)
334.4 v. weak	328.2 cl.	δ (O-W-O) or α-MoO_3
647.8 sh.		α-MoO_3 or - WO_3
704.2 clear	713.5 804.5 v. strong	stretching vibrations W-O in crystalline monoclinic WO_3
826.5 strong		doubly coordinated oxygen, α-MoO_3

It must be pointed out that the line at 704.2 cm^{-1} is broad, with a clearly pronounced shoulder at 647.8 cm^{-1}. The main maximum is connected to stretching vibrations of W-O bonds in crystalline monoclinic WO_3 [7], and the shoulder is associated either with triply coordinated oxygen of α-MoO_3 (this line is seen in the Raman spectrum of pure MoO_3), or with hexagonal WO_3 [8]. The strong maximum at 826.5 cm^{-1} is due to doubly coordinated oxygen corresponding to α-MoO_3. The analysis suggests that MoO_3 crystallized and tungsten oxide is also partly crystalline, only one peak (704.2 cm^{-1}) indicates that.

The annealed MoO_3-WO_3 films from the second set show sharper and intense maxima, the fundamental W-O-W bands of monoclinic WO_3 were detected. They are located at 274.8 and 328.2 cm^{-1}, and stronger lines at 713.5 and 804.5 cm^{-1} [9]. The weak bands below 200 cm^{-1} are attributed to lattice vibrations of MoO_3 and WO_3. The 230.9 cm^{-1} peak is related to the deformation modes of monoclinic MoO_3 [6].

The Raman results lead to the conclusion that CVD MoO_3-WO_3 films obtained from $Mo(CO)_6$:$W(CO)_6$ = 1:6 and a gas flow ratio 1/32 crystallize in monoclinic WO_3 with small inclusions of MoO_3. Raman data show that these particular mixed oxide films possess the highest degree of crystallization compared to the other studied CVD films. The second set contains a greater fraction of W oxide. The pure oxide films crystallize at higher temperatures (CVD WO_3 remains predominantly amorphous after 500°C treatment [5]), but in the mixed oxide system its crystallization is induced by the presence of a small amount of MoO_3.

The optical properties of the mixed oxide films are suitable for electrochromic applications, as they reveal a high initial transmittance. The as- deposited films of MoO_3-WO_3, obtained from the precursor 1:4 and gas flow ratio 1/32, show an optical transmittance of up to 80 % in

the visible spectral range. The films from the other set (precursor $Mo(CO)_6$:$W(CO)_6$ = 1:6) exhibit transmittances of 70 % and 78 % for gas flow ratios of 1/16 and 1/32, respectively. The reflectance is 25 % and 17 % for these samples. An interesting tendency is observed after annealing of the films. The transmittance of the films from the first precursor, together with the MoO_3-WO_3 ($Mo(CO)_6$:$W(CO)_6$ = 1:6; Ar/O_2 = 1/16) decreased after high temperature annealing above 400°C. The films from the second set with higher oxygen content behaved as the single oxide films, improving their optical transparency after post deposition annealing. This could be in some way connected with the film chemical composition and a mass transfer during rearrangements of the structure during annealing.

Table 2. Colour efficiency (CE) and optical modulation (ΔT) values of the CVD MoO_3-WO_3 films.

MoO_3-WO_3 films	λ [nm]	CE [cm^2/C]		ΔT [%]	
		As dep.	Ann. 500°C	As dep.	Ann. 500°C
Precursor 1:4; Ar/O_2=1/32	500	50.1	86,7	71,7	52.2
	550	196,6	114,7	72,3	52.4
	600	103,6	102.0	66,2	38,2
Precursor 1:6; Ar/O_2=1/16	500	32,7	28,8	17,8	28,8
	550	37,3	43,7	20,0	43,7
	600	29,0	23,4	15,9	23,4
Precursor 1:6; Ar/O_2=1/32	500	51,6	51,6	20,3	26,9
	550	140,8	86,3	73,2	20,0
	600	75,6	75,6	29,7	28,1

The EDX analyses show that the first set of samples has a Mo/W ratio 0.32. The second set revealed values such as 0.12 (gas flow rate 1/16) and 0.05 (gas flow rate 1/32). Obviously, when the MoO_3 component in the film composition is very small, the optical properties are similar to those of pure oxides. The chemical composition affects the electrochromic behaviour. In Table 2, the colour efficiency (CE) and the optical modulation (ΔT), derived from cyclic voltammetry data are summarized. The highest electrochromic characteristics are manifested by MoO_3-WO_3 films obtained from the precursor 1:4 and a gas flow ratio Ar/O_2=1/32. Other authors reported that mixed oxide systems expressed better electrochromic performance, when the single oxides are in the optimal range of ratios [10].

4. Conclusions

The structure of MoO_3-WO_3 films is found to be influenced by the precursor mixture ratio and oxygen content during film growth. The structure of the films is fine grained. The initial transparency is high, suggesting a high optical modulation. The mixed Mo/W based oxide films show an electrochromic effect, resulting in high colour efficiency and optical modulation values. A higher oxygen gas flow rate during the deposition process leads to better optical and electrochromic properties of the as-deposited MoO_3-WO_3 films. APCVD mixed W/Mo based oxide films may serve for successful electrochromic device applications.

Acknowledgements

The financial support of the Ministry of Education and Science is acknowledged under the National Research Program DO1-377/NTE-04/16.06.2006, module 2.

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