

OPTICAL AND ELECTROCHROMIC CHARACTERIZATION OF MULTILAYERED MIXED METAL OXIDE THIN FILMS

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The paper presents results on the preparation and study of the structure, optical and electrochromic properties of sol-gel derived thin films of WO_3 , MoO_3 , and mixed films on based upon these. The films were deposited in a simplified sol-gel process. Raman spectra results showed that WO_3 and the mixed films were predominantly amorphous, while crystallization of the MoO_3 films was detected. All films showed an electrochromic effect. Color efficiencies were in the range 58 to 100 cm^2/mC for a wavelength of 550 nm, reaching a value of 130 cm^2/mC for the WO_3 film. The results confirm that the simple sol-gel process which has been developed is promising for low cost applications in electrochromic smart windows.

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1. Introduction

Electrochromic thin film materials have the ability to modify their optical properties reversibly under a small applied voltage. This characteristic is very important for "smart windows" and display applications. Transmittance modulation (a persistent and reversible color change induced by an electrical field) can be reached by inserting/extracting small alkali ions into the electrochromic film. Investigations of metal oxide films are connected with their application as the active layer in electrochromic devices, mainly smart windows. An important requirement for a thin film to exhibit an electrochromic effect is for it to have a highly porous structure, permitting easy intercalation of ions.

Recently, comparative studies involving molybdenum and tungsten based oxide films pointing out the advantages of each of them. [1,2]. Different techniques are used for preparation of molybdenum oxide, tungsten oxide and mixed MoO_3 - WO_3 films. The sol-gel process is a promising technique, permitting deposition not only of single layers but also of multilayered MoO_3/WO_3 systems [3, 4].

The aim of this study was to use a sol-gel process to deposit transition metal oxide thin films, with structural optical and electrochemical properties suitable for large scale, large area and low cost applications. A simplified variant of the sol-gel process was employed to deposit films of MoO_3 , WO_3 and mixed films based upon them, avoiding some of the stages of the typical sol-gel process. The film structures were studied by Raman spectroscopy. The electrochromic behavior of the films was characterized by cyclic voltammetry.

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2. Experimental details

Molybdenum oxide, tungsten oxide and mixed MoO_3/WO_3 oxide films have been prepared by a sol-gel technological process. The solutions were prepared by dissolving the metal powder in 30% hydrogen peroxide (H_2O_2), cooled in a water bath during addition of the metal powder, and continuously stirred until all metal was dissolved. This solution was dried at 40°C for about 24 hours, until a xerogel was produced. 10 grams of this xerogel were dissolved in 100 ml ethanol and aged for 24 hours. A similar process is described in [5] for MoO_3 . The films were deposited by spin coating at 2000 rpm on ITO-covered conductive glass. After spin coating, the substrate was dried at 150° in air for 30 min. Since one deposition cycle led to a film thickness of about 40 nm, this procedure was repeated five times in order to achieve a film thickness of about 200 nm. After the coating procedure, the films were finally annealed at 270°C for one hour, in air.

The thin films were investigated by Raman spectroscopy. Ellipsometric measurements were applied to determine the spectral dependence of the refractive index. The electrochromic behavior was studied by cyclic voltammetry performed using a standard three-electrode arrangement. A platinum electrode was used as a counter electrode, and the reference electrode was a saturated calomel electrode (SCE). The film transmittance changes were investigated in the spectral range of 400–850 nm, as a result of coloring under an applied voltage.

3. Results and discussion

Information about the structure of the films studied was obtained from Raman measurements. Fig. 1 presents the Raman spectra of pure MoO_3 and WO_3 films, compared with mixed oxide films.

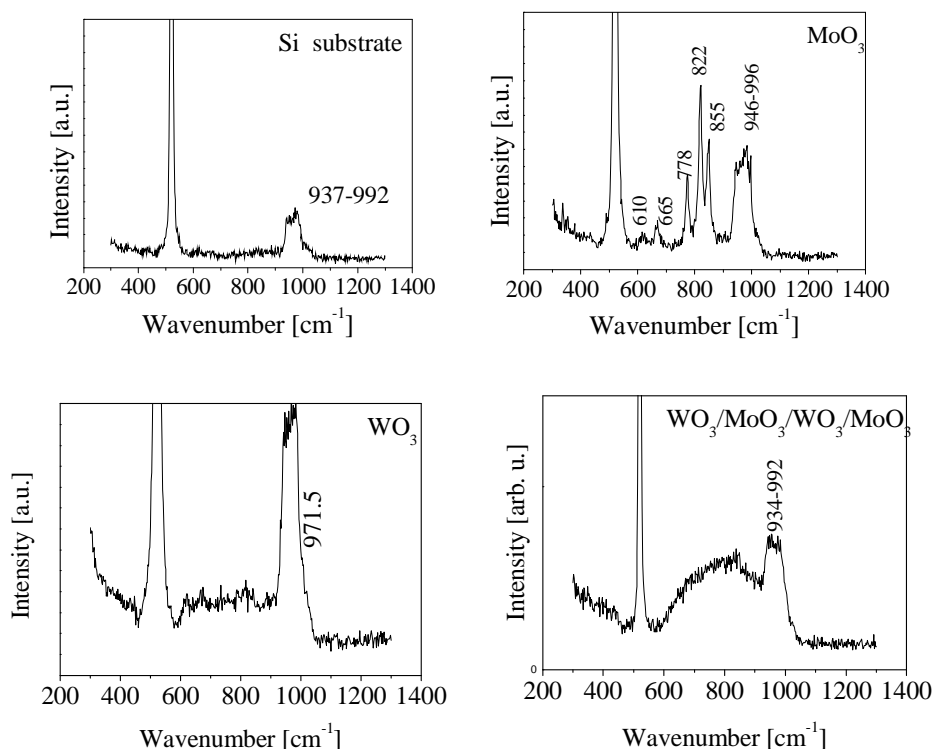


Fig. 1. Raman spectra of sol-gel derived thin films of MoO_3 , WO_3 and mixed oxide film based on them.

The Raman spectrum of the MoO_3 film revealed crystallization. The peak at around 610 cm^{-1} can be assigned to a broad and a complex band involving the stretching vibration of the

Mo-O-Mo bond, and it is characteristic for the orthorhombic (α) MoO_3 structure [6-8]. The observed band at 665 cm^{-1} was also attributed to α - MoO_3 . The strong peak at 778 cm^{-1} is due to the stretching vibration of the corner-sharing octahedral Mo-O-Mo units. This Raman band can also be assigned to the monoclinic modification. The strongest peak at 820 cm^{-1} comes from the stretching vibration of Mo-O-Mo bonds in α - MoO_3 . The 885 cm^{-1} band can be attributed to the same type of vibrations in β - MoO_3 [6]. The broad band at $946\text{--}886\text{ cm}^{-1}$ obviously overlaps with the pure substrate spectrum, and an increase of the band intensity was observed. This suggests that there were also contributions from double Mo=O bonds. It can be concluded that pure MoO_3 films crystallize in a mixture of two structural modifications, with a prevailing orthorhombic phase. The Raman spectrum of the WO_3 film exhibited a very strong band at 971 cm^{-1} , assigned to double W=O bonds. As a whole, the WO_3 film had an amorphous-like structure. The Raman spectrum of $\text{MoO}_3/\text{WO}_3/\text{MoO}_3/\text{WO}_3$ showed a broad band in the range of $600\text{--}850\text{ cm}^{-1}$, centered at 713 cm^{-1} . This peak is one of the most cited bands typical for WO_3 [7]. In this region, bands appeared due to different Mo-O and W-O vibrations. Obviously, the film was amorphous and the tungsten component was dominant.

From the Raman investigation, it can be concluded that a comparatively low annealing temperature (270°C) leads to the crystallization of the MoO_3 structure, and even some degree of crystallization of the WO_3 structure is observed (Fig. 1). Obviously, WO_3 and the mixed oxide films require higher temperatures to crystallize. Similar behavior was observed for CVD films, for which MoO_3 crystallized at 300°C , while mixed oxide films stayed predominantly amorphous even after annealing at 500°C [2, 8].

The optical band gap energies and the optical constants derived from the ellipsometry data confirmed the conclusions from the Raman study. As an example, an optical band gap value of 3.07 eV was obtained for the mixed films. This value is often cited for amorphous WO_3 [2,9]. Modelling, applying the effective medium approximation theory, shows an approximately 28% volume fraction of MoO_3 and 72 % of WO_3 in the mixed oxide films.

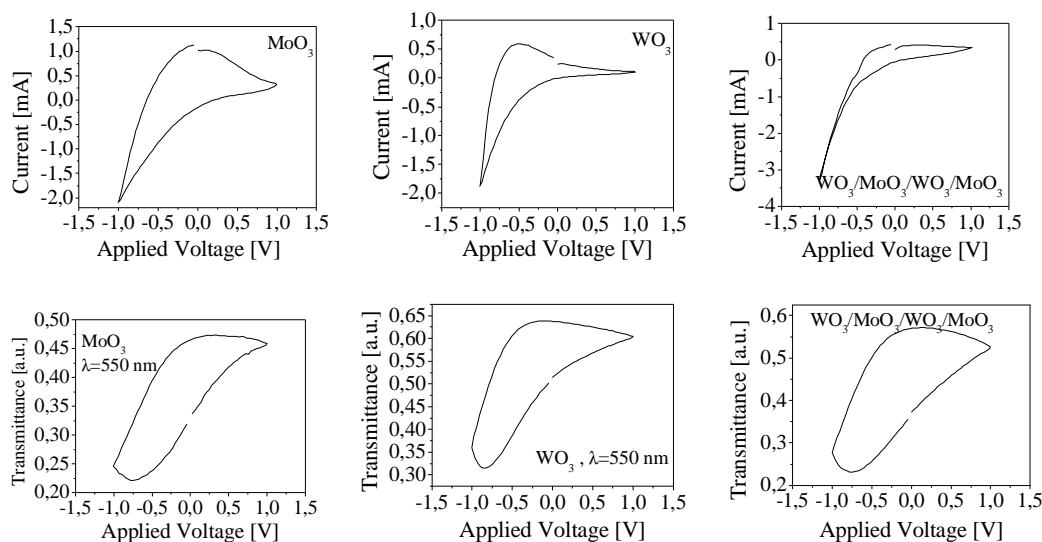


Fig. 2. Cyclic voltammograms and variation of the transmittance for the coloration of MoO_3 and WO_3 films, and one based on a multilayered structure of mixed W/Mo oxides.

The measured voltammograms are presented in Fig. 2, showing the dependence of the electrical current on the applied voltage (-1.5 V to $+1.5\text{ V}$) between the working electrode and the reference electrode. Very good reversibility was observed: the films changed from a transparent state to an almost opaque one. For all the films a deep blue coloration, especially intense in the case of WO_3 films, was observed under an applied DC voltage. The electrochemical reduction of MoO_3 and WO_3 films results in the formation of a molybdenum or tungsten bronze, of the form $\text{Li}_x\text{Mo(W)O}_3$. This process increases the number of Mo^{5+} or W^{5+} ions, and hence the number of color centers [8].

No peaks were observed in either the cathodic or the anodic modes, as is typical for the amorphous structure.

The dependence of the coloration efficiency on the wavelength (Fig. 3) is very important, since there was a considerable change in the coloration due to an increased optical absorption at certain wavelengths. The color efficiency of the WO_3 film increased with increasing wavelength, reaching the highest value in the IR region. Its optical absorption is known to be in this spectral range [9]. The best values for the color efficiency are those found for WO_3 at 800 - 130 cm^2/mC . For the MoO_3 and mixed sol-gel W/Mo based thin films, the maximum in color efficiency around 550 nm (~ 2.25 eV) is a valuable result, since this energy coincides with the maximum of the solar spectrum, and is also close to the maximum of the eye sensitivity curve.

The color efficiency values for the sol-gel films studied were in the same range as those of our CVD films [10] and those obtained by physical vapor deposition technique [9].

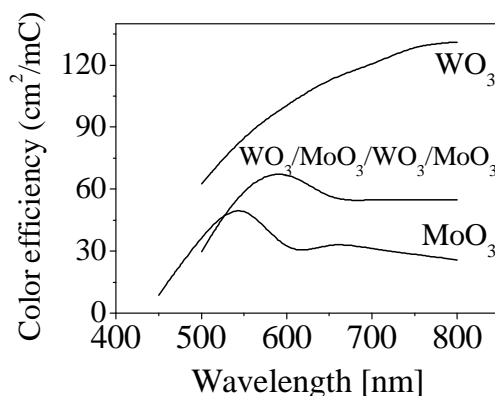


Fig. 3. Spectral dependence of the color efficiency of MoO_3 and WO_3 films, and of a multilayered mixed W/Mo based oxide film.

4. Conclusions

The experimental results have shown that thin films of MoO_3 , WO_3 and mixed oxide films can be deposited by simple sol-gel method. After annealing at 270 °C, the films possessed structural and optical properties defining good electrochromic behavior. All the films had color efficiencies of 60-120 cm^2/mC , which is in the range required for electrochromic device applications.

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