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# THERMALLY INDUCED STRUCTURAL TRANSFORMATIONS IN CVD TRANSITION METAL OXIDE THIN FILMS

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Thin films of molybdenum, tungsten and mixed $MoO_3$-$WO_3$ oxides, obtained by atmospheric pressure chemical vapor deposition, were investigated by Raman and XRD measurements. All of the films were prepared using identical technological parameters, and were annealed at 400 $^oC$. Analysis of the Raman and XRD spectra for the three types of film shows that molybdenum oxide films crystallized as orthorhombic $MoO_3$, with a small fraction of $MoO_{2.89}$ sub-oxide, while the annealed tungsten oxide films were triclinic $WO_3$ with less than 2 % of the sub-oxide of $W_{20}O_{58}$. The Raman spectra of the mixed $MoO_3$-$WO_3$ films indicated the crystalline phases of molybdenum and tungsten oxides in an amorphous network. In addition, the XRD results showed that the structure of the mixed oxides followed the crystallization of $WO_3$, and Mo atoms were suggested to substitute for W in the $WO_3$ lattice.

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## 1. Introduction

Transition metal oxides are largely studied with respect to their electrochromic properties, for applications as smart windows and display devices. Molybdenum trioxide, compared to tungsten trioxide, has a comparatively lower coloration efficiency. However, the closer position of its optical absorption peak to the human eye sensitivity peak makes this material a very attractive electrochromic material [1,2]. Mixed films based on W/Mo oxides are expected to exhibit an enlarged optical absorption band. This could originate from increased electron transitions between the two types of metallic site in the two-component material.

Investigations of metal oxide films are connected with their application as the active layers in electrochromic devices, mainly smart windows. A very important feature of the films is their optimal structure (crystalline orthorhombic with a unique layered structure of the $MoO_3$ film and an amorphous, porous structure in the cases of $WO_3$ and mixed $MoO_3$-$WO_3$ films), all permitting easily intercalation of ions. For an electrochromic device, a high optical transmittance of the active metal oxide layer is very important. To improve the initial transmittance, structural changes of the films are necessary. This is done by post-deposition annealing at temperatures of 300-500 $^oC$ [3-5].

In this investigation, the structure of $MoO_3$, $WO_3$ and mixed $MoO_3$-$WO_3$ oxide thin films after annealing at 400 $^oC$ was studied by Raman and XRD methods. The temperature of 400 $^oC$ was

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chosen since it is compatible with glass substrate technology and is optimal for a suitably porous film structure.

## 2. Experimental details

Films of $MoO_3$, $WO_3$ and mixed $MoO_3$-$WO_3$ oxide were deposited on conductive glass (Donnelly type $SnO_2$:Sb) and Si substrates, by atmospheric pressure pyrolytical decomposition of the corresponding hexacarbonyls, $W(CO)_6$, $Mo(CO)_6$, or their suitable physical mixtures. The sublimator temperature of 90 °C was controlled to an accuracy of ± 1°C. The selected flow rate of argon through the sublimator assured a constant supply of precursor vapor. Oxygen entered separately into the reactor. The chosen ratio of flow rates of argon to oxygen was 1:32. The deposition temperature was 200 °C. This was a crossing point of the deposition temperatures for the three kinds of metal oxide film [5]. The deposition time was kept constant (40 min) and because of the different growth rates the film thickness was about 300 nm for $MoO_3$, 120 nm for $WO_3$ and 400 nm for mixed oxide films. Apparently, the presence of two components in the deposition chemical reactions changes the growth kinetics, leading to an increased growth rate of the mixed oxide films at a low CVD temperature (200°C), at which pure $WO_3$ grows very slowly [3].

After deposition, the films were annealed in air for 1 hour at 400°C. This temperature was selected because of the glass substrates, used also for practical applications in electrochromic windows. Moreover, some cracking effects caused by higher annealing temperatures were observed in the films [2].

For films deposited on silicon substrates, Raman measurements were carried out using a Dilor XY triple monochromator with a multichannel optical detector. During recording of the Raman spectra in the range of 100-1100 $cm^{-1}$, the intensity of the He-Ne laser ($\lambda$ = 632.8 nm) excitation was controlled to an accuracy of 1%. The excitation power on the sample surface was 0.5 mW, and the excitation spot diameter was 3 $\mu$m. Additional information about the crystalline phases was obtained for films deposited on conductive glass substrates, applying X-ray diffractometry using Philips X'Pert equipment. The crystalline phases were identified using data from the ASTM system [6].

## 3. Results and discussion

The development of crystalline phases in the CVD metal oxide films, due to thermal annealing, was analyzed by large-angle XRD measurements. The results are summarized in Fig. 1, where the XRD patterns for the $MoO_3$, $WO_3$ and $MoO_3$-$WO_3$ films are given. The appearance of sharp peaks above the broad amorphous one shows that all three kinds of sample contain crystalline phases. However, it is difficult to separate the crystalline part from the amorphous one, because the structure of the glass substrates is also amorphous.

In the case of the $MoO_3$ films, orthorhombic molybdenum trioxide and triclinic $MoO_{2.89}$ sub-oxide were identified among the crystalline phases (Fig.1). From the analysis of the ratio of the peak intensities, it was established that the orthorhombic $MoO_3$ crystallites prefer to grow in the <010> direction. The sub-oxide percentage, however, could not be determined because the corresponding X-ray lines coincided with the strongest XRD peak of the crystalline $SnO_2$ used as a conductive layer on the glass substrate. This $SnO_2$ peak appeared in all the XRD spectra. The larger part of the crystalline phases in the tungsten oxide films consisted of triclinic $WO_3$, and there was less than 2 % of $W_{20}O_{58}$ sub-oxide (Fig. 1). The XRD pattern of the mixed $MoO_3$-$WO_3$ film was very similar to that of the $WO_3$ film. Although the peak positions were the same, the peak intensity was strongly enhanced, because W atoms are partly substituted by Mo atoms. Obviously, in the mixed oxides, $(W,Mo)O_3$ crystallites are present with the same triclinic modification found for the pure $WO_3$ film. The Mo atoms replace some of the W atoms in the triclinic $WO_3$ lattice.

Our previous Raman investigations have shown that films in the as-deposited state are predominantly amorphous [2]. After annealing at 400 °C, the structure of these films underwent different degrees of crystallization, as shown in Fig. 2. The Raman spectra of the $WO_3$ and $MoO_3$-

$WO_3$ films indicate an amorphous-like structure, with superimposed peaks revealing some degree of crystallization. The spectrum of the annealed $MoO_3$ film corresponds to a thoroughly crystalline structure. In the spectrum of the $MoO_3$ film, the peaks in the range 600-1000 $cm^{-1}$ and below 400 $cm^{-1}$ down to 120 $cm^{-1}$ are attributed respectively to the stretching and bending vibrations of Mo-O bonds in the orthorhombic modification [7]. A detailed study of the effect of different annealing temperatures on the $MoO_3$ film structure has been presented elsewhere [1].

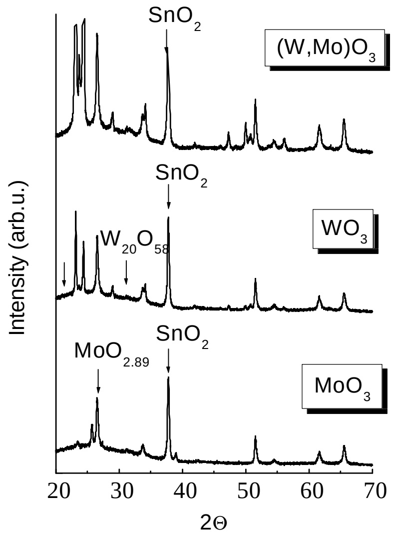

Fig. 1. XRD spectra for $MoO_3$, $WO_3$ and mixed $MoO_3$ -$WO_3$ oxide films deposited on glass substrates at 200 °C and annealed at 400 °C. Most of the peaks are specific for the corresponding trioxides. The non-specific peaks are pointed out in the spectra.

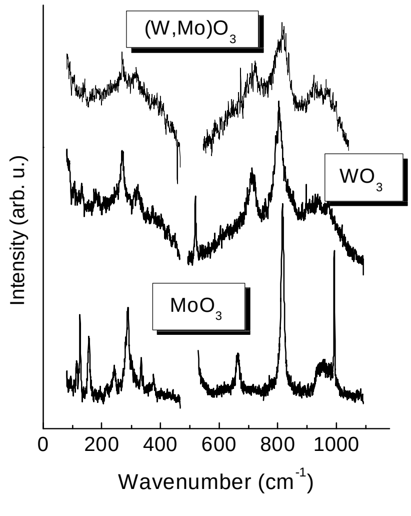

Fig. 2. Raman spectra of $MoO_3$, $WO_3$ and mixed $MoO_3$-$WO_3$ oxide films, deposited on Si substrates at 200 °C and annealed at 400 °C.

The peaks in the spectrum of the $WO_3$ film at 717 and 803 $cm^{-1}$ are connected with the W-O stretching vibrational bands [8]. The similar position of these Raman peaks is related to the monoclinic modification [9]. $WO_3$ in crystalline form is often cited as either having a monoclinic, orthorhombic or triclinic modification [10]. This is because$WO_3$ in these modifications has main diffraction peaks at one and the same d-spacings. However, the XRD spectra clearly show a triclinic modification, as discussed above.

In the Raman spectrum of the $MoO_3$-$WO_3$ mixed oxide film, there was a very broad band in the range 600-1000 $cm^{-1}$, centered at around 800 $cm^{-1}$. This band is also characteristic of the annealed $WO_3$ film, and it indicates that the mixed film structure was basically a tungsten trioxide amorphous framework. The peaks superimposed over this band are attributed to the crystalline phases of the pure components $MoO_3$ and $WO_3$. The peak at around 727 $cm^{-1}$ is related to W-O stretching vibration bonds [11]. The most pronounced peak at 817 $cm^{-1}$ could be assigned to the stretching vibration of the Mo-O-Mo groups. The peak at 940 $cm^{-1}$ is related to the double Mo=O bond vibration in the orthorhombic modification of $MoO_3$ [7]. These results are in a good agreement with the XRD data, and present additional proof that Mo atoms substitute for W atoms in the $WO_3$ network.

Additional information about the effect of annealing on these materials is the optical bandgap, $E_{.g,.}$ data from ellipsometric measurements, described in detail elsewhere [2.12]. It is empirically established that structural transformation from the amorphous to the crystalline phase causes an increase in the energy band gap for $MoO_3$ [1,13,14] and a decrease for $WO_3$ [13,15]. For the annealed $MoO_3$ films, the $E_{.g.}$ value of 2.9 eV is related to crystalline $MoO_3$. The value of 3.1 eV for the annealed $WO_3$ films is a characteristic of the amorphous structure of this material. Almost the same value is obtained for mixed $MoO_3$-$WO_3$ films (3.0 eV), giving new evidence that the mixed films are predominantly amorphous and are similar to tungsten trioxide.

## 4. Conclusions

Raman and XRD data analysis showed that the annealing of CVD W/Mo based metal oxide thin films at 400°C leads to crystallization of $MoO_3$ films in an orthorhombic modification. In the case of $WO_3$, crystallization occurs in the triclinic modification. For mixed $MoO_3$-$WO_3$ oxide films, the structure was dominated by amorphous tungsten trioxide, including the crystalline phases of $MoO_3$ and $WO_3$, and the Mo atoms are suggested to substitute for W atoms.

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