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Structure and optical properties of CVD molybdenum oxide films for electrochromic application

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Abstract Vibrational and optical properties of MoO₃ thin films have been studied by Raman and infrared spectroscopy. The films were deposited onto Si substrates at a temperature of 150 °C by chemical vapor deposition of Mo(CO)₆ at atmospheric pressure and different amounts of oxygen in the reactor. The Raman and IR spectral analyses show that the as-deposited films are in general amorphous. Post-deposition annealing at 300 and 400 °C leads to crystallization and the MoO₃ film structure is a mixture of orthorhombic and monoclinic MoO₃ modifications. Transformation of the monoclinic crystallographic modification to a thoroughly orthorhombic layered structure is observed for films heated at temperatures above 400 °C.

Keywords Chemical vapor deposition · Molybdenum oxide · Thin films · Raman spectroscopy · Infrared spectroscopy

Introduction

Transition metal oxides of WO₃ and MoO₃ exhibit various important properties, including electrochromism. This effect is widely studied in these materials because of their possible applications in display devices and “smart windows” [1]. MoO₃ can exist in different crystalline polymorphs. The thermodynamically stable orthorhombic α -MoO₃ and the metastable monoclinic β -MoO₃ modifications are the mostly studied ones. The orthorhombic MoO₃ has a layered structure consisting

of double layers of MoO₆ octahedra held together by covalent forces [2, 3]. Some researchers [3] have studied, in a systematic way, the IR and Raman spectra of powder samples of molybdenum trioxides (orthorhombic and monoclinic) as well as molybdenum trioxide hydrates. Others [4] have investigated the temperature dependence of the phonon spectrum of orthorhombic MoO₃ crystals by measuring transmittance and reflection spectra from 20 to 600 cm⁻¹. In recent years there have been some separate studies on vibrational properties of MoO₃ thin films obtained by different methods, but still there is a lack of detailed investigation on the dependence of the process parameters, both those concerned with the growth process and the process of post-deposition annealing. Recently, Raman spectra of CVD MoO₃ thin films and their changes with annealing temperature (200–500 °C) have been studied in detail [5]. In the present paper the influence of the oxygen content on the structure and vibrational properties of as-deposited and annealed CVD molybdenum oxide films is reported.

Experimental

Thin films of MoO₃ were obtained by pyrolytic decomposition of Mo(CO)₆ vapor in an argon-oxygen gas mixture at atmospheric pressure in a horizontal CVD reactor with cold walls. The powder precursor of Mo(CO)₆ was placed in a sublimator immersed in a silicon oil bath, the temperature of which was maintained at 90 °C and controlled with an accuracy of ± 1 °C. Through a separate line, oxygen (99.95%) entered the reactor. The amount of Mo(CO)₆ precursor vapor was kept constant by keeping constant the argon carrier gas flow rate through the sublimator. The oxygen amount during the film growth was varied by changing the flow rate of the oxygen, so different ratios of carrier argon to oxygen flow rates were used, namely 1:20, 1:28 and 1:40. Silicon substrates were placed on a graphite susceptor heated by a high-frequency generator. The substrate temperature, which is the deposition temperature, was kept at 150 °C with an accuracy of ± 10 °C. The samples were annealed by heating at temperatures of 300 and 400 °C in air for 1 h.

The Raman scattering spectra (wavenumber range of 100–1100 cm⁻¹) were measured in pseudo-back-scattering geometry by a Dilor XY triple monochromator with a multichannel optical detector. During the recording the intensity of the He-Ne laser

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($\lambda=632.8$ nm) was controlled with an accuracy of 1%. The excitation power on the sample surface was 0.5 mW and the excitation spot diameter was 3 μm . The IR spectral measurements were carried out on a Perkin-Elmer 1430 IR spectrophotometer. A Talystep profilometer was used for thickness determination. The growth rate of the films was around 10 nm min^{-1} . Thicknesses used were in the range 320–400 nm.

Results and discussion

The results presented in this study refer to MoO_3 films annealed at 300 and 400 $^\circ\text{C}$ and the difference in the Raman bands as a result of changes in one technological parameter, i.e. the gas flow rates ratio. No data for the as-deposited MoO_3 films are given here. We note that when the films are deposited on an amorphous substrate (glass), our early RHEED results have shown that MoO_3 films in the as-deposited state are generally amorphous [6]. However, when the substrate is crystalline silicon, some crystallization takes place even during the film growth, indications of which are small peaks superimposed over broad band regions in the Raman spectra (not presented) of the as-deposited MoO_3 films.

The results of Raman and IR measurements are given in Figs. 1, 2, 3, and the characteristic bands are summarized in Table 1. The spectral analysis is based on the fact that the structure of MoO_3 is formed by MoO_6 octahedra, for which the stretching and bending vibrational Raman and IR active modes occur in the 500–1000 cm^{-1} and 200–400 cm^{-1} regions, respectively. The terminal double $\text{Mo}=\text{O}$ bonds are characterized by narrow Raman and IR bands occurring in the 920–1000 cm^{-1} range [3]. Some authors consider this region as 885–1007 cm^{-1} [7]. For the CVD MoO_3 films studied, the corresponding Raman band was observed at around 947 cm^{-1} . Bands in this range are associated with stretching modes of the $\text{Mo}=\text{O}$ terminal. The intense Raman line observed at 847 cm^{-1} in films prepared at the highest oxygen amount (1/40 gas flow ratio) could be assigned to vibration of bridging oxygens linked to two Mo atoms in a three-dimensional arrangement of monoclinic MoO_3 . A similar Raman peak at 849 cm^{-1} has been related to vibrations in monoclinic MoO_3 [8]. Moreover, it has been stated that the more intense Raman lines are the 848 and 776 cm^{-1} ones for monoclinic MoO_3 [3]. These lines are assigned by the same authors to the stretching vibrations of the metal-oxygen bonds of $\text{Mo}-\text{O}-\text{Mo}$ units in the corner-sharing octahedra. Bands around 816 and 828 cm^{-1} for MoO_3 prepared at oxygen contents defined by gas ratios of 1/20 and 1/28, respectively, could be assigned to vibrations in the orthorhombic MoO_3 film structure. For samples obtained at the highest amount of oxygen, 1/40, and annealed at 300 $^\circ\text{C}$ and 400 $^\circ\text{C}$ (see Figs. 1c and 2c), a characteristic peak is observed at about 768–772 cm^{-1} . A strong Raman peak at 774 cm^{-1} has been observed by other authors [8] and they assigned it to monoclinic MoO_3 . It is seen that higher amounts of oxygen somehow favor formation of monoclinic MoO_3 . A very

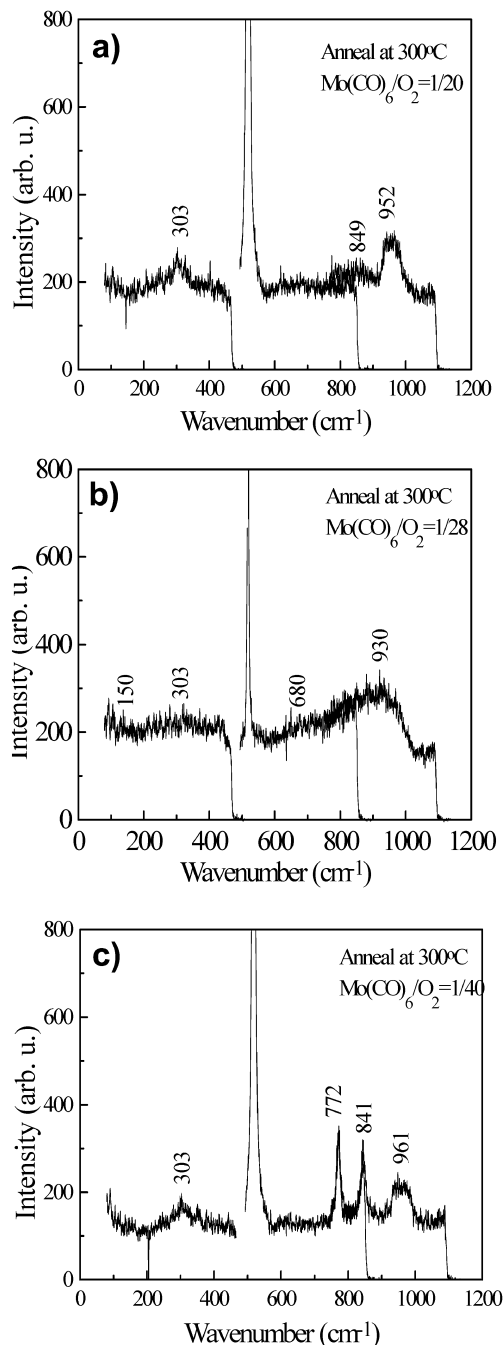


Fig. 1. Raman spectra of annealed (300 $^\circ\text{C}$) CVD thin films of MoO_3 deposited at 150 $^\circ\text{C}$ and atmospheric pressure with three different amounts of oxygen, defined by the oxygen/argon gas ratios of (a) 1/20, (b) 1/28 and (c) 1/40

narrow Raman line at 663 cm^{-1} appears in samples obtained at the highest amount of oxygen, produced with a gas ratio of 1/40 and heated at 400 $^\circ\text{C}$ (Fig. 2c). This line is also observed in Raman spectra of our CVD MoO_3 films obtained at gas ratios of 1/32 and 1/36 [5]. For lines in the range 660–700 cm^{-1} , Seguin et al. [3] refers to the stretching vibrations of bridging oxygen atoms linked to three metal atoms in orthorhombic MoO_3 . The line at 667 cm^{-1} has also been assigned to

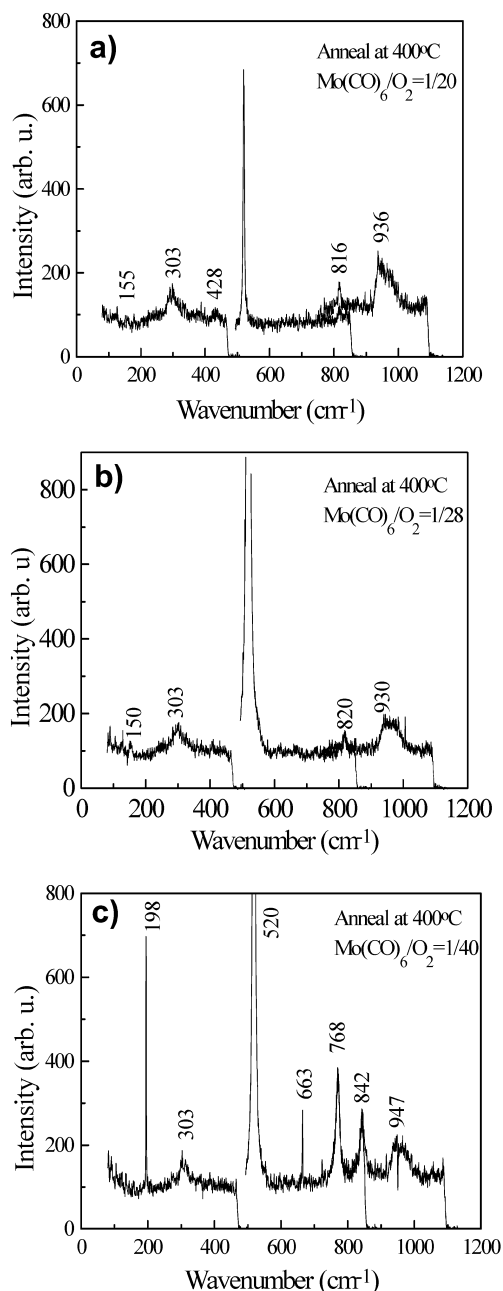


Fig. 2. Raman spectra of annealed (400 °C) CVD thin films of MoO_3 deposited at 150 °C and atmospheric pressure with three different amounts of oxygen, defined by the oxygen/argon gas ratios of (a) 1/20, (b) 1/28 and (c) 1/40

orthorhombic MoO_3 [8]. The intense peak at 520 cm^{-1} corresponds to the vibrations of the optical phonons of silicon. For all the studied MoO_3 films, a comparatively enlarged band existing in the Raman spectrum is observed at 303 cm^{-1} . This has been assigned as a very strong IR-active mode for a monoclinic MoO_3 modification. Bands under 400 cm^{-1} are assigned as deformation modes. The very narrow line observed at 198 cm^{-1} has been assigned [3] to that kind of vibrational mode.

It is considered that orthorhombic MoO_3 can be obtained from any hydrated metal oxides by heating at

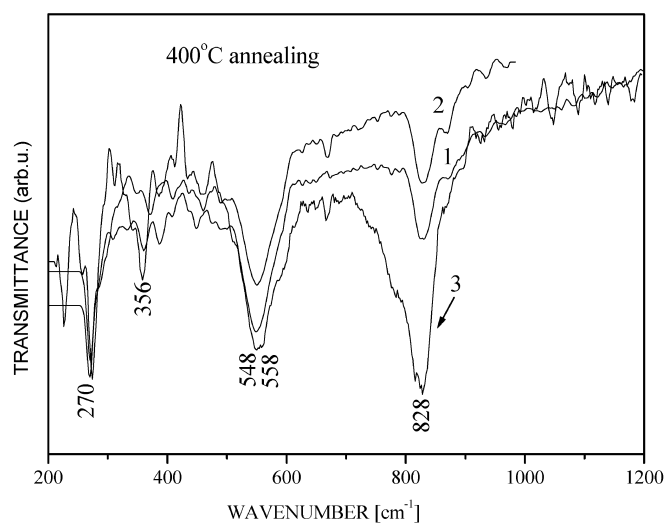


Fig. 3. IR transmittance spectra of annealed (400 °C) CVD thin films of MoO_3 deposited at 150 °C and atmospheric pressure with three different amounts of oxygen, defined by the oxygen/argon gas ratios of (1) 1/20, (2) 1/28 and (3) 1/40

around 400 °C for several hours [3, 9]. Even at lower temperatures, slightly above 350 °C, in air for 4 hours it has been possible to convert MoO_3 films into an orthorhombic crystalline modification [9]. The oxygen content in the gas stream during the film growth influences the structure and the bond configuration of the film. However, from the results it seems that the terminal double bonds are not strongly influenced by the amount of oxygen; nor does the annealing temperature have an effect, because almost equally shaped Raman bands are observed in the range $930\text{--}960\text{ cm}^{-1}$ in all the MoO_3 films studied. When the gas flow ratio is 1/28, flattening in the Raman bands was observed for the annealed films, especially the ones annealed at 300 °C (Fig. 1b). Similar featureless Raman spectra are observed for $\text{Mo(CO)}_6\text{-LPCVD MoO}_3$ films [10]. It can be supposed that the featureless character is due to mass transfer, leading to orthorhombic phase formation. When the oxygen flow doubles in comparison with the initial amount (i.e. the ratio increases from 1/20 to 1/40), then well-expressed Raman peaks in the annealed films were observed.

The IR spectra (not presented) of the as-deposited films are featureless; there are no absorption bands. After annealing at 300 and 400 °C, an absorption band at 828 cm^{-1} , typical for orthorhombic MoO_3 , appears. This band is well expressed in the spectrum of the sample heated at 400 °C, as is seen in Fig. 3. A very strong IR band at 820 cm^{-1} has been observed in powder samples [3], which was assigned to vibrations of oxygen atoms connected to two Mo atoms in the orthorhombic MoO_3 structure. In the IR spectra of the annealed samples at 300 and 400 °C, absorption bands appeared in the range $548\text{--}564\text{ cm}^{-1}$. These bands could be related to transverse optic (TO) vibrations of Mo-O-Mo bonds. A band has been observed at 545 cm^{-1} and assigned to oxygens linked to two metal atoms in an orthorhombic MoO_3

Table 1. Results from the analysis of the Raman and IR spectra of CVD MoO₃ thin films deposited at 150 °C and atmospheric pressure with different amounts of oxygen defined by the oxygen/argon gas flow rate ratios of 1/20, 1/28 and 1/40 after annealing at 300 °C and 400 °C

Gas flow rate ratio	IR absorption bands (cm ⁻¹)		Raman absorption bands (cm ⁻¹)	
	T _{anneal} = 300 °C	T _{anneal} = 400 °C	T _{anneal} = 300 °C	T _{anneal} = 400 °C
1/20	268	270	–	155 (w)
	–	356	303 (m)	303 (m)
	564	558	–	428 (w)
	710	828 (s)	849 (w)	816 (m)
1/28	–	–	952 (s, broad)	936 (s)
	–	270	150 (w)	150 (w)
	–	356	303 (w)	303
	564	558 (s)	680 (w)	–
	710 (very broad)	–	–	–
	–	828 (s)	–	820 (m)
1/40	–	–	930 (m, broad)	930 (s, broad)
	–	–	–	198 (vs)
	229	270	303 (w)	303 (m)
	380	356	–	–
	–	548 (splitting 558 cm ⁻¹ into two bands)	–	–
	–	–	–	663 (s)
	–	–	772 (s)	768 (stronger)
	823	828 (s)	841 (s)	842 (s)
–	–	961 (s, broad)	947 (s, broad)	

modification [7]. The IR band at 356 cm⁻¹ observed in the IR spectra of films obtained at the highest oxygen amount (gas flow ratio of 1/40) and annealed at 400 °C could be connected with monoclinic MoO₃, as pointed out [3] for the very weak peak observed at 352–358 cm⁻¹. It can be emphasized that, as a result of increased oxygen content, the formation of monoclinic modification is encouraged. This is obvious only if the annealing temperature is high enough (400 °C). Even at 400 °C annealing, in order to obtain MoO₃ films with only orthorhombic structure the duration should be several hours, as is often cited. Our experiments have shown that, at increased temperatures up to 500 °C, one hour annealing is enough to form films of only orthorhombic structure, although some shortcomings like film cracking appear [5].

Conclusions

MoO₃ films deposited at 150 °C by CVD of Mo(CO)₆ possess vibrational properties, which change considerably by varying the parameters of the CVD and post-annealing processes. Raman and IR spectra showed that the MoO₃ films grown at the given deposition conditions and annealed at 300 and 400 °C are a mixture of orthorhombic and monoclinic MoO₃ modifications. The influence of the oxygen content is noticeable only after applying thermal annealing. This influence is basically

on the vibration of the bonds of oxygen with two or three metal atoms and is less pronounced for terminal double Mo=O bonds.

The results clearly show that if the annealing temperature does not exceed 400 °C, then several hours of heating are necessary to convert the MoO₃ structure into the layered structure of the orthorhombic modification. Such a layered structure would permit easy intercalation of ions, an important parameter for provoking the electrochromic effect.

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