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ORIGINAL PAPER

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# Spectroscopic ellipsometry study of CVD molybdenum oxide films: effect of temperature

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**Abstract** The optical properties of CVD $MoO_3$ films were studied by ellipsometry in the spectral range 280–820 nm. The films were deposited on silicon substrates by pyrolytic decomposition at atmospheric pressure of $Mo(CO)_6$ at 150 and 200 °C. To optimize the film structure, annealing was performed at temperatures of 300 and 400 °C. The refractive index for as-deposited $MoO_3$ films varies within 1.8–2.2 and the optical band gap energies in the range 2.87–2.98 eV. After annealing, the latter values slightly increase to 2.85–3.05 eV, depending on the annealing temperature. The band gap energies are typical for a polycrystalline material. Peaks in the spectral dependence of the absorption coefficient were observed. Their position and intensity are found to be affected by the process temperature.

**Keywords** Chemical vapor deposition · Molybdenum oxide · Thin films · Spectroscopic ellipsometry · Optical constants

## Introduction

Molybdenum oxide ($MoO_3$) films are interesting switchable materials because of their application in electrochromic devices and smart windows [1]. The technological process is decisive for the fabrication of films with a disordered and sufficiently porous structure, a necessary basis for the electrochromic effect. Different growth techniques are currently used for $MoO_3$ thin film deposition, such as thermal evaporation [2, 3], sputtering [4], chemical vapor deposition (CVD) [5, 6], electrodeposition [7] and flash evaporation [8, 9]. Our experience in applying CVD technology has shown that direct deposition of $MoO_3$ is possible by pyrolytic decomposition of molybdenum hexacarbonyl [$Mo(CO)_6$] at atmospheric pressure [10]. One of the main advantages of this process is the high deposition rates and the possibility to cover large areas in a flow-through process. Numerous experimental results [1, 3, 11] are available for the optical characterization of $MoO_3$ films prepared by evaporation and/or the sputtering technique, while CVD $MoO_3$ films are less studied and need data regarding their structural and optical properties.

In the present paper the optical properties of chemical vapor deposited $MoO_3$ films are studied by spectroscopic ellipsometry. The changes in the optical parameters resulting from varying the temperature of the growth and annealing processes are considered.

## Experimental details

Thin $MoO_3$ films were deposited by pyrolytic $Mo(CO)_6$ decomposition proceeding in argon/oxygen at atmospheric pressure in a CVD reactor with cold walls. The pyrolysis takes place on Si substrates heated at 150 and 200 °C. The sublimator filled with $Mo(CO)_6$ powder was immersed in a silicon oil bath heated at 90 °C with an accuracy of 1 °C. The vapor amount of $Mo(CO)_6$ was kept constant by keeping constant the Ar carrier gas flow rate through the sublimator. The oxygen amount during the film growth was also constant, so the ratio of carrier argon to oxygen flow rates was 1:12.

The $MoO_3$ films were deposited on either Si or glass substrates. The film thickness, controlled by Talystep profilometer, varied in the range 270–360 nm.

The ellipsometric measurements of the films on Si substrates were performed on a Rudolph Research ellipsometer in the spectral region 280–820 nm at an angle of incidence of 70°. The accuracy of the angles of the polarizer, analyzer and light incidence was within 0.01°. A single-layer model was applied for determination of the

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complex refractive index of the $MoO_3$ films. In the calculations a thin (~2 nm) film of native $SiO_2$ on Si was not taken into account since the films studied are significantly thicker. In the iteration procedure the optical constants of the silicon substrate [12] were kept as fixed parameters and the refractive index ($n$) and extinction coefficient ($k$) of the films were the parameters to be searched. From the least-squares fitting the values of $n$ and $k$ were obtained at a minimum error of the sum of squares.

The transmittance spectra of the films on glass substrates were registered in the range 325–900 nm on a double-beam spectrophotometer (Shimadzu UV-190).

## Results and discussion

The higher deposition temperature (200 °C) results in a decrease of the growth rate owing to a vapor phase reaction proceeding in the reactor space [10]. As a result, the thickness of the 200 °C samples was smaller (~270 nm), compared to that for the 150 °C samples (~360 nm).

In Fig. 1 the transmittance and reflectance spectra of the as-deposited $MoO_3$ films annealed at 400 °C films are presented. The reflectance spectra are calculated from the refractive index ($n$) and extinction coefficient ($k$) obtained from the ellipsometric data. The results show that the lower temperature films ($T_{dep} = 150$ °C) have lower transmittance. After annealing, the transparency of these films increases; the transmittance values become close for the two kinds of film. Obviously, during annealing in air, additional oxidation proceeds, yielding a stoichiometric $MoO_3$ possessing higher transparency. Additional oxidation also explains the obtained increase with ~10% film thickness.

The spectral dispersion of the refractive index and the extinction coefficient for the as-deposited samples are given in Fig. 2. These curves possess specific character. The $n$ and $k$ values are close for the films deposited at the two temperatures: the $n$ values are within 1.8–2.2 and $k$ values vary around 0.2. The observed maxima in the refractive index dispersion curves could be related to inhomogeneities in the film structure. Based on the results from Raman and IR experiments [13, 14], the structure of the obtained $MoO_3$ films is a mixture of amorphous and crystalline phases; the fraction of the latter varies with the deposition temperature. The comparatively high deposition rates also contribute to inhomogeneities in the films. The maxima in the extinction spectral dependences indicate that proper-type defects are present.

After annealing, the spectral dependence of the refractive index becomes featureless (Fig. 3). This is an indication for improved structure uniformity. The refractive index values are within 1.8–2.0. In comparison

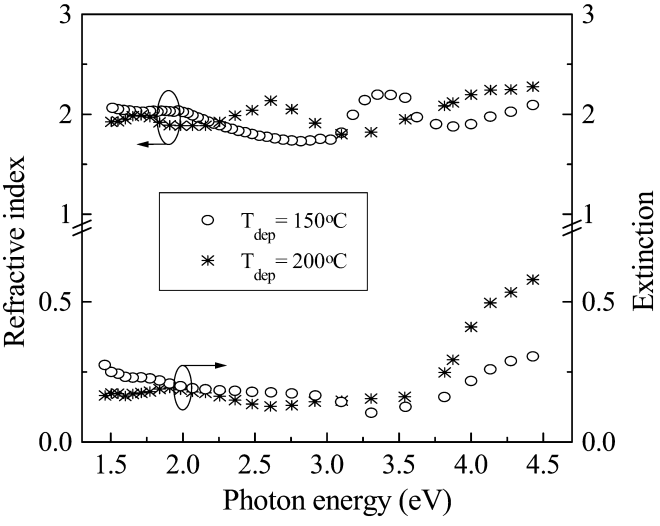


**Fig. 2.** Refractive index and extinction coefficient spectra for as-deposited CVD $MoO_3$ films at 150 °C (*circles*) and 200 °C (*stars*)

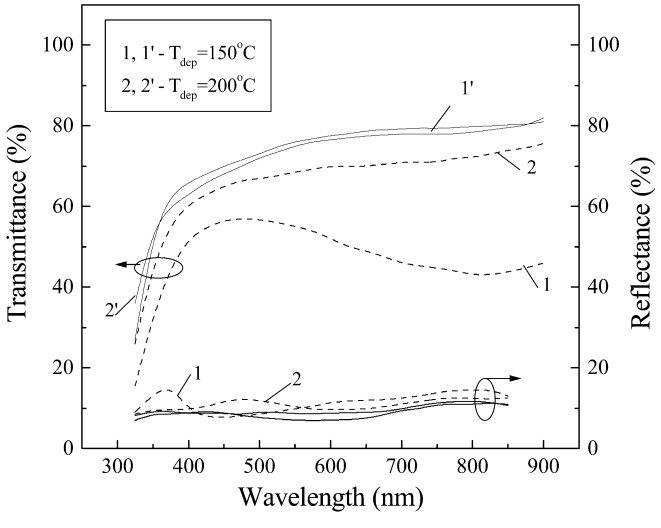


**Fig. 1.** Transmittance and reflectance spectra of the as-deposited CVD $MoO_3$ films (*dashed lines*) at 150 °C (*1*) and 200 °C (*2*) and after annealing (*full lines*) at 400 °C (*1′*, *2′*)

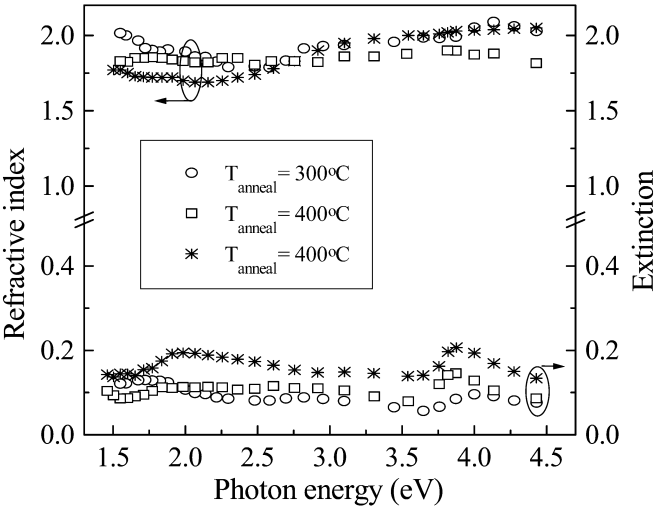


**Fig. 3.** Refractive index and extinction coefficient of CVD $MoO_3$ films: deposited at 150 °C and annealed at 300 °C (*circles*); deposited at 150 °C and annealed at 400 °C (*squares*); deposited at 200 °C and annealed at 400 °C (*stars*)

with Fig. 2, from Fig. 3 it is seen that the extinction values considerably decrease for $MoO_3$ films deposited at 150 °C, while for films deposited at 200 °C the shape of the curve changes and only a slight decrease in the $k$ value is observed. These results are in good agreement with those of the transmittance spectra, where an increase of film transparency is registered (see Fig. 1).

The coefficient of absorption ($\alpha$) was calculated from the corresponding $k$ values ($\alpha = 4\pi k/\lambda$). The spectral dependence of the absorption coefficient of the as-deposited and annealed $MoO_3$ films is presented in Fig. 4. Correspondingly to the extinction (Figs. 2 and 3), the absorption in the annealed films is smaller than for the as-deposited films. For the 150 °C films, absorption peaks appear around 1.8 and 2.75 eV and their intensity decreases after annealing. For films deposited at 200 °C, an absorption peak around ~2.0 eV is observed, which after annealing disappears. Apparently, air oxidation decreases the amount of defects owing to saturation with oxygen of dangling Mo bonds.

The plots of $(\alpha h\nu)^{1/2}$ versus photon energy for the as-deposited films are presented in Fig. 5. The observed maxima in the energy range below the optical band gap energy could be related to proper-type defects. For the higher deposition temperature, the maximum position moves towards the lower energy region. This suggests that the bond configuration at the defect sites is affected by temperature. Absorption bands in the same energy range have been observed [8] and the authors associate the maxima with absorption by defects of oxygen-ion vacancies in the $MoO_3$ film. The observed shape of the absorption spectrum can be related to such oxygen-ion vacancies defining different energy levels in the energy gap of $MoO_3$.

Extrapolating the linear part of the plot of $(\alpha h\nu)^{1/2}$ versus photon energy toward zero absorption, the intercept with the energy axis determines the optical band gap energy ($E_{og}$) value. For the as-deposited films the $E_{og}$ values are 2.87 eV ($T_{dep} = 150$ °C) and 2.98 eV ($T_{dep} = 200$ °C). The optical band gap energies found elsewhere [5, 15] have similar values, ascribed to a polycrystalline structure of the $MoO_3$ films. The optical band gap energy values of the as-deposited CVD $MoO_3$ films are given in Table 1.

In Fig. 6 the plots of $(\alpha h\nu)^{1/2}$ versus photon energy for the annealed $MoO_3$ films are shown. After extrapolation of the linear part of the curves, the optical energy gap values for the annealed $MoO_3$ films are found in the range 2.85–3.05 eV (see Table 1). Comparison of these results with those obtained before annealing indicates that only a small increase of $E_{og}$ is the result of annealing, which could be related to crystallization. Raman spectral analysis of the $MoO_3$ films has shown [13] that, in films annealed at these temperatures, crystalline phases of monoclinic and orthorhombic modifications exist.

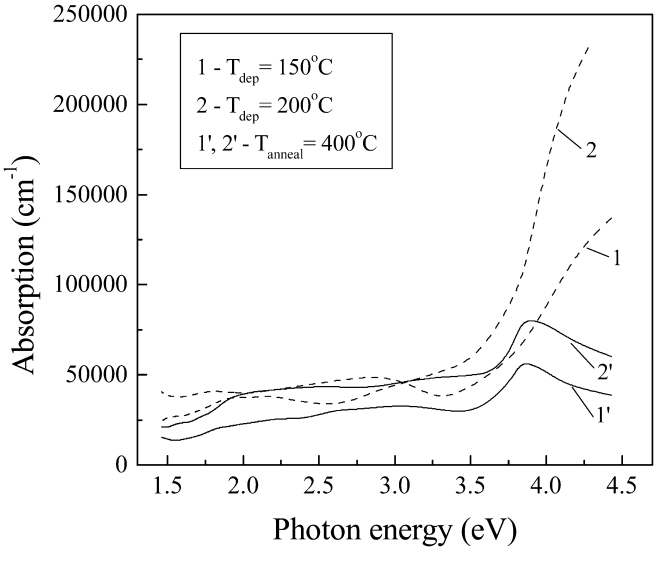


**Fig. 4.** Spectral dependence of the absorption coefficient of as-deposited CVD $MoO_3$ films (*dashed lines*) at 150 °C (*1*) and 200 °C (*2*) and after annealing at 400 °C (*full lines*)

## Conclusions

The optical constants of CVD thin $MoO_3$ films, which depend on the process temperatures, were studied by spectral ellipsometry. The results show that as-deposited

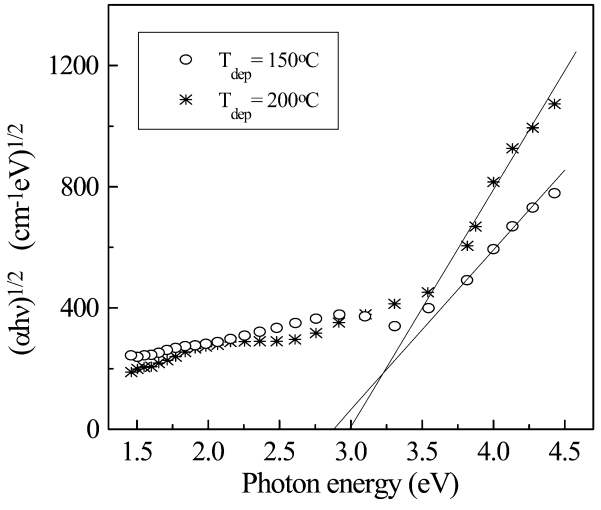


**Fig. 5.** Plot of $(\alpha h\nu)^{1/2}$ versus photon energy for as-deposited CVD $MoO_3$ films at 150 °C (*circles*) and 200 °C (*stars*)

**Table 1.** Optical band gap energy values of CVD $MoO_3$ films in dependence on the process temperature

| Annealing temperature (°C) | Optical band gap energy (eV) | |
|---|---|---|
| | $T_{dep} = 150$ °C | $T_{dep} = 200$ °C |
| As-deposited state | 2.87 | 2.98 |
| 300 | 2.85 | 3.09 |
| 400 | 2.92 | 3.05 |

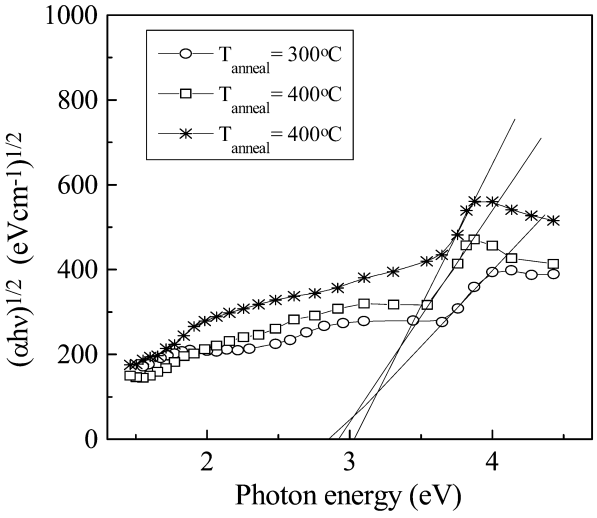


**Fig. 6.** Plot of $(\alpha hv)^{1/2}$ versus photon energy at 300 °C (*circles*) and 400 °C (*squares*) for CVD $MoO_3$ films deposited at 150 °C and after annealing at 400 °C for films deposited at 200 °C (*stars*)

films at 150 and 200 °C have inhomogeneous and defective structures which define specific maxima in the spectral dependence of the optical constants. The observed absorption bands are evidence for the existence of proper-type defects, most probably oxygen vacancies. Their energy position in the band gap depends on the process temperature.

The effect of the annealing temperature (300 and 400 °C) is detected by an increase of the transmittance, by flattening of the refractive index dispersion curves and by a decreased absorption coefficient in the whole spectral region. A slight increase of the optical band gap energy is observed.

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