Thermo-optical Properties of MoO_3 thin films in the mid-infrared and phonon frequency shift

Alessandro Bile[1,], Daniele Ceneda[1], Marco Centini[1], Federico Vittorio Lupo[2], Maria Pia Casaletto[3], Roberto Macaluso[2], Koray Aydin[4] and Maria Cristina Larciprete[1]*

[1]Department of Basic and Applied Sciences, Sapienza University of Rome, Rome, 00161 Italy.

[2] Department of Engineering, University of Palermo, Palermo, 90128, Italy.

[3] National Research Council (CNR), Institute for Nanostructured Materials (ISMN), Palermo, 90146, Italy.

[4] Department of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois 60208, USA.

Abstract. MoO_3 is extensively studied in the mid infrared range due to the strong anisotropy of its optical properties. We investigate the mid-infrared thermo-optical properties of polycrystalline alpha-phase Molybdenum trioxide (α-MoO_3) thin films grown onto SiO_2 substrates in the temperature range 20°C-250°C reporting a thermo-optic coefficient of the mean order of 10^{-4} K^{-1}.

Keywords: Optoelectronics, Electro-Optical Devices, Electro-Optical Materials, Optical Materials, Optical Properties, Opto-Electronic Properties, Electrochromic Properties, Optical Constants, Ellipsometry, Thin Films

1 Introduction

MoO_3 has been extensively studied in the mid infrared range due to the strong anisotropy of its optical properties. In addition, MoO_3 exhibits various chromogenic properties such as thermochromism [1], photochromism [2] and electrochromism [3]. Specifically, thermochromia is the process of changing the optical transparency or reflectance of a material under heating.
MoO_3 has been reported to exhibit a colour change from transparent white to bluish when the temperature of the material increases from room temperature up to 300 °C [4]. Another consequence of annealing MoO_3 films in an argon atmosphere is a significant narrowing of their energy forbidden band [4].
More interestingly, thermo-optical properties are reported in the reference for thermally evaporated MoO_3 thin films using ellipsometry [5]. The values of thermo-optical coefficients dn/dT and dk/dT were found to be negative and positive, respectively, in the temperature range 295-460 K. Refractive index dependence on temperature of MoO_3, investigated in the visible range, revealed a variation between 6.24 to $0.91 \cdot 10^{-4}$ K^{-1} [5]. In the same range the extinction coefficient showed a positive variation in the range $0.1\text{-}3.1 \cdot 10^{-5}$ K^{-1} [5]. The trend for the obtained temperature-dependent n values of MoO_3, i.e., monotonic and linear decrease, is characteristic of the material in which the optical indices are associated with thermal expansion and thus with material density.
Here we report a dependence of refractive index (n) and extinction coefficient (k) on temperature in the mid-infrared range.

2 Experimental and Theoretical Methods

MoO_3 films were deposited onto fused silica substrates by pulsed laser deposition (PLD) at 400 °C and 10^{-1} mbar oxygen pressure. Structural characterisation of the films was performed by x-ray diffraction (XRD), as reported in [6]. A Bruker INVENIO-R FTIR spectrometer operating in 64-scan mode per measurement was used to study the reflectance spectrum at a fixed angle (15°) and at a fixed polarization (0°). Fig. 1 reports the x-ray diffractogram of a MoO_3 films. All the peaks can be assigned to the orthorhombic (alpha) phase of MoO_3 (ICDD 01-078-4612 card).

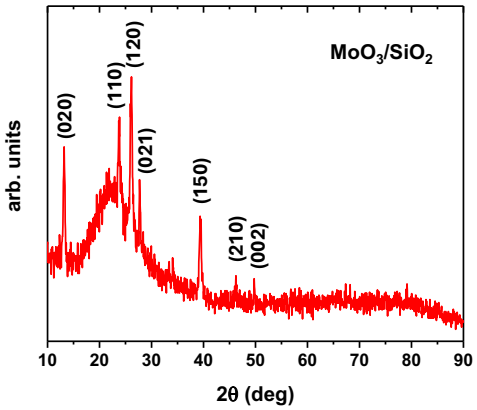

Fig. 1. XRD pattern of a α-MoO_3 film deposited at 400 °C and 10^{-1} mbar oxygen pressure onto a fused silica substrate.

The material's response to four different temperatures was studied: T0 = 20 °C, T100 = 100 °C, T200=200 °C and T250= 250 °C. All measurements were normalized using a gold

* Corresponding author: alessandro.bile@uniroma1.it

reference mirror as the background signal under the same experimental conditions. For each temperature, reflectance spectra of the gold reference mirror was performed. The measured spectral reflectance curves of the MoO_3/SiO_2 structure for the four different temperatures are shown in Figure 2. The polycrystalline nature of the laser-deposited MoO_3 films simultaneously reveals, even at near-normal incidence, the three Reststrahlen bands (RBs) associated with the alpha phase of bulk MoO_3, as also highlighted in ref [5].

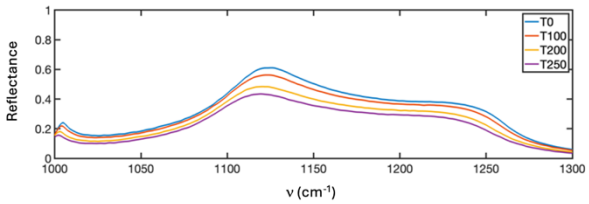

Fig. 2. Temperature-dependent reflection FT-IR spectra measured at θ =15° incidence angle and polarization 0° from α-MoO_3 film, grown on fused silica substrate by PLD.

In this study, we focused our attention on the region 1000-1300 cm^{-1}, around the RB of SiO_2 where reflectivity is more sensitive to the temperature. We also note a narrow band reflection peak at 1006 cm^{-1} due to MoO_3 optical phonon. As shown by reflectance measurements, this peak is highly tunable with temperature, i.e. by increasing temperature the reflectivity is reduced while the phonon frequency corresponding to this peak shifts from 1006 cm^{-1} to 1002 cm^{-1}. To fully evaluate the temperature dependence of the MoO_3 film, the reflectance of the SiO_2 substrate as a function of temperature was also examined. Substrate modelling is indeed important to extract the true thermo-optical behaviour of MoO_3 from the experimental data. As a first step, the temperature dependent electric permittivity of the SiO_2 substrate has been reconstructed by fitting the experimental reflectivity with an isotropic Lorentz model with three oscillators:

$$\varepsilon(\omega) = \varepsilon_{inf} + \sum_{i=1}^{3} \frac{s_i \omega_i^2}{\omega_i^2 - i\gamma_i \omega - \omega^2} \qquad (1)$$

Where the resonance frequencies ω_i, oscillator strengths s_i, damping coefficients γ_i, with i = 1,2,3, and ε_{inf}, are determined as fitting parameters by minimizing the RMS deviation between the calculated and measured reflection spectra.

Afterwards, the temperature dependent electric permittivity of the MoO_3 film on SiO_2 was retrieved by considering a similar Lorentz model for the polycrystalline, isotropic, MoO_3 and using the previously determined parameters to model the SiO_2 substrate at different temperatures. Reconstructed real and imaginary part of the MoO_3 refractive index is reported in figure 1 for T0=20°C and T250=250°C. In order to investigate the dependence of the refractive index on temperature variation, we selected two frequencies: one (1095 cm^{-1}) in a transparency range for MoO_3 (which falls within the RB of SiO_2) and the other close to phonon resonance of MoO_3 (998 cm^{-1}). In these regions we have computed the thermo-optic coefficient, dn/dT.

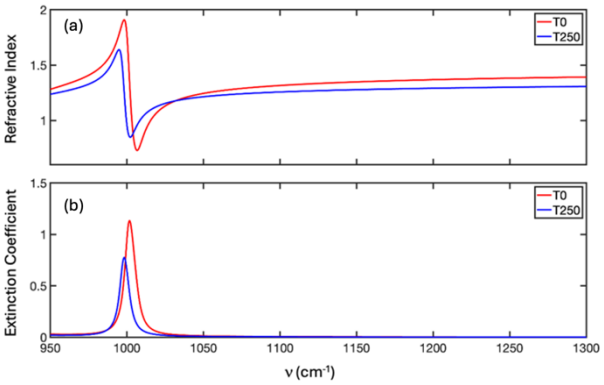

Fig. 3. (a) Reconstructed MoO3 refractive indices at room temperature and maximum heating temperature (250 °C); (b) Reconstructed MoO_3 dispersion coefficients for the two temperatures. Note the phonon frequency shift due to the temperature increasing.

In particular, from the obtained experimental results α-MoO_3 films show a refractive index variation of $dn/dT = (-1.73 \pm 0.02) \cdot 10^{-4}$ K^{-1} at 1095 cm^{-1}. When approaching the phonon resonance frequency (at 998 cm^{-1}) we also found that the absolute value of thermo-optical coefficient is increased to $dn/dT = (-3.09 \pm 0.04) \cdot 10^{-3}$ K^{-1}.

3 Conclusions

In conclusion, we have shown that optical properties of thin films of α-MoO_3 are highly tunable as a function of temperature. Our results obtained in the mid-IR range are of the same order of magnitude of the literature results achieved in the visible range, expanding the interest for MoO_3 as a tunable polaritonic material for IR photonics and thermal radiation management.

Acknowledgments
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