Pulsed laser deposited α-MoO_3 thin films for mid-infrared photonic applications

Roberto Macaluso*
Thin Films Laboratory (TFL)
Department of Engineering
University of Palermo
Palermo, Italy
email: roberto.macaluso@unipa.it
* Corresponding author

Martina Mercurio
Department of Basic and Applied Sciences
Sapienza University of Roma
Roma, Italy
email:
martina.mercurio@uniroma1.it

Federico Vittorio Lupo
Thin Films Laboratory (TFL)
Department of Engineering
University of Palermo
Palermo, Italy
email:
federicovittorio.lupo@unipa.it

Nunzio Timpanaro Pirrina
Thin Films Laboratory (TFL)
Department of Engineering
University of Palermo
Palermo, Italyemail:
nunzio.timpanaropirrina@community.unipa.it

Daniele Ceneda
Department of Basic and Applied Sciences
Sapienza University of Roma
Roma, Italy
email:
daniele.ceneda@uniroma1.it

Maria Pia Casaletto
National Research Council (CNR)
Institute for Nanostructured Materials (ISMN)
Palermo, Italy
email: mariapia.casaletto@cnr.it

Dominique Persano Adorno
Department of Physics and Chemistry 'E. Segré'
University of Palermo
Palermo, Italy
email:
dominique.persanoadorno@unipa.it

Isodiana Crupi
Thin Films Laboratory (TFL)
Department of Engineering
University of Palermo
Palermo, Italy
isodiana.crupi@unipa.it

Mauro Mosca
Thin Films Laboratory (TFL)
Department of Engineering
University of Palermo
Palermo, Italy
email: mauro.mosca@unipa.it

Marco Centini
Department of Basic and Applied Sciences
Sapienza University of Roma
Roma, Italy
email:
marco.centini@uniroma1.it

Maria Cristina Larciprete
Department of Basic and Applied Sciences
Sapienza University of Roma
Roma, Italy
email:
mariacristina.larciprete@uniroma1.it

***Abstract*— Alpha-phase molybdenum trioxide (α-MoO_3) has recently attracted much attention in the nanophotonics community because of its strong ability to excite surface phonon polaritons (SPhPs), exploitable in many applications ranging from the sensing of biomolecules to the realization of polarizers and filters in the mid-infrared. In this paper, we report on fabrication, characterization and optimization of alpha-phase MoO_3 thin films grown by pulsed laser deposition. Different process conditions were tested through structural and optical characterization to obtain the most suitable films for mid-infrared photonic applications.**

Keywords—MoO_3, mid-infrared photonics, surface phonon polaritons, hyperbolic materials, pulsed laser deposition

I. Introduction

Molybdenum trioxide (MoO_3) and more specifically its thermodynamically stable orthorhombic alpha phase (α-MoO_3) has drawn much interest in recent years due to its ability to support surface phonon polaritons (SPhPs) in the mid-infrared spectral range [1-4]. Due to its crystal structure, consisting of unique double layers of distorted MoO_6 octahedral units [5], α-MoO_3 exhibits strong in-plane anisotropy which is responsible for its unique polaritonic behavior. Consequently, α-MoO_3 is characterized by a natural in-plane hyperbolicity with the real part of the dielectric permittivity displaying opposite sign in different crystallographic directions [2, 6]. This makes MoO_3 a promising candidate for the next generation of nanophotonic devices usable for sensing, light manipulation at subwavelength scales, infrared polarizing elements, and thermal management. The orthorhombic crystallization of α-MoO_3, normally achieved at temperature larger than 400 °C, is characterized by MoO_3 layers interacting with each other through both electrostatic and weak van der Waals forces. This means that it is very easy to exfoliate MoO_3 into very thin flakes, which are however difficult to handle afterwards for practical applications. Besides α-MoO_3, molybdenum trioxide can exist also in other two metastable crystalline forms, namely the monoclinic β-MoO_3 phase and the hexagonal h-MoO_3 phase [7]. These crystalline polymorphs are, however, not useful for polaritonic applications.

MoO_3 has been synthetized over the last years with different techniques, including thermal evaporation [8], hydrothermal growth [9], sputtering [10], and pulsed laser deposition (PLD) [11]. The latter has proven to be a very good technique for obtaining large area α-MoO_3 thin films onto stable and easily handled substrates [3, 12]. Moreover, PLD is a technique compatible with semiconductor fabrication, allowing, for

This work has been financed by the European Union-NextGenerationEU, PNRR M4 - C2- investment 1.1 (PRIN 2022, Project code: 2022ZRN4LX, "*C-MOOVO: Combined Molibdenum trioxide/Vanadium dioxide structures for a new class of tunable photonic devices in the mid infrared",* CUP: B53D23009060006). The opinions expressed are those of the authors only and should not be considered representative of the European Union or the European Commission's official position. Neither the European Union nor the European Commission can be held responsible for them.

example, the integration of MoO_3 films into a multilayer structure. Deposition conditions, such as oxygen pressure and temperature, address very clearly films growth, therefore for obtaining α-MoO_3 thin films suitable for polaritonic applications it is important to employ appropriate process parameters. These can be obtained by comparing different deposition conditions with the structural and optical properties of the corresponding deposited films. In this work, MoO_3 films fabricated by PLD at different conditions are structurally characterized to identify α-phase MoO_3 films and then optically characterized to check polaritonic behavior in the mid-infrared.

II. Samples Fabrication

All MoO_3 thin films were deposited onto fused silica substrates by PLD using a pulsed Nd:YAG laser (Q-SMART 850 model, λ = 355 nm, pulse width 6 ns, energy per pulse 230 mJ). The density of energy was 7.4 J cm^{-2} with a repetition rate of 5 Hz. Films deposition was carried out by using a 99.9% pure MoO_3 target (1 inch diameter, 0.25-inch thickness). Before deposition, substrates were sonicated in acetone, then rinsed with isopropanol, and dried with compressed air. Five different MoO_3 films were deposited at different oxygen pressures and temperatures, as reported in Table I.

TABLE I. Deposition conditions for the MoO_3 films

Sample	Deposition temperature (°C)	Oxygen pressure (mbar)
A	200 °C	10^{-1}
B	400 °C	10^{-2}
C	400 °C	10^{-1}
D	450 °C	10^{-1}
E	500 °C	10^{-1}

III. Results and Discussion

A. Structural characterization

X-ray diffraction (XRD) analysis was carried out to assess the crystalline phase of the deposited MoO_3 films by using a D5005 diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with a Cu Kα (1.5406 Å) source. All measurements were performed with a 0.05° step, in a 10° - 80° 2θ angular range. All XRD patterns are reported in Fig. 1.

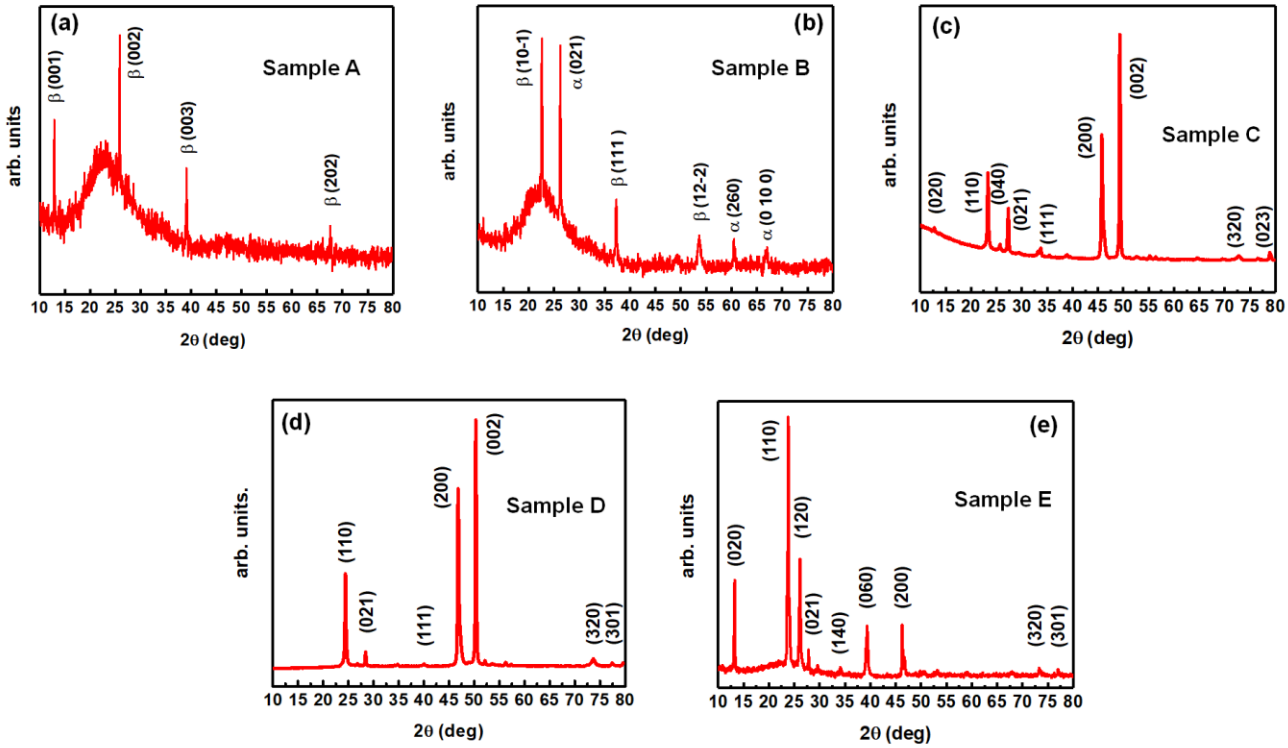

Fig. 1. X-ray diffraction patterns of all deposited MoO_3 films: sample A (a), sample B (b), sample C (c), sample D (d), and sample E (e). XRD peaks were assigned by using ICDD 01-078-4612 and 01-085-9501 cards. Where not specifically indicated, XRD peaks are assigned to the α-phase of MoO_3.

.

XRD analysis shows that the stable orthorhombic α-phase of MoO_3 is obtained only for higher O_2 pressure (10^{-1} mbar) and deposition temperature starting from 400 °C (Figs. 1 (c), (d), (e)). Low temperature (200 °C) and low O_2 pressure (10^{-2} mbar) lead instead to the monoclinic metastable β-phase of MoO_3 (Fig. 1(a)) and to a mixed α and β phase (Fig. 1(b)), respectively. It is noteworthy that, unlike results reported in [11], where α-MoO_3 films were obtained only at 500 °C and 10^{-1} mbar O_2 pressure, here we achieve α-MoO_3 films already at 400 °C and same O_2 pressure.

B. Morphological characterization

Morphological characterization of α-MoO_3 films was performed with a FEI Versa 3D scanning electron microscope

(SEM). In Fig. 2 the top view of samples C, D, and E are reported. All films are crack free and reveal a sort of nano structuration, with average grain sizes increasing from 450 nm (sample C) to 550 nm (sample D), up to 700 nm (sample E), which reveals an improvement of the material's quality. The latter is corroborated by the preferential (110) orientation indicated by XRD measurements (Fig. 1 (e)).

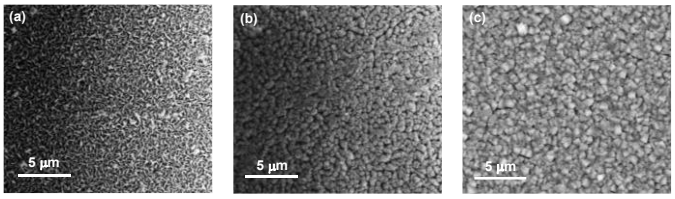

Fig. 2. SEM top view images of sample C (a), sample D (b), and sample E (c). All SEM images were taken at 20000X magnification.

C. *Polarization-dependent reflectance measurements*

IR reflectance measurements were carried out at θ = 45° incidence angle, for different linear polarization angles (ϕ) of the light by using a FTIR interferometer (Invenio-R, Bruker) equipped with an IR source constituted by a glow-bar, and a deuterated triglycine sulfate (DTGS) pyroelectric detector. All the measurements were performed in the 6000–400 cm^{-1} spectral range. Mid-infrared reflectance measurements, reported in Fig. 3, confirm the polaritonic response of the α-MoO_3 films and allow us to identify the most suitable deposition conditions for photonic applications. Sample A,

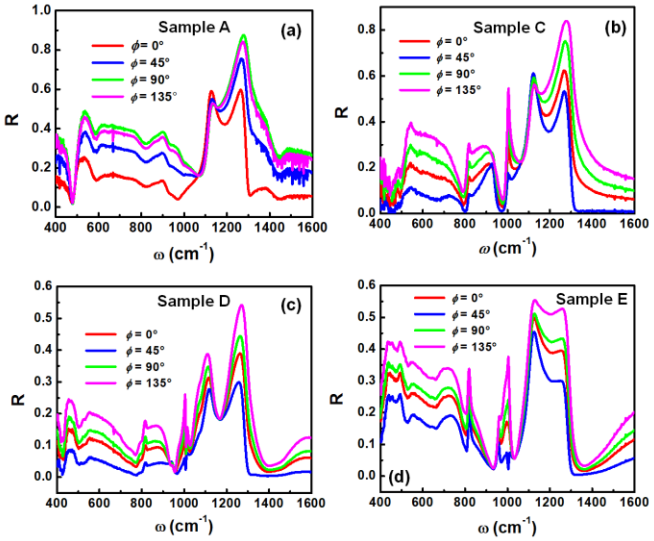

Fig. 3. Polarization-dependent reflectance FT-IR spectra recorded at 45° incidence angle from sample A (a), sample C (b), sample D (c), and sample E (d).

belonging to the β-phase, shows a spectrum completely different than the α-phase films. In particular, peaks in the 1070 – 1300 cm^{-1} range correspond to the Reststrahlen band of the fused silica substrate while no phonon resonances can be attributed to the MoO_3 film. On the contrary, all the single α-phase films (C, D, and E) exhibit specific features in the 800 – 1100 cm^{-1} frequency range. In particular, sample C, grown at 400 °C, shows a well-defined resonance at about 1006 cm^{-1} indicating a high-quality polaritonic response. Furthermore, its deposition temperature is lower compared to sample E, thus enabling cost-effective and scalable processing. Notably, sample E shows a stronger polarization-dependent modulation around 818 cm^{-1}, which could be beneficial for applications requiring polarization sensitivity. This pronounced peak, corresponding to x-phonon frequency, may have strengthened due to the higher deposition temperature (500 °C) which promoted a preferential growth direction (Fig. 1(e)), as well as an increase of the MoO_3 film's crystalline grain sizes (Fig. 2(c)). In particular, larger crystallites could have enhanced the anisotropic phonon response by reducing the contribution of grain boundaries and defects, which tend to broaden or suppress vibrational features. Thus, the enhanced peak at 818 cm^{-1} likely reflects a stronger phonon mode activity along the x-direction due to the improved structural coherence at the microscopic scale.

Overall, sample C offers the best compromise between material quality, well-defined phonon resonances and moderate fabrication temperature, making it the most promising candidate for scalable α-MoO_3-based mid-infrared photonic devices.

IV. Conclusions

We have demonstrated the successful fabrication of α-phase MoO_3 thin films by PLD at different temperature and oxygen pressure conditions. Structural characterization via XRD confirms that single α-MoO_3 is obtained for deposition temperatures of 400 °C and above, at an oxygen pressure of 10^{-1} mbar. SEM images reveal an increase in grain size with temperature, consistent with previous reports.

References

[1] S. Puebla, R D'Agosta, G. Sanchez-Santolino, R. Frisenda, C. Munuera, A. Castellanos-Gomez, "In-plane anisotropic optical and mechanical properties of two-dimensional MoO_3, npj 2D Mater Appl, vol. 5, 37, pp. 1-7, 2021. https://doi.org/10.1038/s41699-021-00220-5.

[2] S. A. Dereshgi, T-G Folland, A.-A. Murthy, X. Song , I. Tanriover, V.-P. Dravid, J.-D. Caldwell and K. Aydin, "Lithography-free IR polarization converters via orthogonal in-plane phonons in α-MoO3 flakes", Nat. Commun., vol. 11, 5771, 2020.

[3] M. C. Larciprete, D. Ceneda, C. Yang, S. A. Dereshgi, F. V. Lupo, M. P. Casaletto, R. Macaluso, M. Antezza, Z. M. Zhang, M. Centini, and K. Aydin, "Large-area polycrystalline α-MoO3 thin films for IR photonics", J. Phys. D: Appl. Phys., vol. 57, 135107, 2024.

[4] C. R: Gubbin, S. De Liberato, and T. G. Folland, "Surface phonon polaritons for infrared optoelectronics", J. Appl. Phys., vol. 131, 030901, 2022.

[5] H. Ding, K. G. Ray, V. Ozolins, M. Asta, "Structural and Vibrational Properties of-MoO3 from van der Waals Corrected Density Functional Theory Calculations", Phys. Rev. B, vol. 85, 012104, 2012.

[6] N. R. Sahoo, S. Dixit, A. Kumar Singh, S. H. Nam, N. X. Fang, and A. Kumar, "High Temperature Mid-IR Polarizer via Natural In-Plane Hyperbolic Van der Waals Crystals", Adv. Optical Mater., vol. 10, 2101919, 2022.

[7] C. C. Zhang, L. Zheng, Z. M. Zhang, R. C. Dai, Z. P. Wang, J. W. Zhang, and Z. J. Ding, “Raman studies of hexagonal MoO3 at high pressure”, Phys. Status Solidi B, vol. 248, No. 5, pp. 1119–1122, 2011. DOI 10.1002/pssb.201000633

[8] C. Battaglia, X. Yin, M. Zheng, I.D. Sharp, T. Chen, S. Mc Donnell, A. Azcatl, C. Carraro, B. Ma, R. Maboudian, R.M. Wallace, A. Javey, “Hole selective MoOx contact for silicon solar cells”, Nano Lett., vol. 14, pp. 967–971, 2014, https://doi.org/ 10.1021/nl404389u.

[9] G. Song, J. Shen, F. Jiang, R. Hu, W. Li, L. An, R. Zou, Z. Chen, Z. Qin, J. Hu, “Hydrophilic molybdenum oxide nanomaterials with controlled morphology and strong plasmonic absorption for photothermal ablation of cancer cells”, ACS Appl. Mater. Interfaces, vol. 6, pp. 3915–3922, 2014 https://doi.org/10.1021/am4050184.

[10] J.M. Pachlhofer, C. Jachs, R. Franz, E. Franzke, H. Kostenbauer, J. Winkler, C. Mitterer, “Structure evolution in reactively sputtered molybdenum oxide thin films”, Vacuum, vol. 131, pp. 246–251, 2016, https://doi.org/10.1016/j. vacuum.2016.07.002.

[11] J. Holovský, E. Horynova, L. Horak, K. Ridzonova, Z. Remes, L. Landova, R. Kumar Sharma, “Pulsed laser deposition of high-transparency molybdenum oxide thin films”, Vacuum, vol. 194, 110613, 2021.

[12] A. Bile, D. Ceneda, M. Centini, F. V. Lupo, D. Persano Adorno, R. Macaluso, K. Aydin and M. C. Larciprete, “Thermo-optical properties of α-MoO3 thin films in the mid-infrared and phonon frequency shift”, J. Phys. Photonics, vol. 7, 025015, 2025.