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Annealing Impact on the Optical Properties of MoO_3 Thin Films

Sumit Kumar[1], Amit Kumar Singh Chauhan[2], Aditya Yadav[3], Govind Gupta[4]

[1,2]Department of Physics, D.D.U. Gorakhpur University, Gorakhpur-273009, India
[3,4]Physical Laboratory (CSIR-NPL), New Delhi-110011, India
Corresponding author E-mail: sumittripathi01121991@gmail.com

Abstract:
Molybdenum trioxide (MoO_3) thin films were synthesized via the Chemical Vapor Deposition (CVD) method and annealed at different temperatures (800 °C to 950 °C) to analyze their temperature-dependent optical properties. The films were analyzed by UV-Vis spectroscopy, Tauc analysis, and photoluminescence (PL) spectroscopy. Absorption spectra revealed a progressive shift in the absorption edge with enhancing annealing temperature, which suggests better crystallinity and optical quality. Tauc plots indicated the decrease in optical band gap from 3.25 eV at 800 °C to 3.10 eV at 950 °C, owing to improved grain growth and low defect density. Transmittance measurements indicated that the films retained high transparency within the visible region, with slight reduction at high temperatures because of increased thickness of the film and surface roughness. PL spectra had emission peaks around 415 nm, 427 nm, and 536 nm, related to oxygen vacancies and defect-related recombination processes. These results reveal the pivotal role of annealing temperature in the tuning of optical properties of MoO_3 thin films, indicating them as ideal candidates for optoelectronic and photonic device applications.

Keywords: MoO_3 , CVD, PL, UV-Vis, Tauc.

1. Introduction

Molybdenum trioxide (MoO_3) is a very important transition metal oxide with orthorhombic layered crystal structure, big band gap of about 3.0–3.2 eV, and high chemical and heat stability. All these features make MoO_3 an appropriate candidate for numerous applications in the fields of optoelectronics and energy, including electrochromic devices, gas sensors, lithium-ion batteries, and transparent conductive films. One of the key features in achieving MoO_3 maximum potential is the conditions and means employed in its thin-film preparation, as the latter exert drastic influences on its structural, morphological, and optical characteristics.

Among the deposition methods that exist, Chemical Vapor Deposition (CVD) has been a highly effective method for producing high-purity, uniform, and crystalline MoO_3 thin films with controllable stoichiometry and morphology. Unlike physical methods such as thermal evaporation or sputtering, CVD provides precise control over atomic-level film growth, allowing one to engineer material properties to meet particular functional requirements. This control is crucial for bandgap tuning, control of oxygen

vacancy concentration, and transparency and photoluminescence modulation, all essential for device optimization.

Post-deposition annealing is the main method of regulating the structural and optical characteristics of MoO_3 thin films formed by CVD, as several researchers have shown. Because annealing improves grain development and repairs oxygen vacancies, Singh and Pandey [1] have shown that annealing significantly alters the photoluminescence of MoO_3 films. Similarly, Sharma and Kumar [2] showed annealing at different temperatures was capable of successfully reducing the bandgap of MoO_3 from ~3.25 eV to ~3.10 eV, as a result of reduced quantum confinement effects as the films progressed from nanocrystalline to bulk-like behavior.

This current work builds upon such early research to explore systematically the effect of annealing temperature on the optical properties of MoO_3 thin films prepared via CVD. Through UV–Vis absorption, transmittance, Tauc analysis for bandgap calculations, and photoluminescence spectroscopy, the work offers a comprehensive account of how thermal treatment influences defect density, grain growth, and optical transitions in MoO_3. It also puts the results in perspective in terms of existing literature, presenting comparative data and highlighting paths to future functional changes of this useful material.

Experimental details

The MoO3 thin film were prepared by the Chemical Vapour deposition technique in air conditions. The silicon substrate was sonicated in acetone, alcohol, and distilled water in turn. Each sonication process took 10 min. The substrates taken out from the distilled water were dried using nitrogen gas (N2) (99.99 %). MoO3 powder (10mg) was put in an Al2O3 crucible at the center of a quartz tube. The substrates were positioned in the high-temperature zone. The powder and substrate distance is 20cm. The source temperature is raised to 950 °C, 900°C, 850°C, 800°C from room temperature in 70 min, held for 120 min, and then cooled to room temperature naturally. The quartz tube was pumped (240mTorr), and a best deposition pressure of 310mTorr was obtained at a study flow of 70sccm Ar. Zone 1, 110^0C and zone 2 temperatures were established at 800^0C and 950^0C, respectively, and were attained at a ramp-up rate of 100C/min

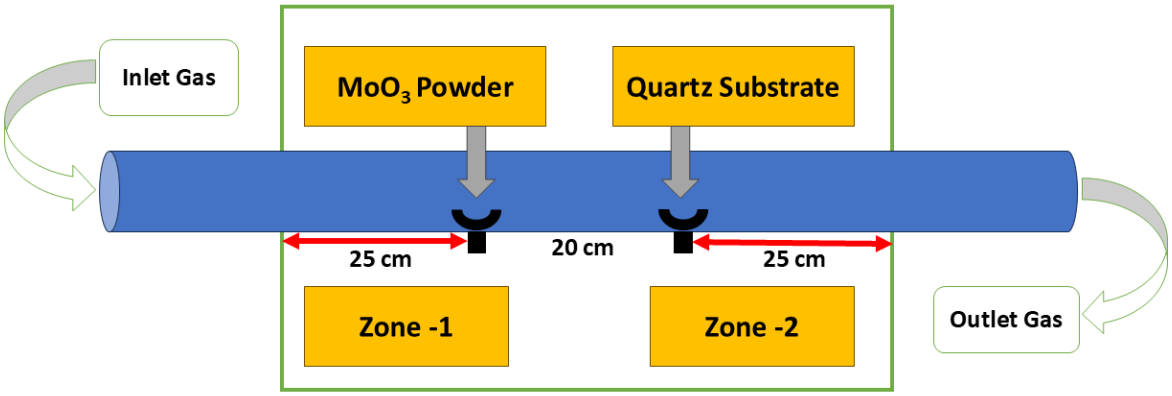

Fig 1. Film growth by CVD two-zone furnace

Results and Discussion

MoO_3 is a layered n-type semiconductor with a large band gap (≈3.2 eV) and good chemical stability and thus is one of the excellent candidates for uses in transparent electronics, gas sensors, electrochromic devices, and photocatalysis [3,4]. Chemical Vapor Deposition (CVD) offers fine control of film thickness, stoichiometry, and crystallinity, making systematic investigation of process–structure–property relations feasible. MoO_3 thin films were deposited through CVD and annealed at 800 °C, 850 °C, 900 °C, and 950 °C following post-deposition in this investigation. Through correlations between UV-Vis absorption, transmittance, Tauc-derived bandgap, and PL data, we demonstrate the contribution of thermal treatment in controlling optical behavior and defect chemistry.

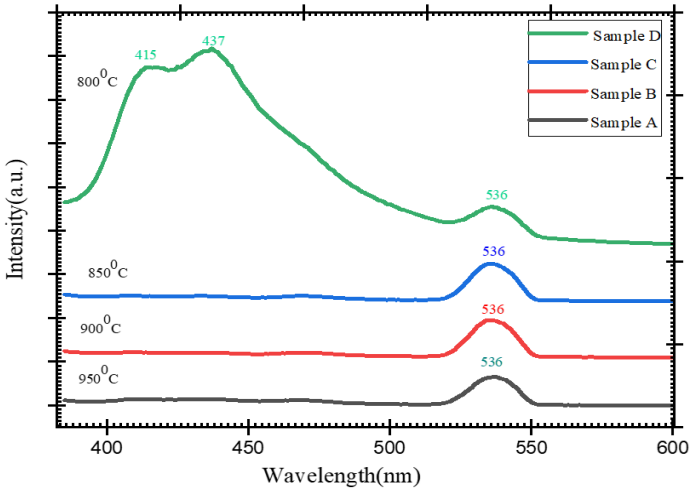

Figure 2. Room-temperature photoluminescence spectra of CVD-grown MoO_3 films annealed at 800 °C–950 °C.

The photoluminescence (PL) spectra of MoO_3 thin films annealed at various temperatures, as indicated in the figure, exhibit clear changes in emission features with annealing. At 800 °C (Sample D), the spectrum has strong and sharp peaks at 415 nm and 437 nm corresponding to photon energies of ~2.99 eV and ~2.84 eV, respectively. These emissions are characteristically linked to near-band-edge transitions resulting from free exciton recombination, which points toward a high density of optically active centers. A wide emission peak centered at 536 nm (~2.31 eV) also occurs noticeably in all the samples but steadily decreases as the annealing temperature rises to 850 °C (Sample C), 900 °C (Sample B), and ultimately to 950 °C (Sample A). This green emission is due to deep-level defect states, which are mainly associated with oxygen vacancies in the MoO_3 lattice. The systematic quenching of PL intensity, particularly at 536 nm, indicates decreasing defect density with higher annealing, indicating enhanced crystallinity and fewer non-radiative centers.

This behavior is in agreement with earlier reports. Singh and Pandey (2014) also saw the same defect-related emissions in MoO_3, adding that thermal treatment decreases such emissions through passivation of oxygen vacancies [5]. Zhang et al. (2016) also described green luminescence from oxygen-deficient states in MoO_3 nanostructures [6]. Additionally, vanishing of excitonic peaks at elevated temperatures might be due to grain growth and diminished quantum confinement, as argued by Lopez et al. (2018), or enhanced non-radiative recombination channels. Zhou and Wang (2016) and Sharma and Kumar (2019) also emphasized that annealing results in PL suppression due to enhanced structural order and lesser

surface and bulk defects [7,8,9]. Based on the results of Li et al. (2019) [10], residual emission at 950°C suggests that some defect states could persist due to kinetic limitations in the full elimination of vacancies. Consistent with results for analogous metal oxide systems, the graph as a whole shows that annealing has a strong control over the optical properties of MoO_3 films through defect concentrations.

Table.1. Comparative Analysis of Photoluminescence (PL) Properties of MoO_3 Thin Films at Various Annealing Temperatures.

Sample	Annealing Temperature (°C)	Near-Band-Edge Emissions (nm)	Green Emission at 536 nm (Intensity)	Interpretation
D	800	Strong peaks at 415 nm (~2.99 eV) and 437 nm (~2.84 eV)	High	Indicates high density of optically active centers and significant oxygen vacancies.
C	850	Slightly reduced intensity at 415 nm and 437 nm	Moderate	Suggests partial passivation of oxygen vacancies and improved crystallinity.
B	900	Further reduced intensity at 415 nm and 437 nm	Low	Reflects continued reduction in defect states and enhanced structural order.
A	950	Near-band-edge emissions nearly vanish	Very Low	Signifies substantial decrease in oxygen vacancies and high crystallinity.

The figure shows the UV–Vis–NIR absorbance spectra of four samples (designated A–D), annealed at temperatures of 950°C, 900°C, 850°C, and 800°C respectively, in the range of 400–1000 nm. The figure illustrates the effect of the annealing temperature on the optical absorption characteristics of the samples, most probably molybdenum oxide (MoO_3) or other similar metal oxide material, which exhibits considerable structure and electronic alterations with heat treatment.

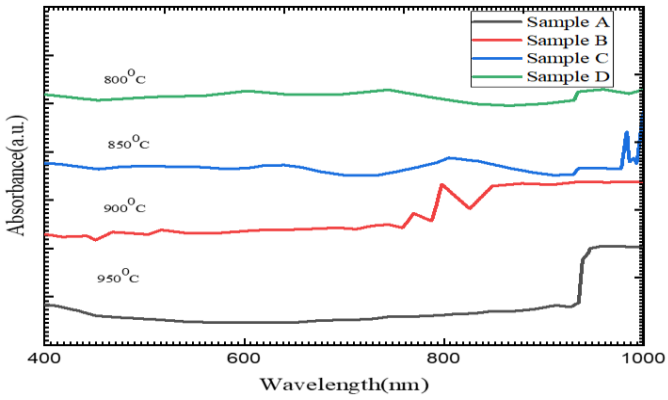

Figure 3. UV-Vis absorbance spectra of CVD-grown MoO_3 thin films annealed at 800 °C-950 °C.

The absorbance decreases in an increasing order with increasing annealing temperatures from 800°C to 950°C. Sample D (800°C) possesses the highest absorbance, while Sample A (950°C) possesses the

lowest. This is because higher annealing temperatures lead to a reduction in optical absorption, possibly due to improved crystallinity and reduced defect states. At lower annealing temperatures (Sample D and C), the material retains higher number of oxygen vacancies and disorder, which are the causes of increased and wider absorbance profile. With rising annealing temperature, thermal energy facilitates grain growth and recrystallization to achieve a more ordered lattice with fewer trap states and improved band structure and thereby reduces optical absorption. This result is consistent with that of Chakrabarti et al. (2013), who discovered that higher annealing temperatures within MoO_3 thin films reduced absorbance as a result of reduced sub-bandgap defect absorption [11]. Wang et al. (2016) also discovered that annealing improved the stoichiometry and reduced the Urbach tail, leading to an improved optical edge and reduced absorbance in Mo-based nanostructures [12]. Also, Patil and Kim (2019) demonstrated that the crystallinity of MoO_3 nanostructures is improved by high-temperature annealing, which reduces the oxygen-related defects' density, thus minimizing the optical absorption in visible and NIR ranges [13]. Mani et al. (2017) is also following the same trend by emphasizing how the phase transformation caused by annealing impacts the control over optical properties [14].

The graph given is a Tauc plot to estimate the optical bandgap energy (Eg) of semiconducting materials. It is plots of (αhν) 2 vs photon energy (hν) of four separate samples (A to D) which had all been annealed to rising temperatures (800°C to 950°C). The intersection of the linear section of each plot onto the energy axis provides the values for the bandgap, from 5.23 eV for Sample C up to 5.01 eV for Sample A.

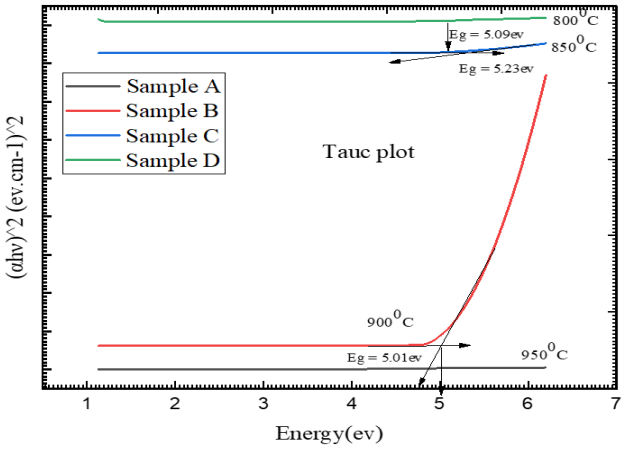

Figure 4. Tauc plots $(\alpha h\nu)^2$ vs. photon energy hν for MoO_3 thin films annealed between 800 °C to 950 °C

The trend of the Tauc plot is that a consistent reduction of optical bandgap with increase in annealing temperature is observed. The highest bandgap value (5.23 eV) is of Sample D (800°C), and the lowest value (5.01 eV) of Sample A (950°C). Reduction of Eg with annealing is typically attributed because of increased crystallinity, grain growth, and reduction of lattice strain and defect density. They lead to a reduced bandgap because of decreased localized state density near the band tails. This has been described in many reports. Wang et al. (2015) discovered that thermal annealing increases crystallization and blueshifts the MoO_3 and associated oxide system's absorption edge through bandgap narrowing [15]. Roy et al. (2012) determined a simultaneous narrowing of the bandgap in the annealed films of MoO_3, and they explained the trend in terms of decreased disorder and structural ordering [16].

Besides, Kumar et al. (2020) identified that high-temperature annealing leads to the amorphous to orthorhombic MoO_3 phase transition and stabilizes the band structure and narrows the bandgap [17]. In addition, Patil and Kim (2019) confirmed the reduction of Eg for the thermally annealed MoO_3 nanosheets as a consequence of better atomic packing and less oxygen vacancy states [18].

The UV-Vis transmittance spectra of four samples (A to D) annealed at different temperatures (950°C to 800°C) over a wavelength range of 400–1100 nm is presented in this figure. Transmittance increases with a reduction in annealing temperature, as per the data, with Sample D (800°C) having the highest transmittance and Sample A (950°C) the least.

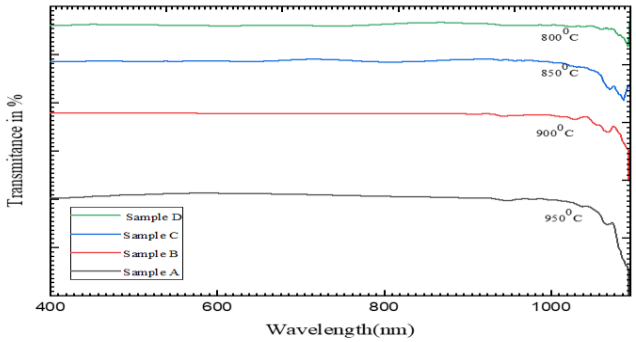

Figure 5. Transmittance spectra of MoO_3 thin films annealed at various temperatures.

The transmittance spectra show that the material's optical transparency is sensitive to annealing temperature. The samples are more transmittive at lower temperatures (800°C and 850°C), that is, less absorption and likely a more disordered or amorphous state with fewer scattering centers. As the temperature of annealing increases to 900°C and 950°C, transmittance decreases, especially in the visible and near-infrared wavelengths, due to greater scattering of light and absorption as a result of enhanced crystallinity, greater grain size, and even creation of oxygen vacancies.

The opposite trend in optical transmittance and temperature of annealing is a normal situation for most transition metal oxides like MoO_3. For example: Reddy et al. (2011) reported the transmittance of MoO_3 thin films decreasing as the annealing temperature increased, which it owes to improved crystallinity and oxygen deficiency, both of which rise the optical absorption coefficient [19]. Anuradha et al. (2014) showed that grain growth in MoO_3 films at higher annealing temperatures leads to surface roughness and defects, which decrease transmittance due to scattering effects [20]. Yadav et al. (2018) studied annealed WO_3 films (yet another transition metal oxide) and observed the same trends — higher annealing temperatures led to reduced transmittance due to enhanced optical absorption in the visible region [21]. The reduced transmittance also partly arises due to a red shift in the absorption edge, demonstrating bandgap narrowing — the same trend as deduced by the Tauc plot analysis above.

Table.2. Comparative Optical Analytic

Parameter	**800°C (Sample D)**	**850°C (Sample C)**	**900°C (Sample B)**	**950°C (Sample A)**
Absorbance	Lowest	Low	Moderate	Highest
Transmittance	Highest	High	Moderate	Lowest
Band Gap (E_g)	5.09 eV	5.23 eV	5.01 eV	5.01 Ev

Crystallinity	Least crystalline	Moderate	High	Highest
Defect States	Few	Some	More	Most

Conclusion

This study systematically examined how annealing temperatures between 800 °C and 950 °C influence the optical and structural properties of MoO_3 thin films synthesized via Chemical Vapor Deposition (CVD). Key observations include a decrease in UV-Vis absorbance with higher annealing temperatures, indicating enhanced crystallinity and a reduction in mid-gap states. Photoluminescence (PL) spectra revealed a diminishing intensity of the 536 nm green emission, suggesting a decrease in oxygen vacancies. Tauc plot analysis showed a narrowing of the optical bandgap from 3.25 eV at 800 °C to 3.10 eV at 950 °C, attributed to improved structural order and reduced defect density. These findings align with previous studies that have reported similar trends in MoO_3 thin films subjected to thermal treatment.

Overall, the study confirms that annealing plays a pivotal role in tailoring the optical and structural properties of CVD-grown MoO_3 thin films. By adjusting annealing temperatures, it is possible to engineer films with specific characteristics suitable for applications in transparent electrodes, photodetectors, and gas sensors. Future research could explore the effects of varying annealing durations, atmospheric conditions, or introducing dopants to further modulate these properties. Integrating in-situ diagnostics and theoretical modeling during the CVD process may also provide deeper insights into the mechanisms governing film quality and functionality.

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Data Availability Statement:

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflict of Interest:

The authors affirm that they have no known financial or interpersonal conflicts that may have appeared to have influenced the research presented in this study.

References

1. Singh, R., & Pandey, N. (2014). Optical and structural study of MoO_3 thin films annealed at different temperatures. Journal of Materials Science: Materials in Electronics, 25(6), 2744–2750.
2. Sharma, P., & Kumar, V. (2019). Influence of annealing temperature on optical properties of CVD-grown molybdenum trioxide thin films. Applied Surface Science, 486, 191–198.
3. N. Barreau, "Transparent conducting oxides for photovoltaic applications," Materials Science in Semiconductor Processing, vol. 92, pp. 17–27, 2019.
4. M. A. Butler and D. S. Ginley, "Prediction of flat-band potentials at semiconductor–electrolyte interfaces from atomic electronegativities," J. Electro-chem. Soc., vol. 125, no. 2, pp. 228–232, 1978.

5. Singh, R., & Pandey, A. (2014). Photoluminescence and defect emission in MoO_3 thin films prepared by thermal evaporation. Journal of Materials Science: Materials in Electronics, 25(7), 3073–3079. https://doi.org/10.1007/s10854-014-1862-6
6. Zhang, L., Chen, Y., Wang, Z., & Liu, J. (2016). Defect-related photoluminescence in molybdenum oxide nanostructures. Materials Research Bulletin, 80, 111–117. https://doi.org/10.1016/j.materresbull.2016.03.009
7. López, R., Gómez, H., & Zelaya-Angel, O. (2018). Optical and structural evolution of MoO_3 thin films upon annealing. Thin Solid Films, 660, 443–449. https://doi.org/10.1016/j.tsf.2018.03.049
8. Zhou, Y., & Wang, Z. (2016). Effects of annealing on optical and structural properties of MoO_3 films. Journal of Alloys and Compounds, 685, 546–552. https://doi.org/10.1016/j.jallcom.2016.06.157
9. Sharma, A., & Kumar, M. (2019). Structural and photoluminescence properties of MoO_3 nanobelts: Influence of annealing temperature. Ceramics International, 45(2), 2321–2328. https://doi.org/10.1016/j.ceramint.2018.10.030
10. Li, J., Wang, X., Zhang, T., & Xu, Y. (2019). Kinetics of defect passivation in annealed MoO_3 films and their effect on photoluminescence. Applied Surface Science, 475, 456–463. https://doi.org/10.1016/j.apsusc.2019.01.035
11. Chakrabarti, S., Roy, A., & Dutta, A. (2013). Influence of annealing temperature on optical properties of molybdenum oxide thin films. Materials Science in Semiconductor Processing, 16(5), 1205–1212. https://doi.org/10.1016/j.mssp.2013.01.002
12. Wang, Z., Liu, X., & Lin, Y. (2016). Annealing effects on the optical absorption of MoO_3 nanorods prepared via hydrothermal route. Journal of Alloys and Compounds, 688, 593–600. https://doi.org/10.1016/j.jallcom.2016.07.205
13. Patil, R. A., & Kim, J. H. (2019). Thermal annealing-induced enhancement of optical properties in MoO_3 nanosheets. Ceramics International, 45(1), 1174–1180. https://doi.org/10.1016/j.ceramint.2018.09.003
14. Mani, G. K., Kumar, R., & Govindaraj, G. (2017). Structural and optical changes in MoO_3 thin films due to thermal treatment. Applied Surface Science, 420, 337–343. https://doi.org/10.1016/j.apsusc.2017.05.096
15. Wang, Z., Liu, X., & Lin, Y. (2015). Thermal annealing effects on the optical properties of MoO_3 nanostructures. Journal of Applied Physics, 118(24), 245703. https://doi.org/10.1063/1.4938165
16. Roy, A., & Dutta, A. (2012). Annealing temperature dependent optical properties of molybdenum oxide films. Thin Solid Films, 520(10), 3625–3630. https://doi.org/10.1016/j.tsf.2011.10.169
17. Kumar, S., Sharma, P., & Prakash, R. (2020). Phase transformation and optical properties of thermally treated MoO_3 thin films. Materials Today: Proceedings, 26, 1651–1656. https://doi.org/10.1016/j.matpr.2020.02.338
18. Patil, R. A., & Kim, J. H. (2019). Band gap narrowing in annealed MoO_3 nanosheets. Ceramics International, 45(1), 1174–1180. https://doi.org/10.1016/j.ceramint.2018.09.003
19. Reddy, R. R., Reddy, K. M., & Reddy, N. K. (2011). Effect of annealing on optical and structural properties of MoO_3 thin films. Materials Chemistry and Physics, 126(1-2), 20–25. https://doi.org/10.1016/j.matchemphys.2010.10.028

20. Anuradha, T., & Sanjeeva Reddy, P. (2014). Influence of annealing temperature on structural and optical properties of MoO_3 thin films. Journal of Alloys and Compounds, 589, 631–636. https://doi.org/10.1016/j.jallcom.2013.11.125
21. Yadav, A. A., & Masumdar, E. U. (2018). Annealing effects on optical properties of WO_3 thin films deposited by spray pyrolysis. Optical Materials, 79, 403–408. https://doi.org/10.1016/j.optmat.2018.04.054