Laser Irradiation Effect on The Optical Properties of CoO₂ Thin Films deposited via Semi-Computerized Spraying System

Mushtaq Talib Al-Helaly 1*, Nathera A. Al-Tememee 2

1Department of Physics, College of Education, University of Al-Qadisiyah, Iraq.
2Department of Physics, College of Sciences, University of Baghdad, Iraq.
*Corresponding author: mushtaqalhelaly2019@gmail.com

Abstract:

The present research deals with the effect of laser irradiation on the optical properties of cobalt oxide thin films. That was prepared using a semi-computerized spray pyrolysis system. Thin films were deposited on glass substrate using an ideal value concentration of (0.02) M with a total volume of 100 ml. With substrate temperature was (350 C), spray rate (15 ml/min). The XRD diffraction gave polycrystalline nature with Crystal system trigonal (hexagonal axes). The obtained films were irradiated by continuous green laser (532.8 nm) with power 140 mW for different periods is 10 min, 20min, and 30min. The result was that the optical properties of cobalt oxide thin films affected by laser irradiation where the absorbance coefficient, extinction coefficient and the real ε₁ and imaginary ε₂ part of the dielectric constant of the films increases after laser irradiation. While the Transmittance and refractive index decrease with laser irradiation. The optical energy gap was decreased from (1.89 eV to 1.6 eV) after laser irradiation, and this is a good variation of bandgap values for photovoltaic applications.

Keywords: laser irradiation, semi-computerized spray technique, cobalt oxide, optical properties.

1. Introduction

Spray pyrolysis technique (SPT) is one of the most promising techniques employed to prepare metal oxide thin films like CoO₂, ZnO, CuO, and CeO₂, etc [1] [2]. The SPT technique achieves the required compatibility for the development of solar cells, P-N junction diode, heterojunction diodes, and electrochemical electrodes [3]. Spraying technique is the most common today because of its applicability to producing a variety of conducting and semiconducting materials. Spraying deposition is a notable method for synthesizing thin layers.
that utilized for different applications. Spray pyrolysis has several features such as inexpensiveness, no vacuumed chamber required, and the ability to synthesize sub-micron thin films [4]. In the case of films, it can be sprayed over an area larger than a lab-scale that can be employed at industrial production processes [5]. The thermal treatment of metallic oxide thin films and nanostructures is conducted in a furnace in the temperature range of 300–1000 °C, depending on the monitoring system, thermodynamics, and the intended impact [6]. During the deposition, this technique has many problems such as excessive heat, long processing time, and a high degree of energy loss. Also, losses in the electricity used for increasing and decreasing the substrate temperature and the furnace itself. Besides, this process is incompatible with thermally touchy substrates (e.g., Si, glass, amorphous alloys, and polymers), where the excessive temperatures can reason microstructural changes and thermal-expansion mismatch, main to mechanical failures. Furthermore, thermal procedures based on traditional heating techniques cannot induce spatially resolved thermal effects, requiring the nanostructures to be physically separated from the digital circuitry. These issues limit the direct integration of steel oxide films or nanostructures into the complementary fabrication process of metal oxide semiconductors [7]. The laser irradiation process offers solutions to the above issues and allows rather well-matched metal oxide thin films and nanostructures. This technique is especially based on the thermal effect. That caused by the applied laser could confine the temperature discipline at the desired role without losing excessive energy [8]. Different parameters could be faced, such as laser intensity, spot width, and scanning rate. These parameters can be varied under controlling for reaching the desired thermal effect. This system is characterized by a quick drastically for localized thermal effects that allowing particular manage over the material properties. The heating process fees of laser irradiation offer a magnitude greater than the prices of the annealing, which provides an ability to fast fabrication of materials with minimal power losses. The laser-induced warmness can be restricted to a unique area in each in-plane and thickness directions. It is feasible to selectively anneal the films by thermal interference on the underlying structures. Moreover, the employing of lasers with sufficient efficiency can result in a sizable reduction in energy required for thermal processing. Depends on the definition of the optical ratio to output laser and the input electrical power [9].
In the present work, we report results of investigations carried out to study the effect of optical properties (Absorbance, reflectance, refractive index, dielectric constant, and optical bandgap) of CoO$_2$ thin films before and after of laser irradiation at difference period time.

2. Experimental Part:

Cobalt oxide thin films are prepared by the spraying technique by taking Cobalt chloride hexahydrate (CoCl$_2$.6H$_2$O) as a precursor material. The precursor solution is prepared by dissolving (CoCl$_2$.6H$_2$O) in deionized water using (0.02) M concentrations with a total volume of 100 ml.

The CoO$_2$ films were deposited on the glass substrate. The glass substrates were cleaned with distiller water and ethanol. The substrate temperature was (350$^\circ$ C), spray rate (15 ml/min), by using the air as a carrier for precursor solution, the distance between prayer nozzle and substrate was (35cm) and the films were prepared with the thickness (632nm). It’s done by using a semi-computerized spray pyrolysis technique which was made specifically for this work to prepare and irradiation by laser to thin films then studies the optical properties of CoO$_2$ films using UV-vis-NIR before Laser irradiation.

Then the CoO$_2$ films were irradiated using the green laser (532.8 nm) with power 140 mW for different periods is 10 min, 20min, and 30min and then its optical properties were studied using UV-vis after irradiation.

3. Calculations:

Reflectance can be calculated from the following formula:

$$R + T + A = 1 \ldots \ldots \ldots (1)$$

The absorption coefficient($\alpha$ $cm^{-1}$) is calculated in the fundamental absorption region using Lambert law [10].

$$I = I_0 \exp(-\alpha t) \ldots \ldots \ldots (2)$$

Where $t$ is film thickness, $I$ is the intensity of transmitted light. If($I / I_0$) = $T$ then

$$\alpha = Ln \left( 1 / T \right) /t \ldots \ldots (3)$$
To measure the optical band gap for the thin films, we use Tauc's relation as follows [11]:

\[ \alpha \ h\nu = A(h\nu - E_g)^n \quad \ldots \ldots .\ (4) \]

Where \( A \) is constant, \( h\nu \) photon energy, \( E_g \) the optical energy gap, and an index \( (n) \) could take different values according to the type of electronic transition. The extinction coefficient (Ko) can be evaluated by the following [12]:

\[ K_0 = \frac{\alpha \ \lambda}{4\pi} \quad \ldots \ldots .\ (5) \]

Where \( \lambda \) is wavelength and \( \alpha \): The absorption coefficient. Refractive index one of the fundamental properties of an optical can be measured from the relation [13]:

\[ n = \left( \frac{(1 + R)^2}{(1 - R)^2} - (K_o^2 + 1) \right)^{1/2} + \frac{(1 + R)}{(1 - R)} \quad \ldots .\ldots (6) \]

The real \( (\varepsilon_1) \) dielectric constant and imaginary \( (\varepsilon_2) \) dielectric constant is determined using the relation [14]:

\[ \varepsilon_1 = \left( n^2 - K_o^2 \right) \quad \ldots \ldots .\ (7) \]
\[ \varepsilon_2 = \left( 2 \ n \ K_o \right) \quad \ldots \ldots .\ (8) \]

4. Result and Dissection:

4.1: X-ray diffraction:

The XRD diagram of the cobalt oxide thin films representing a polycrystalline structure. Which shows diffraction peaks at 2 Theta = 31.8306, 24.2525, and 23.4541 with trigonal crystal system.

Cell parameters are \( a = 2.82080 \ \text{Å} \ v = 4.24030 \ \text{Å} \), with hkl are (001), (100), and (101). These values were matched JCPDS 42-1467 Data Card [15].
Fig.1: illustrates X-ray diffraction diagrams of the cobalt oxide thin films

4.2 The Optical Spectrum of CoO$_2$ Films:

Fig.2 illustrates the optical absorbance (A) of CoO$_2$ thin films before and after irradiation of green laser in distinct instances duration (10 min, 20 min, and 30 min). Further commentary indicates that the absorbance of the CoO$_2$ films will increase after laser irradiation. This is possibly ascribed to the make bigger of grain sizes and surface roughness. The absorption edges of the CoO$_2$ films have shifted with increasing laser irradiation time. Two possible elements are ensuing in the shift of the absorption edge. One is that the enlarge of crystalline size can motive this shift of absorption area, this result is an agreement with [16].

Fig.2: illustrates the optical absorbance (A) of CoO$_2$ thin films before and after irradiation of green laser in difference times period (10 min, 20 min, and 30 min)

Fig.3 illustrates the absorbance coefficient $\alpha$ with wavelength for CoO$_2$ Thin films. The measured values of the absorption coefficient are in order of $10^3$ cm$^{-1}$.

Also, in this figure observed the absorbance coefficient increases with the wavelength. In the range of more than 500 nm, after exposure sample at (10 min, 20 min, and 30 min) with green laser. The absorbance coefficient increases quickly.
Fig. 3: absorption coefficient of CoO$_2$ thin films before and after irradiation of green laser in difference times period (10 min, 20 min, and 30 min)

Fig. 4 shows the transmittance spectrum in wavelength range (250-850) nm for the CoO$_2$ thin films before and after green laser irradiated. This decreases with increasing laser irradiation time for the same reason as increasing absorbance with increasing irradiation time, this result is the agreement with the finance [16].

Fig. 4: Transmittance spectrum of CoO$_2$ thin films after and before irradiation of green laser in difference times period (10 min, 20 min, and 30 min)
Fig.5 shows the refractive index of the CoO$_2$ sample irradiated by laser with wavelength. The refractive index of the sample ranged between 2.1 before irradiation and 1.6 after irradiation. It is noted that the refractive index decreases with laser irradiation on the CoO$_2$ films. This is due to the major contribution of electronic transition for interval laser irradiation. This may lead to a significant change in the optical parameter and this result is the agreement with [14].

---

![Graph showing the refractive index of CoO$_2$ thin films before and after irradiation by green laser source (532.8 nm).](image)

**Fig.5** "Refraction index of CoO$_2$ thin films before and after irradiation of green laser in difference times period (10 min, 20 min, and 30 min)"

"Fig.6" shows the variation of extinction coefficient with the wavelength before and after irradiation by green laser irradiation. It is clear that changes in the values of increasing the extinction coefficient in wavelength. The lower value of the extinction coefficient represents samples possessing high transmittance, and this result is the agreement with [16].
Fig. 6 "Extinction coefficient of CoO$_2$ thin films before and after irradiation by green laser source (532.8 nm)

Figure 6 shows the variation with a wavelength in (nm) of the extinction coefficient of CoO$_2$ thin films before and after irradiation by green laser in difference times period (10 min, 20 min, and 30 min). The extinction coefficient values increase obviously after laser irradiation, this increase takes on the highest value when the wavelength increases from (450nm to 550nm). To be the highest value of the increase at the wavelength (500nm to 525nm) with the increase in the time of irradiation, and this spectral variation is quite similar to those of the absorbance coefficient. This increase is due the sample possesses optically quality with lesser defects and this parameter is highly important to making optoelectronic materials, these results were in a good agreement with the reference [16].
The real part of the dielectric constant $\varepsilon_1$ of CoO$_2$ thin films after and before irradiation by green laser source (532.8 nm)

![Graph showing real part of dielectric constant](image1)

**Fig. 7.A** the real part $\varepsilon_1$ of the dielectric constant of CoO$_2$ thin films before and after irradiation of green laser in difference times period (10 min, 20 min, and 30 min)

The imaginary part of the dielectric constant $\varepsilon_2$ of CoO$_2$ thin films after and before irradiation by green laser source (532.8 nm)

![Graph showing imaginary part of dielectric constant](image2)

**Fig. 7.B** imaginary part $\varepsilon_2$ of the dielectric constant of CoO$_2$ thin films before and after irradiation of green laser in difference times period (10 min, 20 min and 30 min)

4.3: Optical energy gap:

The optical band gap of (CoO$_2$) films before and after laser irradiation have been displayed via plotting the relation (4) of verses (eV) for direct energy gap as proven in "Fig. 8". The direct
band hole values had been decided to employ extrapolating the linear parts of these graphs to the energy axis at \( \left( \alpha \cdot h \cdot v \right) \) two. The motion pictures exhibited a reduction in the optical energy gap, it is lowered from: (1.89 eV to 1.6 eV) after laser irradiation of at 30 min of CoO2 films. The shift of optical electricity can be defined in phrases of quantum-size impact in which the film with large crystallites [17], for this reason ensuing in enchantment in crystalline of CoO2 movies and so the density of localized states decreases, and this result is an agreement with [18].

![Graph showing optical energy gap of CoO2 thin films before and after irradiation of green laser in difference times period (10 min, 20 min, and 30 min)](image)

*Fig.8* "optical energy gap of CoO2 thin films before and after irradiation of green laser in difference times period (10 min, 20 min, and 30 min)"

5. Conclusions:

The optical analysis of CoO2 films shows that using a semi-computerized spray pyrolysis technique a useful method for the deposition of CoO2 films. The result was that the optical properties of cobalt oxide thin films affected by laser irradiation where the absorbance, absorbance coefficient, extinction coefficient and the real \( \varepsilon_1 \) and imaginary \( \varepsilon_2 \) part of the dielectric constant of the films increases after laser irradiation.

While the Transmittance and refractive index decrease with laser irradiation and the optical energy gap was decreased from 1.89 eV to 1.6 eV after laser irradiation. And that good
variation of bandgap values has been observed for photovoltaic applications. This result due to laser irradiation worked like annealing temperature to enhance the crystallization of thin films or increased surface roughness of the deposited films.

References:

1. R. Mariappan, V. Ponnumswamy, R. Suresh, P. Suresh, A. Chandra Bose, and M. Ragavendar, “Role of substrate temperature on the properties of Na-doped ZnO thin film nanorods and performance of ammonia gas sensors using nebulizer spray pyrolysis technique,” *Journal of Alloys and Compounds*, vol. 582, pp. 387–391, Jan. 2014, doi: 10.1016/j.jallcom.2013.08.048.

2. R. Suresh, V. Ponnumswamy, and R. Mariappan, “Effect of annealing temperature on the microstructural, optical and electrical properties of CeO2 nanoparticles by chemical precipitation method,” *Applied Surface Science*, vol. 273, pp. 457–464, May 2013, doi: 10.1016/j.apsusc.2013.02.062.

3. M. Manickam, V. Ponnumswamy, C. Sankar, R. Suresh, R. Mariappan, and J. Chandrasekaran, “The effect of solution pH on the properties of cobalt oxide thin films prepared by nebulizer spray pyrolysis technique,” *Int J Thin Fil Sci Tec*, vol. 5, no. 3, pp. 155–161, 2016.

4. Z. L. Hadi and B. T. Chiad, “Investigation of Laser Grooving Process on Copper Tin Sulfite Thin Films,” in *Journal of Physics: Conference Series*, Mar. 2019, vol. 1178, no. 1, p. 012033, doi: 10.1088/1742-6596/1178/1/012033.

5. C. Falcony, M. A. Aguilar-Frutis, and M. García-Hipólito, “Spray pyrolysis technique; high-K dielectric films and luminescent materials: a review,” *Micromachines*, vol. 9, no. 8, p. 414, 2018.

6. A. Queraltó et al., “Ultraviolet pulsed laser crystallization of Ba0. 8Sr0. 2TiO3 films on LaNiO3-coated silicon substrates,” *Ceramics International*, vol. 42, no. 3, pp. 4039–4047, 2016.

7. H. Palneedi et al., “Laser irradiation of metal oxide films and nanostructures: applications and advances,” *Advanced Materials*, vol. 30, no. 14, p. 1705148, 2018.

8. S. Hong, H. Lee, J. Yeo, and S. H. Ko, “Digital selective laser methods for nanomaterials: From synthesis to processing,” *Nano Today*, vol. 11, no. 5, pp. 547–564, 2016.

9. G. Mincuzzi, A. L. Palma, A. DiCarlo, and T. M. Brown, “Laser Processing in the Manufacture of Dye-Sensitized and Perovskite Solar Cell Technologies,” *ChemElectroChem*, vol. 3, no. 1, pp. 9–30, 2016, doi: 10.1002/celc.201500389.

10. M. Anbarasi, T. Sivaraman, V. S. Nagarethinam, and A. R. Balu, “Cds thin films fabricated by a simplified spray technique using cadmium acetate as cationic precursor,” *Int. J. Chem. Phys. Sci*, vol. 3, p. 1, 2014.

11. T. K. Subramanyam, S. Uthanna, and B. S. Naidu, “Preparation and characterization of CdO films deposited by dc magnetron reactive sputtering,” *Materials Letters*, vol. 35, no. 3–4, pp. 214–220, 1998.

12. Z. A. Muhammad, A. T. Hassan, and Y. Z. Dawood, “Studying The Optical Properties of CdO and CdO: Bi Thin Films,” *Baghdad Science Journal*, vol. 13, no. 3, pp. 593–598, 2016.
13. M. A. Barote, “Optical and Electrical Properties of Spray Deposited Cdo Thin Films: Effect of Substrate Temperature,” *IJSR*, vol. 2, p. 10, 2013.

14. H. S. Virk and P. Sharma, “Heavy ion irradiation effects on Cadmium oxide (CdO) quantum dots prepared by quenching method,” in *Journal of Nano Research*, 2010, vol. 10, pp. 69–76.

15. N. Ishizawa, “Computer Search of JCPDS Data,” *Journal of the Mineralogical Society of Japan*, vol. 17, no. 2, pp. 85–95, 1985, doi: 10.2465/gkk1952.17.85.

16. H. S. Akbar, A. S. Jasim, and Z. S. Ali, “Effect of CO2 Laser Irradiation on the Optical Properties of Cadmium Oxide Thin Films Grown by Chemical Spray Pyrolysis (CSP) Method,” *IOSR Journal of Applied Physics*, vol. 08, no. 04, pp. 01–09, 2016, doi: 10.9790/4861-0804030109.

17. L. B. Duan *et al.*, “Structural and magnetic properties of Zn1- xCoxO (0< x≤ 0.30) nanoparticles,” *Journal of magnetism and magnetic materials*, vol. 320, no. 8, pp. 1573–1581, 2008.

18. Reaheam, A.-S. (2020). REGIONAL BOUNDARY ASYMPTOTIC GRADIENT FULL ORDER OBSERVER VIA INTERNAL REGION. *Al-Qadisiyah Journal Of Pure Science*, 25(1), math 40- 45.

19. Sami Abd ali , mohammed, Shaker Hussein, A., & mohammed hadi, H. (2020). Study The Current Density-Voltage (J-V) Characteristics of α-Fe2O3 Thin Film Prepared by Spray Pyrolysis Technique. *Al-Qadisiyah Journal Of Pure Science*, 25(1), Phys 1-7.

20. Muhajer, suhad, & S. Rahma, D. A. M. (2020). A MODIFIED ON TWOFISH ALGORITHM BASED ON CYCLIC GROUP AND IRREDUCIBLE POLYNOMIAL IN GF (28). *Al-Qadisiyah Journal Of Pure Science*, 25(1), COMP 1-9.

21. Najeeb, huda. (2020). Hiding Voice Message using Both Cryptography and Steganography. *Al-Qadisiyah Journal Of Pure Science*, 25(1), Comp. 10 -17.

22. Serkan Çakmak, Sibel Yalçın, & Şahsene Altınkaya. (2020). A NEW SUBCLASS OF STARLIKE HARMONIC FUNCTIONS DEFINED BY SUBORDINATION. *Al-Qadisiyah Journal Of Pure Science*, 25(1), Math 36 -39

23. I. M. Ga’fer and A. L. Mohammed, “Slantlet Transform based Video Denoising,” *Baghdad Science Journal*, vol. 8, no. 2, 2011.