The Effect of the Number of Laser Pulses on Some Physical Properties Affecting Gas Sensitivity of CdO Thin Films Prepared by PLD Method

Sadiq. B. Nouri[1*], Zuheer. N. Maieed[2], Amer. SH. Mahmood[3]

Abstract

In this research, thin films of cadmium oxide (CdO) were manufactured using pulse laser deposition (PLD) technology on glass substrates under pressure of (0.001 mbar) at room temperature by a laser power effect (800mj/cm) with a number of different laser pulses (N= (150-200-250 and 300)). The optical and synthetic properties of thin cadmium oxide films were studied, as well as their gas sensitivity. The optical properties of thin films were analyzed and studied using absorption spectra (UV-VIS) UV-Visible measurements show that CdO films of different thicknesses have a direct permissible transition with the band gap between (2.51) and (2.22) eV before annealing and after annealing the band gap decreases to become between (2.44) and (2.06). As for synthetic properties, they were analyzed and studied through X-ray diffraction patterns which showed the thin films are multi-crystalline the grain size increase with the increase in the number of pulses from (100) pulse to (300) pulse gradually as for the effect of annealing, it also led to an increase in the size of the particles. While gas sensor properties were studied using static gas sensor system. The results of gas sensor showed that the increase in operating temperature improves film sensitivity. the maximum sensitivity of the pure CdO film to gas (NO2) was found to be 46.16% at 200°C and the number of pulses was (150). After annealing, the gas sensitivity decreased to was (34.25%) for (150) pulses.

Key Words: Thin Films, Pulsed Laser, Deposition, CdO, Optical Properties of Thin Films, X-Rays Diffraction, Measurement of Gas Sensor.

DOI Number: 10.14704/nq.2022.20.3.NQ22255 **NeuroQuantology 2022; 20(3):271-278**

Introduction

PLD is increasingly used to prepare a variety of thin films. In the simplest work of PLD, the material to be deposited is vaporized by irradiating the target material with a high-density beam of pulsed laser light. Then, the film is produced by collecting this vapor on a nearby substrate fixed on the target [Aadim, et al 2014]. Since the emergence of high-temperature ceramic superconductors, the global effort to produce high-quality thin layers of these materials has led to a wide range of investigations on applicable techniques. PLD is ranked as one of the most successful techniques, due to its high control and relatively low costs. The cadmium oxide film is considered as a semiconductor with a faceted crystalline (cubic) structure. It exists in nature in two forms, namely, crystalline and random (non-crystalline). The crystalline structure is brown or red, while random structure is colorless [Al-Ogili, et al 2011].

Corresponding author: Sadiq. B. Nouri
Address: [1*,2,3] Physics Department, College of Education for Pure Sciences, Tikrit University, Tikrıt, Iraq.
E-mail: [1*]sadiq.b.nouri@st.tu.edu.iq; [2]zuheer1976@tu.edu.iq; [3]Amershaker5@tu.edu.iq
Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Received: 12 January 2022 **Accepted:** 18 February 2022

As for the classification of the compound in semiconductors, it is considered negative of (n) type due to oxygen vacuums resulting from molecular incompatibility of compounds. Cadmium oxide belongs to II-VI of the periodic table, a energy gap of (2.21-2.95) volts at room temperature of (300) kelvins [Hadaate, et al 2017].]. It is used as a thin film in the manufacture of photovoltaic cells, crystalline displays, transistors with thin films, LED lamps, infrared detectors, anti-reflection coatings, and reflective coatings [Eman, et al 2015]. PLD is commonly used to create thin films from crystalline (NPS) from different high-quality materials at one stage with lower costs than any other process [Ayad, et al 2018]. In this research, the films of cadmium oxide will be prepared using pulsed laser deposition technology and the effect of laser pulse number and annealing on them.

Experimental Part

High-purity cadmium oxide powder of a (3gm) weight was compressed by a hydraulic compressor on a circular disc with a diameter of (11mm) and under pressure of (5) tons so that the sample had a diameter of (10.7 mm) and thickness (4.2 mm). PLD was used for the preparation of thin films using a laser (ND: YAG) with a wavelength of (1064 nm). The sample was placed in a glass chamber under pressure of ($10^{-3}mbar$). The distance between the laser gun and the sample in the chamber was (15 cm) at an angle of (45) degree, while the distance between the sample and the glass substrate was (3cm). The laser power used in this research was (800 mj) for a number of different pulses (150-200-250 and 300) with a frequency of (6 Hz). Figure (1) shows a scheme for the system:

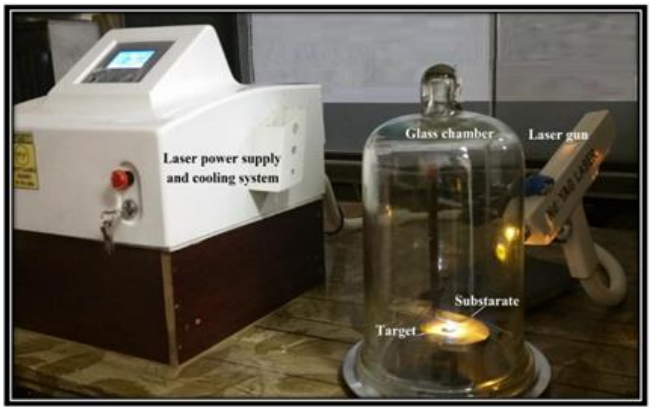

Figure 1. The system used in this work

Results and Discussion

Figures (2-a,2-b) show the transmittance spectrum as a function of the wavelength for the different deposition energies before and after annealing, Figure (2-a) represents transmittance spectrum before annealing. It is observed that transmittance spectrum changes and gradually decreases with the increase in number of pulses. This is due to the increase in film thickness because of the increase in the number of pulses[Nasir, et al 2019], i.e., there is inverse proportionality between them. While figure (2-b) represents transmittance spectrum after annealing. It is clear that transmittance spectrum of each thin film analyzed increases with the increase in annealing temperature. This may be due to improving the crystalline size, or low reflection caused by variation in particles size[Ali, et al 2006].

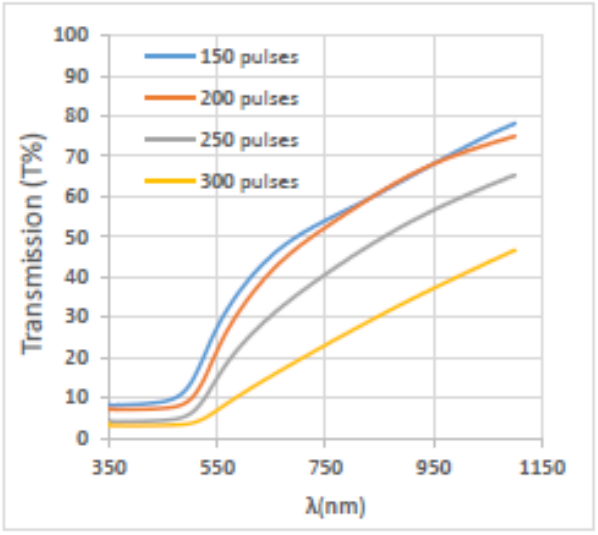

Figure 2-a. Transmittance spectrum before annealing

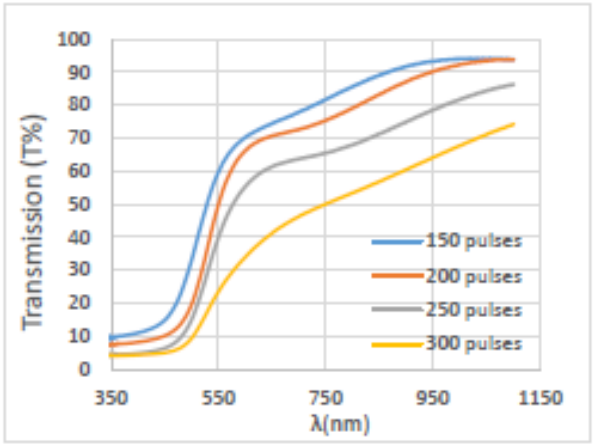

Figure 2-b. Transmittance spectrum after annealing

Figures (3-a,3-b) shows absorption spectrum as a feature of wavelength before and after annealing. Figure (3-a) shows the absorption spectrum before annealing. It is observed that absorption increases with the increase in the number of pulses. This is due to the removal of particles from the target material when laser is shed, as the removal increases by increasing the number of pulses. Thus, the thickness of the thin films deposited on the glass substrate from the lower surface will increase; therefore, the absorption increases[Santos, et al 2005]. As for figure (3-b), it represents absorption spectrum after annealing. It shows a decrease in absorption compared to absorption before annealing.

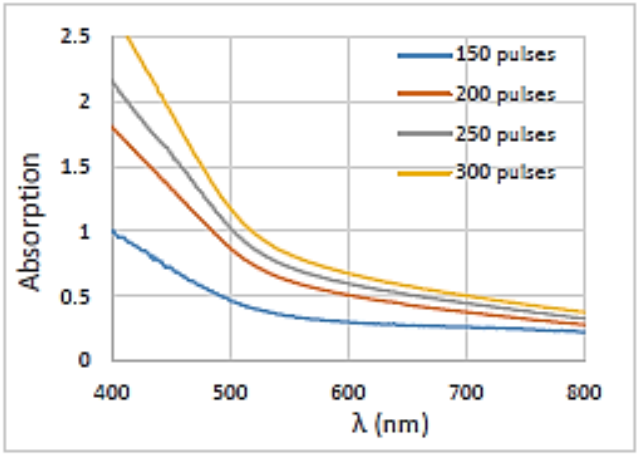

Figure 3-a. Absorption coefficient before annealing

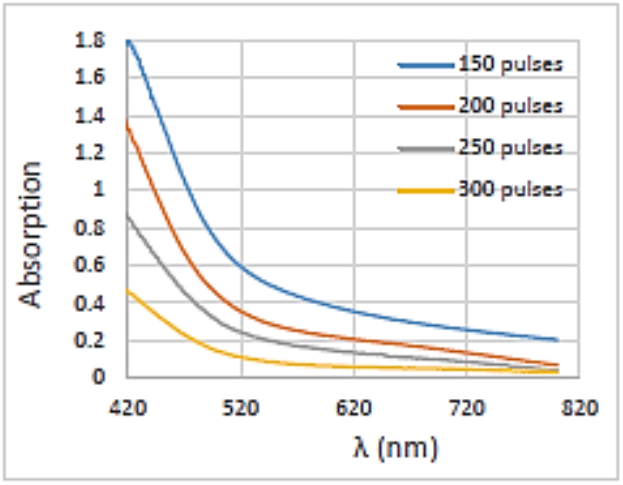

Figure 3-b. absorption coefficient after annealing

Figures (4-a,4-c) shows absorption coefficient values as a function of the wavelength of the number of different pulses before and after annealing. Figure (4-a) represents the change of absorption coefficient with the change in the number of pulses before annealing. While figure (4-b) represents the change of absorption coefficient with the change in the number of pulses after annealing. It is observed that the value of absorption coefficient decreases with the increase in the number of laser pulses, due to increased absorption[Fakhri, et al 2014].

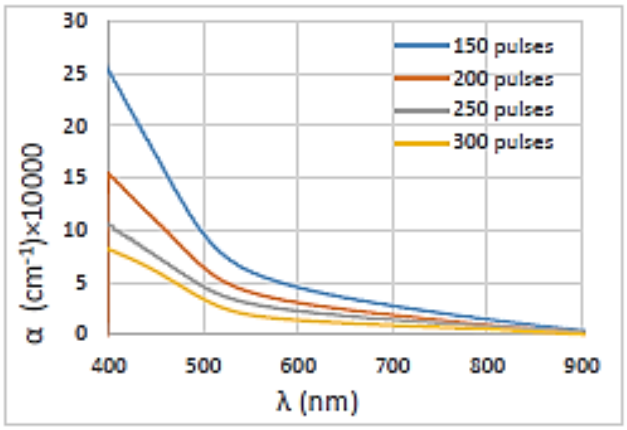

Figure 4-a. Absorption coefficient before annealing

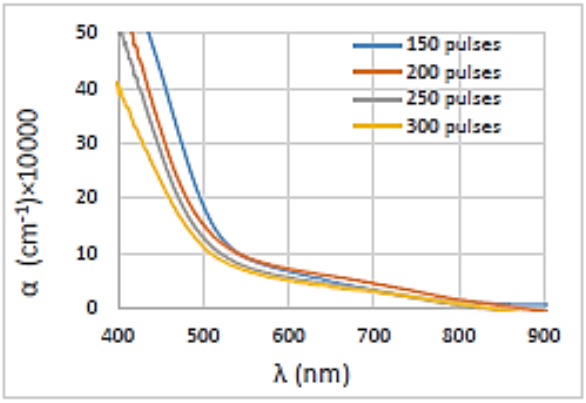

Figure 4-b. Absorption coefficient after annealing

Figures (5-a,5-b) illustrates the values of energy gaps and their relationship with the change in the number of pulses and annealing. Figure (5-a) shows the change in energy gaps with the increase in the number of pulses prior to the process of annealing. It is observed that energy gaps gradually decrease with the increase in laser power. This is due to the increase in the number of laser pulses, which led to the generation of secondary power levels between parity and conduction packages. Thus, this enabled electrons to occupy these local levels as they move from parity package to conduction package[Ali, et al 2006].

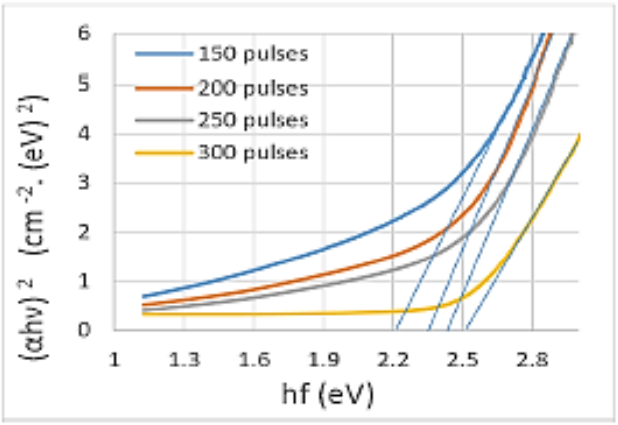

Figure 5-a. Energy gap before annealing

Figure (5-b) represents the change in energy gaps with the change in the number of pulses after annealing. it is clear that energy gaps after annealing decrease as compared with those in the number of pulses before annealing due to the increase in the size of the grains and the decrease in the density of the imbalance. Table 1 shows. Band gaps before and after annealing.

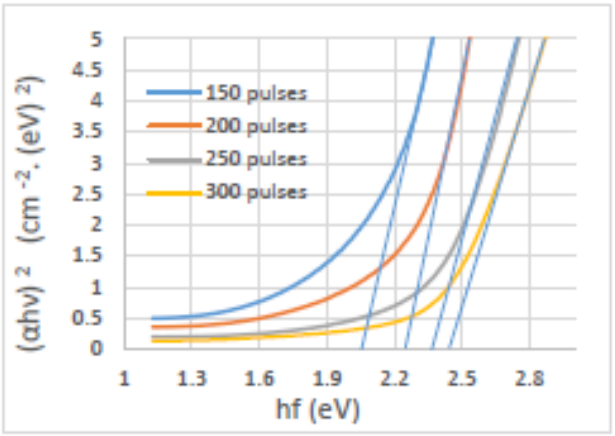

Figure 5-b. Energy gap after annealing

Table 1. Band gaps before and after annealing

Pulses	Eg Before Anneling (eV)	Eg After Anneling (eV)
150	2.22	2.06
200	2.36	2.25
250	2.44	2.37
300	2.51	2.44

Figures (6-a,6-b) shows x-ray diffraction results of the number of different pulses before and after annealing. Figure (6-a) shows x-ray diffraction results before annealing. Hence, there appear five main peaks representing the crystalline levels of the cubic crystalline structure (222), (311), (220), (200), and (111) for numbers of different pulses (150-200-250 and 300). They correspond to the following angles respectively (69.22) (65.90) (55.28) (38.22) (32.92)=2θ, corresponding to the standard file of CdO no. (CdO_00-005-0640_star.pdf)[Wadaa, et al 2019]. The results showed an improvement and increase in the crystalline with the increase in the number of pulses. This is because crystals grow larger when more layers of material are added to the outer surface of the thin film[Jasim, et al 2020]. Figure (6-b) shows the effect of annealing on x-ray diffraction results. It is clear that annealing increases the roughness of the film surface, compression, the improvement in the order of atoms when compared to the same number of pulses before annealing, as well as the change in the crystalline size from (4.2 nm) to (7.5 nm), where the crystalline size is calculated using Scherrer equation [Nasir, et al 2019].

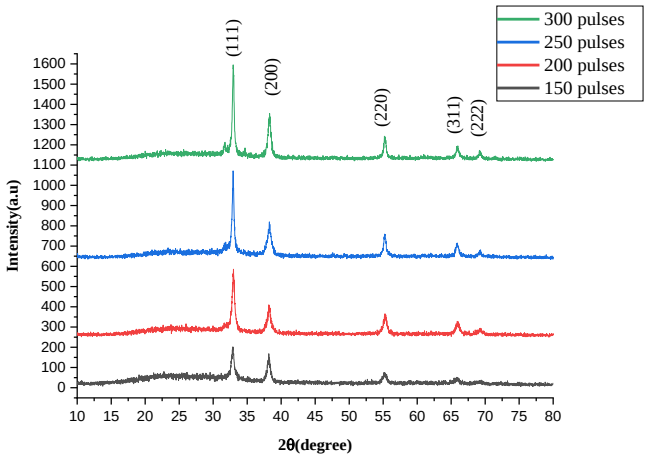

Figure 6-a. X-ray diffraction before annealing

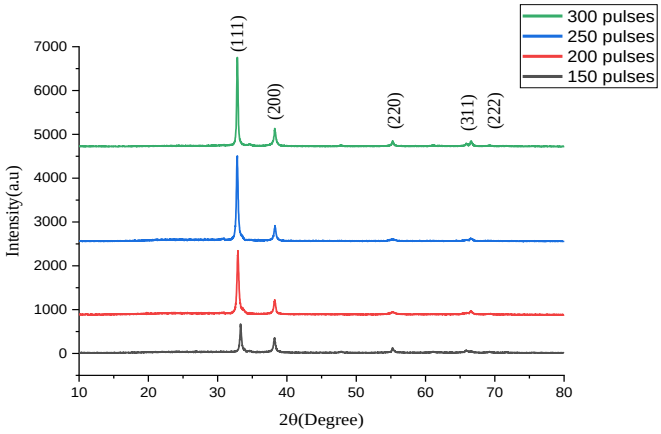

Figure 6-b. X-ray diffraction after annealing

The results of gas sensor showed that the increase in operating temperature improves film sensitivity. In numbers, the sensitivity of all films increases with the increase in operating temperature. This is due to the increase in the rate of surface interaction of film with the target gas. The maximum peak values are seen at certain temperatures called optimal temperature and. The increase and decrease in sensitivity indicate the phenomenon of gases absorption. Sensitivity increases at operating temperature up to 200°C. Figures (7-a,7-b) shows the results of gas sensitivity to a number of different pulses before and after annealing. In figure (7-a), before annealing the maximum sensitivity of the pure CdO film to gas (NO_2) was found to be 46.16% at 200°C and the number of pulses was (150).

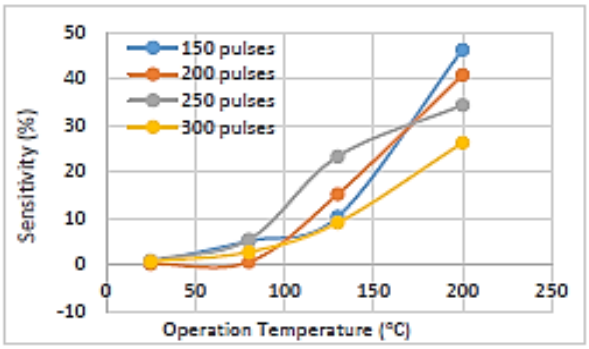

Figure 7-a. Sensitivity before annealing

When increasing the number of pulses, sensitivity decreases, i.e., there is an inverse relationship between the number of pulses and sensitivity. This is due to the size of the grains, which are small at (150) pulses, allowing the space charge to cover a large volume of grains and the large number of grain limits that provide a large area for the adsorption of oxygen molecules (O_2) on the outer surface of thin films. They will extract electrons from the conduction package and confine them to the outer surface of the films, causing an increase in film resistance. Using the relationship ($s=(R_g/R_a) \times 100$ %), sensitivity was calculated, which leads to a decrease in film resistance [Sujitno, et al 2006]. If the number of pulses increases, the crystalline size increases and thus reduces the limits of grains, resulting in a reduction in the area of adsorption of oxygen molecules and thus reduces the change in resistance and decreases sensitivity. Figure (7-b) shows gas sensitivity after annealing, as the greatest sensitivity was (34.25%) for (150) pulses. It is observed that the value of sensitivity after annealing decreased as compared to before annealing due to the improvement and good crystallization that occurred to the film after annealing. Accordingly, the limits of grains decreased more than they were before annealing, which led to a decrease in sensitivity.

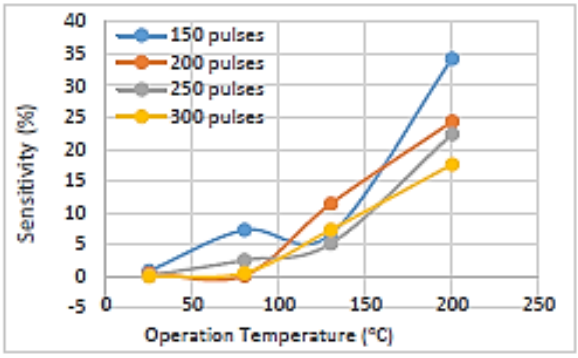

Figure 7-b. Sensitivity after annealing

Figures (8-a,8-b,8-c,8-d) and (9-a,9-b,9-c,9-d) illustrate the relationship between response time and recovery time for a number of different pulses before and after annealing at optimum operating temperature (200°C) and air voltage and bias (5 volt) on the glass substrates of (CdO) films. The speed of response was studied at the temperature at which the sensor showed maximum sensitivity. These two figures clarify that 150 pulses show a rapid response speed (27.7 seconds) and a recovery time (90 seconds) for the glass substrate. This shows that (150) pulses are the best pulses to achieve a rapid response sensor. The rapid response sensor for gas (NO_2) may be caused by faster gas oxidation [Gardem, et al 2010]. Thus, electrons move easily to the conduction range, reducing the resistance of thin films [Gardem, et al 2010]. Increased oxygen absorption on the surface leads to extracting conduction electrons from the nearby surface area, forming an electron-depleting surface layer. This has increased the number of active absorption sites and achieved rapid response time for sensors. When the number of pulses increases, the response time increases due to improvement in granular volume, which reduces the interaction between gas and thin film. In real situations, rapid response time is usually required, but quick recovery time is not very important. In addition, recovery time decreases by increasing the number of pulses. In figure (9) after annealing, the response time is higher than before annealing, also due to the improvement in granular volume, which

leads to a decrease in the interaction between gas and the film surface.

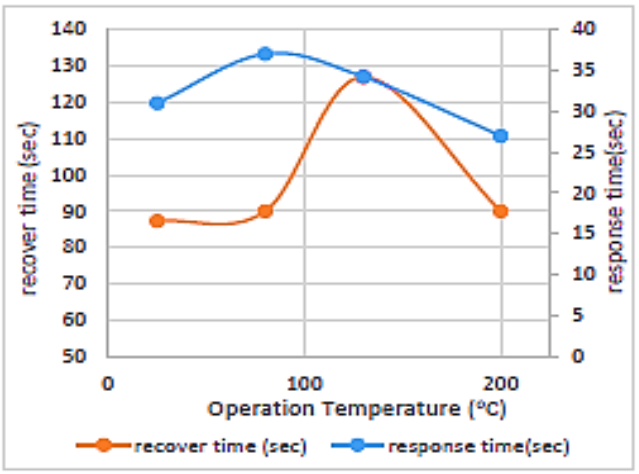

Figure 8-a. Response time and recovery time before annealing (150 pulses)

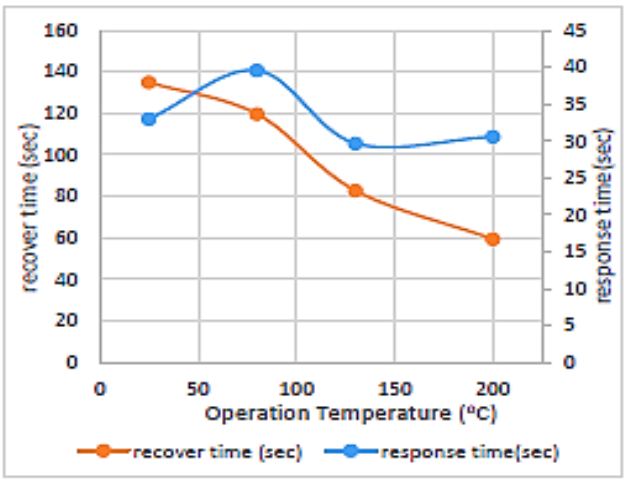

Figure 8-b. Response time and recovery time before annealing (200 pulses)

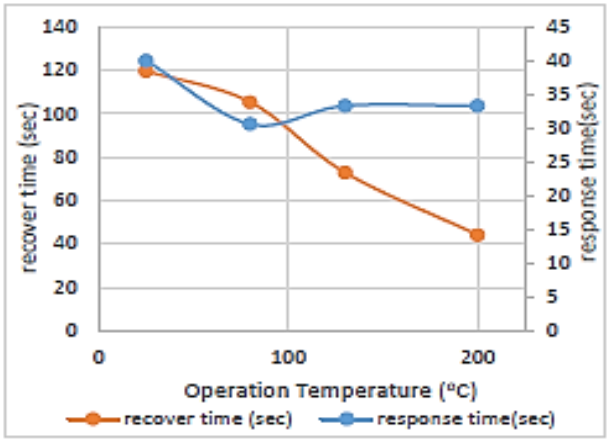

Figure 8-c. Response time and recovery time before annealing (250 pulses)

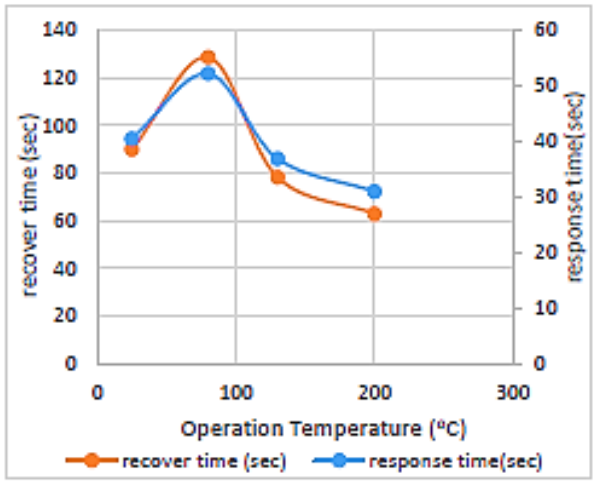

Figure 8-d. Response time and recovery time before annealing (300 pulses)

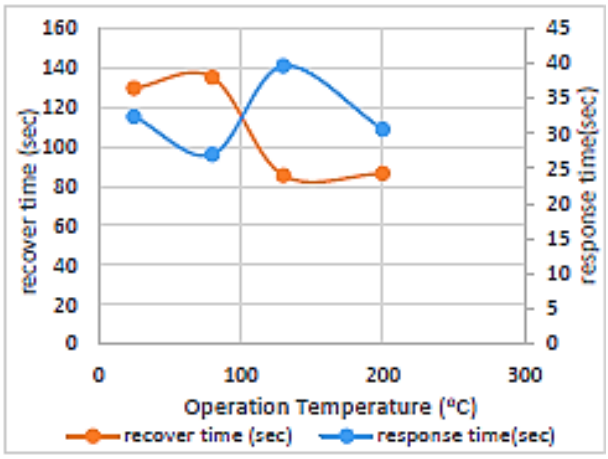

Figure 9-a. Response time and recovery time after annealing (150 pulses)

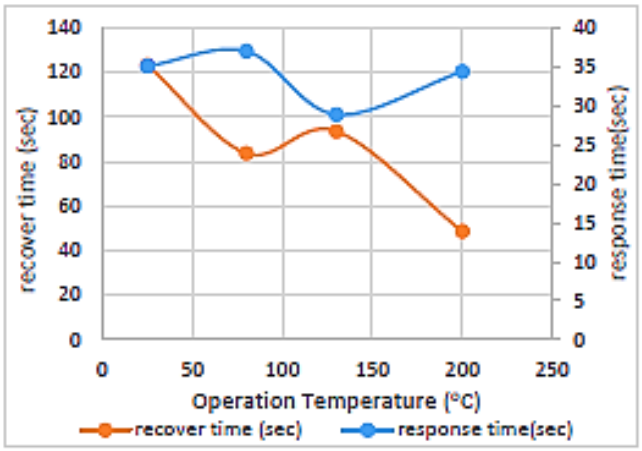

Figure 9-b. Response time and recovery time after annealing (200 pulses)

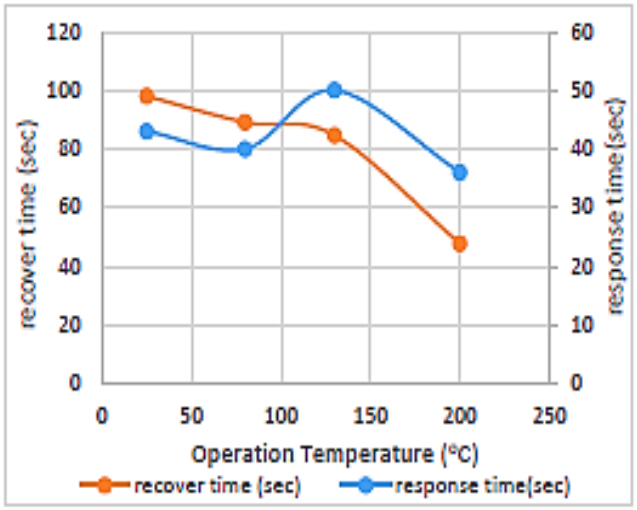

Figure 9-c. Response time and recovery time after annealing (250 pulses)

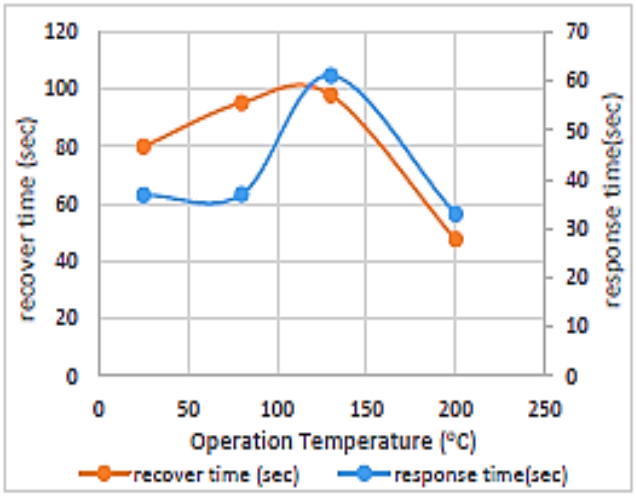

Figure 9-d. Response time and recovery time after annealing (300 pulses)

Conclusion

The optical properties of the thin film (CdO) prepared with pulsed laser deposition technology depend heavily on the number of laser pulses. Perhaps this is due to improvements in crystalline size. Transmittance decreases and absorption increases as the number of laser pulses shed on the target increases, which in turn increases the particles ejected towards the substrate. Energy gap values decrease as the number of pulses for each CDO film prepared with PLD increases due to crystallization growth. X-ray diffraction studies revealed that films are a multicrystal phase and CdO cube. XRD peaks are wider at low temperatures, indicating that quantum confinement is better at low temperatures. As for gas sensitivity studies, they showed that films with fewer pulses have a higher surface area to interact with gas. Grain sizes increase as the number of pulses increases, reducing the area of the surface interacting with gas. A gas sensitivity test for pure CdO film samples shows that they work best at high temperature. CdO pure film sensitivity to gas (NO_2) began at 100°C and maximum sensitivity at 200°C. High sensitivity and rapid response time are achieved at 150 pulses before annealing process. The sensitivity of the samples decreases as the number of pulses increases with annealing as well.

References

Aadim, Kadhim A. "Effect of annealing temperature and laser pulse energy on the optical properties of CuO films prepared by pulsed laser deposition." *Iraqi journal of physics*, 12, 23 (2014): 97-104.

Al-Ogili, H.K.J. "Effect of Thickness to the Structure Properties of CdO Thin Films", *Eng. & Tech. Journal*, 29, 2011, 1536.

Hadaate Ullah, Ridoanur Rahaman, Shahin Mahmud, "Optical Properties of Cadmium Oxide (CdO) Thin Films", *Indonesian Journal of Electrical Engineering and Computer Science*, Vol. 5, 2017, 81-84.

Eman K. Hassan, "Structural and optical properties of CdO and CdO0.99Cu0.01 thin films prepared by pulsed laser deposition technique", *Iraqi Journal of Physics,* Vol. 13, 2015.

Ayad Z. Mohammad, Kadhim A. Aadim and May A. Abduljabbar, "Laser Energy Impact on CdO NPs Prepared by PLD Technique", *Indian Journal of Natural Sciences,* Vol. 8, 2018, 14106-14111.

E. Nasir, H. Al-Lamy, and H. Abdul-Ameer, Optical Properties of CDSE Films at Different Thickness and Annealing Temperatures. *Chalcogenide Letters,* 16 (2019) 485–497.

Ali, H.M., Abd El-Raheem, MM., Megahed, N.M. and Mohamed. H.A. "Optimization of the optical and electrical properties of electron beam evaporated aluminum-doped zinc oxide films for opto-electronic applications." *Journal of Physics and Chemistry of Solids,* 67(8): 2006, 1823-1829.

J. Santos-Cruz, G. Torres-Delgado, R. Castanedo-Perez, S. Jime Nez-Sandoval, O. Jime nez-Sandoval, C.I. Zun iga-Romero, J. Marquez Marın and O. Zelaya-Angel," Dependence of electrical and optical properties of sol–gel prepared undoped cadmium oxide thin films on annealing temperature ", *Thin Solid Films,* Vol. 493, (2005), PP. 83–87.

Fakhri, Makram A "Effect of Substrate Temperature on Optical and Structural Properties of Indium Oxide Thin Films Prepared by Reactive PLD Method." *Engineering and Technology Journal,* 32(5) Part (A) Engineering: 2014, 1323-1330.

Wadaa S.H.; Ala' F.A. and Kadhim A.A.; "*Influence of Laser Energy and Annealing on Structural and Optical Properties of CdS Films Prepared by Laser Induced Plasma*". Department of Physics, College of Science, University of Baghdad, 2019.

Jasim M.H.; Awatif S.J. and Kadhim A. *"Synthesis and Characterization of CdOx-1: MgX films by pulsed laser deposition",* Department of Physics, College of Sciences, University of Baghdad, Iraq, 2020.

E.M. Nasir, Thickness and gamma-ray effect on physical properties of CdO thin films grown by pulsed laser deposition. *Iraqi Journal of Physics (IJP),* 14 (2019) 90–100, doi: 10.30723/ijp.v14i29.225.

Sujitno T, Sudjatmoko S Atom Andonesia 32: (2006), 65-79.

Garde S, Sensors & Transducers 122: (2010), 128-142.