

Study the Effect of CuO Doping on Optical Properties of (MPAMI) Preparation by Pulse Laser Deposition

Shimaa A. J. Farhan, Sahib Neamh Abdulwahid, Abid Allah M. Ali

University of Kufa, College of Education for Girl, Department of Physics, Najaf, Iraq

Abstract: Thin films (MPAMI) doping by copper oxide (CuO) (10%) were prepared on glass bases using the Pulsed Laser Deposition (PLD) technique. The effect of the doping ratio on laser pulses (1000, 3000, 5000) mJ/cm² on the optical properties for these thin films was examined. The energy gap values were shown to decrease by increasing the laser pulse energy to reach 2.2eV for the nanofilm with a pulse about of 5000 mJ/cm². While the permeability property was improved in contrast to the absorbance effect. This improvement is benefited according to application. While photoluminescence is decreased and shift it to blue (towards blue) so that the peaks are low and with an extended plateau and between decreasing reflectivity intensity to increase wavelength in an oscillating manner as well as increase the energy of laser pulses, decreasing intensity but led to the displacement of the peak of the reflectivity spectrum to blue displacement, and can be observed decrease of acute refractive index values at the beginning of the measurement and at the wavelength (320 nm). The behavior of the extinction factor curves is may be an explanation of the waning radiation within the material by two mechanisms, the first being the absorption, and the second the amount of the scattering that is forward or background.

Keywords: Photoluminescence, Optical, CuO nanostructures, PLD, Thin films, Tinged, Laser ablation

1. Introduction

Thin films are used to describe one or several layers of atoms of a substance of very small thickness not exceeding (1 μm) [2, 1]. Because of the thinness of these films are deposited on a solid material such as glass, silicon, some salts, or polymers. Thin films have properties and features that are not available in the compositions of other materials. The fact that their ultrafine thickness and large surface-to-volume ratio gave them a unique physical structure that matches the structure of monocrystalline sometimes, and exceeds it at other times. One of the important techniques for obtaining new properties for materials that are difficult to view and feel when they are in a natural mass form, at the present time thin films receive more attention, for use in many electronic applications in the manufacture of capacitors, diodes, integrated circuits, transistors, resistors and conductive poles [3, 4]. These thin films were also used in the manufacture of light-emitting diodes and plasma display panels, as well as in optical applications for the manufacture of solar cells and sensors [6, 5] and the manufacture of optical fibers used in the transfer of information and communications. As well as in the manufacture of optical filters and anti-reflective coatings to reduce the losses associated with the reflection of light from the surfaces of these cells. It was also used in the manufacture of optical detectors. and also in the manufacture of CDs [7]. In this research, we used the method of laser pulse evaporation for its wide use, and that the first to use the technology of pulsed laser evaporation (PLD) (Smith and Turner) in 1965 where he prepared semiconductors and thin films of insulators [8]. The possibility of obtaining thin films to manufacture the electronic and optical devices made the technology of PLD with a very short pulse duration (ns) take great interest in this time, and that the base temperature (ground, base), gas pressure, laser energy, and vacuum value has an important effect on the properties of the thin film prepared in this way [9, 10]. Figure 1 shows the system used in the work.



Figure 1: The PLD system used in action

2. Theoretical procedure

We can identify the optical applications of the thin films prepared from those materials, and any change in these factors leads to a noticeable change in these properties, especially the deviation of the basic absorption edge towards higher or lower energies, and then a change in the value of the optical energy gap [11]. PL is defined as the emission of light from any type of material after its irradiation with a photo transmitter, i.e. absorption of photons (electromagnetic radiation), and begins by excitement of the material (arousal by photons), hence the name of photo-luminescence usually arousal subject to different relaxation processes and after that photons are re-radiated [12]. The period between absorption and emission may be very short in most semiconductors with a direct gap, which leads to excitation of more energy or equal to the energy gap of the material. Research areas focused on quantifying the quantum dots (QDC) of the semiconductor nanostructures for their good performance [13].

The transmittance (T) is defined as the ratio between the intensity of the transmitted light and the intensity of incident light (I / I_0) and is calculated from the following equation [14].

$$T = \frac{I}{I_0} = e^{-\alpha t} \quad (1)$$

Where, t is the thickness of the material (cm) and α the absorption coefficient (cm^{-1}).

The absorption coefficient (α) is defined as the ratio of the decrease in the radiation energy flux in relation to the distance within the medium toward the propagation of the wave. The absorption coefficient is calculated from the following relationship [15]:

$$\alpha t = 2.303 \log I/I_0 \quad (2)$$

Where the value of $\log (I/I_0)$ represents the absorbance (A), since the intensity of the light falling on the thin films decreases exponentially (exponential function), and the ratio of the decrease in the radiation energy through the thin films material is called the absorption factor (α). It can be calculated from the following relationship:

$$\alpha = 2.303 \left(\frac{A}{t} \right) \quad (3)$$

where, t: Thin films thickness, (A): Absorbance

If the value of the absorption coefficient is $\alpha \geq 10^4 \text{cm}^{-1}$ then the electronic transitions are direct at high energies, but if the value of the absorption coefficient $\alpha \leq 10^4 \text{cm}^{-1}$ at low energies, electronic transfers are indirect.

The energy gap is defined as the amount of energy required to excite (transfer) electrons from the top of the valence beam to the bottom of the conduction beam [16]. As the energy gap is one of the most important optical constants in semiconductor physics

and depends on determining the value of manufacturing many electronic devices such as solar cells, photodiodes and reagents, the optical energy gap ($\alpha h\nu$) can be determined by analyzing permeability and reflectivity data measured at specific wavelengths. The value of the optical energy gap can be calculated from the absorption equation for direct transfers [17]:

$$\alpha h\nu = B(h\nu - E_g)^m \quad (4)$$

where,

($h\nu$) is the energy of the photon, B: Represents the proportional constant, E_g : Represents The allowed or forbidden energy gap for electronic transfers, (m) is a constant gives the type of electronic transmission.

The refractive index (n) is defined as the ratio between the velocity of light in a vacuum (c) to its velocity (v) in any medium and a specified wavelength. The complex (n) consists of the part real and the imaginary part $N = n - ik$. Refractive index is given by:

$$n = \sqrt{\frac{4R - k^2}{(R - 1)^2} - \frac{(R + 1)}{R - 1}} \quad (5)$$

where, R: Represents the reflexivity, which is defined as the ratio between the intensity of the reflected radiation to the intensity of the incident radiation at the boundary between the two different media with the optical density, and is calculated from the following relationship [18].

$$R = 1 - T - A \quad (6)$$

The fictional part of the complex refractive index (N) is called the decay coefficient or extinction (k), and is calculated from the following equation [19].

$$k = \frac{\alpha \lambda}{4\pi} \quad (7)$$

where λ represents the wavelength of the incident radiation.

3. Materials and Methods

MPAMI powder is pressed by hydraulic piston. It is a Chinese origin device used to press or compress samples or materials that are in powder form with a maximum pressure of 6 MPa. The material is placed inside the small still steel container and then press according to the nature of the material. Where each substance has a maximum of pressing. As this material was compressed to a pellets with a thickness of 5mm, with a diameter of 1cm. The samples were deposited on the FTO substrates, these basis's are fixed to the upper of holder of the system inside the sedimentation chamber, which is a distance of 5 cm from the bottom holder on which the target material is placed, which is either pure (MPAMI) or doping with copper oxide (CuO) at a rate of (10%), and the distance has been set with this dimension in order to obtain the best homogeneity of the material that will stick to these substrate after evaporation from the pellets with fixed dimensions for a period ranging from 5 to 10 minutes in order to increase the adhesion of the material. The pressure inside discharge chamber was 2×10^{-2} mbar, where a Nd-YAG laser with a frequency of 10 Hz, energies of 1000, 3000, 5000 Mj, and wavelength of 1064 nm was used. The pulse width was used for deposition is 10 ns. It is fixed to all thin films and to the two materials. This work was performed in the laboratories of Sharif University, Iran. Photoluminescence measurements (PL) (Model: Flex One, zolix) was achieved as shown in Figure 2.



Figure 2: Photograph of the system (PL) used in this study

4. Results and Discussion

The results of the luminous emission spectrum (Luminescence) of pure nanofilm and doping with a CuO layer prepared with different laser pulses (1000,3000,5000) mJ/cm^2 have been recorded using an irritation source. Figure 3 describing the relationship between the luminous intensity as a function wavelength. It can be seen that there are deep sniping levels in which the nanofilms are formed. Likewise, other peaks can be observed at the peak that indicate the emission of peaks from each sample and for each laser pulses, i.e. that one sample radiates different colors, and this can be attributed to the effect of the quantum restriction occurring in the prepared nanofilms. These results are confirmed by the results of FESEM, which are consistent with the results of the research [20]. The effect of all laser pulses (number of pulses) and the fixed percentage of CuO Impurities on the properties of thin nanofilms can be summarized as that they have decreased luminous intensity, but have been displaced by a blue displacement (towards blue) so that the peaks have become low and have an extended plateau.

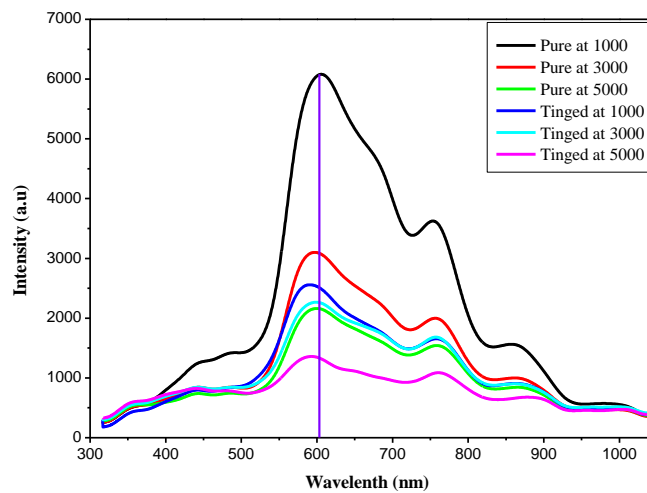


Figure 3: Optical brightness spectrum

Figure 4 shows the permeability curves of pure and doped nanoparticles (MPAMI) films with laser pulses (1000, 3000, 5000) mJ/cm^2 as a function of wavelength. The effect of both laser pulses and CuO can be summarized as having improved the permeability property in contrast to the absorbance effect and this relative improvement may be beneficial and according to the application intended to be used for it. The reasons were the reason for possessing the transmittance curves to a large concave width and over a range of between wavelengths (400-1000) nm and this characteristic has a great benefit in the application of optical reagents and this result is agreeing with research [21].

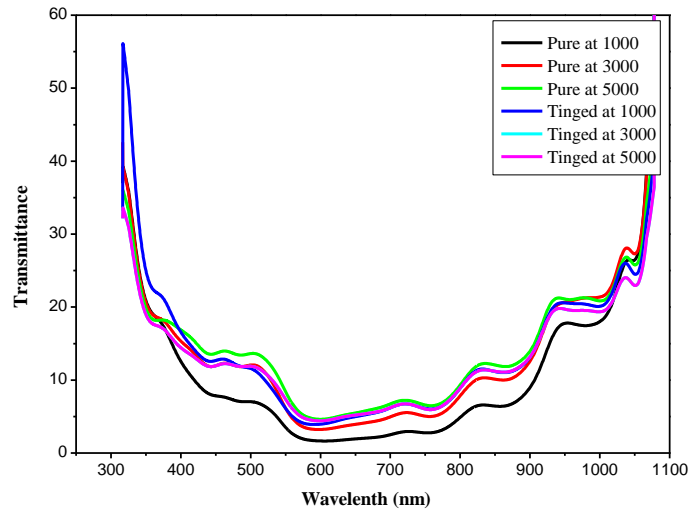


Figure 4: Permeability spectrum for pure and doping nanoparticles

Figure 5 shows the relationship between absorbent films and the wavelength of both the pure and the deformed films in relation to the fixed ratio of CuO. The effect of both deposition and the number of laser pulses on absorbance as a function of the wavelength where we note that the intensity of absorption has decreased after the process of deformation and increase the number of laser pulses from 1000 mj/cm^2 to 5000 mj/cm^2 with a displacement towards (blue displacement) but there was widening the size of the absorbance curve to the plateau of a deformed model and the number of laser pulses (5000 mj/cm^2), and this result is agreeing with research [22].

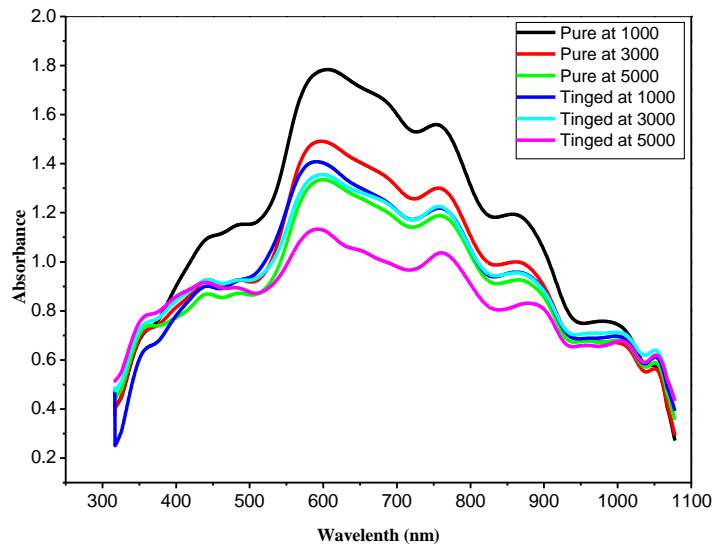


Figure 5: Absorption spectrum for pure and doping nanoparticles

Figure 6 shows the relationship between absorption coefficient and wavelength. We can observe the effect of both the deformation process and the increase in the number of laser pulses on the pure and doping nanofilms. Where we note a decrease in the

absorption coefficient values with an increase in the number of laser pulses from 1000 mj/cm^2 to 5000 mj/cm^2) for both pure and doping films, with a shift towards and an increase in the size of the breadth of the absorption coefficient curve and this result will affect the optical properties in general. As the laser pulses (5000 mj/cm^2) led to the formation of nanocrystals.

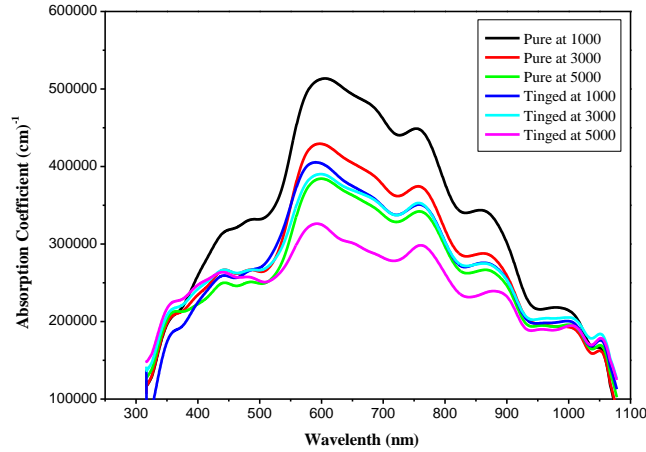


Figure 6: Spectrum of absorption coefficient for pure and doping nanoparticles

Figure 7 shows the relationship between the energy gap and wavelength. The value of the energy gap has been calculated through the intersection of the two tangent curves (the tangent of the upper curved part and the tangent direction of the lower part). It can be seen that the energy gap values decrease as the laser pulse energy reaches of 2.2 eV for the thin-film (5000 mj/cm^2). This can be explained by the fact that laser pulses of (5000 mj/cm^2) have formed nanoparticles with their smallest limits that have reached (25 nm).

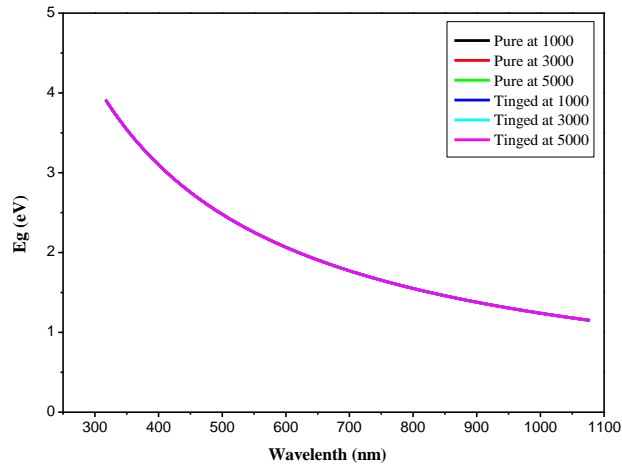


Figure 7: Spectrum of the Energy Gap for Pure and doping Nanoparticles

Figure 8 shows the reflection spectrum change as a function of the wavelength of both pure and CuO-impregnated thin films with respect to the constant by changing the laser pulse energy from $1000\text{-}5000 \text{ mj/cm}^2$. Several changes can be observed due to the effect of CuO on the pure thin films. The decrease in the intensity of the reflectivity by increasing the wavelength. As well as the increase in the energy of laser pulses, led to the displacement of the peak of the reflectivity spectrum by a blue shift.

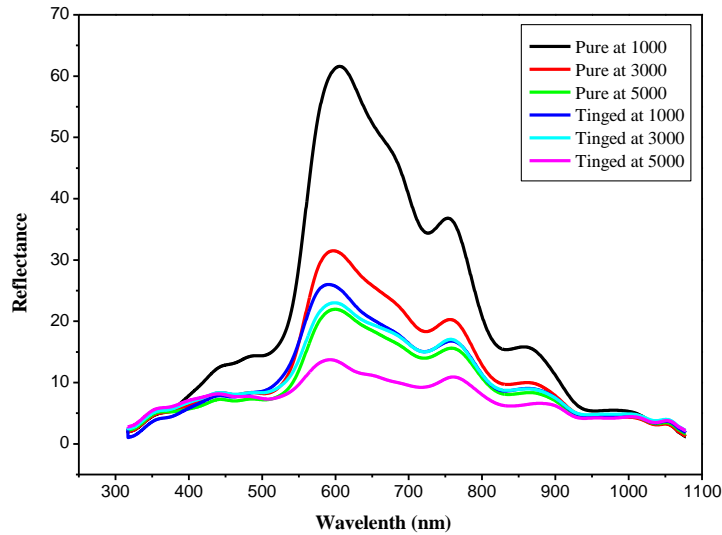


Figure 8: Change in the reflectivity spectrum as a function of the wavelength

Figure 9 shows the behavior of the refractive index spectrum as a function of changing the wavelength of several nanofilms including pure and doping ones, under the influence of CuO and increased exposure to laser pulses in the process of preparing the nanofilms. A sharp decrease in the refractive index values can be observed at the beginning of the measurement and at the wavelength (320 nm), to predict the stability conditions along the range (320-1000 nm) to obtain a value of the refractive index that is almost constant for all nanofilms.

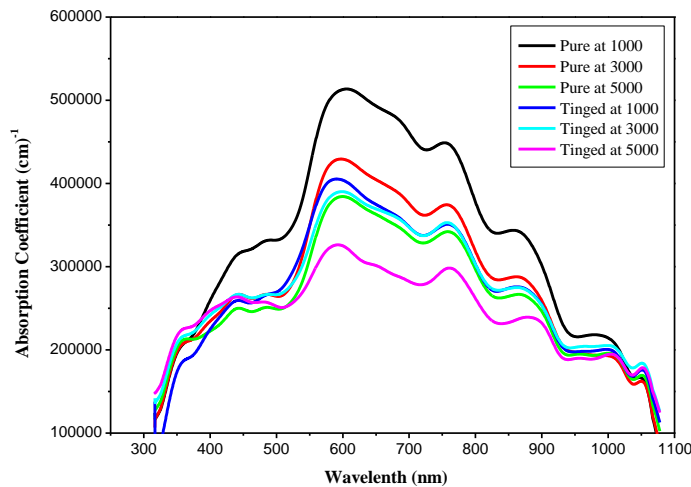


Figure 9: Spectrum of the refractive index of pure and doping nanoparticles (MPAMI)

Figure 10 shows the relationship between the extinction coefficient as a function of the wavelength to change the energy of laser pulses at pure and doping nanofilms. The effect of both distortion and the increase in the energy of laser pulse has led to a decrease in the spectrum (peak) and an increase in the width of the curves, to reach the maximum peak of laser pulse (5000 mj/cm²) in the range of 17×10⁶. A well-known represents the extent of the scattering of the radiation entering the thin films, where the reducing

of the rays within the material is explained by two mechanisms, the first being absorption and the second the amount of scattering that is forward or/and background [23].

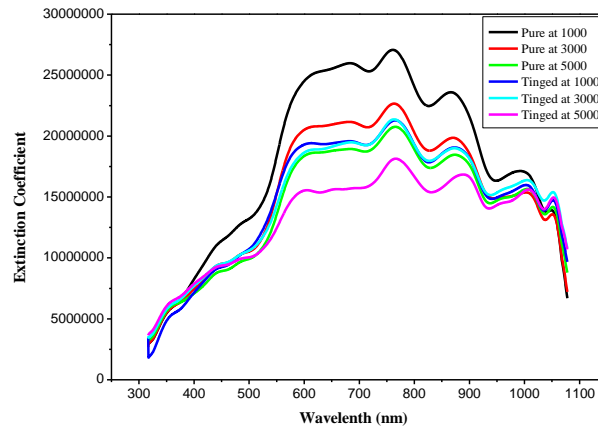


Figure 10: The extinction coefficient as a function of the pure and doping nanoparticles (MPAMI)

Conclusions

1-The behavior of the three curves in the luminance spectrum of the nanofilms prepared by laser pulses (1000, 3000, 5000 mj/cm^2) is explained by the presence of deep sniping levels in which the nanofilms are formed and the observation of other peaks at the top (peak) indicates the emission of the range of peaks from each specimen and each at laser pulses, i.e. one sample radiates different colors, and this can be attributed to the effect of the quantum restriction occurring in the prepared nanofilms, and the fixed percentage of CuO deformation on the properties of the nanofilms that they have reduced the luminous intensity but were displaced by a blue displacement, so that the peaks became low and extended plateau.

2- The permeability at the limits of the beginning of low wavelengths has ability, i.e. with high energy and within the limits of the region (300-350 nm), after which the transmittance after the wavelength (350nm) falls to the limits of 550nm in order to record the lowest value of transmittance at the wavelength (600 nm) which reflects the best absorption state and which subsequently caused the best luminance, so this can be explained by quantitative restriction. The effect of both laser pulses and doping CuO has improved the permeability property in contrast to the effect of absorbance and this relative improvement may be beneficial and according to the application to be used for it.

3- The spectrum of the doping nanofilms with a laser pulse energy of 5000 mj/cm^2 has more effect. Where the semi-flat has an undetermined value (peak) that the surface of the thin films concerned becomes rough with a so-called plateau, where increases absorbance and reduces reflexivity, as reflexivity reaches the semi-saturation behavior due to the nanoscale size of the particles leading to the phenomenon of quantitative restriction.

Acknowledgment

The authors acknowledge the financial support of University of Kufa, Iraq. The author is grateful to Dr. Basim Almayahi, University of Kufa (basimnajaf@yahoo.com) for assisting me throughout conducting the present research.

References

1. K, Seeger. Semiconductor Physics. Wien, New York, (1978)
2. J. R.Son, "Thin Film Technology", 2nd Ed., (1986).
3. S. A. Kandela, "Laser physics", University of Baghdad, (1988).
4. Luque, Antonio, and Gerardo L. Araújo. Solar cells and optics for photovoltaic concentration. A. Hilger, (1989).
5. S. M. Sze, "Semiconductors devices physics and technology", translated by F. G. Hayat H. A. Ahimed, University of Mousal, (1990)

6. A. S. Jabbar, "A Study of Some Physical Properties of (Cd) Films deposited by locally fabricated D.C. Sputtering "University of Technology, thesis, (2006).
7. Jef Poortmans, Vladimir Arkhipov, " Thin Film Solar Cells: Fabrication, Characterization and Applications", published by John Wiley & Sons publications (2006).
8. Sze, Simon Min. Semiconductor devices: physics and technology. John wiley and sons, 2008.
9. Eckertova, Ludmila. Physics of thin films. Springer Science & Business Media, 2012.
10. Panda, S. K., and C. Jacob. "Preparation of transparent ZnO thin films and their application in UV sensor devices." *Solid-State Electronics* 73 (2012): 44-50.
11. Wasan A. Al-Taa'y, Saad F. Oboudi, Emad Yousif, Mohammed Abdul Nabi, Rahimi M. Yusop, and Darfizzi Derawi. "Fabrication and characterization of nickel chloride doped PMMA films." *Advances in Materials Science and Engineering* (2015).
12. Vigneshkumar, M., Suganya, S. M., Pandiarajan, J., Saranya, A., & Prithivikumar, N "Structural and optical properties of nanocrystalline nickel oxide thin film by spray pyrolysis technique." *International Journal of Technical Research and Applications* (2016): 52-56.
13. Chen, X., Chen, Y., Yang, Y., Jia, H., Zhang, J. M., Chen, S., & Huang, Z.. "The structure and electrical properties of PbPdO₂ thin films with preferred orientation prepared by PLD." *Ceramics International* 43.13 (2017): 10428-10433.
14. Abed Ahmed Khalefa AL -Hammdany . "study the structural ,optical and electrical properties of (Li_xNi_{2-x}O₂) Compound and thin films prepared by pulse laser deposition and use as a gas sensor " University of Tikrit, Faculty of Education and Pure Sciences, 2017.
15. Othman, A. A., Osman, M. A., Ibrahim, E. M. M., Ali, M. A., & Abd-Elrahim, A. G. "Mn-doped ZnO nanocrystals synthesized by sonochemical method: Structural, photoluminescence, and magnetic properties." *Materials Science and Engineering: B* 219 (2017): 1-9.
16. Murtadha La. Sheqnaab. Study the Characteristics and Nonlinear Optical Properties of Semiconductors Prepared by Pulsing Laser Ablation." Department of Physics University of Al-Qadisiyah, 2018.
17. Mustafa, Dhia Aldin Sleibi, and Rawaa Isam Mohammed Al-Rawi. "Structural and Optical Properties for Zn Doped CdO Thin Films Prepared by Pulse Laser deposition." *Iraqi Journal of Science* 59.2B (2018): 839-846.
18. Harb, Noha H. "The Structure and Optical Properties of Ag doped CdO Thin Film Prepared by Pulse Laser Deposition (PLD)." *Baghdad Science Journal* 15.3 (2018): 300-303
19. Yin, H., Zhao, Y., Li, J., Yang, Q., & Wu, W. (2020). "Optical and electrical properties of Ag: Cu₂O nanocomposite films prepared by pulse laser deposition." *Materials Chemistry and Physics* 241 (2020): 122399.
20. S.Mahajan, Meenu Rani, R.B.Dubey and J.Jagrati Mahajan, "Synthesis and Characterization of Zn selenide Nanoparticles at various Reaction Time " *International journal of latest research in science and technology*, 2,(2013)457-459.
21. Neupane Dipesh. "Structural and Optical investigation CdSe dots, Kathmandu university journal of science, engineering and technology", 8,2,(2012).
22. Elizabeth M. Boatman and George C. Lisensky, " A Safer Easier, Faster Synthesis for CdSe Quantum Dot Nanocrystals", *Journal of Chemical Education*, 82,(2005)11.
23. N.Jeyakumar, B.Natarajan, S.Ramamurthy and V.Vasu, "Structural and optical properties of n-type porous silicon-effect of etching time ", *International Journal of Nanoscience and Nanotechnology*, (2007) 45-51.