Al-Mustansiriyah Journal of Science
ISSN: 1814-635X (print), ISSN:2521-3520 (online) Volume 32, Issue 4, 2021 DOI: http://doi.org/10.23851/mjs.v32i4.993

Research Article **Open Access**

Dependence of the Structural and Optical Properties of Gallium Oxide Nanostructures on Laser Fluency

Khalid H. Jebur, Nadheer J. Mohammed*

Department of Physics, College of Science, Mustansiriyah University, Baghdad, IRAQ.

*Correspondent contact: nadheerphys@uomustansiriyah.edu.iq

Article Info

Received
10/05/2021

Accepted
27/05/2021

Published
20/11/2021

ABSTRACT

In this research, thin films of gallium oxide β-Ga_2O_3 nanostructures were prepared by pulsed laser ablation in distilled water (PLAL). Then, deposited on quartz substrate by the drop-casting method at 90 ºC. The Nd-YAG laser was used with a wavelength of 1064 nm and a repetition rate of 5 Hz. The effect of increasing laser fluencies on the structural and optical properties was investigated by, Transmission electron microscope (TEM), Atomic force microscopy (AFM), X-ray diffraction (XRD), scanning electron microscopy (SEM) and spectrophotometer microscopy (UV-VIS). Crystallite size for all samples increased with the increasing the fluency of laser excepting at the fluency of laser 5.57 J/cm^2 was 9.78 nm. The formation of nanoparticles, spindle-like, nanosheet and core-shell of β-Ga_2O_3 have been observed by the images of TEM at the fluencies of laser 4.77, 5.57, 5.97, and 6.36 J/cm^2, respectively. The nanocluster and nanoroads of the β-Ga_2O_3 thin films can be seen by the SEM images at the all fluencies of laser 4.77, 5.97, 6.36 and 5.57 J/cm^2. The results of XRD investigations showed that the diffractions patern of β-Ga_2O_3 transformed from the monoclinic phase with (-201),)-402(, and)-603(into orthorhombic phase with)002(,(004), and)006(when increased the fluency of laser. The energy bandgap decreased with the increase of laser fluencies, and the absorption peak was located in the UV region.

KEYWORDS: Gallium oxide Ga_2O_3 nanoparticles; distilled water; laser ablation; nanostructure.

الخلاصة

في هذا البحث تم تحضير أغشية رقيقة من الهياكل النانويةلاوكسيد الغاليوم β-Ga_2O_3 عن طريق القشط بالليزر النبضي في الماء المقطر (PLAL) على ركيزة الكوارتز بطريقة الصب بالتنقيط عند **90** درجة مئوية. تم استخدام ليزر Nd-YAG بطول موجة **1064** نانومتر ومعدل تكرار **5** هرتز. تم فحص تأثير زيادة كثافة طاقة الليزر على الخصائص التركيبية والبصرية بواسطة ، المجهر الإلكتروني النافذ (TEM)، مجهر القوة الذرية (AFM)، حيود الأشعة السينية (XRD)، المجهر الإلكتروني الماسح (SEM) ومجهر المطياف الضوئي (UV-VIS). أزاد الحجم البلوري لجميع العينات مع زيادة كثافة طاقة الليزر باستثناء الطاقة **5.57** جول\سم^2 كانت **9.78** نانومتر. تم ملاحظة تكوين الجسيمات النانوية ، جسيمات شبيهة بالمغزل ، الورقة النانوية والقلب-قشرة لـ β-Ga_2O_3 بواسطة صور TEM عند طلاقة الليزر **4.77** و **5.57** و **5.97** و **6.36** جول\سم^2 ، على التوالي. يمكن رؤية العناقيد النانوية والقضبان النانوية لكل لأغشية الرقيقة β-Ga_2O_3 بواسطة صور SEM عند كثافة طاقة الليزر **4.77** و **5.97** و **6.36** و **5.57** جول\سم^2. أظهرت نتائج تحقيقات XRD أن نماذج الحيود لـ β-Ga_2O_3 تحولت من الطور أحادي الميل مع (**201**-) ، (**402**-) ، (**603**-) إلى طور تقويمي التركيب مع (**002**) ، (**004**) ، و (**006**) عند زيادة كثافة طاقة الليزر. انخفضت فجوة الطاقة مع زيادة كثافة طاقة الليزر ، وكانت ذروة الامتصاص تقع في منطقة الأشعة فوق البنفسجية

INTRODUCTION

Numerous different polymorphs can be created from Ga_2O_3, which are assigned as α- ,*β-, γ- ,δ-, and ε -*Ga_2O_3 [1]. Out of all the available forms ,β-form is the most popular polymorph of Ga_2O_3. β-Ga_2O_3 is the only stable polymorph out of all the forms over a wide temperature *range till its melting point 1795* ºC. The remaining polymorphs are unstable and transform into the *β* form at temperatures above *750-900* ^{0}C. It is known that the properties of materials are highly dependent on the chemical nature and crystal structure in particularly, because of the overlapping of atomic or molecular orbitals to the components of the material. Solids consist of a large number of atoms, and they characterized by the existence of energy beams that are responsible for most of the physical and chemical properties for solids.

Nanomaterial's of a range of granular size between 1-100 nm, a group of atoms becomes so small that the power beams are modulated electronic hugely and differently, which strongly influences on alter all physical properties of materials [3]. Nanoparticles can be produced in different liquids media [4]. As well as, the PLAL is a novel method to produce nanoparticles biologically by using nanoparticles as food to the bacteria serrate [5]. Monoclinic gallium oxide semiconductor β-Ga_2O_3 possesses wide-band gap Eg = 4.9 eV, and possesses conduction, and luminescence properties, and thus has probable applications in optoelectronic devices which include flat-panel displays, solar energy transformation devices, optical limiter for ultraviolet, and high temperature stable gas sensors [6]. The preparation of Ga_2O_3 thin films have been finalized by low-pressure chemical vapor deposition (LPCVD) [7], mist chemical vapor deposition (mist-CVD) [8], metal-organic chemical vapor deposition (MOCVD) [9]. In this study, we reported a new method to demonstrate a great potential in controlling the shape of nanostructures by changing the laser fluency. Where the increase in laser energy led to the formation of nanostructures represented by nanoparticles, spindle-like, nanosheet and core-shell nanostructures of β-Ga_2O_3 without using toxic chemical methods [2, 3].

EXPERIMENTAL

To produce Gallium oxide Ga_2O_3 nanoparticles, a pellet of Gallium metal (99· 99%, purity) located at the bottom of quartz vessel, containing 2 ml of distilled water, was irradiated with the focused yield of fundamental wavelength (1064 nm) of nanosecond pulsed Nd :YAG laser, the quartz vessel was rotated with a stepper motor (6 rpm) to avoid the drilling effect due to laser ablation. The distance between the gallium (target) and the laser lens is 10 cm, the number of pulses is 1000pulses and repetition rate)5 Hz(as in Figure1 and2]10].

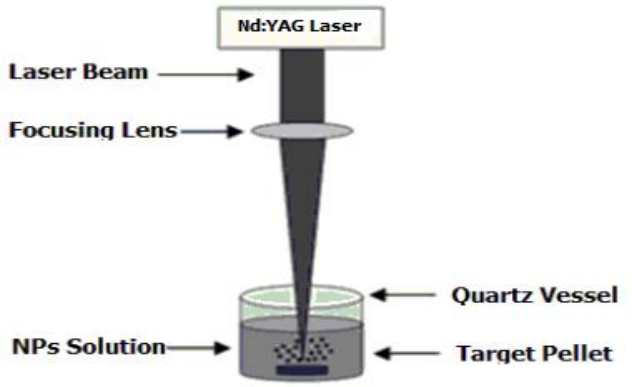


Figure 1. Colloid of β-Ga_2O_3 nanostructures formation by PLAL

A light yellow colored the colloidal solution was obtained after ablation. The quartz substrate are cleaned with distilled water and alcohol to remove grease and dust from them, and they are placed on a hot plate at a temperature of 90 ^{0}C and using a drop casting method**,** thin films are prepared as in figure (2).

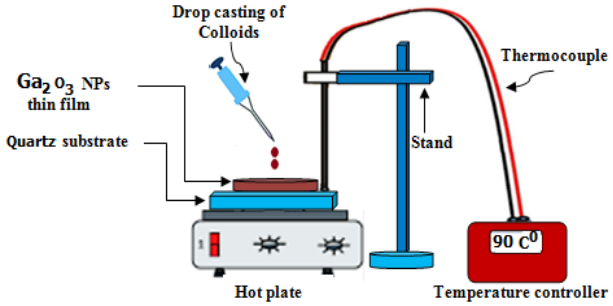


Figure 2. Drop casting method on a quartz substrate with a heater of β-Ga_2O_3 colloidal solution.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) spectra of β-Ga_2O_3 nanostructures thin films grown at various laser fluencies (4.77, 5.57, 5.97, and 6.36 J/cm^2). All the diffraction peaks in Figure 3 can be indexed to the polycrystalline structure according to the JCPDS card no. 00-043-1012 for β-Ga_2O_3 (a= 12.2213 Å, b= 3.0713 Å, c= 5.586 Å). It clearly shows that the crystalline structure of β-Ga_2O_3 nanocrystalline transformed from the β-Ga_2O_3 monoclinic phase with (-201), (-402), and (-603) into Ga_2O_3 orthorhombic phase with (002), 004), and (006) for all laser fluencies values.

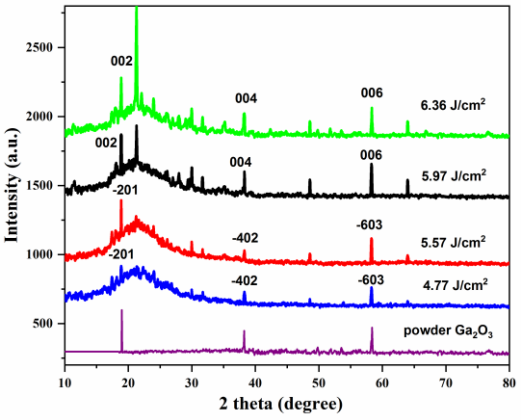


Figure 3. X-ray diffraction patterns of β-Ga_2O_3 nonostructure thin films at different laser fluencies ,)4.77, 5.57, 5. 97and 6. 36J/cm^2).

The crystallite size can be calculated from the Scherer equation, which is expressed as:

$$D = 094\lambda/\beta cos\theta \quad (1)$$

where (D) is the crystallite size, (θ) is the diffraction angle, (β) is the FWHM of diffraction peak, λ = 1.5406°A is the wavelength of Cu Kα radiation and Scherrer's constant is (K= *0.94*). Using the equation (1), the crystallite size of β-Ga_2O_3 was calculated for different fluencies of laser, as shown in Table 1.

The AFM images give some quantitative data about the surface roughness (R) and the maximum height of the β-Ga_2O_3 nanostructurs thin films were prepared at different laser fluencies, the films had a strong granular surface consisting of an irregular grain agglomeration of tens of nanometers as shown in Figures 4. surface roughness increases when the laser fluencies increase which is the result of the movement of the atoms or molecules on the film's surface]11[.

Table 1: Crystallite size at various laser fluencies of β-Ga_2O_3 nanostructure thin films.

Laser fluency (J/cm^2)	Crystallite size (nm)
4.77	33.6
5.57	9.78
5.97	74.7
6.36	*91*.4

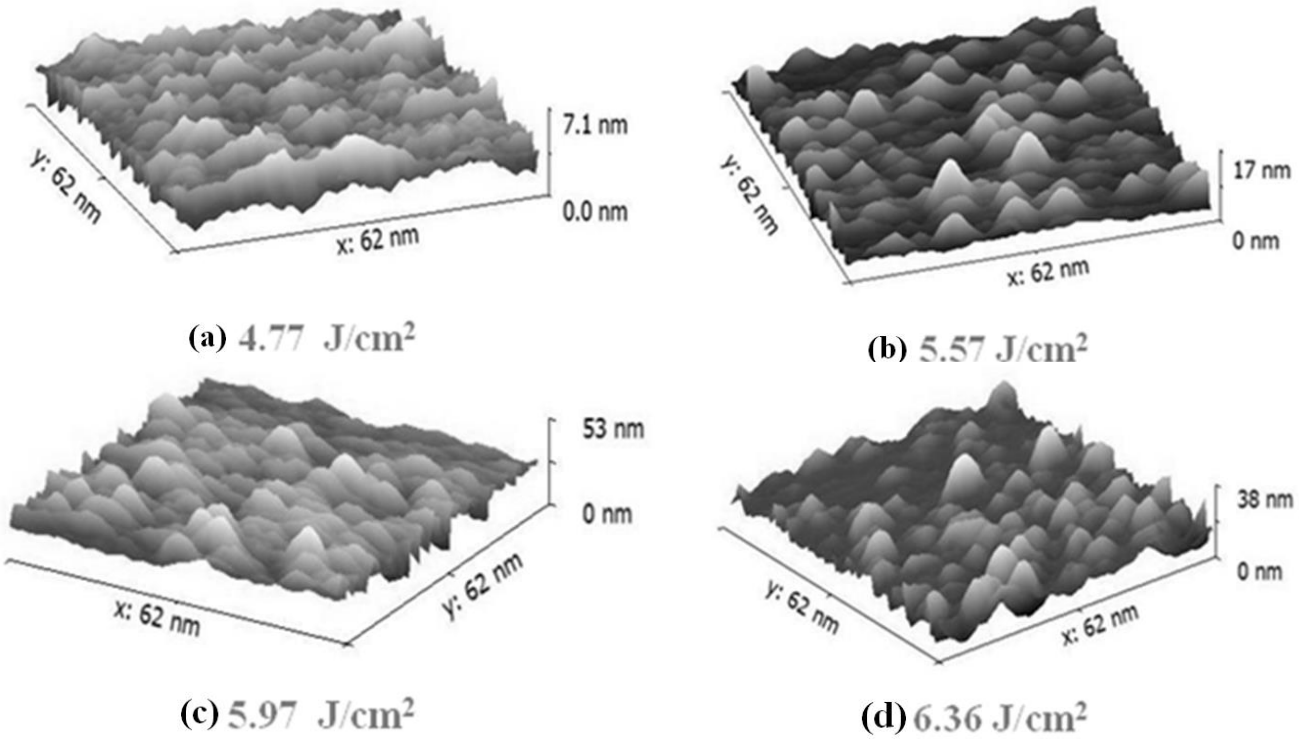


Figure 4. The AFM images of β-Ga_2O_3 nanostructure thin films prepared by increasing laser fluencies: ((a) 4.77, (b) 5.57, (c) 5.97 and (d) 6.36) J/cm^2.

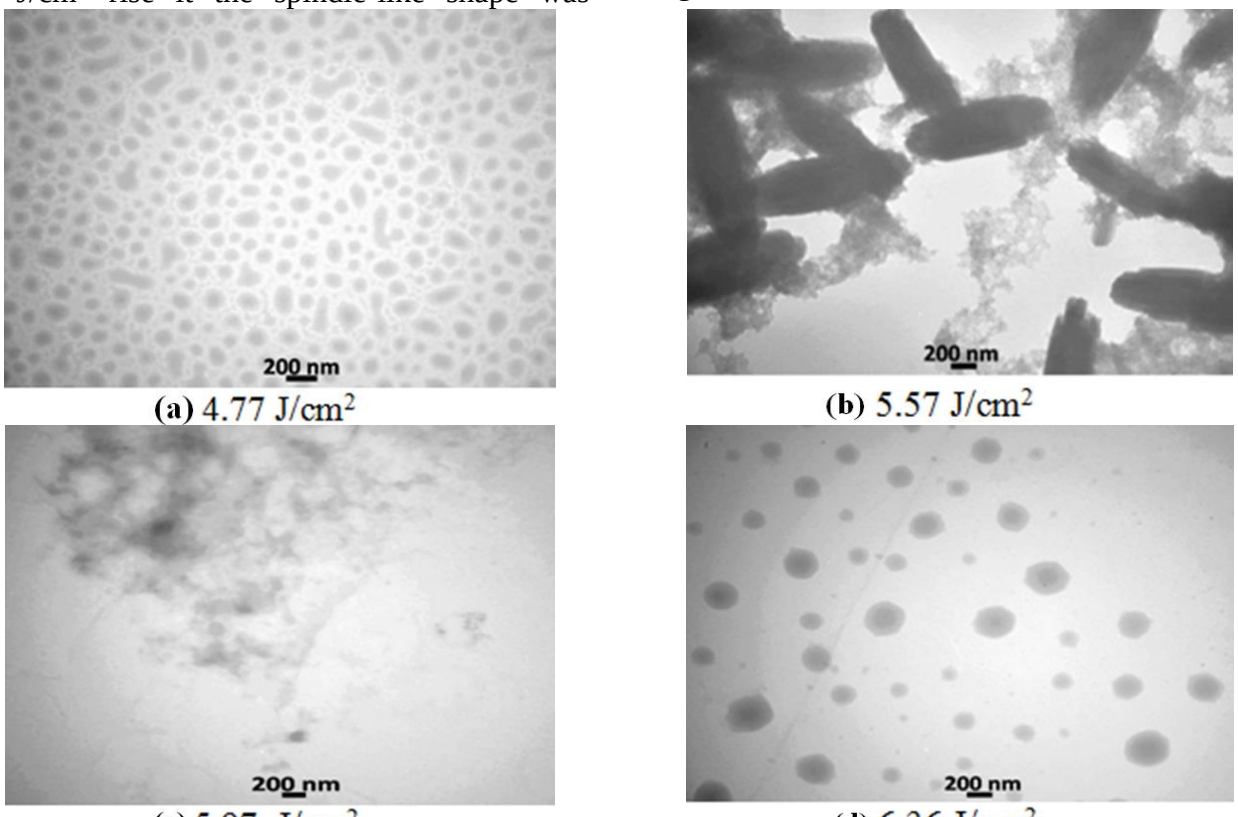
The obtained of surface roughness (R) values showed in Table 2.

Table 2. Morphological characteristics from AFM images for β-Ga_2O_3 nanostructure thin films

Laser fluency (J/cm^2)	Roughness (R) (nm)
4.77	3.537
5.57	40.84
5.97	5.421
6.36	9.581

In the Figure 5, noticed that the TEM images of β-Ga_2O_3nanostructures at various laser fluencies, (4.77, 5.57, 5.97 and 6.36 J/cm^2) respectively. At the laser fluency of about 4.77 J/cm^2, can observe that the produced nanoparticles are spherical without any assembly. At the laser fluency of about 5.57 J/cm^2 rise it the spindle-like shape was appeared. Small nanoparticles are formed with some clusters of these particles due to the aggregation with the increasing of laser fluencies. At the laser fluency of about 5.97 J/cm^2, can be observed of nanosheets structure, while formed a spherical core-shell nanoparticle at the fluency of about 6.36 J/cm^2.

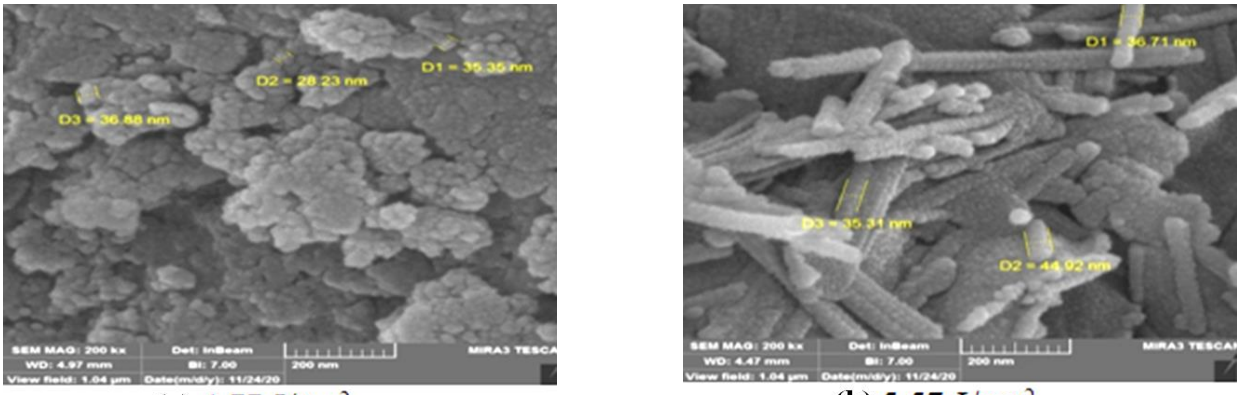
The heat deposition at 90^{o}C was affected strongly on the shape of the prepared films nanostructures, where the images of the SEM showed the aggregate of nanoparticles of β-Ga_2O_3 in nanometer size into cluster structure for the fluencies (4.77 and 6.36 J/cm^2). Also, for the fluencies (5.57 and 5.97 J/cm^2) were observed the formation of nanocorn-like and nanosheet structures, respectively, as shown in the Figure 6.



(a) 4.77 J/cm^2 (b) 5.57 J/cm^2

(c) 5.97 J/cm^2 (d) 6.36 J/cm^2

Figure 5.: TEM images of β-Ga_2O_3 nanostructure thin films at different laser fluencies ((a) 4.77, (b) 5.57, (c) 5.97 and (d) 6.36) J/cm^2).



(a) 4.77 J/cm^2 (b) 5.57 J/cm^2

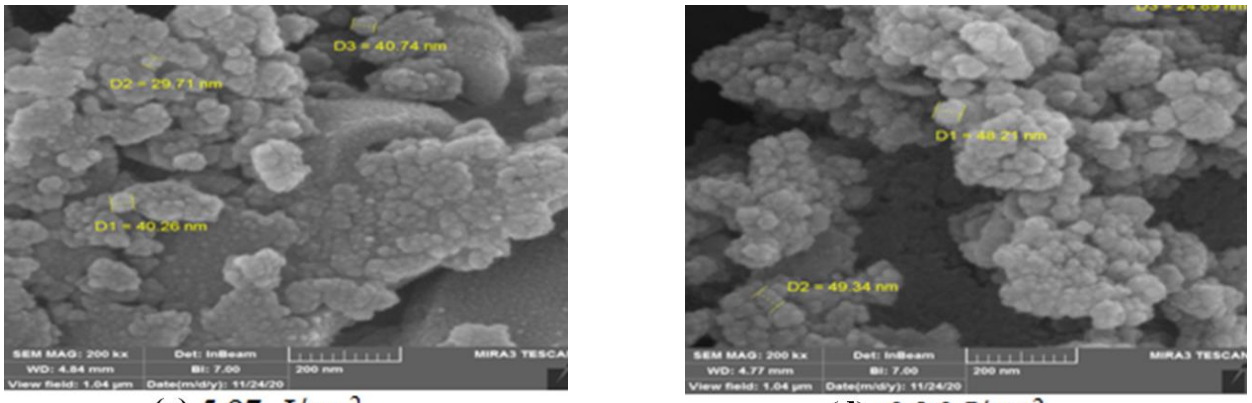


Figure 6. SEM images of β-Ga_2O_3 nanostructure thin films at different laser fluencies ((a) 4.77, (b) 5.57, (c) 5.97 and (d) 6.36) J/cm^2)

The transmittance spectra and absorbance as a function of the wavelength in the range between (***200***-1100) nm was investigated to the β-Ga_2O_3 nanostructure thin films. By increasing the laser fluencies, a decrease in transmittance can be observed in Figure 7-a, which is due to the increase in the surface roughness which causes scattering of the photons and increasing absorbance of the prepared films as shown in Figure 7-b.

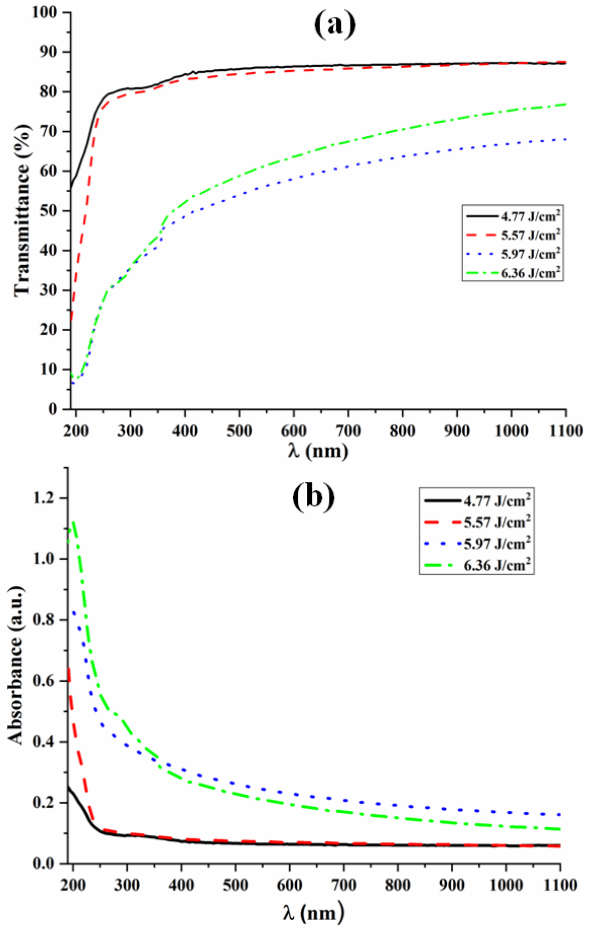


Figure 7. The optical transmittance spectra (a) and the absorbance spectra (b) of β-Ga_2O_3 nanostructure thin films at different laser fluencies (4.77, 5.57, 5.97 and 6.36 J/cm^2).

As the shapes of the formed nanostructures change with the increase of the laser fluency, the transmittance of the prepared samples is found to strongly depend on the aggregate shape. The prepared samples demonstrate more than 80% transmittance at wavelengths longer than 240 nm for the laser fluencies about of (4.77, 5.57 J/cm^2) and decreases sharply below 240 nm that is indicated to the light scattering of the films in this region as the laser fluencies increases [12]. The increasing in the laser fluency, the maximum peak of absorbance will increase due to the increase in the ablation process and crystallization improvement, which leads to an increase in the transfer of electrons from the valence band to the conduction band, and thus the absorbance value increases, as shown in Figure 8.

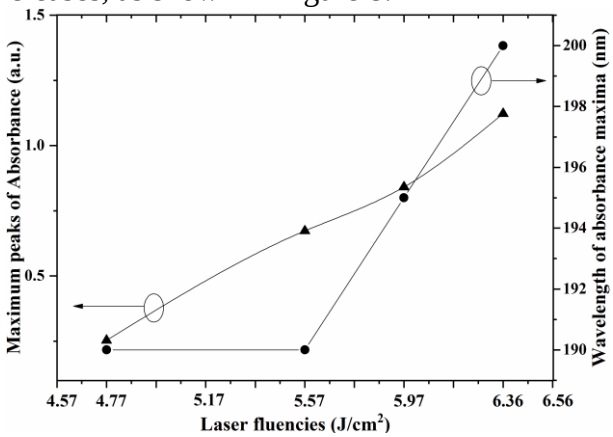


Figure 8: The peak and wavelength of absorbance maxima at different laser fluencies (4.77, 5.57, 5.97 and 6.36 J/cm^2).

As for the wavelength of absorbance maxima, at a fluency from 4.77 J/cm^2 to 5.57 J/cm^2, it is no

shifting in the wavelength and with increasing fluency from 5.57 to 6.36 J/cm^2, the shift to shorter wavelength in the UV rigin can be seen clearly. The optical energy gap of β-Ga_2O_3 is calculated from the model of Tauc [13]:

$$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^n \qquad (2)$$

where(α) absorption coefficient, (B)the transition constant is equal to one, (n) equal (1/2) for the allowed direct transition. The energy bandgap was determined by extrapolating the linear state of the plot of $(\alpha h\upsilon)^2$ versus ($h\upsilon$) on the energy axis, as shown in Figure 9.

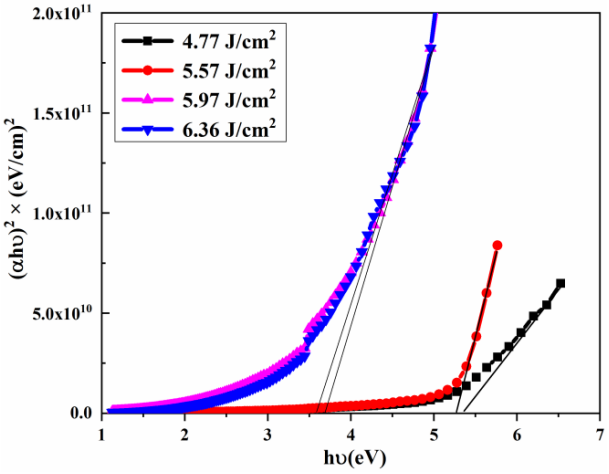


Figure 9: The optical band gap of β-Ga_2O_3 nanostructure thin films at different laser fluencies (4.77, 5.57, 5.97 and 6.36 J/cm^2).

For all samples, the energy band gap decreases when the laser fluencies increase, as shown in Table 3.

Table 3. The optical band gap of β-Ga_2O_3 nanostructures at different laser fluencies.

Laser fluency (J/cm^2)	Band gap (eV)
4.77	5.38
5.57	5.26
5.97	3.70
6.36	3.59

The quality of the prepared films decreases as the laser fluency increases, this study is promising evidence of the principle that the change in the laser fluency can be used in the band gap engineering, and opens the way for the fabrication of wavelength-specific optical electronic devices that work in the UV region.

CONCLUSIONS

According to the results obtained, PLAL is a technique by which the crystal structure phase of β-Ga_2O_3 nanoparticles transformed from monoclinic phase of β-Ga_2O_3 into orthotopic phase of Ga_2O_3 accompanied by an increase in the crystallite size when the laser fluency increases. Where the increase in laser energy led to the formation of nanostructures represented β-Ga_2O_3 NPs, spindle-like, nanosheet and core-shell nanostructures of β-Ga_2O_3 at the fluencies (4.77, 5.57, 5.97 and 6.36 J/cm^2) respectively, without using toxic chemical methods. More of the samples showed an increase in roughness when forming the nanostructures, which made this feature an entry in most applications of gas sensors. In addition, optical investigations of the prepared films showed that the maximum absorption values were within the ultraviolet region, and this could be used in the manufacture of UV-spectrum windows.

ACKNOWLEDGMENTS

This work was done with the possibilities available in the thin film laboratory, Department of Physics, College of Science, Mustansiriyah University, Baghdad, IRAQ.

REFERENCES

[1] S. B. Isukapati "Gallium Oxide Thin Films for Optoelectronic Applications", Master Thesis, Youngstown State University (2018).

[2] S.-D. Lee, K. Akaiwa, and S. Fujita, "Thermal stability of single crystalline alpha gallium oxide films on sapphire substrates", Phys. Status Solidi C, vol. 10, no. 11, pp. 1592–1595, Nov. 2013.

[3] A. Pyatenko, K. Shimokawa, M. Yamaguch, O. Nishimura, M. Suzuki (Synthesis of silver articles by laser ablation in pure water) Applied Physics A. 79. Issue 4-6 pp 803-806 (2004).

[4] Agool, Ibrahim R.; Mohammed, Nadheer J.; Abd Al-Meer, Harth M., "Synthesis and Characterization of CdTe NPs Induced by Laser Ablation in Liquids", Journal of Advanced Physics, Volume 6, Number 2, June 2017, pp. 241-247(7) (2017).

[5] Muslim, D.S.N.; Dham, Z.A.; Mohammed, D.N.J. Synthesis and characterization of nanoparticles conjugated tannase and using it for enhancement of antibacterial activity of tannase produced by Serratia marcescens. Microb. Pathog. 2017, 110, 484–493

[6] L. Binet, D. Gourier, J. Phys. Chem. Solids 59 (1998) 1241.

[7] Rafique, S.; Karim, M.R.; Johnson, J.M.; Hwang, J.; Zhao, H.P. LPCVD homoepitaxy of Si doped β-Ga2O3 thin films on (010) and (001) substrates. App. Phys. Lett. 2018, 112, 052104.

[8] Ma, T.C.; Chen, X.H.; Ren, F.F.; Zhu, S.M.; Gu, S.L.; Zhang, R.; Zheng, Y.D.; Ye, J.D. Heteroepitaxial growth of thick α-Ga2O3 film on sapphire (0001) by MIST-CVD technique. J. Semicond. 2019, 40, 012804.

[9] Oh, S.; Jung, Y.; Mastro, M.A.; Hite, J.K.; Eddy, C.R., Jr.; Kim, J. Development of solar blind photodetectors based on Si-implanted beta-Ga_2O_3.

Opt. Express 2015, 23, 28300–28305. [CrossRef] [PubMed]

[10] [10] Mohammed N, Dagher H F. Synthesis and Characterization of Mercuric Sulfide Nanoparticles Thin Films by Pulsed Laser Ablation (PLA) in Distilled Water (DW). IJMSE. 2020; 17 (3) :11-16.

[11] N. J. Mohammed, H. A. Ahmed, "Effect of Laser Fluence on Structural Transformations and Photoluminescence Quenching of Zinc Selenide Nanoparticles Thin Films", Al-Mustansiriyah Journal of Science, Volume 29, Issue 4, PP 122-127, 2018.

[12] Seyyedi, M., Rostami, A. & Matloub, S. Effect of morphology of nanoparticles on performance of transparent display. Opt Quant Electron 52, 308 (2020).

[13] J.W. Roberts, P.R. Chalker, B. Ding, R.A. Oliver, J.T. Gibbon, L.A.H. Jones, V.R. Dhanak, L.J. Phillips, J.D. Major, F.C.-P. Massabuau, Low temperature growth and optical properties of α-Ga_2O_3 deposited on sapphire by plasma enhanced atomic layer deposition, Journal of Crystal Growth, Volume 528, 2019, 125254.