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

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ABSTRACT

In this research, thin films of gallium oxide \( \beta\)-Ga\(_2\)O\(_3\) nanostructures were prepared by pulsed laser ablation in distilled water (PLAL). Then, deposited on quartz substrate by the drop-casting method at 90 °C. The Nd:YAG laser was used with a wavelength of 1064 nm and a repetition rate of 5 Hz. The effect of increasing laser fluences 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). Crystal size for all samples increased with the increasing the fluency of laser excepting at the fluency of laser 5.57 J/cm\(^2\). The results of XRD investigations showed that the diffractions pattern of \( \beta\)-Ga\(_2\)O\(_3\) transformed from the monoclinic phase with \( \{010\}\), \( \{001\}\), and \( \{002\}\) into orthorhombic phase with \( \{001\}\), \( \{004\}\), 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\(_2\)O\(_3\) nanoparticles; distilled water; laser ablation; nanostructure.

INTRODUCTION

Numerous different polymorphs can be created from Ga\(_2\)O\(_3\), which are assigned as \( \alpha\)-, \( \beta\)-, \( \gamma\)-, \( \delta\)-, and \( \varepsilon\)-Ga\(_2\)O\(_3\) [1]. Out of all the available forms, \( \beta\)-form is the most popular polymorph of Ga\(_2\)O\(_3\). \( \beta\)-Ga\(_2\)O\(_3\) is the only stable polymorph out of all the forms over a wide temperature range till its melting point 1795 °C. The remaining polymorphs are unstable and transform into the \( \beta\) form at temperatures above 750-900 °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 $\beta$-Ga$_2$O$_3$ possesses wide-band gap $E_g = 4.9$ 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$_2$O$_3$ 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 $\beta$-Ga$_2$O$_3$ without using toxic chemical methods [2, 3].

**EXPERIMENTAL**

To produce Gallium oxide Ga$_2$O$_3$ 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 1000 pulses and repetition rate 5 Hz (as in Figure 1 and 2) [10].

**RESULTS AND DISCUSSION**

X-ray diffraction (XRD) spectra of $\beta$-Ga$_2$O$_3$ 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 $\beta$-Ga$_2$O$_3$ (a= 12.2213 Å, b= 3.0713 Å, c= 5.586 Å). It clearly shows that the crystalline structure of $\beta$-Ga$_2$O$_3$ nanocrystalline transformed from the $\beta$-Ga$_2$O$_3$ monoclinic phase with (-201), (-402), and (-603) into Ga$_2$O$_3$ orthorhombic phase with (002), (004), and (006) for all laser fluencies values.
The crystallite size can be calculated from the Scherrer equation, which is expressed as:

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)

where \( D \) is the crystallite size, \( \theta \) is the diffraction angle, \( \beta \) is the FWHM of diffraction peak, \( \lambda = 1.5406 \text{Å} \) is the wavelength of Cu Kα radiation and Scherrer’s constant is \( K = 0.94 \).

Using the equation (1), the crystallite size of \( \beta \)-Ga\(_2\)O\(_3\) 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 \( \beta \)-Ga\(_2\)O\(_3\) nanostructures 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\(^1\)\(^1\).

### Table 1: Crystallite size at various laser fluencies of \( \beta \)-Ga\(_2\)O\(_3\) 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 3.** X-ray diffraction patterns of \( \beta \)-Ga\(_2\)O\(_3\) nanostructure thin films at different laser fluencies (4.77, 5.57, 5.97 and 6.36 J/cm\(^2\)).

**Figure 4.** The AFM images of \( \beta \)-Ga\(_2\)O\(_3\) 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.

| Laser fluency (J/cm²) | Roughness (R) (nm) |
|------------------------|---------------------|
| 4.77                   | 3.537               |
| 5.57                   | 40.84               |
| 5.97                   | 5.421               |
| 6.36                   | 9.581               |

Table 2. Morphological characteristics from AFM images for β-Ga₂O₃ nanostructure thin films.

In the Figure 5, noticed that the TEM images of β-Ga₂O₃ nanostructures at various laser fluencies, (4.77, 5.57, 5.97 and 6.36 J/cm²) respectively. At the laser fluency of about 4.77 J/cm², can observe that the produced nanoparticles are spherical without any assembly. At the laser fluency of about 5.57 J/cm² 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/cm², can be observed of nanosheets structure, while formed a spherical core-shell nanoparticle at the fluency of about 6.36 J/cm².

The heat deposition at 90°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-Ga₂O₃ in nanometer size into cluster structure for the fluencies (4.77 and 6.36 J/cm²). Also, for the fluencies (5.57 and 5.97 J/cm²) were observed the formation of nanocorn-like and nanosheet structures, respectively, as shown in the Figure 6.

Figure 5.: TEM images of β-Ga₂O₃ nanostructure thin films at different laser fluencies ((a) 4.77, (b) 5.57, (c) 5.97 and (d) 6.36 J/cm²).
The transmittance spectra and absorbance as a function of the wavelength in the range between (200-1100) nm was investigated to the β-Ga₂O₃ 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.

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/cm²) 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.

As for the wavelength of absorbance maxima, at a fluency from 4.77 J/cm² to 5.57 J/cm², it is no
shifting in the wavelength and with increasing fluency from 5.57 to 6.36 J/cm², the shift to shorter wavelength in the UV region can be seen clearly. The optical energy gap of β-Ga₂O₃ is calculated from the model of Tauc [13]:

\[ a h \nu = B (h \nu - E_g)^n \]  

where \(a\) 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 \((ah\nu)²\) versus \((h\nu)\) on the energy axis, as shown in Figure 9.

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

| Laser fluency (J/cm²) | 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-Ga₂O₃ nanoparticles transformed from monoclinic phase of β-Ga₂O₃ into orthotropic phase of Ga₂O₃ accompanied by an increase in the crystallite size when the laser fluence increases. Where the increase in laser energy led to the formation of nanostructures represented β-Ga₂O₃ NPs, spindle-like, nanosheet and core-shell nanostructures of β-Ga₂O₃ at the fluencies (4.77, 5.57, 5.97 and 6.36 J/cm²) 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.

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