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Cactus-like Gallium Oxide Nanostructure for Gas Sensor Applications

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ABSTRACT

Pulsed laser ablation technique in distilled water (PLAL) was employed to prepare colloid of spindle-like β-Ga_2O_3 nanostructure and then deposit on the quartz substrate by the drop-casting method to produce cactus-like β-Ga_2O_3 nanostructures at 90^0C. The Nd-YAG Q-Switched laser is the method to formation nanostructure from a gallium metal target by using a wavelength 1064 nm, the repetition rate of about 5 Hz and the fluency of laser about 5.57 J/cm^2. All the investigations of the Transmission electron microscope (TEM) and Scanning electron microscopy (SEM) showed that the formation of spindle-like β-Ga_2O^3 and cactus-like β-Ga_2O_3 nanostructures, respectively. X-ray diffraction (XRD) of the cactus-like β-Ga_2O_3 nanostructures was investigated with a crystallite size of about 9.78 nm. The formation of cactus-like β-Ga_2O_3 nanostructures is the result of transformation from the prepared spindle-like β-Ga_2O_3 nanostructures with the optimum fluency of laser of about 5.57 J/cm^2.

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

الخلاصة

تم استخدام تقنية القشط بالليزر النبضي في الماء المقطر (PLAL) لتحضير بنية نانوية شبيهة بالمغزل تم ترسيبها على ركيزة الكوارتز بواسطة طريقة الصب بالتقطير لإنتاج هياكل نانوية من الغاليوم اوكسايد β-Ga_2O_3 تشبه الصبار عند **90** درجة مئوية. ليزر Nd-YAG Q-Switched هو طريقة لتكوين البنية النانوية من هدف معدن الغاليوم باستخدام الطول الموجي **1064** نانومتر ، ومعدل التكرار حوالي **5** هرتز وكثافة طاقة ليزر حوالي **5.57** جول / سم ^{2}. أظهرت جميع التحقيقات الخاصة بالمجهر الإلكتروني النافذ (TEM) والمجهر الإلكتروني الماسح (SEM) تكوين تراكيب نانوية من الغاليوم اوكسايد β-Ga_2O_3 شبيهه بالمغزل وشبيهة بالصبار على التوالي. تم فحص حيود الأشعة السينية (XRD) للهياكل النانوية من اوكسيد الغاليوم الشبيهه بالصبار Ga_2O_2 بحجم بلوري يبلغ حوالي **9.78** نانومتر. إن تكوين الهياكل النانوية الشبيهة بالصبار من الغاليوم اوكسايد β-Ga_2O_3 هو نتيجة للتحول من الهياكل النانوية الشبيهة بالمغزل المحضرة بكثافة طاقة ليزر بحوالي **5.57** جول/سم ^{2}.

INTRODUCTION

Gallium oxide Ga_2O_3 exist in a different form, α–, β–, γ –, ε–, δ– and κ–phase [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 point1795 ^{0}C. The remaining polymorphs are unstable and transform into theβ form at temperatures above 750-900 C°]2[. Gallium oxide (Ga_2O_3) is a wide band gap (~5 eV) semiconductor material, wide band gap semiconductors present advantages over the polymers currently used for UV detection because of their intrinsic visible blindness, temperature stability, and enhanced radiation hardness [3] and is a promising candidate for novel applications in optoelectronic devices such as field effect transistors (FET) [4], gas sensors [5]. We propose a simple and inexpensive thermal oxidation process to produce Ga_2O_3 thin film and nanoparticle using by pulsed laser ablation in distilled water (PLAL) technique on quartz substrate because the influence of the oxidation parameters[6].

The present work enables us to obtain new nanostructures of β-Ga_2O_3 in an easy and low-cost method. These structures can be controlled and increase the surface reaction by controlling the laser fluency and substrate temperature used accessing nanostructures of cactus-like β-Ga_2O_3 nanostructures with a high surface reaction that can be used in a gas sensor application.

EXPERIMENTAL

Gallium oxide nanostructures were prepared using a gallium metal target (99.99%, purity) placed at the bottom of a quartz vessel containing 2 mL of distilled water, where a nanoscale solution was produced using an Nd-Yag laser of wavelength 1064 nm, frequency 5 Hz and laser fluency about 5.57 J/cm^2. The quartz vessel was in a state of rotation at a rate of 6 rpm in order to avoid the drilling effect produced by 1000 laser pulses, where the distance between the laser lens and the metal target is 10 cm. The solution was precipitated on a glass substrate at 90 °C to obtain a film of nanoscale material as shown in Figure 1 [7].

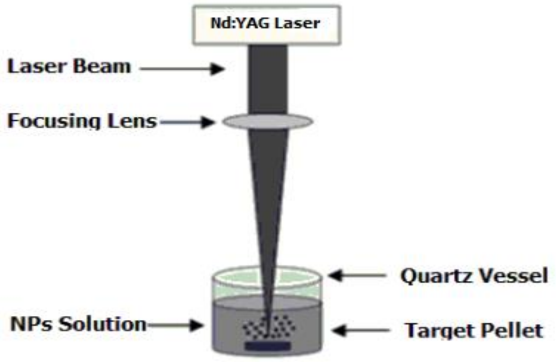

Figure 1. PLAL technique to produce a spindle-like β-Ga_2O_3 nanostructures.

As a result of ablated gallium metal, the suspension of spindle-like β-Ga_2O_3 nanoparticles clusters have a yellow color. This suspension precipitated on substrate of pre-prepared quartz, where they are placed on a hot plate with a precipitation temperature of 90 °C after which we obtain a new structure of cactus-like β-Ga_2O_3 thin film by the drop casting method, as shown in Figure 2.

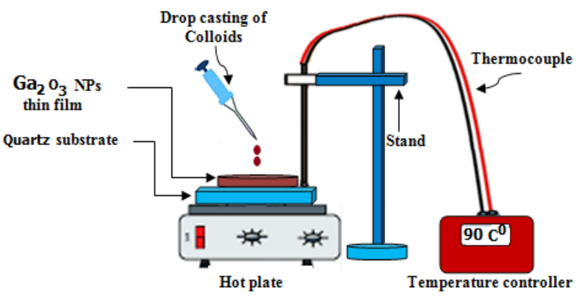

Figure 2. Drop casting method to produce cactus-like β-Ga_2O_3 nanostructures thin film on a quartz substrate at 90^{o}C.

RESULTS AND DISCUSSION

The crystallinity of the cactus-like β-Ga_2O_3 thin film prepared at the laser fluency and substrate temperature of about 5.57 J/cm^2 and 90^{o}C, respectively, can be investigated by the X-ray diffraction (XRD) spectra with the polycrystalline structure as shown in Figure 3. All the observed peaks indicated to the formation of β-Ga_2O_3 orthorhombic phase with (002), 004), and (006), when compared with the JCPDS card no. 00-043-1012 of β-Ga_2O_3 monoclinic phase with (-201), (-402), and (-603).

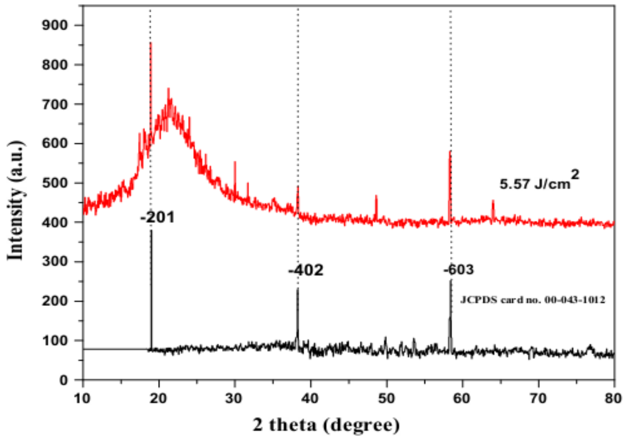

Figure 3. X-ray diffraction patterns of cactus-like β-Ga_2O_3 nanostructure thin films at the laser fluency 5.57 J/cm^2

The calculations of the crystillite size achieved by the Scherer equation [8], as follow:

$$D=0.94\ \lambda/\ \beta\ \cos\ \theta \qquad (1)$$

where (D) is the crystallite diameter, (θ) is the diffraction angle, (β) is the FWHM of diffraction peak, λ = 1.5406 Å is the wavelength of Cu Kα radiation and K = *0.94* is a Scherer's constant. The results of the calculations showed the formation of thin film with a crystallite size equal to about 9.78 nm.

The roughness factor has a great influence on the properties of the prepared film in terms of the application in which it was used. At the laser fluency 5.57 J/cm^2, we notice through the AFM images in Figure 4 the formed film has a high roughness (R) reaches about 40.84 nm that can be used in gas sensor applications.

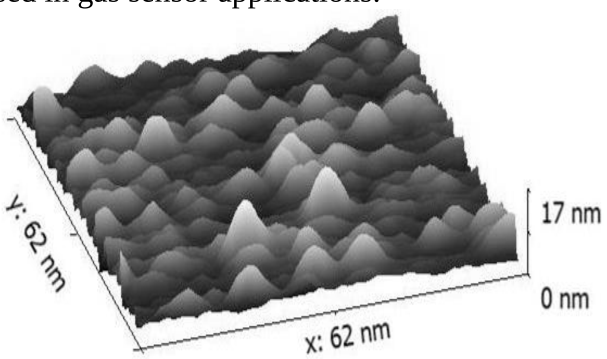

Figure 4. The AFM images of cactus-like β-Ga_2O_3 nanostructure thin films prepared at laser fluency (5.57J/cm^2).

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Obtaining a spindle-like β-Ga_2O_3 nanostructure from ablated gallium metal in distilled water was accomplished at an optimum laser fluence of about 5.57 J/cm^2. As the fluency of the laser has a strong effect on controlling, the shape of the nanomaterial when the target is irradiated and its material melted to transform into groups of nanoparticles, which then coalescence by the influence of the surrounding medium to produce spindle-like β-Ga_2O_3 nanostructures. As shown in Figure 5 of TEM images.

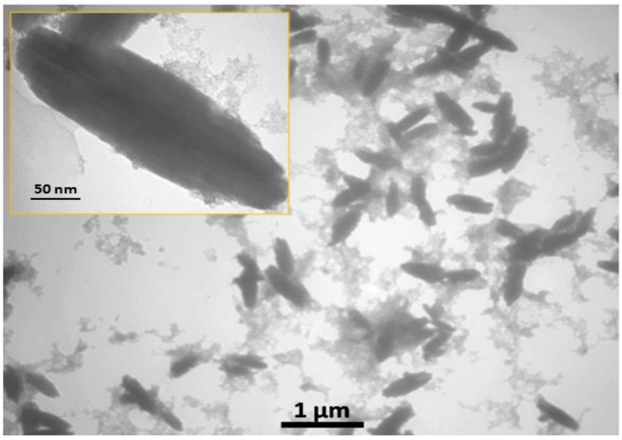

Figure 5. The TEM images of spindle-like β-Ga_2O_3 nanostructure colloids at laser fluency (5.57 J/cm^2).

Where the colloidal solution of the spindle-like β-Ga_2O_3 nanostructure was then deposited on quartz substrate at a temperature of 90 °C by the drop-casting technique to produce cactus-like β-Ga_2O_3 nanostructures and as seen from SEM images in the Figure 6.

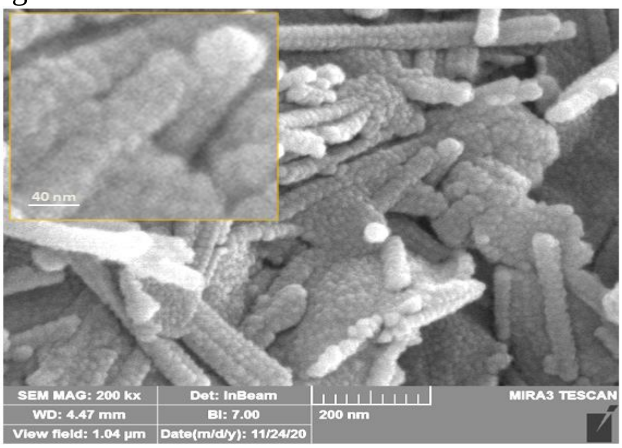

Figure 6. The SEM images of cactus-like β-Ga_2O_3 nanostructure thin films prepared at laser fluency (5.57J/cm^2).

The transmittance spectrum for the cactus-like β-Ga_2O_3 nanostructure thin film at the laser fluency 5.57 J/cm^2 is depicted in Figure 7. Above the absorption edge as in the spectrum of absorbance, then the transmittance is reach to more than 80%, suggesting that the assumption of little reflection or scattering. The transmittance at wavelength longer than the absorption edge 200 nm, seems to increase the transmittance, which could be due to decreased scattering or reflection from the cactus-like β-Ga_2O_3 nanostructure thin film which are crystalline.

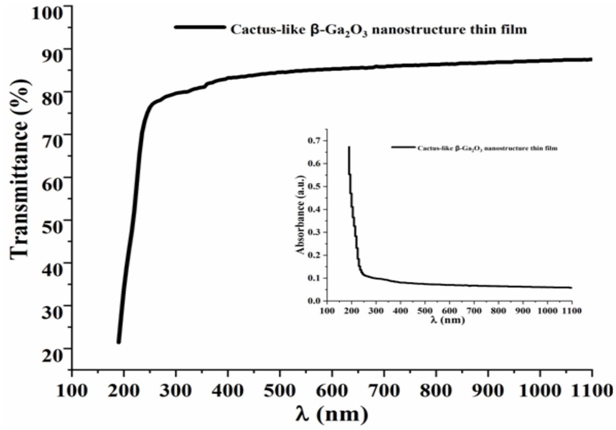

Figure 7. UV-vis transmittance and absorbance spectra of cactus-like β-Ga_2O_3 nanostructure thin films at laser fluency 5.57J/cm^2.

The Tauc model [9] was applied to calculate the optical energy gap for Ga_2O_3 from the eq. (2):

$$\alpha h\upsilon = B(h\upsilon - Eg)^{n} \quad (2)$$

where (α) absorption coefficient, (B) the transition constant is equal to one, (n) equal (1/2) for the allowed direct transition. The optical bandgap of a semiconductor film is an important indicator for voltage electronic device applications. The energy gap 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 8.

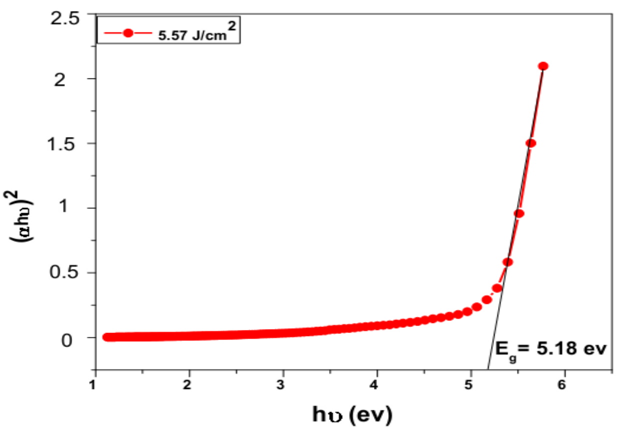

Figure 8. The energy gap of cactus-like β-Ga_2O_3 nanostructure thin films at laser fluency 5.57 J/cm^2..

The bandgap of Ga_2O_3 recorded is 5.18 eV which is larger than 4.84 eV [10]. A large bandgap enables a strong electric field making it possible to use a thinner device for a given voltage. The thinner the device, the lower is the on-resistance and thus high efficiency.

Sensing properties

The performance and efficiency of gas sensors are characterized by various parameters, including response, recovery time and sensitivity. The sensor response S (%) is defined as the ratio between the resistance difference with and without the gas molecules and the original resistance value of the sensor. The sensitivity of the prepared sensor of the cactus-like β-Ga_2O_3 nanostructure at laser fluency 5.57 J/cm^2, was taken place after measuring the thin film resistance in the absence of gas, and then measuring the resistance in the presence of gas as a function of time by applying the equation)3(:

$$S = \frac{R_g - R_a}{R_a} * 100\% \qquad (3)$$

Where R_a is the original resistance of the sensor in air, R_g is the resistance of the sensor when exposing to the gases and S is the sensitivity of the sensor [11]. All the variables of the sensitivity were recorded as shown in Table 1.

Table (1): The variables of sensitivity which was recorded at different concentration of ethanol (0.5, 0.4, 0.25 and 0.1 ppm) for the prepared film at laser fluency 5.57 J/cm^2 of cactus-like β-Ga_2O_3 nanostructure

Concentration (ppm)	Response time (s)	Recovery time (s)	Sensitivity (%)
0.5	70.5	59.3	28 %
0.4	70.5	78.3	21%
0.25	157	67	15,6 %
0.1	86	24.6	7.8 %

As shown in Figure 9, the investigation of the ethanol sensing performance of the cactus-like β-Ga_2O_3 nanostructure thin films was recorded. Different concentrations of ethanol were exposed to the prepared sensor ranging about (0.5, 0.4, 0.25 and 0.1 ppm).

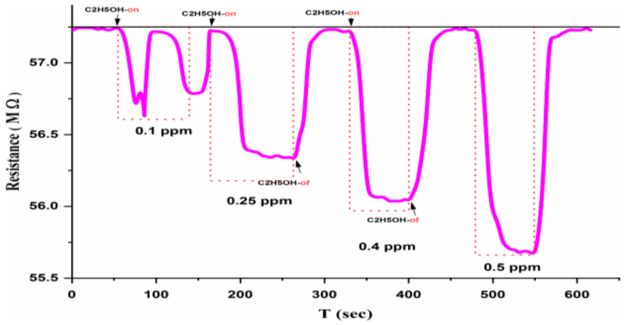

Figure 9. The response of cactus-like β-Ga_2O_3 nanostructure sensor to different concentrations of ethanol gas at laser fluency 5.57J/cm^2.

This sensor exhibited a high sensitivity to ethanol at 0.5 ppm and the sensitivity sensor was 28% at the working temperature of about 246 °C as shown in Figure 10.

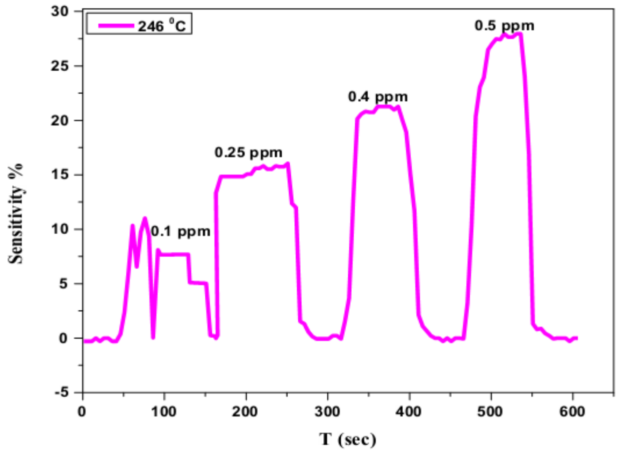

Figure 10 The sensitivity of the cactus-like β-Ga_2O_3 nanostructure thin films sensor to ethanol ranging from 0.1 to 0.5 ppm for 10 min.

CONCLUSIONS

In summary, we have synthesized a new nanostructure of spindle-like β-Ga_2O_3 in an easy and low-cost method. These structures of spindle-like β-Ga_2O_3 nanostructures thin film can be controlled and increase the surface reaction at the optimum laser fluency and substrate temperature of about 5.57 J/cm^2 and 90 °C, respectively, wich were used accessing nanostructures of cactus-like β-Ga_2O_3 nanostructures with a high surface reaction that can be used in a gas sensor application. A highly sensitive and inexpensive ethanol gas sensor fabricated on a quartz substrate and operated at 247 °C. Where the sensor depends on the formation of a new cactus-like β-Ga_2O_3 nanostructure to be highly sensitive reaching 28% when exposed to a small amount of ethanol of about 0.5 ppm. This makes the sensor very useful for the application in analyzing breath for diagnosing intoxicated drivers in addition to the more traditional use of sensitive workplace monitoring of gas leaks.

REFERENCES

[1] L. B. Cheah, R. A. Maulat Osman, "Ga_2O_3 thin films by sol-gel method its optical properties", AIP Conference Proceedings 2203, 020028 (2020).

[2] S.I. Stepanov, V.I. Nikolaev, V.E. Bougrov and A.E. Romanov, "Gallium oxide: properties and applications-A Review", Polytechnic University, (2015).

[3] A. V. Parisi, M. G. Kimlin, D. J. Turnbull, and J. Macaranas, "Potential of phenothiazine as a thin film

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dosimeter for UVA exposures," Photochemical & Photobiological Sciences, vol. 4, no. 11, p. 907, 2005.

[4] K. Matsuzaki, H. Yanagi, T. Kamiya, H. Hiramatsu, K. Nomura, M. Hirano and H. Hosono, "Field-Induced Current Modulation in Epitaxial Film of Deep-Ultraviolet Transparent Oxide Semiconductor Ga_2O_3," Applied Physics Letters, Vol. 88, No. 9, 2006, Article No. 092106. doi:10.1063/1.2179373.

[5] N. D. Cuong, Y. W. Park and S. G. Yoon, "Microstructural and Electrical Properties of Ga_2O_3 Nanowires Grown at Various Temperatures by Vapor-Liquid-Solid Technique," Sensors and Actuators B, Vol. 140, No. 1 2009, pp. 240-244. doi:10.1016/j.snb.2009.04.020.

[6] B. Alhalaili, R. Bunk, R. Vidu and M. Saif Islam, "Dynamics Contributions to the Growth Mechanism of Ga_2O_3 Thin Film and NWs Enabled by Ag Catalyst", (2019).

[7] N. Jassim Mohammed, H. Fakher Dagher, "Synthesis and Characterization of Mercuric Sulfide Nanoparticles Thin Films by Pulsed Laser Ablation (PLA) in Distilled Water (DW)", Thin Films Laboratory, College of Science, Mustansiriyah University, Baghdad, Iraq, (2020).

[8] H. G. Jiang, M. Ruhle and E. J. Lavernia, J. Mater. Res.14, 549 (1998).

[9] Ghose S., Rahman S., Hong L., Rojas-Ramirez J. S., Jin H., Park K., Klie R. and Droopad R. 2017 Journal of Applied Physics 122 095302.

[10] H. Peelaers and C. G. Van de Walle, Phys. Status Solidi B 252, 828 (2015).

[11] Long-Tsong Ju and Shr-Liang Ju, Enhanced oxygen gas sensor by surface-etched gallium oxide, International Journal of the Physical Sciences, Vol. 6(30), pp. 7016 – 7020, (2011).