Int. J. Electrochem. Sci., 10 (**2015**) 9742 - 9750

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

β-Ga_2O_3 Particles Formed of a Complex Organic by Electrolysis

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Received: 26 May 2015 / *Accepted:* 2 September 2015 / *Published:* 30 September 2015

β-Gallium oxide particles were obtained by electrolysis from a complex of gallium-carbohydrazide, using as electrolyte ethanol and subsequently annealing at 900 °C in N_2, O_2, or O_3 atmosphere during 1 hr. The particles were deposited on c-Si wafers for 30 minutes with a current density of 15 mA cm^{-2}. Heat treatment breaks down the complex and lead to the formation of Ga_2O_3, but the amount of oxide formed is modified according to the atmosphere of treatment. It is observed the semiconductor material formation in presence of oxygen, and to a lesser extent in nitrogen or ozone atmospheres. The influence of annealing atmosphere is reflected in the surface morphology and the optical properties of Ga_2O_3 particles, which were investigated by X-ray diffraction (XRD), energy dispersive X-ray (EDS), micro-Raman and UV-Vis spectroscopy.

Keywords: gallium oxide, electrolysis, x-ray diffraction, complex.

1. INTRODUCTION

Monoclinic gallium oxide (β-Ga_2O_3) is a wide band gap semiconductor, which has wide applications as optical windows, semiconducting laser, high-temperature stable gas sensor, dielectric thin film. Gallium oxide occurs in various structures like α, β, γ, σ, ε types, and the monoclinic β-Ga_2O_3 is considered to be the equilibrium phase [1-3]. The β-Ga_2O_3 possesses excellent optical properties, it is highly transparent in visible and near UV range of wavelengths and enhancement of

transmittance could be obtained by increase of oxide layer deposition temperature or appropriate annealing of crystals [4-7].

One of the parameters influencing the band gap is temperature annealing of deposited layer [8]. Recently, several groups have reported the growth of β-Ga_2O_3 by several methods as molecular beam epitaxy (MBE) [9,10], electron beam evaporation [11], spray pyrolysis, rf-magnetron sputtering, low-pressure flame, pulsed laser ablation [12]. There are other methods to obtain gallium oxide, the main ways are: chemical oxidation, thermal oxidation, anodic oxidation, plasma oxidation, etc. These oxidation processes use GaAs and GaN with sources of O_2, N_2O or CO_2, for the oxide formation [8]. The electro-crystallization from aqueous solution is a powerful technique for growing high-quality semiconducting oxides, and offers epitaxial growth as well as low-cost, low-temperature, and scalable process. Recently several binary oxides, such as ZnO, CeO_2, TiO_2, and Ag_2O_2, have been prepared electrochemically [13]. It has been reported that the oxidation of semiconductors using electrochemical anodic process is similar to typical process of oxide layer manufacturing in electrolyte. Anodic process is more efficient if in the semiconductor material holes occur (p type electrical conduction). For n type it is necessary to generate holes in order to get an oxidation; the best is using appropriate photon energy. After anodic process of GaAs there are a mixture of arsenic and gallium oxides, these layers of oxide should be annealed at high temperature (more than 450 °C), because of that high temperature those layers dissociate arsenic oxide and gallium oxide and become crystalline [8]. The anodic oxidation of n-type GaN under laboratory illumination at a constant current density of 5 $mA \cdot cm^{-2}$ and sodium tungstate electrolyte at 298 K was made by Pakes, and obtained an oxide non-uniform and texture with pore-like features [14]. On the other hand, has been reported the combustion synthesis for the production of InGaO powders using hydrazine and the combustion reaction occurred by heating the precursors between 150 and 200°C onto closed vessel filled with an inert gas (Ar) [15]. Recently Ghazali report a synthesis of β-Ga_2O_3 nanostructures over c-Si by electrochemical deposition using a mixture of Ga_2O_3, HCl, NH_4OH and H_2O [16], and K. Girija reports the preparation of β-Ga_2O_3 nanorods through reflux condensation process, with reflux at 90 °C of 12 hours, and to get a calcinations at 900 °C for 3 hours, indicating that there is a phase transition from α-Ga_2O_3 to β-Ga_2O_3 above 600 °C [17]. This document describes the synthesis of gallium complex by the electrolysis technique at room temperature, and we have demonstrated the easier crystallization of this complex to β-Ga_2O_3 particles with annealing at 900 °C in O_2 by an hour. The particles obtained were characterized by XRD, EDS, UV-Vis and micro-Raman spectroscopy.

2. EXPERIMENTAL

The particles were prepared by electrolysis with solutions 0.1 M of gallium nitrate hydrate ($Ga(NO_3)_3$, Aldrich 99.9 %) and 0.1 M of carbohydrazide (CH_6N_4O, Fluka 98 %) reagent grade chemicals and deionized water. As a substrate and anode, a boron doped p-type (100) c-Si wafer with 0.01-0.02 ohm-cm resistivity was used; the substrates were cleaned with xylene, acetone and methanol using an ultrasonic bath. The electrolytic process was carried out using as electrolyte 5 ml of ethanol (99.98%) and 5 ml of a solution prepared of gallium nitrate-carbohydrazide. A power source Keithley

model 2400 was used to deliver the controlled current, working with a constant current density (J) of 15 mA over 1.0 cm^2 of exposed area of the Si substrate for 30 min. After the electrolysis, the deposited material was dried at room temperature. The samples obtained with the same growth conditions were annealed in atmosphere of ozone, oxygen or nitrogen at 900 °C by an hour, in order to observe the effect in the structural and optical properties. The samples were characterized by XRD; with a diffractometer Bruker, AXS-D8 Discover (Cu Kα radiation). The Carl Zeiss Auriga 60, coupled with a Bruker Quantex instrument was using to analysis EDS. The ultraviolet-visible (UV-Vis) spectroscopy was made by an instrument Evolution 600 with a diffuse reflectance accessory and the studies of Micro-Raman were made using a spectrometer Jobin-Yvon (Horiba) with the 632 nm line of a He-Ne laser.

3. RESULT AND DISCUSSION

Figure 1 shows the XRD pattern of four samples; as synthesized and annealed in O_3, O_2 or N_2. The patterns corresponding to annealing samples show all the detectable diffraction peaks identified to β-Ga_2O_3 (according PDF card no. 01-076-0573) phase with lattice constants of a=1.223, b=0.304, c=0.580 nm and α=90°, β=103.7°, γ= 90°.

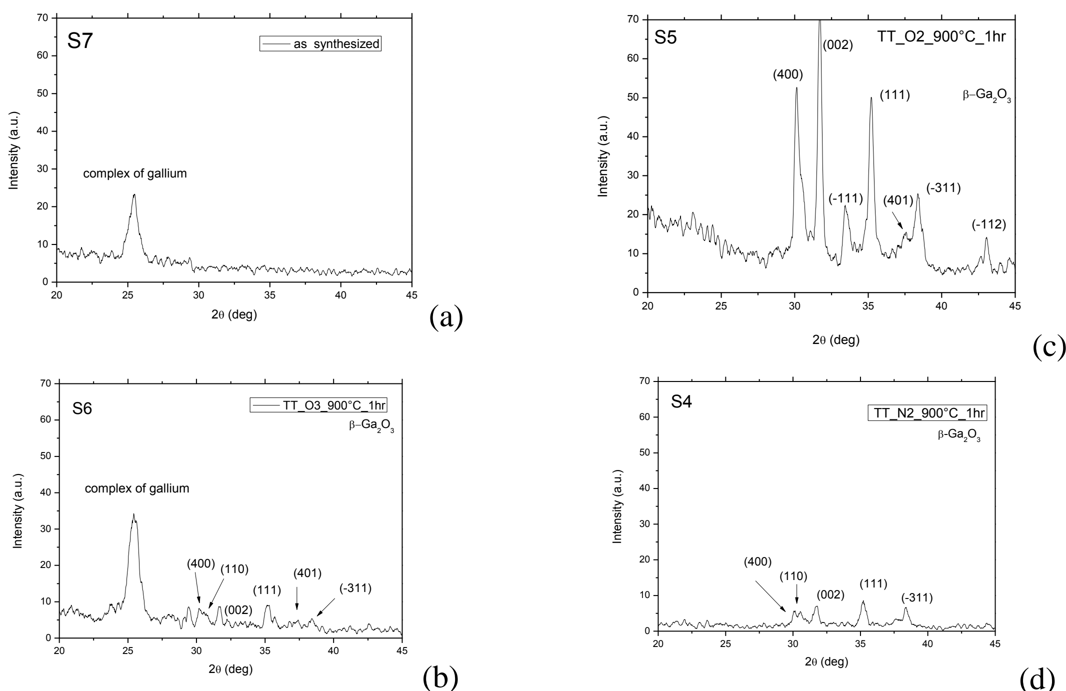
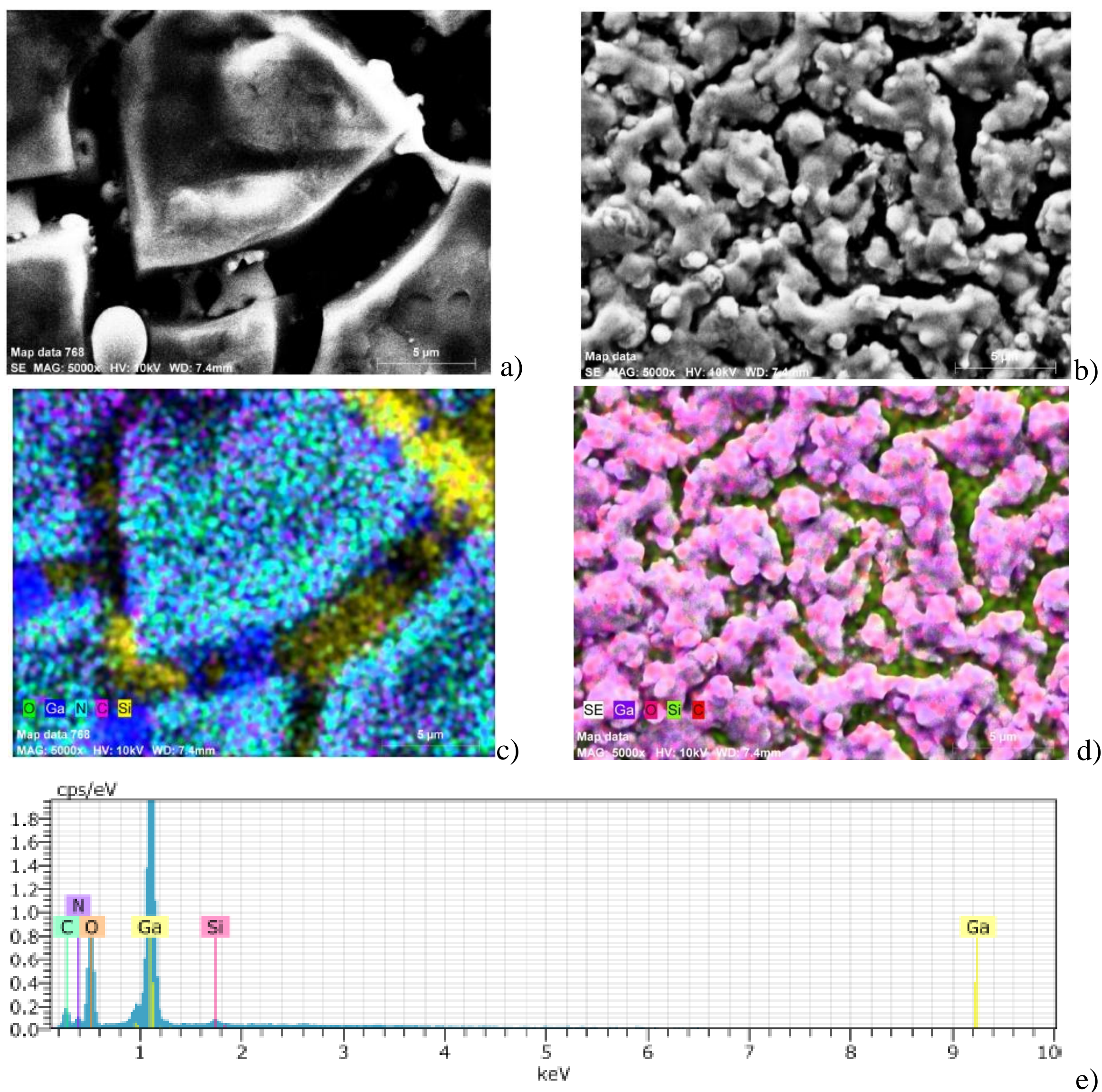


Figure 1. XRD patterns of samples obtained as synthesized (a), and with annealed at 900 °C in b) O_3, c) O_2 and d) N_2.

In the sample as synthesized (S7) (Fig. 1, a) there is a peak of diffraction at 2θ = 25°, which corresponds to the organic impurities deposited. The sample with annealing in ozone (S6) (Fig. 1, b) shows again the peak corresponding to the impurities deposited, in addition lines associated with the β-

Ga_2O_3 phase are observed. The samples annealed with nitrogen and oxygen (S4 and S5 respectively) only present peaks associated to β-Ga_2O_3. An important difference between XRD patterns is observed; the sample annealed in oxygen (S5) shows a major intensity (an order of magnitude higher), therefore a better crystalline quality. The dominant peak in the XRD pattern of sample with annealing in oxygen is β-Ga_2O_3 (002) with $2\theta = 31.7$ °corresponding to base-centered monoclinic structure.

The result of the analysis of EDS for the samples as synthesized and annealed in O_2 is shown in the Figure 2. In the pictures are observed two aspects, the first is the modification of the surface after the heat treatment applied and the second is the distribution of the atomic species contained in the material.



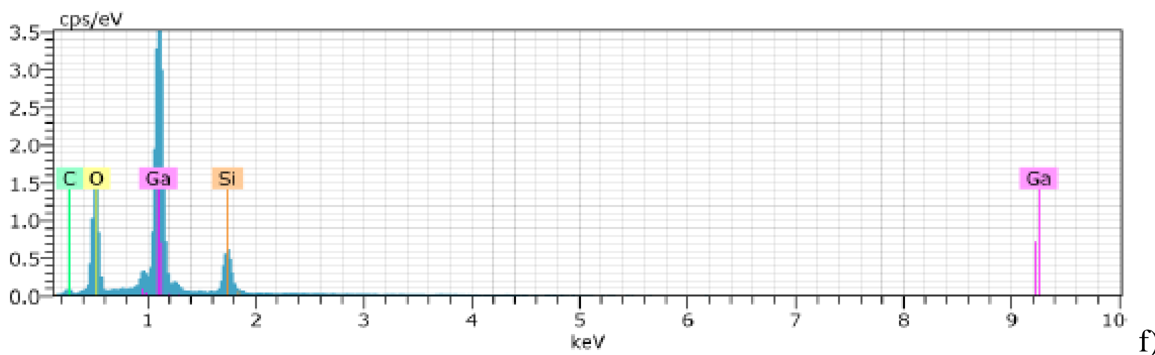


Figure 2. Pictures and EDS spectrum of samples as synthesized (a, c and e) and with annealed at 900 °C in O_2 (b, d and f)

In Figure 2 (a) is observed in the morphology of the sample as synthesized (S7) a texture in the form of plates, and Figure 2 (c) shows the distribution of atomic species that are present in the material, which are gallium, oxygen, nitrogen and carbon. There are three sites with a high concentration of gallium atoms in isolated regions, however this is an anomalous behavior, the characteristic distribution of the atomic species is homogeneous. The image of the sample with heat treatment in oxygen (S5) (Figure 2 (b-d)) shows a rough texture and the distribution of gallium and oxygen atoms is uniform. In the spectrum (Figure 2 (f)) the signal corresponding to the nitrogen is removed and the amount of carbon is significantly reduced, this indicates that these elements were desorbed with heat treatment.

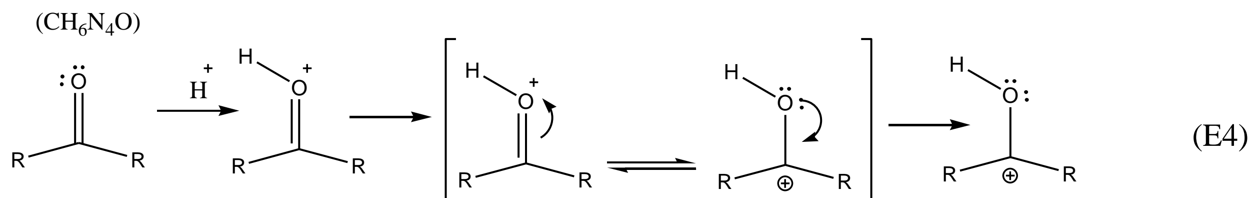
The growth of materials involves the process of precipitation, followed by nucleation and particle growth stage, during the growth stages of β-Ga_2O_3, the process of hydrolysis and condensation takes place [6]. In the electrolysis process it is carried out the precipitation of metal cations, carbohidrazyde and ethanol to obtain the complex of gallium, and it is proposed the following reaction mechanism: the gallium nitrate in water dissociates into gallium ions (Ga^{3+}), and the water provides hydroxyl ions (E1, E2).

$$Ga(NO_3)_3 + H_2O \rightarrow Ga^{3+} + 3NO_3^- \quad (E1)$$

$$H_2O \rightleftharpoons H^+ + OH \quad (E2)$$

The ethanol and carbohydrazide in the presence of H^+ generated ions (E3-E4).

$$2C_2H_5OH \leftrightarrow C_2H_5O^- + C_2H_5OH_2^+ \quad (E3)$$



The ion $N_4H_6C\text{-}OH^+$ is unstable and is considered that the positive charge moves to the atom carbon (E4).

Also it is known that carbohydrazide is an azotic ligand with lone electron pairs, and may coordinate with some metal ions as multidentate forming chelates. Carbohidrazide runs as a tridentade brinder that captures metal by the oxygen and nitrogen of NH_2 groups, as shown in Figure 3 [18].

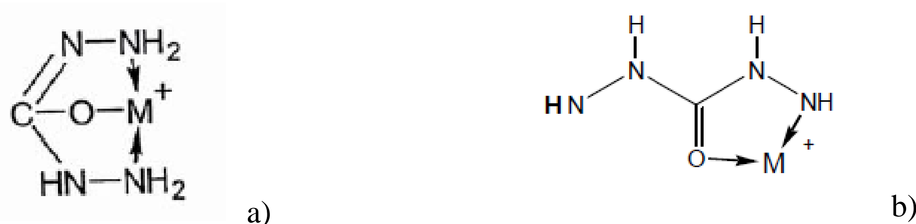


Figure 3. Metal-carbohydrazide complexes [18].

When is applied the current, the positive ions are directed towards the silicon surface and is formed the complex (carbohydrazide-gallium-ethanol).

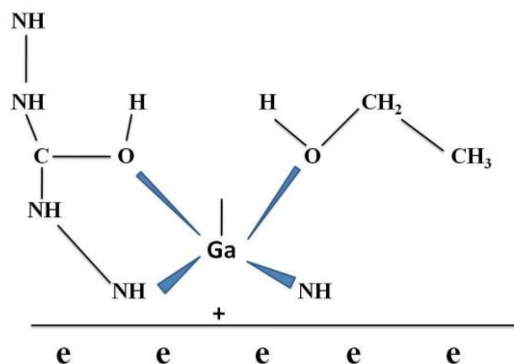


Figure 4. The complex carbohydrazide-gallium-ethanol proposed. Image taken and modified from A. Kagkelari [19].

It is reported that the geometry of the complexes is planar [19]. With applied thermal treatment is carrying out the hydroxylation of metallic ion and subsequent dehydration, forming products in phase gas, and on the surface β-Ga_2O_3 according to the following reaction (E5).

$$2\,[N_4H_6COH\text{-}Ga\text{-}OH\text{-}H_5C_2]_{(s)} + 9O_{2(g)} \rightarrow Ga_2O_{3(s)} + 7H_2O_{(g)} + 6CO_{2(g)} + 4\,N_{2(g)} \quad \text{(E5)}$$

The absorption spectra (Figure 5) clearly exhibit the changes in the absorbance edges corresponding to the energy band gap of β-Ga_2O_3. This semiconductor is a direct-band gap material and the optical band gap can be determined from absorption spectra. It obeys the relation $\alpha h\nu = A(h\nu - Eg)^{1/2}$, where A is a constant, Eg is the optical band gap, and α is the absorption coefficient. By extrapolating a plot of $(\alpha h\nu)^2$ versus hν to α=0, the optical band gap can be obtained. The as-grown sample (S7) shows gradual absorption at 250 nm, indicating that the sample is amorphous, also presents a change in 300 nm (*), which is due to the gallium complex deposited, it is known that the absorption characteristic of group -C=O (π*←n) takes place in 270-290 nm and corresponds to carbohydrazide [20]. The annealing samples in O_3, O_2 and N_2, shows a similar response, but the change in the absorption shifts towards lower wavelength, the signal in 300 nm disappears, the crystallization of the deposited particles were sensitive to the annealing temperature and atmosphere. The optical band gap of the as-grown, O_3, O_2 or N_2 (S6, S5 and S4 respectively) annealed samples are shown in the table 1, where the values in wavelength are approaching the value reported in the band gap of gallium oxide [11].

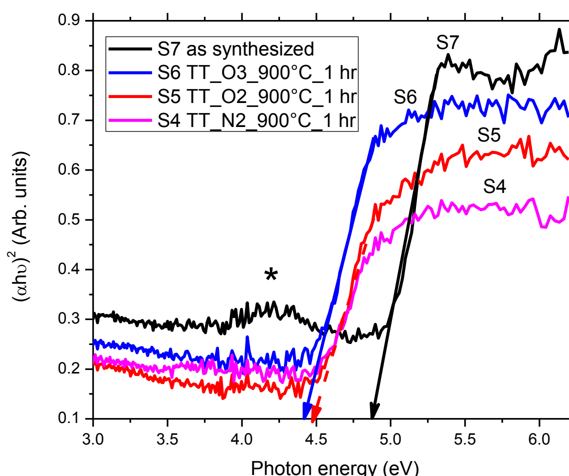


Figure 5. UV-Vis spectra of samples obtained as synthesized and with annealed at 900 °C in O_3, O_2 or N_2.

Table 1. Band gap values obtained

Sample	λ (nm)	Energy (eV)
As synthesized (S7)	250	4.93 eV
Annealed at 900 °C in O_3 (S6)	280	4.41 eV
Annealed at 900 °C in O_2 (S5)	277	4.48 eV
Annealed at 900 °C in N_2 (S4)	277	4.48 eV

The Raman spectra obtained of the samples are shown in Figure 6. All spectra show a signal at 304 cm^{-1} which corresponds to the substrate. The Raman lines active for β-Ga_2O_3 are at 104.7, 163.5, 202.3, 315.8, 339.7, 420.2, 459.4, 607.1, 656.1 and 757.7 cm^{-1} corresponding to the modes of optical vibration [21]. In the samples with thermal annealing can be seen a low intensity signal in 203 cm^{-1}, this value is so close to theoretical value reported characteristics of the monoclinic Ga_2O_3, the intensity is slightly higher in the sample with annealing in oxygen.

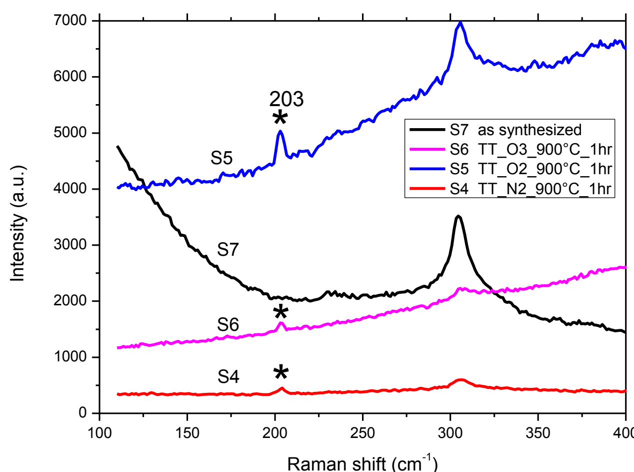


Figure 6. Micro-Raman spectra of samples obtained as synthesized and with annealed at 900 °C in O_3, O_2 or N_2.

4. SUMMARY

It was synthesized and investigated gallium complex on silicon substrates by electrolysis with gallium nitrate as precursor. The particles obtained were complex amorphous and the annealing to 900 °C with oxygen enhances their crystallization. The material obtained was β-Ga_2O_3 with crystalline monoclinic phase and high purity, evidenced from the XRD and Raman analysis. It is proposed that during the process of electrolysis a carbohydrazide-gallium-ethanol organic complex was formed, to according the analysis of EDS and UV-Vis spectroscopy. The temperature and annealing time used in this growth process were lower with respect to the required in another technique.

ACKNOWLEDGEMENTS
The authors wish to thank the VIEP-BUAP for the support given to the development of this project.

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