

Synthesis and Characterization of Monoclinic Gallium Oxide Nanomaterials for High-Concentration Ethanol Vapor Detection

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Abstract. This study was conducted to synthesize Gallium Oxide nanomaterials from its bulk form using a low-cost and repeatable method and investigate on its potential as sensing element for Ethanol (EtOH). Horizontal Vapor Phase Growth (HVPG) Technique was utilized to synthesize monoclinic Gallium Oxide (β -Ga₂O₃) nanowires. Images obtained from the Scanning Electron Microscope showed high density nanowires specifically in the area of highest temperature gradient. SEM also showed that the grown structures using HVPG Technique were at the nanoscale with diameters ranging from 51.60 to 908.38 nm. Higher surface-to-volume ratio was also noted in the area of highest temperature gradient which was subjected to an applied magnetic field. The Gallium to Oxygen ratio was verified via EDX to be approximately 2:3 which agrees with the atomic ratio of Ga₂O₃. The monoclinic structure of the grown nanomaterials was investigated using Raman Spectroscopy. Raman peaks of the samples were at 199 and 486 cm⁻¹ which was accounted to the presence of two Raman-active modes of the b-polymorph of Ga₂O₃. The Raman spectrum of the grown nanowires confirmed that the material is monoclinic in structure and belongs to C_{2/m} space group. The I-V Curve of the grown nanowires were also determined using two-point probe which illustrates a non-linear curve similar to that of a semiconductor material. Furthermore, additional fundamental properties such as resistivity and specific conductance of the materials were also determined via van der Pauw Technique. Results showed that the material has high specific conductance and low resistivity. The synthesized nanomaterial was responsive to Ethanol vapor. Exposure to the said compound increased its resistance. Graphs showed that there is a significant increase in the resistance after exposure to ethanol vapor.

1. Introduction

The synthesis of functional metal oxide nanomaterials has been widely studied due to its extensive potential especially in gas sensing. Semiconducting metal oxide nanostructures that are one-dimensional exhibits unique properties in chemical, optical, electrical and gas sensing. Due to high surface-volume ratio, nanomaterials have higher sensitivity and exhibit more surface reaction. The significant number of surface atoms is also accountable for greater sensitivity and selectivity which is a relevant factor in gas sensing applications. [1, 2] The use of nanotechnology for gas sensing devices results to lower power consumption and ease of use due to its compactness and portability. [3] Studies on Gallium Oxide, a wide-bandgap conductive oxide, are in the early stages, thus, very few reports are made about its crystal growth and material properties.



Successful synthesis of Gallium Oxide nanoparticles using various methods are reported, which include arc discharge, evaporation, and heating. [4, 5] The nanoscale Ga_2O_3 produced showed properties which are distinct from the bulk form. Five polytype of Gallium Oxide have been confirmed. These are denoted α , β , γ , δ and ϵ . The widely studied polytype is the β -polytype which is usually formed into a monoclinic crystal and stable material after undergoing annealing procedure. [6] The monoclinic Gallium Oxide has several useful characteristics, especially the wide bandgap of 4.8-4.9 eV and exhibits a good chemical and thermal stability which makes it an ideal material for gas sensors. [7] The gas sensing properties of the material synthesized in this study was described using Ethanol vapor obtained via static headspace gas sampling.

This paper reports the result of the synthesis of Gallium Oxide nanomaterials from its bulk form using a low-cost and repeatable method such as Horizontal Vapor Phase Growth (HVPG) Technique and investigate its potential as sensing element for Ethanol (EtOH) vapor.

2. Experimental Details

2.1. Synthesis of β - Ga_2O_3

Horizontal Vapor Phase Growth Technique, patented by Santos, et al, was used in the synthesis of the nanomaterial. The method employs a vapor-solid mechanism. Gallium Oxide bulk powder obtained from Sigma-Aldrich was contained in a fused silica quartz tube sealed under high-vacuum system while the pressure was maintained at approximately 1×10^{-6} Torr. Half of the sealed tube was placed in a horizontal tube furnace while the other half extending outside was subjected to a magnetic field (figure 2) to enhance the morphology of the crystal growth. [8] The temperature gradient created a path for the vapor deposition and the crystal growth was expected to be observed on the tube's inner walls at the region of relatively lower temperature. The growing time was set to 8 hours at growth temperature of 1200°C . The furnace was programmed at a ramp time (Δt) of 40 minutes as shown in figure 1. Samples from the two zones indicated in figure 2 were collected for characterization.

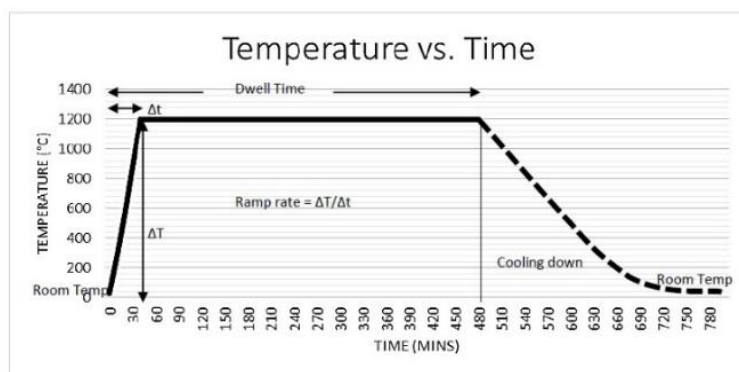


Figure 1. Temperature profile of the horizontal tube furnace with the ramp rate (Δt) set at 40 minutes and maximum temperature of 1200°C at 8 hours' dwell time.

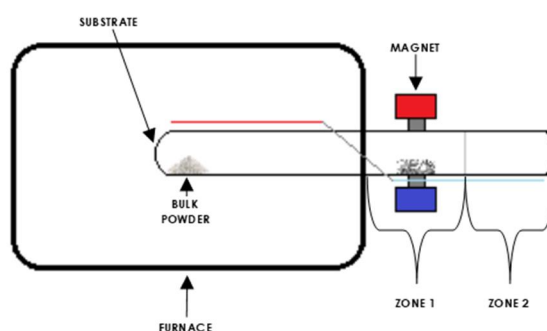


Figure 2. Diagram of the setup in synthesizing the nanostructures.

2.2. Characterization of the Grown Nanomaterials

Phenom Pro Desktop Scanning Electron Microscope was used to capture the SEM micrographs of the samples from zones 1 and 2. Data obtained from the surface morphology analysis were processed in Image J to determine the size and distribution of the as-grown nanomaterials on the inner surface of the substrate.

The samples were analyzed under EDX for elemental composition analysis. The obtained results were used to identify the elements found on the substrate and determine the Gallium to Oxygen atomic ratio.

Van der Pauw (vdP) technique, a general four-point probe technique, was employed to calculate the Resistivity and Specific Conductance of the arbitrarily-shaped samples. Using Keithley Source Measure Unit 2450 four-point probe, the voltage was measured across the substrate. From the readings obtained, Resistivity and Specific Conductance were calculated. Current-Voltage (I-V) curve of the same samples were obtained using Keithley Source Measure Unit 2450 two-point probe. Voltage sweep from -5 volts to +5 volts was graphed.

Raman spectrum of the grown Ga_2O_3 nanomaterials was determined to verify its crystal structure. The Raman peaks identified were cross-referenced with the gathered literatures about fabrication of $\beta\text{-Ga}_2\text{O}_3$.

The gas sensing property, specifically its sensitivity to high percent-by-volume concentration of Ethanol was investigated by measuring the change in resistance of the material when exposed to ethanol vapor. The gas sample was prepared via static headspace gas sampling and the resistance change was recorded using a Keithley Source Measure Unit 2450. Attributes investigated includes response time and sensitivity to the target gas.

3. Discussion

Gallium Oxide nanowires were grown using Horizontal Vapor Phase Growth Technique. SEM micrographs of the samples obtained from the two zones (figure 4) showed significant change in the morphology of the bulk (figure 3) samples after undergoing HVPG Technique. High-density nanowires were found in Zone 1. It was noted that this area has the highest temperature gradient and was also under the effect of an applied magnetic field. These two factors noted were noted to be accountable for the crystal growth zone preference. [8] This factor also contributed to the greater amount of yield in terms of the density of nanostructures found.



Figure 3. SEM micrographs of Gallium Oxide bulk powder.

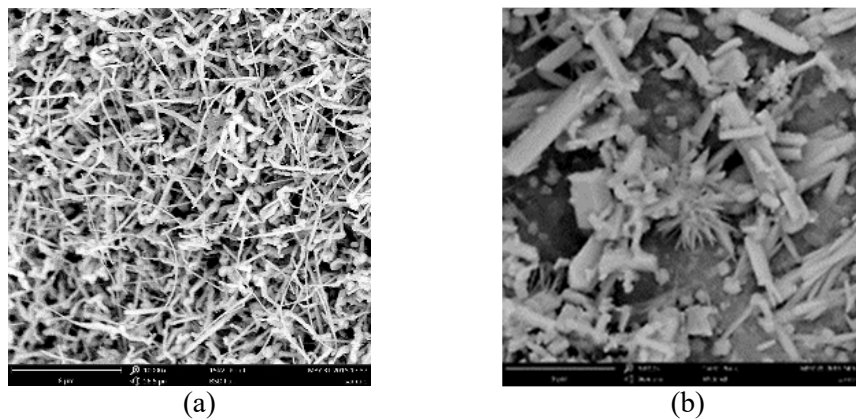


Figure 4. SEM Micrograph of as-grown nanomaterials (a) Zone 1 (b) Zone 2.

Structures deposited in Zone 1 have diameters ranging from 51.60 – 908.38 nm with an average diameter of 237.50 nm. Most of the wires have diameter of 206.50 nm extending up to 435,019.36 nm. On the other hand, structures grown at Zone 2 have measurements between 2000 – 86,800 nm and mean diameter of 19,058.58 nm. A large number of particles have diameter of 16,400 nm in the said zone with maximum span length of 200,802.26 nm.

Higher surface-to-volume ratio was also noted in this area as compared to Zone 2. Note that this zone was subjected to applied magnetic field and the area of highest temperature gradient. The parameters employed to enhance the morphology of the nanowires included the use of 0.25 T variable gap neodymium magnet applied at the region closest to the middle of the tube. In the literature cited, the magnet was positioned in the region near the highest temperature gradient. The presence of the applied magnetic field was noted to assist the growth mechanism from the bulk material which enhanced its morphology. [8]

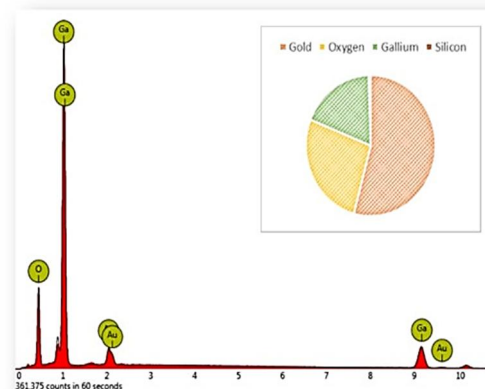


Figure 5. EDX Spectrum of Zone 1 showing peaks of Ga, O, and Au and corresponding pie chart.

Phenom XL Energy Dispersive X-ray Spectroscopy was used to investigate the materials elemental composition. Results confirmed the presence of Gallium, Oxygen and traces of Gold and Silicon found in Zone 1 which is shown in figure 5. Specifically, Zone 1 showed an atomic concentration of 26.65% Gallium, 38.17% of Oxygen and 35.19% of Gold. The traces of Gold atoms were attributed to the Gold sputtering during the sample preparation prior to the analysis, while the traces of Silicon were attributed to the substrate for the nanomaterials synthesis. The Gallium to Oxygen ratio was verified to be approximately 2:3 which agrees with the atomic ratio of Ga_2O_3 .

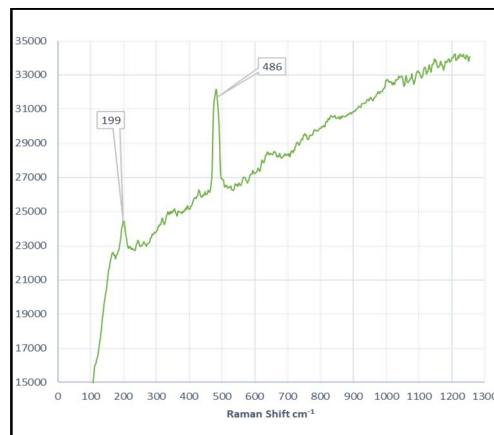


Figure 6. Raman Spectrum of Ga_2O_3 nanowires obtained from Zone 1 synthesized via Horizontal Vapor Phase Technique.

Raman scattering measurements were done using a laser with a wavelength of 565 nm to further investigate the structure of the synthesized nanomaterials. Fifteen Raman modes are expected in the vibrational spectrum of a β -polytype Ga_2O_3 which belongs to the space group $C2/m$ [9]. The Raman-active modes of this polytype are clustered into three groups of frequencies: the low frequency liberation and translation of tetrahedron-octahedron chains with peaks below 200 cm^{-1} , the mid frequency deformation of Ga_2O_6 octahedron with peaks 310 to 480 cm^{-1} and high frequency stretching and bending of GaO_4 tetrahedron whose peaks are found at 500 to 770 cm^{-1} . [10]. Figure 6 shows the Raman spectrum of the grown nanowires synthesized via HVPG Technique deposited on the Silica quartz tube. The position of the sharp peaks at 199 and 486 agrees with the reported Raman peaks in literature for β - Ga_2O_3 . The peak at 199 means that the nanomaterial exhibited the liberation and translation of tetrahedron-octahedron chains. Raman scans also detected the presence of deformation of Ga_2O_6 octahedron chains. The peaks detected in the synthesized nanomaterial also imply that the crystal structures belong to the $C2h$ group symmetry, hence the nanomaterial grown is confirmed to be a β -polytype.

I-V characterization was conducted at room temperature via a two-point probe using Keithley Source Measure Unit. The voltage sweep was set to 200 points and varying the source voltage from -5 to 5 V. The corresponding change in the current was automatically recorded and plotted in a graph using the SMU. Graph is non-linear and resembles the curve of a semiconductor diode. As shown in figure 7 the material has forward and reverse characteristics.

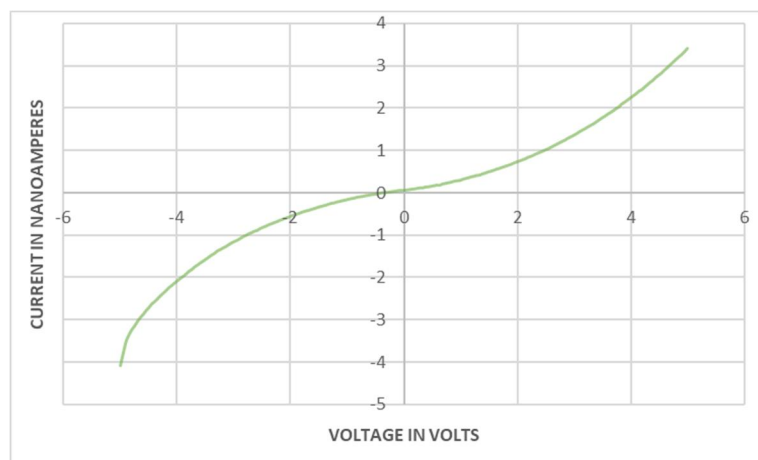


Figure 7. I-V Curve of Ga_2O_3 nanowires obtained from Zone 1.

Four-point probe measurements carried out on the samples also provided additional evidence of the fundamental electrical property of the nanomaterials. Since the sample is an arbitrarily-shaped material, voltage measurements was measured in eight permutations. Volume resistivity specific conductance was expressed in SI unit ohm-meter and Siemens per meter respectively. Results of the vdP Technique shows that the resistivity of the Ga₂O₃ nanomaterials grown in the Silica quartz tube substrate has a low resistivity and very high specific conductance. The materials tested have an average of $4.61 \times 10^{-6} \Omega\text{m}$ volume resistivity and an average of 2.17×10^5 specific conductance.

Investigation on the synthesized nanomaterial's potential use for gas sensing application was conducted at room temperature. Ethanol vapor sensitivity of the synthesized nanomaterial was tested against the headspace gas obtained from 99.99% Ethanol. The exposure time was set to 90 seconds. Using Keithley 2450 SMU, a Resistance vs Time graph was recorded as shown in figure 8.

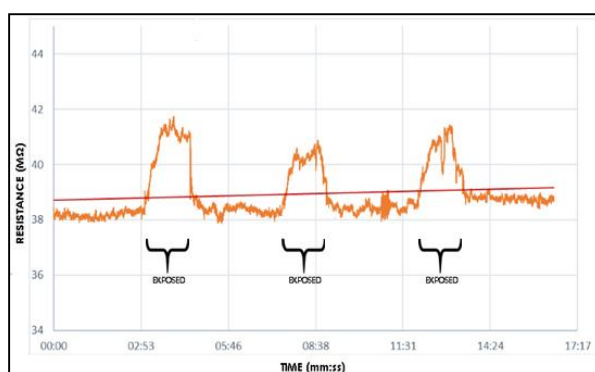


Figure 8. Resistance vs Time graph for the gas reference test at 99.99% concentration conducted at room temperature.

The average change in resistance upon exposure to EtOH vapor was 2.68 MΩ while the average response time recorded was 64.67 seconds. The Sensor Response S_g was determined by the formula

$$S_g = \frac{\Delta R}{R_g} \quad (1)$$

where $\Delta R = R_a - R_g$, R_a is the electrical resistance in air ambient, and R_g is the resistance in Ethanol vapor. [11] The calculated Sensor Response was 0.069175.

4. Conclusion

The results showed that monoclinic Ga₂O₃ nanowires with diameters ranging from 51.60 to 908.38 nm were successfully synthesized via optimized HVPG Technique. The temperature gradient and the applied magnetic field was noted to be the primary contributor in the crystal structure and growth preference of the nanomaterial. The Gallium to Oxygen ratio was verified to be approximately 2:3 which agrees with the atomic ratio of Ga₂O₃. The Raman spectrum of the grown nanowires confirmed that the material is monoclinic in structure and belongs to $C_{2/m}$ space group. This confirms that the grown nanomaterial is a β -polytype. Electrical characterization of the as-grown nanomaterial suggests that it has high specific conductance and low volume resistivity.

The result of gas reference test demonstrates that the nanomaterial is responsive to the presence of ethanol. The data indicates that the resistance increased due to the presence of Ethanol vapor. Overall, the material showed potential for use in gas sensing and gas detection.

Acknowledgement

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