

Optical Sensor Fabricated From Beta Gallium Oxide Nanorods

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ABSTRACT

Beta gallium oxide (β -Ga₂O₃) has attracted lots of attentions for the applications in optical devices. 1-D and 2-D β -Ga₂O₃ can be synthesized by several simple methods such as hydrolysis, sol-gel, electrospinning, and hydrothermal methods. In this study, β -Ga₂O₃ nanorods were prepared via the hydrothermal method. The morphology and crystal structure of β -Ga₂O₃ nanorods were investigated using FESEM image, and XRD patterns, respectively, confirming that Ga₂O₃ has monoclinic structure. FTIR spectrum was utilized to find the representative vibration bands in β -Ga₂O₃ nanorods, illustrating the Ga-O-Ga bending vibration and Ga-O stretching vibration at 670 cm⁻¹ and 450 cm⁻¹, respectively. The optical sensor was successfully fabricated based on β -Ga₂O₃ nanorods powder and graphene oxide powder which served as the medium for charges transport. The sensor was excited with the wavelength of 405 nm and the excitation power of 45mW/cm². It was found that the β -Ga₂O₃ nanorods optical sensor had the rise time and fall time of ~ 1.6 s, and the responsivity of 1.48×10⁻⁴ A/W, providing the applicability of this type of devices. The study shows a solution to fabricate an optical sensor from β -Ga₂O₃ nanorods.

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1. Introduction

Beta gallium oxide (β -Ga₂O₃) has gained a lot of consideration for several applications in power devices, UV photodetectors, photocatalysts, solar cells, and gas sensors because of its ultrawide band gap of 4.8 eV and a high critical field of 8 MV/cm [1], [2]. Because β -Ga₂O₃ can be grown using low cost processes such as Czochralski (CZ) [3], floating zone (FZ), edge-defined film-fed (EFG) methods [4], it has much advantages over other ultra-wide band-gape materials such as SiC and GaN. There are abundant researches focusing on power electronics and optoelectronic devices. The high criteria of highly secure NLOS (Non-Line-of-Sight) in military communications [5] lead to the increase of attentions in the applications of β -Ga₂O₃.

The synthesis and characterization of β -Ga₂O₃ have been conducted in literatures, focusing on 1-D and 2-D morphologies [6]-[8]. These studies have adapted several simple methods based on chemical-reaction-based approaches such as hydrolysis, sol-gel, electrospinning, and hydrothermal methods [9]-[15]. Among available methods, the fabrication of 1-D and 2-D β -Ga₂O₃ using hydrothermal method has been attracted recently due to its simple processes, the flexibilities in changing the fabrication condition, and easy crystallization of β -Ga₂O₃ in specified conditions of high pressure [16], [17]. Besides, β -Ga₂O₃ nanorods and/or nanoparticles formed in hydrothermal chamber have different faces, leading to difference in surface area, volume ratios and/or aspect ratios [18]. It is known that a small change in aspect ratio induces significant variation in optical and electrical properties of 1-D and 2-D β -Ga₂O₃ [13], [19]. Although Ga₂O₃ nanorods have been fabricated with assistants of template and surfactant in hydrothermal methods [20], template-assisted and surfactant-assisted hydrothermal methods expose several disadvantages of cross-contamination, unintentional doping, and increases in product costs [21].

Although the epitaxial growth of $\beta\text{-Ga}_2\text{O}_3$ thin films has had a significant improvement, the solar-blind photodetectors usually gain a high dark current and a slower response speed [22], [23]. Until now, many solar-blind photodetectors have been fabricated on $\beta\text{-Ga}_2\text{O}_3$ nanostructured films [24], [25]. However, all these devices adapted simple metal-semiconductor-metal (MSM) structure, leading to their performance to be still worse than expected.

This work aims to develop optical $\beta\text{-Ga}_2\text{O}_3$ sensors based on $\beta\text{-Ga}_2\text{O}_3$ nano rods fabricated using hydrothermal methods. The $\beta\text{-Ga}_2\text{O}_3$ nano rods powder were mixed into a graphene oxide (GO) medium and then formed a GO/ $\beta\text{-Ga}_2\text{O}_3$ film. A vacuum filtration method was utilized to deposit GO/ $\beta\text{-Ga}_2\text{O}_3$ film on filter paper. The optical sensors were then made on GO/ $\beta\text{-Ga}_2\text{O}_3$ films. Because of the low conductivity of $\beta\text{-Ga}_2\text{O}_3$ nanorods, GO powder was adapted as a medium to transport carriers created in $\beta\text{-Ga}_2\text{O}_3$ nano rods during sensor illumination.

2. Experimental details

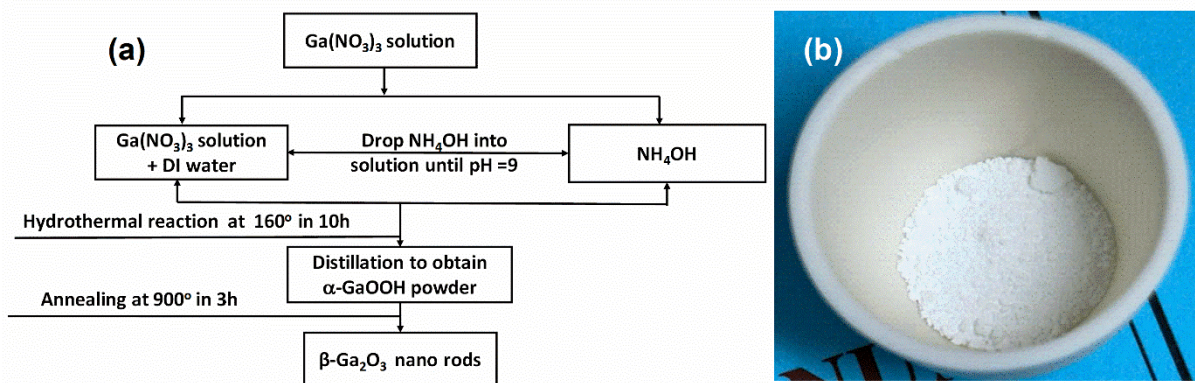


Figure 1. (a) Schematic illustration of the fabrication of $\beta\text{-Ga}_2\text{O}_3$ nanorods using hydrothermal method. (b) $\beta\text{-Ga}_2\text{O}_3$ nanorods powder after annealing.

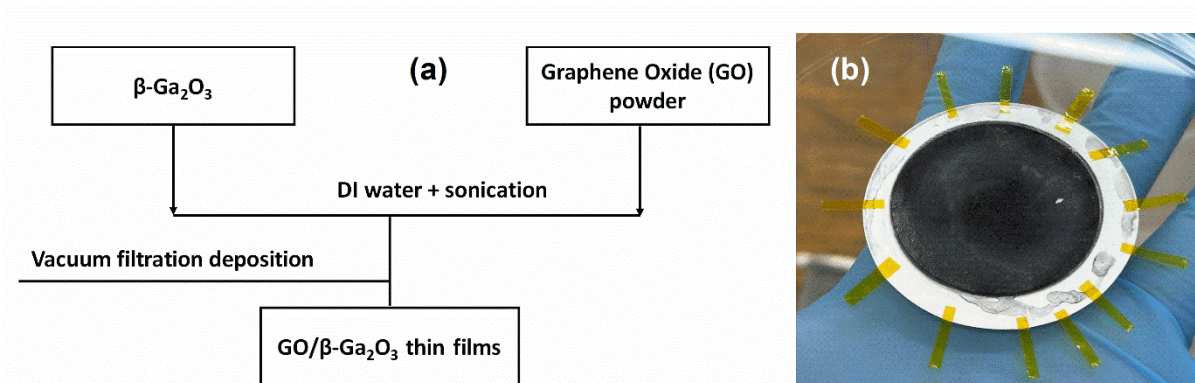


Figure 2. (a) Schematic of preparing GO/ Ga_2O_3 thin film using vacuum filtration method. (b) GO/ Ga_2O_3 thin film on filter paper.

Figure 1(a) shows the schematic of fabrication of $\beta\text{-Ga}_2\text{O}_3$ nanorods powder. First of all, Ga_2O_3 powder (Wuhan Tuocai Technology, China) was dissolved in HNO_3 : HCl (10:1) solution to have $\text{Ga}(\text{NO}_3)_3$ solution. The resultant solution was distilled at 100°C until a white powder of $\text{Ga}(\text{NO}_3)_3$ was obtained. Then 18 ml 0.1 M $\text{Ga}(\text{NO}_3)_3$ solution was prepared and poured into Teflon reactor before NH_4OH 25% solution (Xilong, China) was slowly dropped into the $\text{Ga}(\text{NO}_3)_3$ solution to maintain the pH of mixed solution at ~ 9 for the reaction. The hydrothermal autoclave reactor was annealed at 160°C in 10 hours. The autoclave was then naturally cooled down to room temperature. Finally, Gallium oxide hydroxide $\alpha\text{-GaOOH}$ was collected and washed several times with DI to remove residual reagents.

Finally, α -GaOOH solution was dried at 100°C until obtaining a white powder, which was annealing at 900°C in 3 hours to calcinate and transform α -GaOOH to β -Ga₂O₃ nanorods as shown in Fig. 1(b).

Because β -Ga₂O₃ nanorods distributes discretely, it is needed to have a medium for the transport of carriers. Graphene oxide should be a good choice for this case [26], so GO/Ga₂O₃ thin film was prepared using vacuum filtration method shown in the schematic in Fig. 2(a). The GO/Ga₂O₃ solution was prepared by mixing β -Ga₂O₃ nanorods powder with GO power in DI water with the ratio of GO: β -Ga₂O₃ = 3:1. The solid substances and DI water with the ratio of 3 mg/1ml was sonicated in more than 1 hour, before 3 ml of solution was dropped on the filter paper (size of 0.22 μ m) to deposit GO/Ga₂O₃ thin film shown in Fig 2.(b). Finally, the film was naturally dried at room temperature.

Field emission scanning electron microscope (FESEM) S-4800 (Hitachi, Japan) was utilized to investigate the morphology of β -Ga₂O₃ nanorods. The X-ray Diffraction (XRD) Pattern was investigated using a multipurpose diffractometer Empyrean (Malvern Panalytical, the UK). The chemical structures of the β -Ga₂O₃ nanorods were inspected via Fourier-transform infrared (FTIR) spectroscopy using Nicolet 6700 (Thermo Scientific, the US) - besides, the photocurrent and the responsivity of GO/Ga₂O₃ sensor were measured at 10 V under the excitation of a constant power of incident light (45mW/cm²) using the Ossila P2005A2 source measurement unit (SMU) (Ossila, the UK).

3. Results and Discussion

Figure 3(a) shows a FESEM image of β -Ga₂O₃ nanostructure fabricated using hydrothermal method. It was reported that the reaction between the hydrated gallium as Ga(OH)₃ and ammonium hydroxide in the supersaturated condition led to precipitation of α -GaOOH nanoparticles under the present of alkali [27]. Bigger α -GaOOH nanoparticles were then formed under the effects of van der Waals force [28]. It means that the α -GaOOH nanoparticles absorbed OH⁻ ions on all definite surfaces to form a nanoplate along the privileged direction with a lower surface energy. Ostwald ripening and oriented attachment formed spindle-like α -GaOOH nanorods as shown in Fig. 3(a) [29]. Figure 3(b) shows the distribution of the length in the range from 1.3 μ m to 2.5 μ m with the peak at 2.1 μ m. The distribution of diameter of the nanorods is shown in Fig. 3(c) with the range from 0.15 μ m to 0.45 μ m, leading to the length/diameter (L/D) ratio of ~ 6.

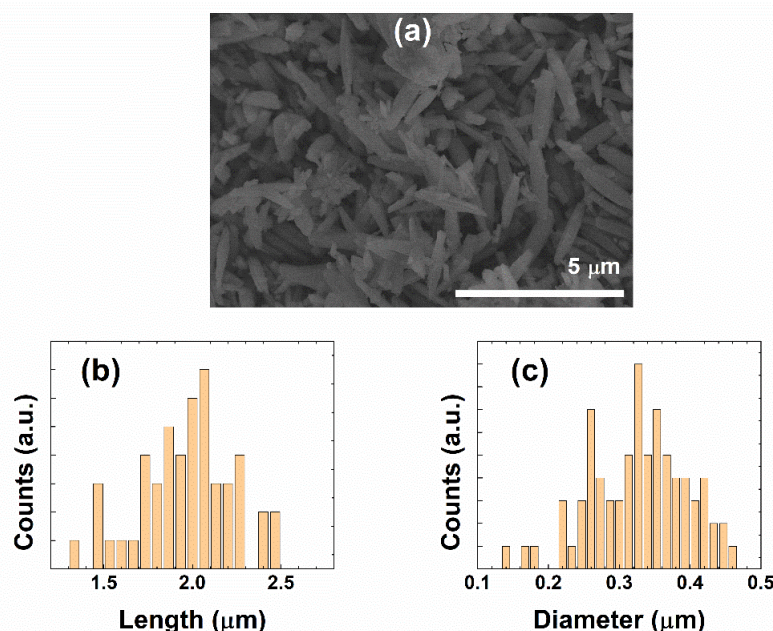


Figure 3. FESEM images of (a) β -Ga₂O₃ nanorods fabricated using hydrothermal method. The distribution of (a) length and (b) diameter of β -Ga₂O₃ nanorods shown in Fig. 3(a).

The crystallinity of the β -Ga₂O₃ nanorods was further characterized using an XRD analysis, as shown in Figure 4. β -Ga₂O₃ nanorods have monoclinic structure which has the lattice parameters of a=12.23 Å, b=3.04 Å, c=5.80 Å, α =90°, β =103.7° and γ =90° (JCPDS 43-1012) [30]. It was reported that

precipitated α -GaOOH nanorods retain their orthorhombic structure after the hydrothermal process, and the crystallinity of the α -GaOOH nanorods was enhanced during the hydrothermal process [31]. Figure 4 indicates that the monoclinic β -Ga₂O₃ nanorods were transformed from hydrothermal-synthesized α -GaOOH after calcinating at 900°C in 3 hours.

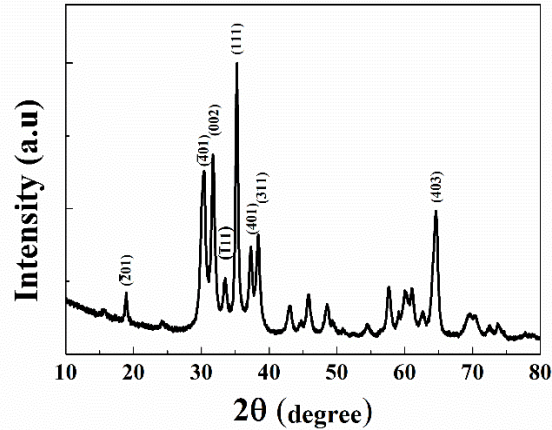


Figure 4. XRD patterns of β -Ga₂O₃ nanorods after calcinating at 900°C in 3 hours.

To investigate the chemical structure of β -Ga₂O₃ nanorods, FTIR spectrum was measured in a wavelength range from 4000 to 400 cm⁻¹ shown in Fig. 5. Strong bands at 3420 cm⁻¹, 1633 cm⁻¹ present the vibration of -OH bonds [32]. These bands are considered to be from the incomplete transformation of α -GaOOH nanorods to β -Ga₂O₃ nanorods. The present the vibration of -OH bonds may also be the adsorption of moisture on β -Ga₂O₃ nanorods during sample preparation for FTIR measurement. The bands at 670 cm⁻¹ and 450 cm⁻¹ represent the Ga-O-Ga bending vibration and Ga-O stretching vibration, respectively [33]. These valleys were observed in both α -GaOOH and β -Ga₂O₃ [33].

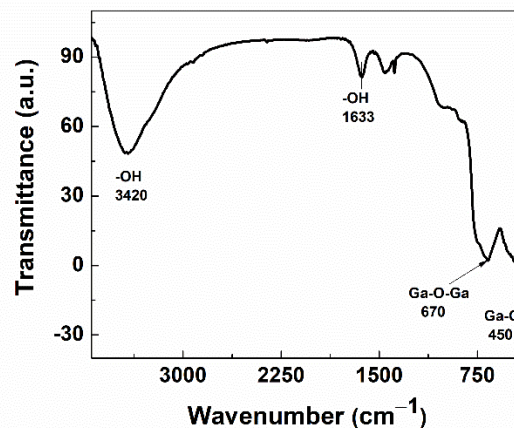


Figure 5. FTIR spectrum of β -Ga₂O₃ nanorods after calcinating at 900°C in 3 hours.

Figure 6(a) shows the image of the GO/Ga₂O₃ nanorods optical sensor. The sensor was fabricated using the shadow mask with the channel distance of 50 μ m. Figure 6(b) illustrates the photocurrent as a function of time, measured at constant power of incident light (45mW/cm²) with the wavelength of 405 nm. The photocurrent is calculated using the formula:

$$I_{ph} = I_{light} - I_{dark}, \quad (1)$$

where I_{ph} , I_{light} , I_{dark} are photocurrent, light current, and dark current, respectively. Figure 4(b) indicates the stability and repeatability of the optical sensor during the measurement. The responsivity of GO/Ga₂O₃ nanorods optical sensor is calculated from [34]:

$$R = \frac{J_{ph}}{P}, \quad (2)$$

where J_{ph} is the photocurrent, and P is the power of the incident light. The responsivity was obtained at 1.48×10^{-4} A/W, indicating the potential application of this sensor. Figure 6(b) also shows the rise time and the fall time of the GO/Ga₂O₃ nanorods optical sensor. The rise time (t_1) is determined from 10% to 90% amplitude of the dark current, and recovery (fall) time (t_2) is extracted from 90% to 10% amplitude of light current. The average rise time and fall time are at ~ 1.61 s at applied voltage of 10 V, which is shorter than those reported in GO optical sensor [26].

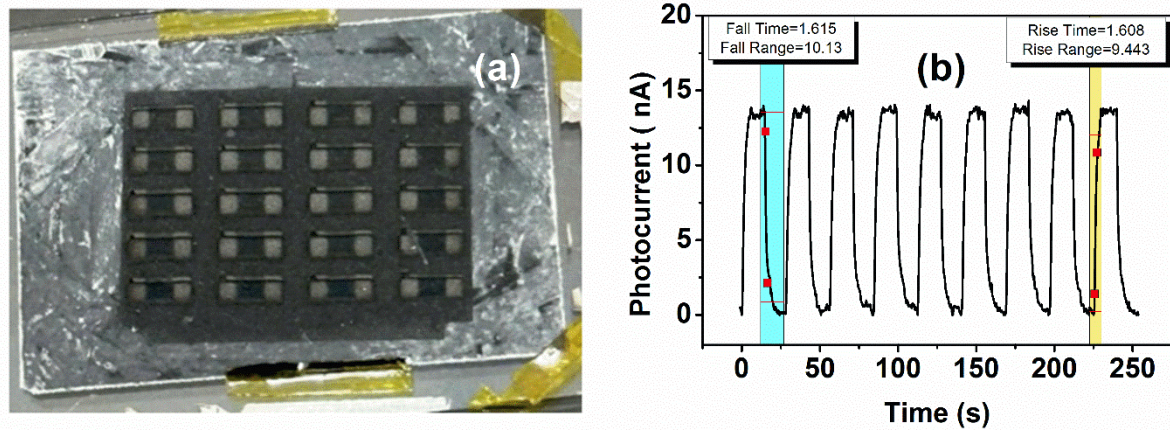


Figure 6. (a) Optical image of GO/Ga₂O₃ nanorods optical sensors after deposition the electrodes, and (b) photocurrent – time characteristics of GO/Ga₂O₃ nanorods optical sensors excited by the wavelength of 405 nm and the power of 45 mW/cm².

4. Conclusions

β -Ga₂O₃ nanorods were fabricated from Ga(NO₃)₃ and NH₄OH via the hydrothermal method, showing the average length of 2.1 μ m extracted from FESEM measurement. XRD patterns indicated that monoclinic β -Ga₂O₃ nanorods was successfully transformed from orthorhombic α -GaOOH nanorods. The chemical structure of β -Ga₂O₃ nanorods was investigated using FTIR spectrum. The result shows the representative bands of β -Ga₂O₃ nanostructures, including the Ga-O-Ga bending vibration and Ga-O stretching vibration at 670 cm⁻¹ and 450 cm⁻¹, respectively. The β -Ga₂O₃ nanorods powder was combined with graphene oxide powder to fabricate an optical sensor. Under the excitation of violet light (45mW/cm²) with the wavelength of 405 nm, the optical sensor exposed the rise time and fall time of ~ 1.6 s. The responsivity was found to be at 1.48×10^{-4} A/W, revealing the potential application of this sensor. The study shows an initial result and solution to fabricate an optical sensor from β -Ga₂O₃ nanorods.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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