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Nafiseh Badiel, Afshin Tarat and Lijie Li

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Nafiseh Badiei, Afshin Tarat, and Lijie Li* (✉)

AFFILIATIONS
College of Engineering, Swansea University, Swansea SA1 8EN, United Kingdom

*Author to whom correspondence should be addressed: L.Li@swansea.ac.uk

ABSTRACT

$\beta$-Ga$_2$O$_3$ is increasingly being used in power electronics and UV sensors. The preparation of $\beta$-Ga$_2$O$_3$ thin films requires costly and time-consuming fabrication processes. Therefore, developing short-time and low-cost fabrication processes of the $\beta$-Ga$_2$O$_3$ thin film has been greatly demanded to quicken the pace of applying this material in practical devices and systems. In this paper, a new fabrication process combining physical vapor deposition and microwave localized annealing has been postulated for $\beta$-Ga$_2$O$_3$ thin films. The experimental results show that after microwave annealing bandgaps have been slightly adjusted, the surface morphology has been improved and extra diffraction peaks appear, which give rise to stronger $\beta$-phase characteristics in the Ga$_2$O$_3$ thin film. Calculation based on density functional theory has been conducted to show the electronic bandstructures, formation energies, and optical absorptions of both types.

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INTRODUCTION

Gallium oxide (Ga$_2$O$_3$) has attracted great attention for its unique semiconductor properties, such as a wide direct bandgap of 4.5–4.9 eV and a large breakdown field strength (8 MV/cm), which offers promising applications in optoelectronic and power electronic devices and systems. Ga$_2$O$_3$ is a polymorphic compound with different crystalline phases ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$); in addition, a transient $\kappa$-Ga$_2$O$_3$ polymorph has been reported. $\beta$-phase gallium oxide ($\beta$-Ga$_2$O$_3$) is regarded as the most thermodynamically stable phase out of its five existing phases. Devices built upon $\beta$-Ga$_2$O$_3$ have promising applications in power electronics, LEDs, and solar-blind photodetectors. Vertical and lateral transistors based on $\beta$-Ga$_2$O$_3$ have been fabricated to demonstrate the feasibility of applying this material in power electronics. The two-dimensional (2D) Ga$_2$O$_3$ has been investigated theoretically due to the potential improvements in tunable bandgap by strain and high surface-area-to-volume ratio against its bulk form. Several theoretical studies have been conducted on 2D Ga$_2$O$_3$ to investigate its electronic and optical properties. Among these crystalline phases, different fabrication techniques and characterization of the $\alpha$- and $\beta$- Ga$_2$O$_3$ have been conducted. Phase transitions among these phases have also been reported using the thermal annealing technique, namely, $\kappa$-Ga$_2$O$_3$ to $\beta$-Ga$_2$O$_3$. $\alpha$-phase to $\beta$-phase at elevated temperature, and reverse transition from $\beta$ to $\alpha$. $\beta$-crystal is the most common and well-studied polymorph of gallium oxide and is the only stable crystal at different temperatures until the melting point at 1900°C. In addition, the studies confirmed that all other crystal forms show a metastable property and transform into $\beta$-crystal structure at a temperature of over 700°C. This thermal stability makes it possible to fabricate either a single crystal or uniform thin films via a high temperature process such as crystallization from a melt or vapor phase epitaxy. Along with other methods, different microwave-assisted techniques have been successfully used to synthesize various gallium oxide hydroxide ($\alpha$-GaOOH) nanorods and nanocrystal structures. The thermal decomposition of 60 min $\alpha$-GaOOH at 600°C in the air for 4 h results in Ga$_2$O$_3$ nanostructures crystalline micrometer/submicron-nanorods. The microwave (MW) irradiation treatment method is a fast, precise, non-contact technology that can induce changes in morphological, chemical, optical, and structural properties during irradiation treatment. Moreover, localized phase changing can be realized based on patterned substrates. When the materials are irradiated by MWs, which have low frequency with low energy, they are hardly damaged. Thus, MW irradiation can be non-destructive and more economical compared to other irradiation treatment methods such as UV radiation, gamma rays, and ion beams. Furthermore, MWs can heat wafers in localized regions...
compared to conventional annealing because energy can be delivered by radiation rather than by conduction or convection. Ultimately, commercial microwave ovens are easily accessible. In this study, for the first time, MW irradiation, in combination with the physical vapor deposition technique, was successfully used to synthesize $\beta$-Ga$_2$O$_3$.

**EXPERIMENTAL METHOD**

Two substrates [100-nm-thick $n$-type Si and fused silica UV grade quartz substrates (Inseto Limited)] were prepared to deposit Ga$_2$O$_3$ thin films. The substrates (four samples of each substrate) were cleaned by ultra-sonication, with the following cleaning sequence: acetone–isopropanol–deionized (DI) water; then, the samples were fully dried using a nitrogen gun and were subsequently heated at 180 °C for 10 min on a hotplate to be completely dehydrated. Then, 300 nm Ga$_2$O$_3$ thin films were deposited onto the substrates (Inseto Limited) by radio-frequency (RF) magnetron sputtering (PVD) at room temperature. As-fabricated samples were treated using a commercial kitchen microwave oven (KENWOOD, Model: K30CSS14, 900 W, 2.45 GHz). The samples were treated for 5, 10, and 20 min and prepared for characterization. For comparison purpose, the samples were synthesized with traditional PVD and furnace annealing; the furnace annealing temperature and time were 700 °C and 40 min, respectively.

**MATERIAL CHARACTERIZATION AND SIMULATION**

Figure 1(a) illustrates the schematic representation of crystal structures of $\alpha$- and $\beta$-phase Ga$_2$O$_3$. The space group of $\alpha$-Ga$_2$O$_3$ is R-3c and that of $\beta$-Ga$_2$O$_3$ is C2/m. It is worth mentioning that, in this experiment, the $\alpha$-Ga$_2$O$_3$ is amorphous as it was grown by PVD at room temperature and the target used in the PVD was amorphous Ga$_2$O$_3$. X-ray diffraction (XRD) is a non-destructive analysis technique used to identify the crystalline structure and phases present in a material and thereby reveal the chemical composition information. The XRD (Bruker D8 Advance x-ray diffractometer) results of the deposited films along with $n$-type Si substrate are shown in Fig. 1(b). The peaks at $\sim$64.4° and $\sim$77.4° correspond to forbidden (512) and (421) plane reflections, respectively. Those are well attributed to the monoclinic $\beta$-phase Ga$_2$O$_3$. The intensity of these peaks is nearly undetectable in non-MW treated sample to the highest intensity in 20 min MW treated one. In Fig. 1(b), subplots (i)–(v) are as-grown, 5, 10, 20 min microwave treated, and using the traditional furnace annealing, respectively. It is clearly shown in Fig. 1(b) that there are many changes in the XRD peaks from as-grown to 5 min MW treatment. For example, peaks at 32.8°, 51.1°, 55.4°, 59.9°, 63.2°, and 65.4° have disappeared, and peaks at 38°, 44.2°, 64.4°, and 77.4° have emerged, reflecting the phase change. It is envisaged that heating on the wafer by the microwave energy anneals the sample, causing phase change from $\alpha$ to $\beta$. Further experiments will be conducted for device applications.

Transmittance measurements of $\alpha$-Ga$_2$O$_3$ (amorphous) and microwave irradiated (crystalline) Ga$_2$O$_3$ thin films were performed on a double-beam UV/Vis/NIR (Perkin-Elmer Lambda 9 spectrophotometer). A $\beta$-Ga$_2$O$_3$ film grown by the PVD with post annealing process within a furnace has demonstrated a bandgap of 4.65 eV [for comparison, see the Tauc plot shown in Fig. 2(a)]. By examining the Tauc plots [Fig. 2(b)] of the MW treated samples, it is shown that the bandgaps of the material are 4.9, 4.8, and 4.75 eV for as-grown from room temperature PVD, 5 min MW treatment, and 20 min MW treatment, respectively. The results display a clear bandgap reduction trend with an increase in the MW treatment time. This aspect potentially reflects that the MW can be a low-cost annealing method to change the crystalline phase from alpha to beta. The XRD and UV–Vis results show a phase change from alpha to beta during microwave treatments; therefore, according to the previous papers, it is estimated that the localized heating on the sample in the microwave unit should be at least 600–700 °C. It was reported previously for the furnace annealing that $N_2$ annealing is better in the passivation, annealing, and sintering begin to be observed. Figure 3(a) shows the sample before MW treatment. After 5 min MW treatment [Fig. 3(b)], samples begin to exhibit annealing and sintering effects, and further annealing can be seen after 20 min MW treatment [Fig. 3(c)].
Density functional theory (DFT) simulation has been performed using the QuantumATK software to better understand the difference between α-Ga₂O₃ and β-Ga₂O₃ in terms of their electronic and optical properties. Both supercells of these two crystalline types have been built and subsequently geometrically optimized. The α-Ga₂O₃ supercell is hexagonal (corundum-like structure, similar to Al₂O₃), contains 12 Ga and 18 O, and the space group belongs to R-3c. The geometrical optimization was made using the exchange correlation of generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) predefined functional. The density mesh cut off was made to 125 Hartree, and k-point sampling was 7 × 7 × 2. During the optimization process, the maximum force tolerance was 0.01 eV/Å and the maximum stress tolerance was 0.001 eV/Å³. The optimized supercell has the lattice parameters as follows: \( a = b = 5.07 \) Å; \( c = 13.62 \) Å; \( \alpha = 90^\circ \); \( \beta = 90^\circ \); \( \gamma = 120^\circ \); Volume = 303.47 Å³. The same geometrical optimization procedure was used to optimize β-Ga₂O₃, whose supercell is monoclinic, and has 8 Ga and 12 O. The exchange correlation and predefined functionals are the same as used in the α-Ga₂O₃ optimization process except the k-point sampling, which was 3 × 9 × 5 for β-Ga₂O₃. The optimized β-Ga₂O₃ has the following lattice parameters: \( a = 12.42 \) Å; \( b = 3.09 \) Å; \( c = 5.89 \) Å; \( \beta = 103.64^\circ \); Volume = 219.46 Å³. After geometrical optimization, the electronic and optical properties of these two phase types have been calculated. In the property calculations, a more accurate algorithm (Meta-GGA) has been used, as the PBE functional usually leads to the underestimation of bandgaps. In the simulation, the exchange correlation is MGGA with \( c \) parameter set to 1.37. The exchange functional of TB09 was used, the density mesh cut off value was 80 Hartree, the broadening was set to 0.1 eV, and the
k-point samplings for both have been the same as in the geometrical optimizations.

It is seen from the DFT simulation results in Fig. 4 that the direct bandgaps of the α-Ga₂O₃ and β-Ga₂O₃ are 5.21 and 4.82 eV, respectively. The bandgap of corundum-like α-Ga₂O₃ has been measured to be in the range of 4.9–5.6 eV, which matches well with the DFT simulation results in this work. It is also found from the density of states (DOS) plots that the valence bands for both types are pretty much similar (both are dominated by electrons on the O 2p orbital) except that the effective mass of β-Ga₂O₃ appears slightly smaller than that of α-Ga₂O₃, which coincides with the experimental results shown in Fig. 2. The DFT simulation has validated that there are phase changes facilitated by the low-cost microwave treatments. In the experiment, the bandgap underwent reductions from 4.9 eV down to 4.75 eV after 20 min of microwave radiation. The bandgap value of 4.75 eV is very much close to the β-Ga₂O₃ [4.65 eV in Fig. 2(a)] obtained by the time-consuming furnace annealing process. A major difference can be found in conduction bands from Fig. 4. For example, the DOS of Ga 4s has a clearer peak and is much stronger in α-Ga₂O₃ than that in β-Ga₂O₃. Moreover, a slightly wider bandgap of the α-Ga₂O₃ indicates that there is a potential application for α-Ga₂O₃ to be used in far UV devices. Inspired by the bandstructure results, further DFT studies have been conducted on the optical absorption spectra of both crystal types. The same simulation parameters were used as in the bandgap calculations. The absorption spectrum can be derived from the imaginary part of the complex dielectric constant, which was calculated from the susceptibility tensor that characterizes the polarization level of the material subjects to an electric field. Previous studies described in detail the procedures for calculating the absorption coefficient. The calculated anisotropic optical absorptions of both crystal phases are shown in Fig. 5. It is shown that for α-Ga₂O₃, the optical absorption spectra in the x- and y-directions are exactly overlapping each other; however, the absorption coefficient in the z-direction is very much different, especially at the wavelength around 150 nm, where there is a peak absorption exceeding 40 μm⁻¹. For the β-Ga₂O₃, the optical absorption coefficients exhibit strong anisotropy in three directions. On comparing these two types of materials, the absorption spectrum of the β-Ga₂O₃ is much wider, corresponding to its narrower bandgap.

More DFT simulation has been conducted to calculate the formation energies for the unit cell of both α-Ga₂O₃ and β-Ga₂O₃. The same computational procedure, as previously described, was used, and the equation $E_f = E_{Ga_2O_3}/n - (2 \cdot E_{Ga} + 3 \cdot E_O)$ was adopted for both types of materials, where $E_f$ is the formation energy of
a unit cell containing 2 Ga and 3 O, and \( n \) is the number of unit cells in a supercell. \( E_{\alpha}, E_{\beta}, \) and \( E_{Ga_2O_3} \) are the total energies of Ga, O, and \( Ga_2O_3 \) supercell, respectively. It is calculated that \( E_{\beta} \) of alpha and beta types are \(-18.226 \) and \(-18.159 \) eV, respectively. The \( E_f \) value of \( \alpha-Ga_2O_3 \) is 67 meV lower than that of \( \beta-Ga_2O_3 \), indicating that extra energy is required to convert \( \alpha \)-to \( \beta \)-phase. This coincides with the fact that \( \alpha \)-phase can be converted to beta at a high temperature.

CONCLUSION

This study aimed to find the possibility of using MW radiation power to induce \( Ga_2O_3 \) phase change. It is found that increasing the MW treatment time results in stronger \( \beta \)-phase character \( Ga_2O_3 \). The XRD results show that the intensity of two peaks at \(-64.4^\circ \) and \(-77.4^\circ \) increased with an increase in the MW treatment time, which are related to forbidden (512) and (421) plane reflections, respectively. This confirms that the \( Ga_2O_3 \) phase changes from room temperature PVD deposited \( \alpha-Ga_2O_3 \) to \( \beta-Ga_2O_3 \). Moreover, transmission measurements of the as-grown \( Ga_2O_3 \) and MW treated \( Ga_2O_3 \) thin films show that treated samples have slightly narrower bandgaps at about 4.8 and 4.75 eV for 5 and 20 min MW treatments, respectively, compared with the \( Ga_2O_3 \) grown by the PVD (4.9 eV), and the \( \beta-Ga_2O_3 \) prepared by the PVD together with post annealing process using furnace at 700°C demonstrating a 4.65 eV bandgap. SEM imaging of the samples before and after 5 and 20 min MW treatments shows that increasing the MW treatment time leads to particle agglomeration, annealing, and sintering, hence improving the crystallinity. Further theoretical study using DFT has been conducted to verify the experiments, which shows that the bandgap of the \( \beta-Ga_2O_3 \) is narrower than that of the \( \alpha-Ga_2O_3 \). The optical absorption of the \( \beta-Ga_2O_3 \) has much stronger anisotropy. The reported experiment paves a way for low-cost fabrication of \( \beta-Ga_2O_3 \).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Nafisah Badiei: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

Afshin Tarat: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal).

Lijie Li: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

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