Epitaxial growth of [beta]-Ga₂O₃/[epsilon]-Ga₂O₃ polymorphic heterostructures on c-plane sapphire for deep-ultraviolet optoelectronics

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ABSTRACT

Thin polymorphic gallium oxide films were grown on *c*-plane sapphire using pulsed laser deposition. The stacked thin films (ϵ -Ga₂O₃ and β -Ga₂O₃) were sequentially grown under the same conditions. Our X-ray diffraction measurements and transmission electron microscopy images confirmed a β -Ga₂O₃/ ϵ -Ga₂O₃ polymorphic heterostructure with rocking-curve widths of 1.4° (β -Ga₂O₃ ($\bar{6}03$)) and 0.6° (ϵ -Ga₂O₃ (006)). The crystallographic orientation relationships between *c*-plane sapphire and the heterogeneously nucleated ϵ -Ga₂O₃ buffer layer, as well as between the ϵ -Ga₂O₃ and β -Ga₂O₃ heterogeneous layers, were determined. Our study will aid in developing novel deep-ultraviolet optoelectronic devices, such as solar-blind and metal–insulator–semiconductor deep-ultraviolet photodiodes.

Keywords: Ga₂O₃, polymorphic heteroepitaxy, epitaxial growth, pulsed laser deposition, deep-ultraviolet, ultraviolet-C, multilayered oxides, optoelectronics.

1. INTRODUCTION

In this proceedings, we present the growth of thin gallium oxide (Ga₂O₃) polymorphic heterostructure on *c*-plane sapphire using pulsed laser deposition (PLD). The heteroepitaxially stacked oxide films (ϵ -Ga₂O₃ and β -Ga₂O₃) were sequentially grown under the same conditions. Our X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) images confirmed a β -Ga₂O₃/ ϵ -Ga₂O₃ polymorphic heterostructure with rocking-curve widths of 1.4° (β -Ga₂O₃ ($\bar{6}03$)) and 0.6° (ϵ -Ga₂O₃ (006)). The crystallographic orientation relationships between *c*-plane sapphire and the heterogeneously nucleated ϵ -Ga₂O₃ buffer layer, as well as between the ϵ -Ga₂O₃ and β -Ga₂O₃ heterogeneous layers, were determined. To our knowledge, this is the first report of a single-crystalline β -Ga₂O₃/ ϵ -Ga₂O₃ polymorphic heterostructure stack. Reports in the literature only demonstrated pure-phase Ga₂O₃ crystals.^{1–5} ϵ -polymorph Ga₂O₃ remains a mysterious material, with various possible emerging applications:

1. ϵ -Ga₂O₃ might be a direct bandgap material, making it possibly suitable for realizing ultraviolet-C light-emitting optoelectronic devices.⁶
2. ϵ -Ga₂O₃ can possibly be utilized to realize efficient high-electron-mobility transistors because the magnitude of its polarization constant is ten times larger than that of gallium nitride (GaN).⁷

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1.1 Epitaxial growth

In this section, we explore the novel growth process involving heteroepitaxially stacked Ga_2O_3 polymorphs: unintentionally doped $\beta\text{-Ga}_2\text{O}_3$ thin films (approximately 130-nm thick) on 1 mol% tin (Sn)-doped $\varepsilon\text{-Ga}_2\text{O}_3$ buffer layers (approximately 400-nm thick). These were grown using PLD at an 800 °C chamber temperature (640 °C substrate temperature), a 5-mTorr argon partial pressure, a 350-mJ pulse energy, and a 5-Hz pulse rate (30k pulses for each film) at a substrate-to-target distance of 80 mm. Figure 1 depicts a schematic of the grown single-crystalline $\beta\text{-Ga}_2\text{O}_3/\varepsilon\text{-Ga}_2\text{O}_3$ polymorphic heterostructure.

Figure 1. Schematic illustration of the grown $\beta\text{-Ga}_2\text{O}_3/\varepsilon\text{-Ga}_2\text{O}_3$ polymorphic heterostructure.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.0.1 Crystallographic orientation relationships and crystal quality

As depicted in Figure 2(a), out-of-plane X-ray diffraction results show that the $\varepsilon\text{-Ga}_2\text{O}_3$ film, when exhibiting both $\text{Cu}(K\alpha_1)$ and $\text{Cu}(K\alpha_2)$ $\varepsilon\text{-Ga}_2\text{O}_3$ (006) doublet peaks (Figure 2(b)), features better crystal quality than does $\beta\text{-Ga}_2\text{O}_3$ when grown under the same conditions. The orientation relationships from the X-ray diffraction measurements and electron microscopy imaging are as follows:

$$\beta\text{-Ga}_2\text{O}_3 (201) \parallel \varepsilon\text{-Ga}_2\text{O}_3 (002) \parallel \alpha\text{-Al}_2\text{O}_3 (0006), \quad (1)$$

$$\beta\text{-Ga}_2\text{O}_3 (102) \parallel \varepsilon\text{-Ga}_2\text{O}_3 (220) \parallel \alpha\text{-Al}_2\text{O}_3 (03\bar{3}0), \quad (2)$$

$$\beta\text{-Ga}_2\text{O}_3 (010) \parallel \varepsilon\text{-Ga}_2\text{O}_3 (100) \parallel \alpha\text{-Al}_2\text{O}_3 (11\bar{2}0). \quad (3)$$

The rocking-curve measurements (Figure 3) revealed that a $\beta\text{-Ga}_2\text{O}_3$ film grown on an $\varepsilon\text{-Ga}_2\text{O}_3$ film achieves a rocking-curve width of about 1.4° (based on $\beta\text{-Ga}_2\text{O}_3$ ($\bar{6}03$) peaks), demonstrating superior crystalline quality to a $\beta\text{-Ga}_2\text{O}_3$ film grown directly on *c*-plane sapphire with rocking-curve widths of approximately 2.2° using pulsed laser deposition and other techniques, per the literature. Therefore, $\varepsilon\text{-Ga}_2\text{O}_3$ films with rocking-curve widths of about 0.6° (based on $\varepsilon\text{-Ga}_2\text{O}_3$ (006) peaks) act as excellent buffer layers for $\beta\text{-Ga}_2\text{O}_3$ film growth.

The atomic force microscopy results depicted in Figure 4 demonstrate that the $\beta\text{-Ga}_2\text{O}_3$ film has a 2.2-nm root mean square roughness value, whereas transmission electron microscopy imaging shown in Figure 5 confirmed the crystallographic integrity of β - and ε -polymorph gallium oxide films stacked on sapphire, with excellent crystallographic qualities and a sharp interface.

Figure 2. (a) XRD measurements of a grown single-crystalline β -Ga₂O₃/ ϵ -Ga₂O₃ polymorphic heterostructure stack. (b) Zoomed-in version of (a) showing the Cu($K_{\alpha 1}$) and Cu($K_{\alpha 2}$) ϵ -Ga₂O₃ (006) doublet peaks.

Figure 3. Rocking curve measurements showing the crystal reflections of grown (a) β -Ga₂O₃ and (b) ϵ -Ga₂O₃ heteroepitaxial stacked crystalline lattices.

Under the typical growth conditions described earlier, a crystallization of β -Ga₂O₃ film was normally observed in either an oxygen or argon ambience when the material target is undoped. However, we observe here that Sn-doped Ga₂O₃ crystallizes as an ϵ -phase film when grown under the same conditions but in an argon ambience. We conjecture that Sn oxidizes by oxygen during pulsed laser deposition, rendering it incapable to act as a catalyst for the growth of ϵ -polymorph gallium oxide crystal. But when grown in an argon ambience, Sn atoms in the Sn-doped gallium oxide materials target eventually act as ϵ -phase catalysts. This is the most plausible hypothesis given the large dispersion in the elemental atomic numbers ($Z_{\text{Sn}} = 50$, $Z_{\text{Ga}} = 31$, $Z_{\text{Si}} = 14$, $Z_{\text{Ar}} = 18$, and $Z_{\text{O}} = 8$).

Figure 4. AFM scan of a grown β -Ga₂O₃ thin film on an ϵ -Ga₂O₃ buffer layer.

Figure 5. Transmission electron microscopy images of the grown β -Ga₂O₃/ ϵ -Ga₂O₃ polymorphic heterostructure—(a) Cross-sectional TEM image of the entire β -Ga₂O₃/ ϵ -Ga₂O₃/sapphire heterostructure stack, and close-up cross-sectional TEM images of the (b) β -Ga₂O₃/ ϵ -Ga₂O₃ and (c) ϵ -Ga₂O₃/sapphire interfaces. The insets to the right of subfigures (b) and (c) show the acquired FFT patterns of the crystalline lattices.

3. CONCLUDING REMARKS

In summary, thin gallium oxide polymorphic heterostructures were grown on *c*-plane sapphire using PLD, comprising a new platform for deep-ultraviolet optoelectronic devices based on β -Ga₂O₃/ ϵ -Ga₂O₃ heterostructures on sapphire. We showed that tin-doped gallium oxide crystallizes as an ϵ -phase film when grown in an argon ambience, allowing the synthesis of phase-pure ϵ -Ga₂O₃ using PLD. Furthermore, the crystallographic orientation relationships between the *c*-plane sapphire and the heterogeneously nucleated ϵ -polymorph gallium oxide

buffer layer, as well as between the ε -polymorph and β -polymorph gallium oxide heterogeneous layers, were determined. Because of the high-quality β -Ga₂O₃ thin films realized heteroepitaxially on an ε -Ga₂O₃ buffer layer in a single growth step using pulsed laser deposition, we expect that this process will aid in the development of novel deep-ultraviolet optoelectronic devices.

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REFERENCES

- [1] Li, K.-H., Alfaraj, N., Kang, C. H., Braic, L., Hedhili, M. N., Guo, Z., Ng, T. K., and Ooi, B. S., “Deep-ultraviolet photodetection using single-crystalline β -Ga₂O₃/NiO heterojunctions,” *ACS Appl. Mater. Interfaces* **11**(38), 35095–35104 (2019).
- [2] Li, K.-H., Alfaraj, N., Kang, C. H., Braic, L., Zoita, N. C., Kiss, A. E., Ng, T. K., and Ooi, B. S., “Deep-ultraviolet β -Ga₂O₃ photodetectors grown on MgO substrates with a TiN template,” in [*2019 IEEE Photonics Conference (IPC)*], 19186548, IEEE (2019).
- [3] Zhuo, Y., Chen, Z., Tu, W., Ma, X., Pei, Y., and Wang, G., “ β -Ga₂O₃ versus ε -Ga₂O₃: Control of the crystal phase composition of gallium oxide thin film prepared by metal-organic chemical vapor deposition,” *Appl. Surf. Sci.* **420**, 802–807 (2017).
- [4] Xia, X., Chen, Y., Feng, Q., Liang, H., Tao, P., Xu, M., and Du, G., “Hexagonal phase-pure wide band gap ε -Ga₂O₃ films grown on 6H-SiC substrates by metal organic chemical vapor deposition,” *Appl. Phys. Lett.* **108**(20), 202103 (2016).
- [5] Oshima, Y., Villora, E. G., Matsushita, Y., Yamamoto, S., and Shimamura, K., “Epitaxial growth of phase-pure ε -Ga₂O₃ by halide vapor phase epitaxy,” *J. Appl. Phys.* **118**(8), 085301 (2015).
- [6] Pavesi, M., Fabbri, F., Boschi, F., Piacentini, G., Baraldi, A., Bosi, M., Gombia, E., Parisini, A., and Fornari, R., “ ε -Ga₂O₃ epilayers as a material for solar-blind UV photodetectors,” *Mater. Chem. Phys.* **205**, 502–507 (2018).
- [7] Kumar, S., Soman, R., Pratiyush, A. S., Muralidharan, R., and Nath, D. N., “A performance comparison between β -Ga₂O₃ and GaN HEMTs,” *IEEE Trans. Electron Devices* **66**(8), 3310–3317 (2019).