Epitaxial Growth of $\beta$-$\text{Ga}_2\text{O}_3$ Thin Films on Si with YSZ Buffer Layer

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ABSTRACT: We report the epitaxial growth of (001)-oriented $\beta$-$\text{Ga}_2\text{O}_3$ thin films on a (001) Si substrate using the pulsed laser deposition technique employing epitaxial yttria-stabilized zirconia (YSZ) buffer layers. Epitaxial $\beta$-$\text{Ga}_2\text{O}_3$ thin films possess a biaxial compressive strain on YSZ single-crystal substrates while they exhibit a biaxial tensile strain on YSZ-buffered Si substrates. Post-annealing improves the crystalline quality of $\beta$-$\text{Ga}_2\text{O}_3$ thin films. High-resolution X-ray diffraction analyses reveal that the epitaxial (001) $\beta$-$\text{Ga}_2\text{O}_3$ thin films on Si have eight in-plane domain variants to accommodate the large difference in the crystal structure between monoclinic $\beta$-$\text{Ga}_2\text{O}_3$ and cubic YSZ. The results provide a pathway to integrate epitaxial $\beta$-$\text{Ga}_2\text{O}_3$ thin films on a Si gold standard substrate, which will expand the application scope beyond high-power electronics.

INTRODUCTION

Recently, $\text{Ga}_2\text{O}_3$ has attracted significant attention as a promising wide-bandgap semiconductor for applications in high-power devices, ultraviolet photodetectors, and gas sensors. Among the five $\text{Ga}_2\text{O}_3$ polymorphs ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$), monoclinic $\beta$-$\text{Ga}_2\text{O}_3$ is the most thermodynamically stable and exhibits excellent physical properties, such as a wide band gap ($\sim$4.9 eV), optical transparency, n-type semiconducting properties, high electrical breakdown voltage ($\sim$8 MV/cm), and radiation resistance.1−3

The epitaxial growth of $\text{Ga}_2\text{O}_3$ thin films is important for the realization of high-performance devices and understanding their intrinsic properties. Thus far, many growth techniques have been reported for the epitaxial growth of $\text{Ga}_2\text{O}_3$ thin films, including pulsed laser deposition (PLD),4,5 molecular beam epitaxy,6 metal–organic chemical vapor deposition (CVD),7 mist-CVD,8 sol–gel,9 and sputtering.10 For high-power devices, homoepitaxial $\text{Ga}_2\text{O}_3$ structures, wherein both the film and substrate are $\beta$-$\text{Ga}_2\text{O}_3$, are desirable because a key feature of high-power electronics is a high resistance to electrical breakdown under high voltage conditions. Several fabrication techniques for $\beta$-$\text{Ga}_2\text{O}_3$ bulk single crystals have been developed, such as Verneuil,11 floating,12 Czechralski,13 edge-defined film growth,14 and vertical Bridgman methods.15 However, $\beta$-$\text{Ga}_2\text{O}_3$ single-crystal substrates are very expensive compared to other single-crystal oxide and semiconductor substrates, which limits the application of homoepitaxial $\text{Ga}_2\text{O}_3$ structures. In addition, heteroepitaxial structures are formed when $\beta$-$\text{Ga}_2\text{O}_3$ thin films are grown on different substrates, such as $\text{MgO}$,16 $\text{CeO}_2$,17 and $\text{Al}_2\text{O}_3$.18 These have also been widely studied.

In this study, we investigated the epitaxial growth of $\beta$-$\text{Ga}_2\text{O}_3$ thin films on Si substrates, the gold standard single crystal of modern electronics19−21 using the PLD technique. (001)-Oriented epitaxial $\beta$-$\text{Ga}_2\text{O}_3$ thin films were grown on yttria-stabilized zirconia (YSZ) and YSZ-buffered Si substrates. Using high-resolution X-ray diffraction (HRXRD), we analyzed domain structures and strain states of monoclinic $\beta$-$\text{Ga}_2\text{O}_3$ thin films on cubic YSZ-buffered Si substrates and demonstrated the improved crystalline quality through a post-annealing process. The results provide a pathway for integrating the functionalities of $\beta$-$\text{Ga}_2\text{O}_3$ thin films onto Si, which can broaden the scope of $\beta$-$\text{Ga}_2\text{O}_3$ applications beyond high-power electronics.

RESULTS AND DISCUSSION

Figure 1a shows schematics of the $\beta$-$\text{Ga}_2\text{O}_3$, YSZ, and Si unit cells. YSZ has a fluorite structure ($\text{Fm}$3$\text{m}$, cubic), with a lattice parameter of 5.143 Å. Owing to the small lattice mismatch with Si ($\text{Fm}$3$\text{m}$, cubic, 5.431 Å), YSZ can be grown epitaxially on Si. The epitaxial YSZ layers on Si can function as a buffer layer to integrate additional functional oxide overlayers onto Si.22−25 Owing to their unique growth process, involving the scavenging effect, epitaxial YSZ buffer layers can be deposited on Si using low-cost deposition processes, such as PLD and sputtering. $\beta$-$\text{Ga}_2\text{O}_3$ belongs to a monoclinic crystal system ($\text{C}$2/m, $a$ = 12.23 Å, $b$ = 3.04 Å, $c$ = 5.80 Å, and $\beta$ = 103.7°) and has a large lattice mismatch with cubic YSZ and Si substrates. Typically, complex...
domain structures evolve when a material with low symmetry is epitaxially grown on a substrate with high symmetry; for example, epitaxial BiFeO$_3$ (rhombohedral) thin films have four structural variants on SrTiO$_3$ (cubic) substrates. Therefore, it is expected that epitaxial β-Ga$_2$O$_3$ thin films on YSZ and YSZ-buffered Si substrates will exhibit a complex domain structure. In addition to the lattice mismatch, thermal mismatch affects epitaxial β-Ga$_2$O$_3$ thin films, particularly their strain state. A large
difference exists in the thermal expansion coefficients of $\beta$-Ga$_2$O$_3$ ($\sim 5 \times 10^{-6}$/K), YSZ ($\sim 9 \times 10^{-6}$/K), and Si ($\sim 3 \times 10^{-6}$/K). Typically, epitaxial oxide thin films grown on Si possess tensile strain at room temperature because of the thermal mismatch due to cooling to room temperature. To study this effect, we grew epitaxial $\beta$-Ga$_2$O$_3$ thin films on both YSZ and YSZ-buffered Si substrates via PLD, as shown in Figure 1b.

$\beta$-Ga$_2$O$_3$ thin films were grown via PLD using a KrF excimer laser ($\lambda = 248$ nm) at 100 mTorr O$_2$ partial pressure with a laser energy density of 1.5 J/cm$^2$ and frequency of 5 Hz at 750 °C. A Ga$_2$O$_3$ ceramic target was used with a sample-to-target distance of 5 cm. Epitaxial $\beta$-Ga$_2$O$_3$ thin films were grown on two different substrates: (001) YSZ and YSZ-buffered (001) Si single-crystal (YSZ-buffered Si) substrates. A 45 nm-thick epitaxial YSZ buffer layer was grown via PLD at 0.1 mTorr O$_2$ partial pressure with a laser energy density of 1.5 J/cm$^2$ and frequency of 5 Hz at 750 °C. Note that the 45 nm-thick epitaxial YSZ buffer layer was selected considering the crystallinity of each thickness sample (Figure S2). A YSZ ceramic target with a composition of 20%Y-ZrO$_2$ was used with a sample-to-target distance of 5 cm. The growth rate was maintained at 6 nm/min.

Before $\beta$-Ga$_2$O$_3$ deposition, both the YSZ and YSZ-buffered Si substrates were cleaned with acetone, isopropyl alcohol, and DI water, followed by N$_2$ drying.

Commercial atomic force microscopy (AFM, Digital Instrument Dimension 3100, equipped with a Nanoscope IV controller) was used to investigate the surface morphology of $\beta$-Ga$_2$O$_3$ thin films in the tapping mode. Figure 2a,b show AFM...
images of β-Ga$_2$O$_3$ thin films grown on YSZ and YSZ-buffered Si substrates, respectively. The β-Ga$_2$O$_3$ film on the YSZ substrate exhibited a smooth surface with a height variation of ±2 nm. In contrast, the β-Ga$_2$O$_3$ film on YSZ-buffered Si substrates exhibited a slightly rougher surface with a height variation of ±4 nm. These results are also supported by SEM results (see Figure S1).

A high-resolution X-ray diffractometer (Bruker Discovery D8) equipped with a two-channel cut Ge(220) and four crystal monochromators ($\lambda = 1.5406$ Å, 30 kV) was used for the structural analysis of the epitaxial β-Ga$_2$O$_3$ thin films. Figure 2c,d show the XRD θ−2θ scan spectra of the β-Ga$_2$O$_3$ thin films deposited on YSZ and YSZ-buffered Si substrates, respectively. In both cases, the XRD θ−2θ patterns show only {201} diffraction peaks. These results clearly indicate that both β-Ga$_2$O$_3$ thin films grown on the YSZ and YSZ-buffered Si substrates are epitaxially grown with a (201) orientation along the out-of-plane direction.

To study the effect of thermal treatment on the crystalline quality and strain states of β-Ga$_2$O$_3$ thin films, we performed post-annealing processes. The samples were annealed in a tube furnace at 1100 °C under O$_2$ flow (20 sccm) for 5 h at a heating and cooling rate of ~1 °C/min. This annealing condition did not cause cracks in β-Ga$_2$O$_3$ films. To evaluate the crystalline quality of the β-Ga$_2$O$_3$ films, we measured the full width at half maximum (FWHM) of the XRD rocking curve of the (201) peak, which is the most intense peak. The strain states of β-Ga$_2$O$_3$ thin films were characterized by a shift in the (603) diffraction peak. Figure 3a,b show the XRD θ−2θ scan ($57$−$61^\circ$) of the β-Ga$_2$O$_3$ thin films deposited on the YSZ and YSZ-buffered Si substrates, respectively, before and after annealing. For both cases, the (603) diffraction peak intensity increased by approximately one order of magnitude owing to thermal annealing, which indicates an improvement in the crystalline quality. The FWHMs of the (201) rocking curves of β-Ga$_2$O$_3$ thin films deposited on the YSZ and YSZ-buffered Si substrates also increased from 1.190 to 0.257 ° and from 1.300 to 0.543 ° (Figure 3c,d), respectively, owing to thermal annealing. This indicates that the crystalline quality of β-Ga$_2$O$_3$ thin films on YSZ substrates is significantly improved through thermal annealing, as shown in Figure 3e.

Notably, the (603) peak position in the θ−2θ scan of β-Ga$_2$O$_3$ thin films on YSZ-buffered Si substrates is higher than that of β-Ga$_2$O$_3$ thin films on YSZ substrates. Moreover, after thermal annealing, the peak of β-Ga$_2$O$_3$ thin films on the YSZ-buffered Si substrate shifted toward a higher angle, which indicates that the out-of-plane lattice parameter became smaller owing to thermal annealing. These results, summarized in Figure 3f, originate from the thermal stress that evolves from the difference in thermal expansion coefficients of β-Ga$_2$O$_3$ and Si.

To investigate the in-plane epitaxial relationship between a β-Ga$_2$O$_3$ thin film, YSZ buffer layer, and Si substrate, we...
performed XRD azimuthal $\varphi$ scans of $\beta$-Ga$_2$O$_3$(401), YSZ (202), and Si(202) peaks, respectively, as shown in Figure 4a. For YSZ and Si, four peaks appear at the same $\varphi$ angles at 90$^\circ$ intervals, indicating in-plane epitaxy with a cube-on-cube epitaxial relationship between the YSZ buffer layer and Si substrate. In contrast, eight $\beta$-Ga$_2$O$_3$(401) diffraction peaks appeared at two distinct intervals of 31 and 28°. Note that the (401) plane is unique without family planes in the monoclinic crystal structure. Therefore, one (401) peak in the $\varphi$ scan represents a particular domain of $\beta$-Ga$_2$O$_3$. Therefore, epitaxial $\beta$-Ga$_2$O$_3$ thin films on YSZ-buffered Si substrates had eight domain variants (Figure 4b). With respect to each of the four {100} directions of the YSZ-buffered Si unictell, two domains exist, with the [102] direction of $\beta$-Ga$_2$O$_3$ rotated by ±31°. Based on the XRD results, all eight domains are summarized in Figure 4b. This complex domain structure is attributed to the large mismatch between crystal structures of $\beta$-Ga$_2$O$_3$ and YSZ. As a potential application of the $\beta$-Ga$_2$O$_3$ films, we carried out photo current test. As shown in Figure S3, the $\beta$-Ga$_2$O$_3$ films on interdigitated electrode clearly showed photo-resistive characteristics which can be potentially applied to photodetector.

In summary, we successfully grew (201)-oriented epitaxial $\beta$-Ga$_2$O$_3$ thin films on Si substrates by employing epitaxial YSZ buffer layers. Biaxial compressive strain evolved in the $\beta$-Ga$_2$O$_3$ thin films on the YSZ substrate, whereas biaxial tensile strain evolved in the $\beta$-Ga$_2$O$_3$ thin films on the YSZ-buffered Si substrate. To further improve the crystalline quality, post-annealing was performed. Finally, we reveal that epitaxial $\beta$-Ga$_2$O$_3$ thin films have a complex domain structure with eight domain variants. These results will provide a pathway to integrate epitaxial $\beta$-Ga$_2$O$_3$ thin films on Si, which can broaden the scope of $\beta$-Ga$_2$O$_3$ applications beyond high-power electronics and toward UV photodetectors and gas sensors.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.2c04387.

Additional experimental results, including SEM, FWHM, and photo-detector data (PDF)

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**Notes**
The authors declare no competing financial interest.

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