Supporting Information

Low Thermal Budget Heteroepitaxial Gallium Oxide Thin Films Enabled by Atomic Layer Deposition

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A) Specification of the substrates:

Table S1. Specification of the substrates.

Single-Side Polished Sapphire Wafer	
Grade	Prime
Orientation	C-plane (0001), 0.2 ± 0.1° off M-axis, 0 ± 0.1° off A-axis
Dopant	Undoped
Thickness	430 ± 25 µm
Front Surface	Epi-polished, $R_a < 0.3$ nm
Back Surface	Fine-ground, $R_a = 0.8 – 1.2$ µm
Single-Side Polished Si (100) Wafer	
Grade	Prime
Orientation	(100) ± 0.5°
Dopant	Boron (p-type)
Resistivity	1 – 10 Ω.cm
Thickness	500 ± 25 µm
Front Surface	Mirror Polished
Back Surface	Lapped, Etched
Single-Side Polished Si (110) Wafer	
Grade	Prime
Orientation	(110) ± 0.5°
Dopant	Boron (p-type)
Resistivity	5 – 10 Ω.cm
Thickness	525 ± 25 µm
Front Surface	Mirror Polished
Back Surface	Lapped, Etched
Single-Side Polished Si (111) Wafer	
Grade	Prime
Orientation	(111) ± 1°
Dopant	Phosphorus (n-type)
Resistivity	320 – 480 Ω.cm
Thickness	500 – 550 µm
Front Surface	Mirror Polished
Back Surface	Lapped, Etched
Glass Slides	
Grade	Precleaned Plain Pearl Microscope Slides
Thickness	1.0 – 1.2 mm

B) X-ray diffraction analysis by 2θ-ω (rocking) scans:

To examine the broadness of thin film peaks for crystalline films on sapphire and examine possible strain in those films, XRD measurements were performed using rocking scans (aka 2θ-ω scans) by using Bruker D8 Discover diffractometers producing K-α radiation of either cobalt or copper, Vantec 500 detectors, and a sample-to-detector distance of 20 cm at an exposure of 140 s/step with 0.4° to 0.5° ω scan steps. To perform the measurements, 2θ was kept constant by moving both the detector and the X-ray source altogether while ω was being scanned. The 2θ angle was chosen such that the three peaks corresponding to α-Al_2O_3 (006), α-Ga_2O_3 (006), and β-Ga_2O_3 ($\bar{4}02$) can be simultaneously captured in each frame.

The resulting patterns are shown in Figure S1 (the data for the bare sapphire and the as-deposited film have been collected using cobalt X-ray source. However, all the patterns have been converted to Cu wavelength for easier comparison with each other and with literature patterns). The small broadness of the thin film peaks in Figure S1 indicates the high crystalline quality of both α-Ga_2O_3 (006) and β-Ga_2O_3 ($\bar{4}02$) in the thin films (film intensity distributions while varying ω in Figure S1 are as narrow as the single-crystal substrate intensity distribution).

Moreover, Figure S1 shows that both the 277°C as-deposited film on sapphire as well as the 550°C annealed film on sapphire are partially strained. The strain in each phase in these epitaxial films was calculated based on the deviation of the film peak positions from expected relaxed peak positions, and the results are listed in Table S2 indicating that the amount of strain in the films is small.

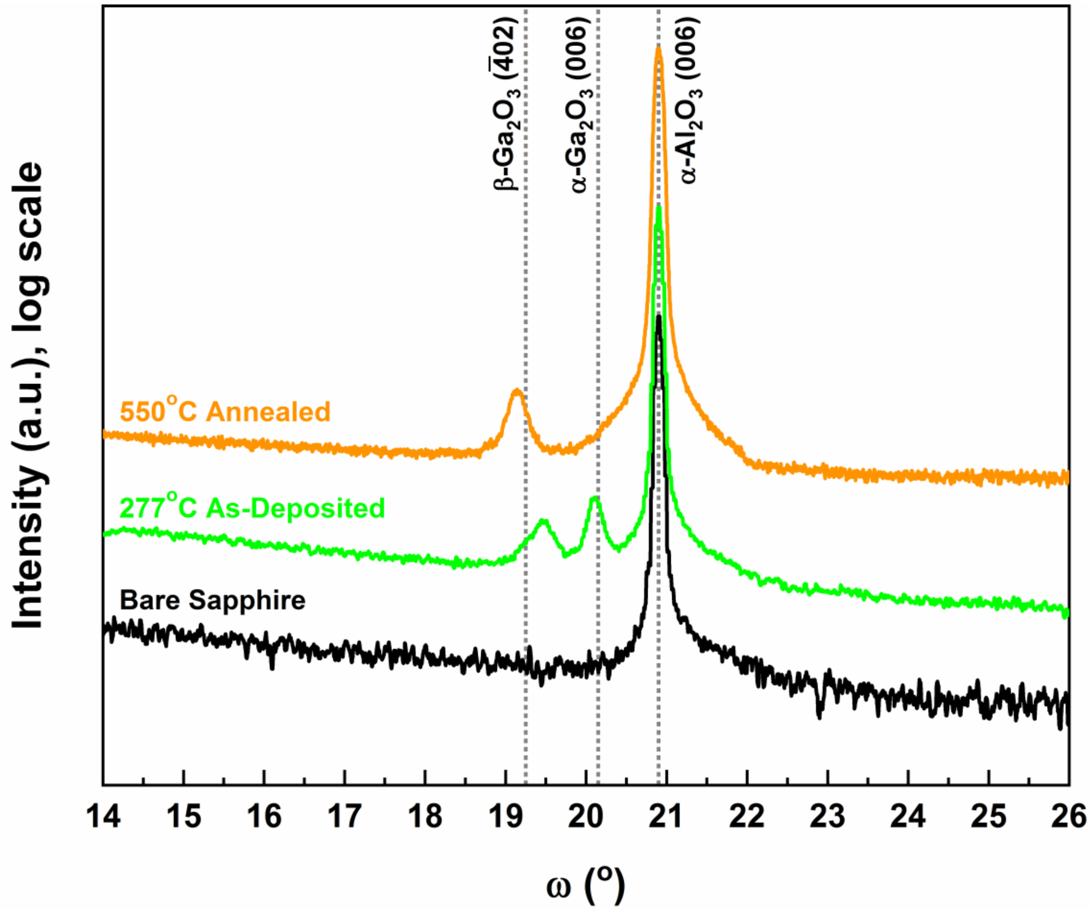

Figure S1. Results of XRD rocking scans (aka 2θ-ω scans) for Ga_2O_3 samples on sapphire collected at $2\theta = 41°$ (based on Cu wavelength). Dotted lines specify peak positions in relaxed crystals. Rocking curve of the bare c-plane sapphire substrate is also included as reference. The data have been collected using either cobalt or copper X-ray source. However, all the patterns have been converted to Cu wavelength for easier comparison with each other and with literature patterns. The intensities in this figure have been normalized such that the intensity of the α-Al_2O_3 (006) peak is the same in all the patterns.

Table S2. The amount of strain in the 277°C as-deposited film on sapphire as well as the 550°C annealed film on sapphire based on deviation of the film peak positions from expected relaxed peak positions observed in XRD rocking curves.

sample (on c-plane sapphire)	crystalline phase and plane	calculated strain
277°C As-Deposited	α-Ga_2O_3 (006)	- 0.19%
	β-Ga_2O_3 ($\bar{4}02$)	+ 1.04%
550°C Annealed	β-Ga_2O_3 ($\bar{4}02$)	- 0.50%

C) In-plane X-ray diffraction analysis by off-specular φ-scans:

In order to study in-plane orientation of β-Ga_2O_3 domains on sapphire (i.e., to study planes that are non-parallel to the sample surface), XRD measurements were performed using off-specular φ-scans by using a Bruker D8 Discover diffractometer equipped with an IμS copper source along with MONTEL optics producing Cu K-α radiation, a LYNXEYE XE detector at exposures ranging from 35 to 50 s/step with 0.25° φ scan steps. More specifically, φ-scans were performed at the 2θ angle of each plane of interest while the sample was tilted to an appropriate χ angle so that the normal to the plane of interest bisects the beam path.

Figure S2 shows the patterns corresponding to α-Al_2O_3 (102) and β-Ga_2O_3 ($\bar{4}01$) planes observed in off-specular φ-scans for the 277°C as-deposited film on sapphire as well as the 550°C annealed film on sapphire. Appearance of three peaks in the α-Al_2O_3 (102) φ-scan reveals the 3-fold symmetry of the underlying sapphire substrate (belonging to the space group R$\bar{3}$c). Meanwhile, considering the centrosymmetric structure of β-Ga_2O_3 (belonging to the space group C2/m) two peaks are expected to be observed in β-Ga_2O_3 ($\bar{4}01$) φ-scan. Appearance of six peaks in β-Ga_2O_3 ($\bar{4}01$) φ-scan each one having 30° φ offset from the α-Al_2O_3 (102) peaks, reveals that there are three in-plane orientations of β-Ga_2O_3 in the film matching the symmetry of the underlying sapphire substrate, with approximately same population, and all with the same normal orientation of β-$Ga_2O_3(\bar{2}01) \parallel \alpha$-$Al_2O_3(006)$. Similar observations for epitaxial β-Ga_2O_3 films on sapphire have been investigated in detail in the literature (see, for example, references 52 to 55 [52-55] for relevant discussions) and have been attributed to the fact that β-Ga_2O_3 has a less symmetric crystal structure than α-Al_2O_3, thereby enabling the formation of more than one in-plane orientation of β-Ga_2O_3 on α-Al_2O_3.

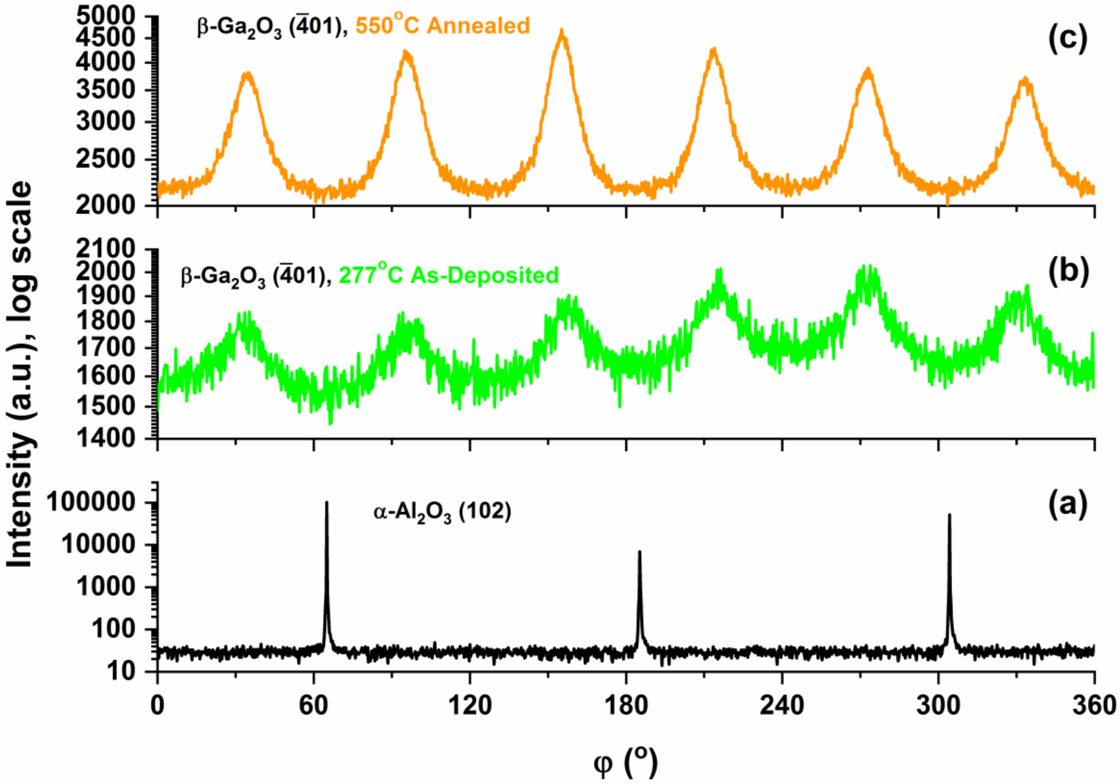

Figure S2. Results of off-specular φ-scans for (a) sapphire (102), (b) β-Ga_2O_3 ($\bar{4}01$) in the 277°C as-deposited film, and (c) β-Ga_2O_3 ($\bar{4}01$) in the 550°C annealed film.

D) Optical properties of gallium oxide on sapphire before and after annealing:

Figure S3 shows the dispersion of refractive index (n) and extinction coefficient (k) for gallium oxide films on sapphire before and after annealing over the entire ellipsomerty spectral range based on Tauc-Lorentz modeling of the ellipsometry data. In addition, Table S3 compares the optical bandgap for those films, their refractive index (n) at the selected photon energy of 632.8 nm (equivalent to 1.96 eV, at which light absorption does not occur in gallium oxide), and their maximum value of extinction coefficient (k_{max}).

As evident from both Figure S3 and Table S3, the 550°C annealed film on sapphire has a larger bandgap, larger k_{max}, and overall larger refractive indices compared to the starting film (i.e., the 190°C as-deposited film). These results are consistent with the fact that annealing the 190°C as-deposited film (which is at the onset of crystallinity) at the temperature of 550°C has transformed the film to a highly oriented β-gallium oxide film.

Furthermore, considering that α-Ga_2O_3 has higher packing density of atoms (therefore, larger refractive index) than β-Ga_2O_3 and based on the refractive index values reported in Table S3 (in this Supporting Information file) and Figure 2 (in the main manuscript), it is worth noting that while the as-deposited films that have high crystalline quality and a higher amount of the α-phase mixed with the β-phase (see the film deposited at T_{sub} = 277°C as an example) can have slightly larger refractive index values compared to the 550°C annealed film due to the absence of the α-phase in the 550°C annealed film, the 550°C annealed film still has reasonably large refractive index ($n > 1.9$ at 632.8 nm) compared to the reported value of 1.97 for bulk β-Ga_2O_3 wafers.[43] Meanwhile, as mentioned in the manuscript, the best as-deposited film properties on sapphire were obtained at T_{sub} = 277°C, beyond which the crystal structure slightly degraded and the bandgap decreased; it is worth noting that the 550°C annealed film still has a larger bandgap than the films deposited at T_{sub} > 277°C, which is an indication of the relatively low defect density in the 550°C annealed film as a pure β-phase epitaxial film with no α-Ga_2O_3 inclusions that could be detected by XRD in the film.

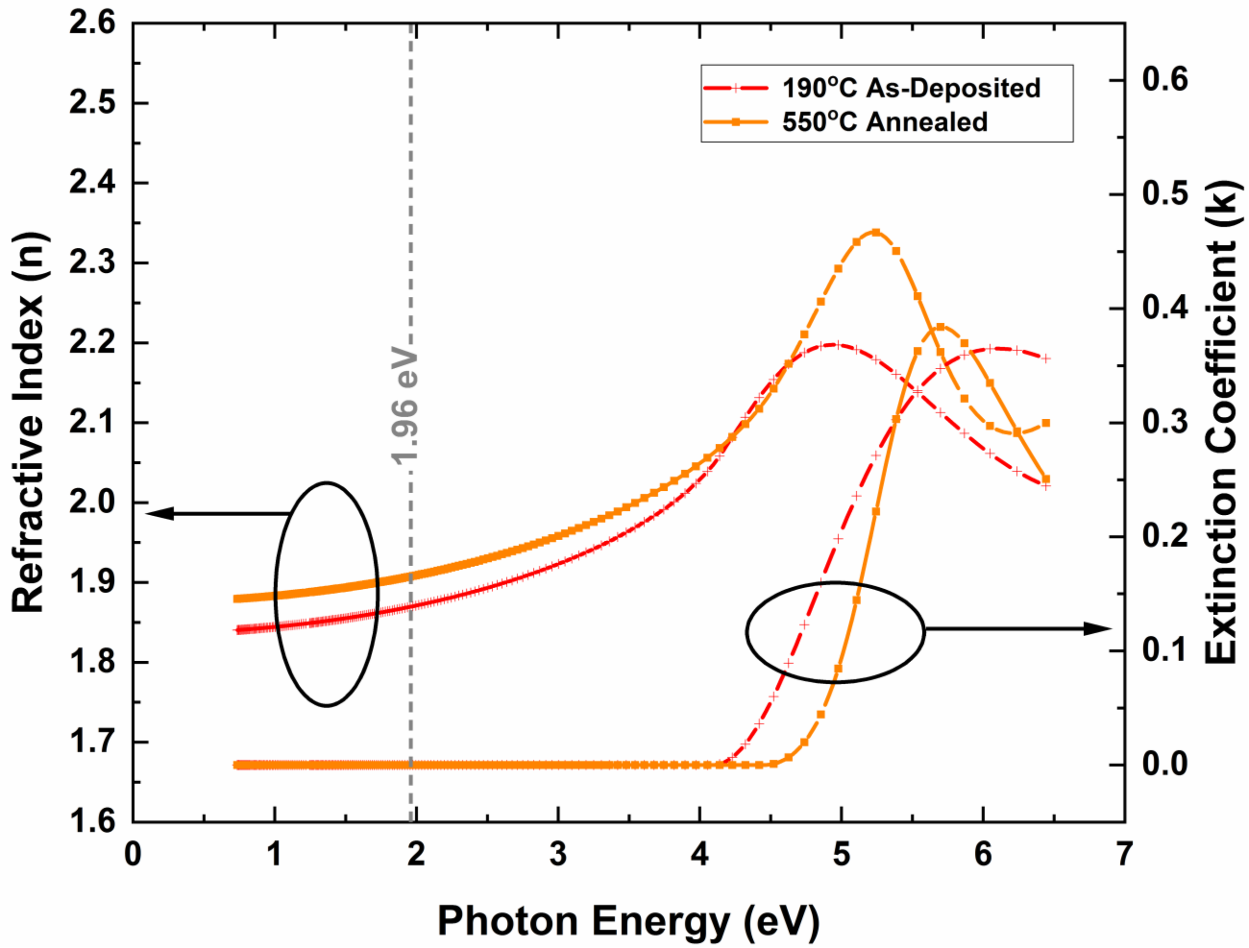

Figure S3. Optical constants of Ga_2O_3 films on sapphire before and after annealing as a function of photon energy based on Tauc-Lorentz modeling of the ellipsometry data. The photon energy corresponding to 632.8 nm (i.e., 1.96 eV) has been identified by a dashed line for reference.

Table S3. Comparison of optical properties for ~38 nm Ga_2O_3 films on sapphire before and after annealing based on Tauc-Lorentz modeling of the ellipsometry data. The error in refractive index and extinction coefficient values is limited to ±0.001 in all cases.

sample	E_g (eV)	n at 632.8 nm	k_{max}	MSE
190°C As-Deposited	4.094 ± 0.014	1.870	0.365	2.837
550°C Annealed	4.447 ± 0.014	1.908	0.384	1.892