1. Introduction

Beta-polymorph gallium oxide ($\beta$-Ga$_2$O$_3$) has the widest known bandgap that can attain controllable n-type doping. Based on its high breakdown field strength and availability of high-quality native substrates, there has been tremendous interest in Ga$_2$O$_3$ for power electronics applications. Other than power electronics, another potential application for Ga$_2$O$_3$ is in deep-ultraviolet (DUV) photodetectors. Over the years, DUV photodetection incorporating Ga$_2$O$_3$ thin films has been investigated chiefly for its possible applications in efficient solar-blind radiation detection. This technology has the potential to open a new paradigm in early missile threat detection and interception, indoor fire-alarm systems, outdoor fire surveillance for civil defense, forest-fire detection, and ultraviolet-C solar radiation observation in ozone-monitoring stations. Still, reports in the literature have not thoroughly examined growth processes of heteroepitaxial monocrystalline thin films on transition metal nitride interlayers. Owing to their intrinsic structural order and electronic properties, transitional metal ceramics combine superior corrosion resistance and mechanical hardness with high electrical conductivity, facilitating the high temperature growth and utilization of emerging oxide semiconductors on nonconductive substrates for fabricating vertically oriented optoelectronic devices.

DUV photodetectors incorporating $\beta$-Ga$_2$O$_3$ thin films have been the subject of extensive studies since the introduction of epitaxial deposition techniques for group III-oxide materials because they enhance photosensitivity and solar-blind photodetection characteristics. However, previous research...
has never investigated the hybrid integration of β-Ga$_2$O$_3$ on transition metal nitride lattice templates, which offers excellent electrical conductivity and catalytic properties. With respect to optoelectronics, most researchers have so far focused on ultrawide-bandgap group III-oxides-based devices grown and fabricated directly on bulk hexagonal phase alpha-polymorph aluminum oxide (i.e., α-Al$_2$O$_3$ or sapphire) substrates,[4,5] which are suitable for hexagonal phase material epitaxy and suffer from considerably lower thermal conductivity and relatively higher thermal expansion coefficients than other inorganic platforms.[6]

Areas of DUV photodetection that lack progress include the fabrication of DUV photodetectors on thermally conductive platforms to enhance their quantum efficiencies and the hybrid integration of semiconductors on emerging material platforms to realize new device architectures that enable higher photoconductive gains and possibly faster response times. Therefore, newly developed platforms for the growth of high-quality β-Ga$_2$O$_3$ thin films have become necessary to the realization of high-efficiency and low-cost hybridized optoelectronics and reliable and high-performance power electronics with integral heat sinks. In particular, monocrystalline titanium nitride (TiN) would constitute an excellent current-spreading layer because of its superior electrical conduction characteristics. TiN can also form an antidualfusion[9] and refractory metal layer,[7,8] enabling higher numbers of operating cycles of a device and increased operating temperatures. TiN is also an excellent thermal conductor and an anticorrosive ceramic material.[9–14]

TiN is often classified as a barrier metal, despite the fact that it is evidently a refractory ceramic from a chemomechanical point of view.[5] Given its compatibility with complementary metal–oxide–semiconductor (CMOS) processes, low resistivity, high thermal stability, and mechanical durability, TiN has emerged as a particularly critical element in the semiconductor microelectronics industry. It has been used as an electromigration blocking layer for metal interconnects in modern integrated circuit chips,[16–18] providing conductive channels between a device’s metal contacts and its active region while acting as a diffusion barrier to prevent the diffusion of metal atoms into the substrate. TiN crystallizes as a diamond cubic crystal structure (Pearson symbol: cF8; cubic crystal family, all face-centered with 8 atoms in its unit cell) as sodium chloride (NaCl) does. It has a cubic unit cell lattice constant $a$, a face diagonal length $d_f$, and a body diagonal length $d_b$ of about 4.236–4.241 Å, 5.998, and 7.364 Å, respectively,[21–23] It follows naturally that the lattice mismatch between TiN ($a = 4.236–4.241 \text{ Å}$) and magnesium oxide (MgO) ($a = 4.210–4.212 \text{ Å}$)[24–27] is less than 0.97%, given that they are both cubic phase crystals. Thus, MgO substrates are an excellent choice for cubic phase material epitaxy, whereas sapphire substrates are more suitable for hexagonal phase material epitaxy.[1,28] Furthermore, MgO exhibits higher thermal conductivity than that of sapphire. Thus, we anticipate that the hybrid integration of β-Ga$_2$O$_3$ on TiN lattice templates grown heteroepitaxially on MgO can assist in achieving low-cost and efficient vertically structured DUV photodetectors if the cubic phase TiN thin film interlayer plays an excellent electrically conductive lattice growth template for monoclinic phase β-Ga$_2$O$_3$ heteroepitaxial growth, thus causing enhanced photocurrent generation and improved device performance upon light illumination.

In this work, we report on the growth of a hybrid thin film stack comprising monocrystalline unintentionally doped β-Ga$_2$O$_3$ layers on a TiN/MgO lattice template by pulsed laser deposition (PLD).[29,30] Several characterization techniques were employed to investigate the heterostructure, including X-ray diffraction (XRD), scanning and high-resolution transmission electron microscopy (STEM and HRTEM), and energy-dispersive X-ray (EDX) spectroscopy. EDX analysis[31] combined with STEM and high-angle annular dark-field (HAADF) micrography were used to confirm the chemical composition of each deposited film. We observed the sharp layer transitions and high quality of interfaces in the heterostructure stack of β-Ga$_2$O$_3$/TiN through HRTEM micrography. We also fabricated a solar-blind DUV photodetector based on the resulting metal–semiconductor heterojunctions. Our photodetectors exhibited an average peak spectral responsivity of 276.62 A W$^{-1}$ at 15 V reverse-bias voltage for a 250 nm $\lambda_{in}$ and $P_{in} = 70 \mu$W cm$^{-2}$. Figure 1A shows a schematic illustration of the photodetector fabrication process. Figure 1B depicts a cross-sectional view of the device’s structural configuration; the inset in Figure 1B shows a top view of the top electrode design. Given the formation of self-trapped holes (i.e., polarons), p-type doping in Ga$_2$O$_3$ has not been demonstrated. Therefore, optoelectronic devices based on Ga$_2$O$_3$ p–n homojunctions are not feasible. Thus, the MSM photodetector is the main structure on which this work focused.

Wakabayashi et al. reported on the heteroepitaxial growth of β-Ga$_2$O$_3$ thin films on (100)-oriented MgO substrates using PLD and studied their structural and electronic properties as a
The grown films were found to comprise metastable cubic $\gamma$ and rotation twin-domain structure monoclinic $\beta$-phases of $\beta$-Ga$_2$O$_3$ when grown at temperatures exceeding 500 °C. However, no detailed crystallographic analysis in terms of electron microscopy imaging were provided, and an optoelectronic device based on the heteroepitaxially grown $\beta$-Ga$_2$O$_3$ thin films was not fabricated given the insulating and multiphase natures of MgO substrates and the grown films, respectively. Therefore, the incorporation of TiN interlayer in our present work allows for the successful hybrid integration of stable-state $\beta$Ga$_2$O$_3$ thin films on inexpensive and common semiconductor substrates for realizing vertically oriented DUV photodetectors. The metastable $\gamma$-phase crystal was formed in the Ga$_2$O$_3$ thin films grown by Wakabayashi et al. because they were synthesized at temperatures around or below 600 °C and at a relatively low laser fluence of 0.2 J cm$^{-2}$, rendering any attempt to fabricate an efficient and reliable DUV photodetector inconceivable. Through the vaporization of Ga under O$_2$ plasma, Nakagomi et al. reported similar results.[33] Matsuo et al. also investigated the epitaxial growth of $\beta$-Ga$_2$O$_3$ directly on bulk MgO using molecular beam epitaxy (MBE) and studied the energy band alignment at the heterointerface, but their study lacks insight into the fact that bulk MgO surfaces are incomparable to those of epitaxially grown MgO dielectric layers; therefore, practical device demonstration based on their surface science study was impossible.[34] Similarly, Wang et al. investigated the epitaxial growth of $\beta$-Ga$_2$O$_3$ on bulk potassium tantalum oxide (KTaO$_3$) using metalorganic vapor-phase epitaxy.[35] Given that KTaO$_3$ is nonconductive, in the absence of a conductive interlayer, realization of a practical optoelectronic device using this junction is infeasible. However, Chen et al. studied the effect of O$_2$ partial pressure on the crystallographic orientation of deposited polycrystalline $\beta$-Ga$_2$O$_3$ thin film on c-plane sapphire using PLD.[36] They also fabricated a laterally oriented MSM DUV photodetector that achieved a spectral responsivity of 0.6 A W$^{-1}$ at 25 V reverse bias ($V_{bias}$). This relatively inadequate device performance was a result of poor material quality. Thus, the novelty of our work is rooted in the growth of monocrystalline $\beta$-Ga$_2$O$_3$ thin films on monocrystalline TiN conductive templates; the detailed examination of crystallographic and electric interface characteristics of this novel heterojunction, and the realization of an ultrahigh-gain vertical DUV photodetector with unprecedented photoreceptive performance.

2. Results and Discussion

2.1. Electron Microscopy Analysis

Figure 2A-I shows a cross-sectional TEM micrograph of an epitaxially grown $\beta$-Ga$_2$O$_3$/TiN/MgO hybrid stack for the a-plane zone axis, confirming the high interface qualities exhibited at the $\beta$-Ga$_2$O$_3$/TiN and TiN/MgO interfaces through the sharp layer transitions, whereas the HRTEM micrographs and fast Fourier transform (FFT) patterns in Figures 2A-II and 2A-III confirm the structural integrity and symmetry of the lattice fringes on the cross sectional TiN/MgO [(200), (220), and (020) FFT plane spots] and $\beta$-Ga$_2$O$_3$ [(400), (512), and (112) FFT plane spots] HRTEM micrographs, respectively. The purpose of the marked glue protection layer, composed mainly of platinum (Pt), was to protect the TEM sample during focused ion beam (FIB) milling. Figure 2B-I displays a cross-sectional STEM micrograph of the sample; Figure 2B-II shows an HAADF micrograph with EDX spectra that confirm each layer’s composition and thickness and the low thermally induced interdiffusion characteristics during layer growth. In the EDX mapping shown in Figure 2B-II, Mg X-ray artificial emission peaks were detected at the $\beta$-Ga$_2$O$_3$ layer because Mg exhibits peaks at 1.254 keV ($K_{\alpha}$) and 0.048 keV ($L_{\alpha}$), whereas Ga peaks at 9.250 keV ($K_{\beta}$) and 1.098 keV ($L_{\beta}$). Mg $K_{\beta}$ and Ga $L_{\beta}$ EDX spectra peak in close proximity to each other, and, as such, the EDX detector cannot intrinsically distinguish between Mg $K_{\alpha}$ and Ga $L_{\alpha}$ emission peaks.[37–39] If Mg diffused from the substrate into the $\beta$-Ga$_2$O$_3$ layer, the same Mg $K_{\alpha}$ signal would have been detected in the TiN layer. Figure 2C displays each created crystal model of $\beta$-Ga$_2$O$_3$ (Figure 2C-I), TiN (Figure 2C-II), and MgO (Figure 2C-III), along with their simulated FFT patterns. When we carefully examine the simulated FFT pattern of a $\beta$-Ga$_2$O$_3$ rotated exactly 45° in Figure 2C-I, we can observe that it does not closely match the acquired FFT pattern shown in Figure 2A-II because these FFT pattern simulations were based on the expected crystal orientations we initially depicted when a monoclinic phase $\beta$-Ga$_2$O$_3$ is grown heteroepitaxially on cubic phase TiN. This issue warranted this study’s careful consideration, as we elaborate here and in upcoming sections. In short, the grown $\beta$-Ga$_2$O$_3$ layer exhibited two unit cell configurations that were not exactly 45° to the left/right; rather, it exhibited rotational twin domains (i.e., 45° ± 0.85° rotation to the left/right). The lattice parameters $b$ and $c$ for $\beta$-Ga$_2$O$_3$ are around 3.03–3.04 Å and 5.80–5.87 Å, respectively. The distance of the nearest-neighbor N atoms on (100) TiN is 2.995 Å, whereas the distances on (100) $\beta$-Ga$_2$O$_3$ along the [010] and [001] directions are $b = 3.03–3.04$ Å and $c = 5.80–5.87$ Å, respectively. Therefore, considering the singlet particular situation, the mismatches along the $\beta$-Ga$_2$O$_3$ [010] and [001] directions are $(−) 2.465$ –2.803% and $(+)$0.748–1.932%, respectively.[40] The distances of the diagonal N atoms (the second nearest-neighbor pairs) are $a = 4.236–4.241$ Å on (100) TiN and 4.263 Å on (100) $\beta$-Ga$_2$O$_3$, resulting in a mismatch of about 1.01%, significantly lower than that of the nearest-neighbor N atoms. We conjecture that the twin domains were formed because of the reflection symmetry of the N sublattice. More details about the crystal alignment are provided in the Supporting Information.

Because the $\beta$-Ga$_2$O$_3$/TiN heterojunction was grown on (001)-oriented bulk MgO, analysis of HRTEM micrographs for the zone axis with FFT patterns in Figures 2A-II and 2A-III reveal the zone axes of MgO, $\beta$-Ga$_2$O$_3$, and TiN to be a-plane (020), (112), and (020), respectively. In each FFT pattern, the upward and rightward directions correspond to the directions of the $c$- and $a$-axis, respectively, given the mathematical descriptions that govern FFT spectra because physical and inverse coordinates are correlated. Therefore, the orientation relationships between $\beta$-Ga$_2$O$_3$ and TiN were determined to be

$$\beta$-Ga$_2$O$_3$ || (200) TiN || (200) MgO \hspace{1cm} (1)$$

and

$$\beta$-Ga$_2$O$_3$ || (020) TiN || (020) MgO \hspace{1cm} (2)$$

The determined orientation relationship in Equation (1) is in agreement with the out-of-plane XRD results presented in Figure 6A,
which provides the orientation relationship along the c-axis, as the plane relationships in equations (1) and (2) were resolved by FFT analysis, through which we could examine the crystal a-axis configuration. The first observed spots located right above the center of each indexed FFT pattern were used to attribute the Miller indices to the observed spots because our homogeneous crystalline thin films were aligned in the epitaxy orientation.

In Figure 3, we display original (left) and plane-filtered (right) HRTEM micrographs taken from regions of the β-Ga₂O₃ layer (Figure 3A), β-Ga₂O₃/TiN interface (Figure 3B), and TiN/MgO interface (Figure 3C). The plane-selective HRTEM micrographs were acquired from FFT patterns by first masking the unrelated FFT spots originating from all planes, except for the ones corresponding to the planes we were interested in examining.
Then, we calculated the inverse FFT of the filtered FFT patterns, producing the plane-selective HRTEM micrographs. In Figure 3A, we show an HRTEM micrograph that corresponds to the region of β-Ga₂O₃ inside the orange square in Figure 2A-I. One can observe abrupt transition in the unit cell configuration within the grown β-Ga₂O₃ film on TiN/MgO (marked with a transparent red dashed line). These column-shaped structures become more manifest as we transit farther away from the β-Ga₂O₃/TiN interface in the direction of layer growth. Therefore, we hypothesize that the monoclinic phase β-Ga₂O₃ layer grows thicker on cubic phase TiN, the dispersion in unit cell configuration becomes more distinct. For β-Ga₂O₃ in Figure 2A, we applied a mask to observe all the plane reflections we were interested in (see Supporting Information); therefore, we generated the filtered version of the HRTEM micrograph in the right-hand side. When the filtered HRTEM micrograph is compared to its original counterpart, one can observe that the latter is sharper, and one can distinguish observe the boundary between the two hypothesized unit cell configurations. As illustrated on the figure, the two superimposed unit cell configurations are separated by stacking faults, as opposed to defect-free disordering of crystallographic planes, giving rise to double twofold crystallographic symmetry. We believe that the slow response times exhibited by the fabricated photodetectors are caused by such high-density defects. In Figure 3B, we consider the inverse FFT pattern generated at the β-Ga₂O₃/TiN interface and formed by masking the FFT spots corresponding to all planes except that of the (020) TiN and (112) β-Ga₂O₃ planes. We observe interplexing and convoluted lines that resemble edge dislocations that we attribute to the lattice mismatch between β-Ga₂O₃ and TiN. The (020) TiN and (112) β-Ga₂O₃ planes are pure a-axis; therefore, the application of inverse FFT reveals edge dislocations. Similarly, in Figure 3C, we examine the inverse FFT pattern generated at the TiN/MgO interface and formed by masking the FFT spots corresponding to all planes except that of the (020) planes of TiN and MgO. We also observe interplexing and convoluted lines that resemble edge dislocations that can be attributed to the small lattice mismatch between TiN and MgO. Detailed FFT and line profile analysis, including a discussion on the universality of observed edge and stacking fault dislocations, are provided in the Supporting Information (Sections 1 and 2).

The (200) plane spacings (d_{200}) of MgO, β-Ga₂O₃, and TiN were estimated using the HRTEM micrographs and found to be 2.056, 5.793, and 2.091 Å, respectively, which closely matches the reported values in the literature. We believe that the slow response times exhibited by the fabricated photodetectors are caused by such high-density defects.

Figure 4 shows our FFT pattern simulation of a β-Ga₂O₃ lattice exhibiting a twin domain structure with a further unit cell rotation of ±0.85°. When we further rotate the crystal structure by ±0.85°, the resulting simulated FFT pattern for β-Ga₂O₃ matches that of the acquired FFT pattern in Figure 2A-II.

Finally, in Figure 5, we schematically illustrate the hypothesized unit cell configuration of β-Ga₂O₃ on TiN with a top-view depiction of the atomic positioning of the heteroepitaxially grown β-Ga₂O₃ film on TiN interlayer on MgO. Because Ga is a metal, it will bond with N; likewise, O will bond with Ti to form covalent bonds. The brighter green atoms in Figure 5A-II (cross-sectional image of the (400) β-Ga₂O₃ plane) resemble the Ga atoms that are located above the cross-section, whereas dimmer atoms are located below the cross-section. The two coexisting β-Ga₂O₃ unit configurations caused double twofold crystallographic symmetry that is further manifested and proven by the XRD analysis based on φ scans for asymmetric reflections in the next section.

2.2. X-Ray Diffraction Characterization of Grown Thin Films

Figure 6A shows the out-of-plane XRD traces of the hybrid material stack comprising a 400 nm thick, heteroepitaxially grown β-Ga₂O₃ thin film on a TiN interlayer grown heteroepitaxially on a (100)-cut MgO substrate under the conditions described earlier. As our out-of-plane XRD experimental set up was not equipped with a monochromator, peaks diffracted from the (200) and (400) MgO planes by a spectrum of X-ray wavelengths emitted by the tube, including fluorescence lines, can be observed in the substrate’s XRD pattern. The pattern contains (400) β-Ga₂O₃ and (200) TiN plane reflections at 2θ≈29.99° and 42.53°, respectively, after the β-Ga₂O₃ thin film growth, indicating that the TiN film is textured with [100]
of TiN aligned with [100] of MgO. The diffraction resolution-limited lattice constant \( a \) of TiN from this trace was determined to be 4.248 Å. Because an out-of-plane XRD measurement, whereby parallel diffracting planes are detected irrespective of their rotations, indicates how the crystal axes are aligned with respect to each other in terms of normal vectors and a family of lattice planes, one can confirm the following c-axis crystallographic plane relationship between the grown films and MgO substrate from Figure 6A:

\[
(400) \beta\text{-Ga}_2\text{O}_3 \ || (200) \text{TiN} \ || (200) \text{MgO}
\]

XRD doublets at \( 2\theta = 45.55^\circ, 62.04^\circ, \) and 101.12° correspond to (600), (800), and (1200) \( \beta\text{-Ga}_2\text{O}_3 \) plane Bragg reflections, respectively, whereas XRD doublets at \( 2\theta = 42.53^\circ \) and 92.75° correspond to (200) and (400) TiN plane Bragg reflections. The (1000) \( \beta\text{-Ga}_2\text{O}_3 \) plane Bragg reflection is in destructive interference with the X-ray source and therefore is not detected. Figure 6B-I and Figure 6B-II show the XRD rocking curve (RC) measurements of the (400) \( \beta\text{-Ga}_2\text{O}_3 \) and (200) TiN plane Bragg reflection, respectively. We used a Gaussian distribution to fit the XRD RC reflection profiles. The (400) \( \beta\text{-Ga}_2\text{O}_3 \) and (200) TiN plane Bragg reflection exhibited an FWHM value of around 1.144° and 0.255°, respectively, demonstrating very high-quality epitaxial TiN thin film by virtue of the low lattice mismatch with MgO. On the other hand, the (400) \( \beta\text{-Ga}_2\text{O}_3 \) plane Bragg reflection exhibited a relatively broad reflection profile given the heteroepitaxial growth nature of the \( \beta\text{-Ga}_2\text{O}_3 \) thin film. This relatively broad reflection profile can reasonably be associated to the double twofold crystallographic symmetry, which may lead to columnar growth and the introduction of more grain boundaries. However, we do not believe that the grown \( \beta\text{-Ga}_2\text{O}_3 \) thin films exhibited columnar growth given that they did not display abnormally rough surface morphology (see Section 4, Supporting Information) and because of the absence of nanowire-like structures.

Loosely referred to as “in-plane” XRD measurements in literature, \( \phi \)-scan asymmetric XRD measurements, whereby parallel diffracting planes are detected with respect to their rotations, reveal how the crystal axes are aligned azimuthally with respect to each other. Figure 7A-I shows the asymmetric XRD
Figure 6. A) Out-of-plane XRD measurements of the heteroepitaxially grown layers (β-Ga2O3/TiN/MgO and TiN/MgO) and bulk MgO in semilogarithmic scale. B) XRD RC measurements of the (400) β-Ga2O3 (I) and (200) TiN (II) plane Bragg reflection.

measurements of the grown β-Ga2O3 film and the TiN on MgO substrate. Four (420) β-Ga2O3 asymmetric Bragg reflections that are separated by 45° were observed, indicating that the planes are orthogonal to each other; however, when we combine these XRD results with our earlier observations from TEM analysis and crystal model simulations, we conjecture that there are two β-Ga2O3 unit cell configurations that provide double twofold symmetry: Two (420) β-Ga2O3 Bragg reflections that originate from the configuration rotated about 45° to the right, and the other two (420) β-Ga2O3 Bragg reflections originating from the configuration rotated about 45° to the left. Otherwise, if there were no multiple-unit cell configurations were present in the grown lattice, we would observe only two XRD Bragg reflections in Figure 7A-I. Also, once we zoom in on any of the plane Bragg reflection pairs (as shown in Figure 7A-II, the first Bragg reflection pair consists of the first and third Bragg reflection peaks), we discover that the (420) β-Ga2O3 plane Bragg reflection split because the β-Ga2O3 lattice’s two configurations exhibit further rotation of 0.85° to the left/right (twin-domain structure). From the electron microscopy date analysis and structure simulations presented in the previous section, we observed a further rotation by ±0.85° in addition to the ±45° rotation in both β-Ga2O3 unit cell configurations. As can be seen in Figure 7A-II, the (420) β-Ga2O3 plane Bragg reflection is not well aligned with that of (222) TiN; it rotates about 0.85° to the left/right presumably because of the strain caused by the small lattice mismatch. Therefore, our XRD analysis confirms our earlier hypothesis that when β-Ga2O3 is grown epitaxially on TiN, the grown layers exhibit unit cell rotation of 45° ± 0.85° to the left/right.

More details are provided in Section 3, Supporting Information. By aligning the observed Bragg reflections, we can deduce the following crystallographic plane relationship between the grown β-Ga2O3 grain at the interface and TiN grain on MgO:

\[
(020) \beta-\text{Ga}_2\text{O}_3 \parallel (022) \text{TiN} \parallel (022) \text{MgO}
\]  

Figure 7B-I,II depicts the XRD RC measurements of the (420) β-Ga2O3 and (222) TiN/MgO Bragg reflections, where a split in the (420) β-Ga2O3 plane reflection can be observed. We conjecture that because the monoclinic β-Ga2O3 layer grown on cubic TiN has two unit cell configurations, it has become intrinsically highly defective. Growth-induced oxygen vacancies and carbon impurities from the PLD target also contributed to such higher levels of defect densities. The (222) TiN plane Bragg reflection exhibited an FWHM of around 0.240°, further confirming a high-quality epitaxial TiN thin film. RC measurements of (222) TiN and MgO Bragg reflections nearly overlap because their lattice constants are remarkably close in value.

2.3. Photocurrent Characteristics and DUV Photodetection

This section investigates the DUV photodetection characteristics of fabricated photodetectors based on the heteroepitaxially grown β-Ga2O3 on a TiN ceramic template. The solar-blind photodetectors exhibit an average peak \( R_{\lambda} \) of 276.72 A W⁻¹ at 15 V reverse bias, for \( \lambda_{\text{in}} = 250 \text{ nm} \) and \( P_{\text{in}} = 70 \mu \text{W cm}^{-2} \). Average ultraviolet-to-visible rejection ratios \( (R_{395\text{nm}}/R_{423\text{nm}}) \) of 9.53 × 10² and 2.03 × 10³ were attained for \( P_{\text{in}} = 423 \pm 60 \mu \text{W cm}^{-2} \) (high \( P_{\text{in}} \) level) and \( P_{\text{in}} = 13 \pm 2 \mu \text{W cm}^{-2} \) (low \( P_{\text{in}} \) level), respectively. The photodetector characteristics were measured at low and high \( P_{\text{in}} \) levels to broadly analyze its sensitivity and the transport mechanism to avoid electronic saturation at high impinging power levels. Given a reverse-biased heterojunction under a uniform incident-light illumination of a particular wavelength \( \lambda_{\text{in}} \) and optical power density \( P_{\text{in}} \), the spectral responsivity \( R_{\lambda_{\text{in}}} \) of the resultant photodetector is a parameter that quantizes the internal quantum efficiency \( \eta_{\lambda_{\text{in}}} \) and the photoelectric gain \( g \) of a photodetector, which are determined by the generated number of carriers per incident photon as a result of the absorption of incident light and the number of carriers that
conduct current through the electrical contact per generated electron–hole pair\textsuperscript{[44,45]} and can be estimated using
\[ R_{\text{V}_{\text{in}}, P_{\text{in}}} = \frac{q \eta_{\text{V}_{\text{in}}, P_{\text{in}}} \lambda_{\text{in}}}{h c} = \frac{I_{\text{V}_{\text{in}}, P_{\text{in}}} - I_{\text{dark}}}{P_{\text{IL}}}, \]  
(5)

where the product \( g \eta_{\text{V}_{\text{in}}, P_{\text{in}}} \lambda_{\text{in}} \) represents the external quantum efficiency (EQE), \( h \) is Planck’s constant, \( c \) is the speed of light in a vacuum, and \( P_{\text{IL}} \) is the effective illuminating power in W (\( P_{\text{IL}} = P \times (S/A) \)), where \( P \) is the total power of the irradiating beam, \( S \) is the effective irradiation area of the photodetector, and \( A \) is the area of the incident-light beam. By manipulating equation (5), the EQE can be expressed as
\[ \text{EQE} = g \eta_{\text{V}_{\text{in}}, P_{\text{in}}} = R_{\text{V}_{\text{in}}, P_{\text{in}}} \times \frac{hc}{q P_{\text{in}}} \]  
(6)

The signal-to-noise ratio (SNR) exhibited by a photodetector with an effective irradiation area \( S \) of 1 cm\(^2\) at an incident-light power of 1 W with an electrical bandwidth of 1 Hz is quantified through the specific detectivity (\( D' \)), as follows
\[ D_{\text{V}_{\text{in}}, P_{\text{in}}} = R_{\text{V}_{\text{in}}, P_{\text{in}}} \times \sqrt{\frac{S}{2 q I_{\text{dark}}}} \]  
(7)

where herein \( S \) is expressed in cm\(^2\), yielding the customary specific detectivity unit of cm/(\( \sqrt{S \cdot W} \)), or Jones. We should note that in Equations (5) and (7), we are underestimating \( R_{\lambda} \) and \( D' \) values because \( S \) was taken as the total device area without subtracting the area of the nontransparent metal contacts. Considering this and referring to the inset in Figure 1B, the effective device area was taken as 550 \( \times \) 500 \( \mu \)m\(^2\).

Figure 8 depicts measured photocurrent density versus \( V_{\text{bias}} \) (\( J_{\text{ph}}-V_{\text{bias}} \)) for a representative photodetector at an \( P_{\text{in}} = 13 \pm 2 \mu W \) cm\(^{-2}\) (Figure 8A, low \( P_{\text{in}} \) levels) and \( P_{\text{in}} = 423 \pm 60 \mu W \) cm\(^{-2}\) (Figure 8B, high \( P_{\text{in}} \) levels); measured \( P_{\text{in}} \)-dependent \( J_{\text{ph}}-V_{\text{bias}} \) curves for the photodetector at an \( \lambda_{\text{in}} = 250 \) nm are shown in Figure 8C. The representative device exhibited dark-current densities (\( J_{\text{d}} \)) of \( 9.32 \times 10^{-10} \) A cm\(^{-2}\) at zero bias, \( 5.02 \times 10^{-6} \) A cm\(^{-2}\) at 5 V reverse bias, and \( 8.29 \times 10^{-5} \) A cm\(^{-2}\) at 15 V reverse bias. From Figure 8C, one can observe that the photodetector exhibited photo-to-dark-current ratios of above 10\(^4\).

Figure 9 plots the evolution of the representative photodetector performance at low (Figure 9A) and high (Figure 9B) \( P_{\text{in}} \) levels. In both cases, the photodetector performance peaked at \( \lambda_{\text{in}} = 250 \) nm. We conjecture that the photodetector exhibited such high gain values (EQE > 10\(^4\)% because of the existence of trap-related deep-acceptor levels within the grown \( \beta \)-Ga\(_2\)O\(_3\) film as additional photoexcited electrons can be created from

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Asymmetric XRD measurements of grown \( \beta \)-Ga\(_2\)O\(_3\) and TiN layers on bulk MgO—A) Asymmetric (\( \alpha \)-plane) XRD measurements of grown \( \beta \)-Ga\(_2\)O\(_3\) and TiN layers on bulk MgO (I), and a zoomed-in version of the blue-shaded portion (II). B) XRD RC measurements of the (420) \( \beta \)-Ga\(_2\)O\(_3\) (I) and (222) TiN/MgO (II) Bragg reflections.}
\end{figure}
these defect states.\textsuperscript{[4,46]} Another hypothesis for such high gain values is the presence of a trap-related deep-acceptor level at the metal–semiconductor interface. This may have caused a reduction in the barrier height owing to charge neutrality and thus increased extracted photocurrent levels.\textsuperscript{[47]}

Figure 10A plots the evolution of average $R_A$ values with increasing $P_{in}$ levels up to 7,363 $\mu$W cm$^{-2}$ at an $\lambda_{in} = 250$ nm and a $V_{bias} = 5$ and 15V. Beyond 70 $\mu$W cm$^{-2}$, average $R_A$ values converge to 23.18 and 125.45 A W$^{-1}$ after peaking at 40.30 and 276.72 A W$^{-1}$ at 5 and 15 V, respectively, indicating a limit for ultraviolet-C photons to excite the photoelectrons from the valence band to the conduction band in the $\beta$-Ga$_2$O$_3$ film. The photodetector $R_A$ values decreased in a nonlinear manner, demonstrating nonlinear absorption characteristics. This is attributed to the dampening of the net built-in electric field by opposite electric fields as a result of the increasing number of accumulated photogenerated charges, which caused less efficient photogenerated carrier separation because the $P_{in}$ increased and manifested a self-limiting gain mechanism to prevent electronic saturation at higher impinging power levels. As such, we argue that our photodetectors require ultraviolet-C light with only about 70 $\mu$W cm$^{-2}$ $P_{in}$ level to operate with optimal gain. Figures 10B and 10C plot the calculated $D^*$ and EQE average values, respectively, for $\lambda_{in} = 250$ nm and $V_{bias} = 5$ and 15 V. The photodetectors exhibited average peak $D^*$ and EQE values of $5.31 \times 10^{13}$ Jones and $1.37 \times 10^6$% for $\lambda_{in} = 250$ nm and $P_{in} = 70$ $\mu$W cm$^{-2}$ at 15 V reverse bias.

Figure 11 plots the intensity-modulated transient photore- sponse current measurements of the representative $\beta$-Ga$_2$O$_3$/ TiN photodetector. We note that current rise and decay processes in Ga$_2$O$_3$-based photodetectors are biexponential; that is, they comprise two components, a fast- and a slow-response component for any given $V_{bias} \neq 0$ (i.e., nonzero bias), whereas for $V_{bias} = 0$, the rise and decay processes are monoeXponential.
in nature and characterized by only one fast-response component. Broadly speaking, when light illumination is the only external disturbance field on the photodetector system, rapid changes in photogenerated carrier concentration occur, with which the fast-response component can be associated. It follows that carrier trapping/releasing processes caused by the existence of defect states in $\beta$-Ga$_2$O$_3$ photoabsorptive thin films dominate the slow response.\[48\] To extract the decay constant, we fitted the decay portion of the first cycle in the time-dependent photoresponse curve using the biexponential relaxation equation

$$I(t) = I_0 + A_1 e^{-t/\tau_{1}} + A_2 e^{-t/\tau_{2}}$$

where $I_{\text{IMPh}}$ is the intensity-modulated photocurrent, $I_0$ is the stable state current, and $A_1$ and $A_2$ are fit model slow- and fast-component amplitude constants, respectively, that establish component dominance; and $t$ is time and $\tau_{1}$ and $\tau_{2}$ are the slow- and fast-response components, respectively, of the decay constants. The photodetector demonstrated $\tau_{2}$ of 581 ms, with $A_2 \gg A_1$. It is conjectured that strong persistent photoconductivity (PPC) results in large internal gains in Ga$_2$O$_3$-based photodetectors because of the slow process of carrier detrapping.\[48\] Besides the presence of two superimposed unit cell configurations separated by stacking faults (resulting in a more defective ordering of crystallographic planes), the time constant of the transient decay is influenced by the depth of electronic trap states, and traps in wide-bandgap semiconductors, such as Ga$_2$O$_3$, are deep; therefore, the time constant is relatively long. Hence, the slow time response is attributed to the high density of trap states that impeded carrier recombination and caused slow recovery time.

Table 1 summarizes our photodetector performance and provides performance comparison with select Ga$_2$O$_3$-based photodetectors operated at room temperature, as reported in the literature. In short, our DUV photodetector is the only monocrystalline Ga$_2$O$_3$-based optoelectronic device to date that employs a vertical device structure without resorting to the use of native Ga$_2$O$_3$ substrates.\[50\] Furthermore, when compared to hexagonal-phase $\varepsilon$- and $\kappa$-Ga$_2$O$_3$, the integration of a monoclinic-phase $\beta$-Ga$_2$O$_3$ thin film into our device architecture facilitated vertical device realization albeit its entropic nucleation and growth process. Vertical device structures are more desirable because they enable the monolithic integration of devices for novel functionalities not possible with lateral device structures, given the latter’s sensitivity to inherent and processing-induced surface-related effects.\[51\]

3. Concluding Remarks

The research focus on $\beta$-Ga$_2$O$_3$ has significantly surged given its potential to achieve ultrahigh-gain DUV photodetection. However, achieving optimal device performance requires extended optimization of material quality, device design, and process technology to compete against the technologically mature silicon carbide (SiC)- and gallium nitride (GaN)-based commercial devices.\[52–59\]

Herein, we focused on the development of an ultrahigh gain DUV photodetector by integrating monocrystalline $\beta$-Ga$_2$O$_3$ on conductive ceramic templates, namely, TiN interlayers heteroepitaxially grown on bulk MgO. The main novelty of this work lies in the development of monocrystalline $\beta$-Ga$_2$O$_3$ growth procedure on (100)-cut MgO substrates using high-quality monocrystalline TiN as a conductive lattice template. The advantage of this structure is rooted in the use of the near-lattice matching between TiN and $\beta$-Ga$_2$O$_3$, along with
the close-lattice matching between TiN and MgO. In addition, both TiN and MgO have significantly higher thermal conductivities than $\beta$-Ga$_2$O$_3$. XRD and HRTEM were used to characterize the materials grown. The fabricated photodetectors show an average peak spectral responsivity of 276.72 A W$^{-1}$. While our initial device performance seems promising, challenges exist and these include achieving optimal response speeds and the development of the ability to produce large-area optoelectronic devices using current material synthesis and device fabrication methodologies.

4. Experimental Section

Thin Film Growth and Device Fabrication: Commercially procured (100) MgO single crystalline substrates from CrysTec GmbH (Germany), 10 mm × 10 mm × 0.5 mm in size, and having a lattice constant of $a = 0.4212$ nm, were used as growth substrates for the $\beta$-Ga$_2$O$_3$/TiN thin film heterostructures. The TiN and $\beta$-Ga$_2$O$_3$ thin films were deposited in different chambers. The MgO substrates were ultrasonically cleaned in a bath of acetone and isopropyl alcohol (IPA), then introduced into a magnetron sputtering processing chamber for the deposition of 180 nm thick TiN templates. The substrates were first degassed for 60 min at 300 °C, etched for 30 min at 800 °C in a 50 W radio frequency (RF) plasma generated in a 5 mTorr argon (Ar) ambience, and further annealed in vacuum at 800 °C for 30 min. The TiN films were deposited at a substrate temperature and bias of 800 °C and −120 V, respectively, using RF magnetron co-sputtering of two Ti targets operated at a power of 180 W each, in an Ar-nitrogen (N$_2$) reactive atmosphere of 5 mTorr total pressure fed by 18.5 sccm of Ar and 1.5 sccm of N$_2$. The TiN deposition rate was about 1.5 nm min$^{-1}$. Two Ti targets were used to increase the deposition rate and enhance the film uniformity. A TiN thickness of 180 nm corresponds to a deposition duration of about 120 min and is high enough to ensure adequate electrical conductivity because the resistivity of metallic thin films with thicknesses lower than 100 nm is dominated by interface scattering effects. The TiN thicknesses above 250 nm were observed to exhibit stacking faults that lead to the loss of in-plane orientation. Therefore, we limited the thickness to 180 nm to suppress the formation of such dislocations. Next, unintentionally-doped $\beta$-Ga$_2$O$_3$ films were grown at a substrate temperature of 640 °C, an oxygen (O$_2$) partial pressure of 5 mTorr, a laser pulse frequency of 50 Hz with an average power of 33 W. Furthermore, the system exhibits an energy stability (1 sigma) of 0.75% at 248 nm, with a pulse duration of 25 ns. The beam dimensions (V × H, FWHM) were 24 × 10 mm$^2$, with a beam divergence of (V × H, FWHM) ≤ 50 mrad at 248 nm. The beam pointing stability (1 sigma) at shutter plane over 2000 pulses was ≤50 μrad.

X-Ray Diffraction Crystallography: Crystal structure properties of the deposited thin films were examined by Bruker D8 Advance (out-of-plane incidence diffraction, without a monochromator given the high sensitivity of the set up) and Bruker D8 Discover (asymmetric XRD diffraction, equipped with a monochromator) X-ray diffractometers using Cu Kα ($\lambda = 1.5405$ Å) radiation.

Transmission Electron Microscopy: HRTEM micrographs and FFT patterns were acquired using a FEI Titan 80-300 transmission electron microscope operating at 300 keV. A FFT pattern simulation of each material was created based on the created crystal model and matched to the FFT pattern extracted from HRTEM micrographs. The EDX detector configuration requires the TEM specimen to be rotated 15° to receive signals during EDX mapping. Moreover, analysis of HRTEM and STEM micrographs, including FFT masking/filtering, inverse FFT, and line profile analyses, were carried out using Gatan DigitalMicrograph. The TEM specimens were prepared using a FEI Helios G4 dual-beam focused ion beam-scanning electron microscope (DBFIB-SEM) system equipped with an OmniProbe micromanipulator and a Ga ion source.

Crystal Visualization: 3D crystallographic representation and visualization of structural models and crystal morphologies were created using the computer software program Visualization of Electronic and Structural Analysis (VESTA).
Extraction of Plane Spacing: The plane spacing values for cubic TiN and MgO and monoclinic \( \beta \text{Ga}_2\text{O}_3 \), respectively, were calculated using the following relations:

\[
d_{\text{TiN,MgO}}^{(hkl)} = \frac{a^2}{\sqrt{h^2 + k^2 + l^2}} \tag{9}
\]

and

\[
d_{\beta \text{Ga}_2\text{O}_3}^{(hkl)} = \left[ \frac{1}{\sin^2 \beta} \left( \frac{k^2 + l^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \right]^{1/2} \tag{10}
\]

where \( h, k, \) and \( l \) are Miller indices, \( a, b, \) and \( c \) are axis-specific lattice parameters, and \( \beta \) is the angle between the \( a-\) and \( c-\)axes.

Electronic Properties: The electrical properties of TiN, namely the chargecarrier density \( (N) \) and mobility \( (\mu) \), as well as the electrical resistivity \( (\rho) \) and Hall coefficient \( (R_H) \), were determined at room temperature in a van der Pauw configuration of electrodes using an Ecopia HMS-3000 Hall Measurement System with a constant magnetic flux density of 0.55 T. Hall measurement results are presented in the Supporting Information.

Device Measurements: The photoelectrical performance of the photodetectors was tested under DUV illumination using a 500 W broadband mercury-xenon arc lamp (Newport’s 66142 Hg(Xe) Arc Lamp). Before illuminating the photodetector, the broadband light passed through an Oriel Cornerstone 260 monochromator fitted with a Newport 74060 diffraction grating. The light intensity was precalibrated using a Si-based photodetector and controlled using a set of neutral-density filters. The \( I-V \) characteristics were extracted using Kelvin (four-wire) resistance measurement setup and an Agilent 4156 C device parameter analyzer.

Atomic Force Microscopy: The surface morphology of deposited crystals was assessed using an Innova atomic force microscope operating in tapping mode. The images were recorded from 5 \( \mu \text{m} \times 5 \mu \text{m} \) areas with a resolution of 1024 \times 1024 pixels at a scan rate of 0.7 Hz, using a commercial pyramidal p-doped silicon probe. The results are presented in Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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