Quasi-Epitaxial Growth of $\beta$-Ga$_2$O$_3$-Coated Wide Band Gap Semiconductor Tape for Flexible UV Photodetectors

Xiao Tang, Kuang-Hui Li, Yue Zhao, Yanxin Sui, Huili Liang, Zeng Liu, Che-Hao Liao, Wedyan Babatain, Rongyu Lin, Chuanju Wang, Yi Lu, Feras S. Alqatari, Zengxia Mei, Weihua Tang, and Xiaohang Li

ABSTRACT: The epitaxial growth of technically important $\beta$-Ga$_2$O$_3$ semiconductor thin films has not been realized on flexible substrates due to the limitations of high-temperature crystallization conditions and lattice-matching requirements. We demonstrate the epitaxial growth of $\beta$-Ga$_2$O$_3$($\beta$-201) thin films on flexible CeO$_2$(001)-buffered Hastelloy tape. The results indicate that CeO$_2$(001) has a small bi-axial lattice mismatch with $\beta$-Ga$_2$O$_3$($\beta$-201), inducing simultaneous double-domain epitaxial growth. Flexible photodetectors are fabricated on the epitaxial $\beta$-Ga$_2$O$_3$-coated tape. Measurements reveal that the photodetectors have a responsivity of $4 \times 10^4$ mA/W, with an on/off ratio reaching 1000 under 254 nm incident light and 5 V bias voltage. Such a photoelectrical performance is within the mainstream level of flexible oxide semiconductor devices in the future.

KEYWORDS: epitaxial growth, flexible, semiconductor, $\beta$-Ga$_2$O$_3$, photodetector

INTRODUCTION

The daily lives of humans are increasingly dependent on the applications of various electronics. In this context, portable, wearable electronics development has become unprecedentedly significant because it can provide people with real-time communication, remote control, and monitoring of diverse potential environmental and health hazards, regardless of the location and time. To accommodate such practical applications, the semiconductor electronics system must be mechanically flexible to tolerate the applied bending stress caused by curvilinear surfaces and movement.

The straightforward route for fabricating flexible electronics is the direct in situ growth of semiconductor thin-film materials on flexible substrates. Until now, such an in situ growth process has been readily realized for a limited number of materials, including carbon nanotubes, transition-metal dichalcogenides, organic compounds, and perovskites. These semiconductor materials do not require a high processing temperature (>300 °C) or high crystallinity (regarding the grain size and orientation). Thus, growth can be easily achieved on a wide range of polymer substrates, such as polyimide, polyethersulfone, polyetherimide, and polyethylene naphthalate.

However, mono-oriented oxide thin films comprise another class of semiconductors that includes $\beta$-Ga$_2$O$_3$, Cu$_2$O, ZnO, and SnO$_2$. These oxides demonstrate superior performance compared with the above low-temperature-processed semiconductor materials in terms of band gap, thermal stability, long-term stability, and nontoxicity, making them irreplaceable in semiconductor applications.

The material growth of flexible electronics based on such oxide materials is challenging for two reasons. First, the mono-oriented oxide semiconductors require a high processing temperature for crystallization. Hence, the above-mentioned polymer substrates can hardly serve as deposition templates due to their low decomposition transition temperature, as summarized in Figure 1. Second, mono-orientation of oxide thin films can only be achieved by epitaxial growth, in which a low lattice mismatch between the growing layer and template is essential. Therefore, although metal foils (e.g., aluminum, copper, and Hastelloy) have much higher processable temperatures, as illustrated in Figure 1, they are also incapable of directly serving as epitaxial templates due to their polycrystalline nature.

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A representative of such oxide semiconductor materials is β-Ga$_2$O$_3$, which has an ultra-wide band gap (~4.9 eV), decent mobility, a high breakdown field (8 MV/cm), and good thermal stability. These attributes make it promising for applications in power devices and ultraviolet (UV) photodetectors (PDs). However, the material growth of high-quality flexible β-Ga$_2$O$_3$ devices is also hindered by the high crystallization temperature and epitaxy requirements. In this view, the “post-growth transfer” process is developed as a compromise technique. The monocrystalline β-Ga$_2$O$_3$ thin film is obtained via a high-temperature epitaxial deposition on conventional rigid wafer templates (e.g., sapphire and -Ga$_2$O$_3$ single crystal) and then transferred to various flexible polymer substrates through a “lift-off paste” procedure. However, device fabrication is limited on the wafer scale and is time-consuming due to its reliance on small wafer templates and cumbersome manual operation involved in the “lift-off paste” process. Hence, in the current developing stage, the post-growth transfer technique is not ideal for large-scale production.

A flexible substrate must be provided that can simultaneously meet two requirements to achieve direct in situ growth of mono-oriented oxide thin films for flexible devices. First, robust thermal stability allows a high-temperature reaction. Second, the desired crystal structure suitable for the epitaxial growth of the mono-oriented layer is needed. Figure 1 reveals that Hastelloy intrinsically has robust thermal stability, making it suitable for crystallizing various oxide semiconductor thin films. Thus, they can be employed as an ideal flexible template if endowed with epitaxial capability.

Hastelloy functionalized by CeO$_2$(001) is demonstrated as effective for the epitaxial growth of mono-oriented β-Ga$_2$O$_3$(~201). The X-ray diffraction (XRD) ϕ-scan and pole figure indicate that CeO$_2$(001) has a bi-axial small-lattice mismatch with the β-Ga$_2$O$_3$ (~201) plane, inducing simultaneous double-domain growth of the β-Ga$_2$O$_3$ thin film. The β-Ga$_2$O$_3$ thin film is fabricated into PDs by depositing micrometer-sized Ti/Au contacts. The PDs exhibit a responsivity of 4 × 10$^3$ mA/W, with an on/off ratio reaching 1000 under 254 nm incident light and 5 V bias voltage. Such photoelectrical performance remained essentially unchanged against more than 20,000 bending-test cycles.

The excellent semiconducting and mechanical performance suggests that the epitaxial β-Ga$_2$O$_3$ layer-coated tape is widely applicable for wearable ozone monitoring, high-temperature flame detection, and biological hazard detection. Moreover, this technique also allows the direct in situ epitaxial growth of other flexible oxide semiconductor devices (e.g., flexible Ga$_2$O$_3$ thin-film transistors) in the future.

**RESULTS AND DISCUSSION**

First, the thermal stability of Hastelloy tape and the epitaxial ability of the CeO$_2$(001) thin film for growing β-Ga$_2$O$_3$(~201) layers were tested, as displayed in Figures S1 and S2 in the Supporting Information, respectively. By applying the ion-beam-assisted deposition (IBAD) technique, the Hastelloy tape was functionalized with a textured CeO$_2$ layer with (001) preferred orientation. Then, β-Ga$_2$O$_3$ was deposited on top of the CeO$_2$ layer. Figure 2a illustrates the structural configuration of the β-Ga$_2$O$_3$-coated tape.

The stacked structure is generally built based on C-276 Hastelloy tape that is 10 mm in width and 50 μm in thickness. After an electropolishing procedure, the tape was first coated with amorphous Al$_2$O$_3$ (80 nm) and Y$_2$O$_3$ (20 nm) layers successively using reactive RF sputtering. The Al$_2$O$_3$ layer serves as a barrier layer to minimize the diffusion of the metallic elements during the following high-temperature treatments, whereas the Y$_2$O$_3$ layer serves as a seed layer for the following depositions of crystallized epitaxial layers. Next, a highly crystallized MgO layer (5 nm) with (001) orientation was realized using the IBAD technique. The mechanism for
forming bi-axially textured (with both out-of-plane and in-plane preferred orientation) MgO on amorphous templates using IBAD has been described in previous reports.\textsuperscript{33} Afterward, LaMnO\textsubscript{3} (20 nm) and CeO\textsubscript{2} (200 nm) layers were successively deposited using magnetron sputtering. The LaMnO\textsubscript{3} layer creates a lattice gradient from MgO to CeO\textsubscript{2} and enhances the bi-axial texture of CeO\textsubscript{2}.\textsuperscript{34}

The XRD patterns measured on the Hastelloy tapes coated with Al\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}/Y\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}/Y\textsubscript{2}O\textsubscript{3}/MgO, and Al\textsubscript{2}O\textsubscript{3}/Y\textsubscript{2}O\textsubscript{3}/MgO/LaMnO\textsubscript{3} buffer layers are presented in Figure S3a. The reflection high-energy electron diffraction (RHEED) pattern obtained during the deposition of the MgO layer is depicted in Figure S3b, suggesting that the MgO layer is crystallized with a preferred orientation. Due to the epitaxy provided by the crystallized MgO layer, the deposited LaMnO\textsubscript{3} and CeO\textsubscript{2} layers naturally obtain a preferred orientation along (001). At this step, the deposition of the stacked buffer-layer structure was accomplished. Then, the β-Ga\textsubscript{2}O\textsubscript{3} thin film was deposited on top of the CeO\textsubscript{2} layer via pulsed laser deposition (PLD). The thickness of the β-Ga\textsubscript{2}O\textsubscript{3} thin film was systematically optimized, and the results are presented in Figure S4 in the Supporting Information. Figure 2b,c shows a batch of the buffered Hastelloy tape before β-Ga\textsubscript{2}O\textsubscript{3} deposition mounted on a PLD sample holder with a 2 in. opening and the same tape after β-Ga\textsubscript{2}O\textsubscript{3} deposition (reflected from the greenish area), respectively.

Figure 3a displays the XRD 2θ patterns of β-Ga\textsubscript{2}O\textsubscript{3}-coated tape and buffered tape. For the buffered tape, the strong (002) and weak (111) peaks of CeO\textsubscript{2} are observed in the pattern. Moreover, another two peaks at higher diffraction angles correspond to (002) and (111) diffractions of Hastelloy C276. When coated with β-Ga\textsubscript{2}O\textsubscript{3}, the pattern is characterized by the appearance of a series of strong diffraction peaks from the {201} planes of β-Ga\textsubscript{2}O\textsubscript{3} without any other diffraction peaks (e.g., β-Ga\textsubscript{2}O\textsubscript{3}(400) at approx. 30°). The result indicates the successful epitaxial growth of single (−201) oriented β-Ga\textsubscript{2}O\textsubscript{3} thin films on the (001) oriented CeO\textsubscript{2} buffer layer.

In addition, the same 2θ measurements were performed on the whole deposition area in Figure 2c. The results are represented in Figure S5 in the Supporting Information and demonstrate a high uniformity of the sample crystallization quality. The rocking curves obtained around the (−201) plane of β-Ga\textsubscript{2}O\textsubscript{3} and (002) plane of CeO\textsubscript{2} are depicted in Figure 3b, with a full-width at half maximum (fwhm) value of 2.93 and 1.74°, respectively. The fwhm value for β-Ga\textsubscript{2}O\textsubscript{3} is higher than the values of the β-Ga\textsubscript{2}O\textsubscript{3} thin films deposited on the conventional sapphire single-crystal substrates by PLD.\textsuperscript{33,34}

This outcome can occur for two reasons. First, an fwhm value of 1.74° for the underlying CeO\textsubscript{2} layer suggests that CeO\textsubscript{2} is not technically a single crystal but only a highly crystallized thin film with a preferred orientation. Thus, the crystal quality and epitaxial ability of the CeO\textsubscript{2}(001) layer are not comparable to those of the sapphire substrates. Second, the thin films are based on the flexible Hastelloy substrate; thus, bending is technically inevitable despite pasting on a rigid and flat holder during the XRD measurement. Such bending is invisible to the naked eye; however, it can be clearly detected using atomic force microscopy (AFM). This bending can result in a certain de-planarization of the (−201) plane of the β-Ga\textsubscript{2}O\textsubscript{3} thin film, contributing to a greater fwhm value of the rocking curve.

The β-Ga\textsubscript{2}O\textsubscript{3}-coated tape is also subjected to XRD ϕ-scan measurements to investigate the in-plane epitaxial relationship between the CeO\textsubscript{2}(001) and β-Ga\textsubscript{2}O\textsubscript{3}(−201) layers, as illustrated in Figure 3c. The ϕ-scan of CeO\textsubscript{2}(111) manifests four peaks, representing a typical four-fold symmetry along the [001] axis of its cubic structure. The β-Ga\textsubscript{2}O\textsubscript{3} film has 12 reflection peaks with a separation of 30° between each of them. For single-crystal β-Ga\textsubscript{2}O\textsubscript{3} (−201) thin films epitaxially grown on sapphire substrates, six peaks evenly separated by 60° are often observed because of the six-fold symmetry along the [102] axis of the crystal structure.\textsuperscript{21} Hence, the 12 peaks observed in the sample suggest that the β-Ga\textsubscript{2}O\textsubscript{3} film has two domains, and the β-Ga\textsubscript{2}O\textsubscript{3}(−401) peaks that come from such
two domains appear alternately throughout the 0 to 360° scan. Therefore, the two domains are laid perpendicularly in the CeO2(001) plane, with a rotation angle of 90° between them.

In addition, all four CeO2 peaks are located precisely at the midpoint between the two adjacent β-Ga2O3(−401) peaks. Thus, at the β-Ga2O3/CeO2 interface, the intersection between the CeO2(111) and CeO2(001) planes always forms a 45° angle with that between the β-Ga2O3(−401) and β-Ga2O3(−201) planes. The β-Ga2O3(−401) and CeO2(111) pole figures of the β-Ga2O3-coated tape are displayed in Figure 3d,e, respectively. The 12 peaks at ω = 19.76° for the β-Ga2O3(−401) pole figure suggest that the β-Ga2O3(−201) plane constitutes two groups of hexagonal structures, corresponding well to the ω-scan measurement.

The large-scale cross-section high-resolution transmission electron microscopy (HRTEM) image of the β-Ga2O3-coated tape is presented in Figure 4a, where the distinct interfaces between the Hastelloy substrate, buffer layers, and Ga2O3 layer throughout the stacked structure are evident. However, due to the low contrast between Y2O3 and Al2O3 and the ultra-low thickness (5 nm) of MgO, the Y2O3 and MgO layers cannot be recognized in the cross-sectional TEM image.

Energy dispersive X-ray (EDX) spectroscopy was performed, and the results are shown in Figure 2b. The results indicate a diffusion of Mn from the LaMnO3 layer to the CeO2 layer, however, no diffusion of Ce occurred from the CeO2 layer to the β-Ga2O3 layer. Therefore, the material purity of the Ga2O3 layer should have been ensured.

An X-ray photoelectron spectroscopy (XPS) measurement was also performed on the Ga2O3-coated tape sample, as revealed in Figure 5 in the Supporting Information, suggesting no Ce in the Ga2O3 layer. Figure 4c presents the cross-sectional HRTEM image of the β-Ga2O3/CeO2 interface. The sharp interface between the Ga2O3 thin film and CeO2 buffer layer is apparent. The corresponding fast Fourier transform (FFT) diffraction patterns of the CeO2 thin film and Ga2O3 buffer layer were obtained, as depicted in Figure 4d,e, respectively. The CeO2 layer presents clear lattice fringes and FFT diffraction patterns, indicating a cubic phase of CeO2. For the Ga2O3 layer, the lattice fringes are blurred. The (−201) diffraction pattern can be observed in the FFT pattern; however, the poly ring is also observed, suggesting that the Ga2O3 thin film is polycrystalline with a preferred (−201) orientation.

We also examined the plane-view HRTEM on the β-Ga2O3-coated tape. The β-Ga2O3-coated tape was etched from the bottom and thinned to 20 to 30 nm to acquire clear images; thus, only the upmost layer of the β-Ga2O3 thin film was preserved. The large-scale image is presented in Figure 4f. The image proves that the β-Ga2O3 thin film is polycrystalline with grain sizes ranging in tens of nanometers. Figure 4g,h presents images of representative grains with higher magnification. By increasing the magnification, clear lattice fringes and the FFT pattern can be obtained, as depicted in Figure 4i,j, respectively. The (010) diffraction pattern is recognized from the FFT pattern, demonstrating the formation of the (−201) plane of β-Ga2O3.

Based on the understanding above, the epitaxial relationship between the CeO2(001) and β-Ga2O3(−201) planes is illustrated in Figure 5. The gray and red dots represent the oxygen atom distribution in the CeO2(001) and β-Ga2O3(−201) planes, respectively. The intersection between the CeO2(111) and (001) planes coincides with the CeO2[110] direction (dashed black line). The intersection between the β-Ga2O3(−401) and (−201) planes coincides with the β-Ga2O3[010] direction (dashed black line).
oxygen atoms in the planes of care

Figure 5. Proposed in-plane epitaxial relationship between CeO2(001) and β-Ga2O3(-201). The gray and red dots represent the oxygen atom distribution in the CeO2(001) and β-Ga2O3(-201) planes, respectively. The orange and green areas highlighted in the two domains represent the smallest six-fold symmetric hexagon units in the β-Ga2O3(-201) plane for Epitaxy A and B, respectively.

fore, relating to the ϕ-scan result, the CeO2[110] and Ga2O3[010] directions form a 45° angle either clockwise or counterclockwise, resulting in two perpendicularly laid domains, as presented on the left (Epitaxy A) and right (Epitaxy B) sides, respectively. The orange and green areas highlighted in the two domains represent the smallest six-fold symmetric hexagon units in the β-Ga2O3(-201) plane for Epitaxy A and B, respectively. By superimposing them, a twelve-fold symmetric geometry is observed, which is reflected from the ϕ-scan result.

To better understand the mechanism for the epitaxial growth of the two perpendicularly laid β-Ga2O3 domains, we carefully examined the distance between the neighboring oxygen atoms in the planes of β-Ga2O3(-201) and CeO2(001). According to the calculations in previous reports, distances between neighboring oxygen atoms along the CeO2[100] direction measure 2.7 Å, whereas those along the β-Ga2O3[100] and [010] directions are 3.04 and 5.26 Å, respectively. The atom distance along the β-Ga2O3[100] direction approximately corresponds to that along CeO2[100], giving a lattice mismatch of 11%. In contrast, the atom distance along the β-Ga2O3[010] approximately corresponds to two times that along CeO2[100] (5.4 Å), resulting in a lattice mismatch of only 2.6%. For the conventional epitaxial growth of β-Ga2O3 thin films on the sapphire substrate, the lattice mismatch between β-Ga2O3[010] and Al2O3[1120] reaches 10.7%. Therefore, the lattice mismatch between either β-Ga2O3[100] or [010] and CeO2[100] is small enough for epitaxial growth. Thus, two perpendicularly laid β-Ga2O3 domains form simultaneously on the CeO2(001) surface.

Figure 6a,b presents the representative three-dimensional (3D) AFM images of the buffered tape and β-Ga2O3-coated tape. The corresponding height profiles measured along the dashed black lines are represented in Figure 5c,d. Like the XRD measurements, the tape samples are also pasted onto a rigid substrate using double-sided tape glue for the AFM scans.

Nevertheless, the bending of the tape is evident because the height change (as indicated by the geometry of the 3D AFM images and the texture values in the height profiles) in the two samples is due to the waviness rather than the intrinsic roughness of the samples. First, the curvature could increase the fwhm value of the rocking curve in Figure 3b, as the out-of-plane alignment of the grains primarily governs it. Second, after reducing the waviness of the baseline, the CeO2-buffered tape and β-Ga2O3-coated tape have an RMS roughness of 0.4 and 5.5 nm, respectively. The roughness significantly increased after β-Ga2O3 deposition; however, the value is still relatively low, so that the β-Ga2O3 semiconductor tape can be fabricated into various photoelectronic devices.

Subsequently, the device was fabricated. Coplanar interdigital Ti (50 nm)/Au (195 nm) electrodes with a spacing of 10 μm were deposited on the β-Ga2O3-coated flexible tape to form metal–semiconductor-metal-structured PDs. Figure 6a,b depicts a simplified configuration and photograph of the bent flexible PD, respectively.

Due to the low surface roughness of the β-Ga2O3 layer, the deposited Ti/Au electrode array has an intact structure with a smooth surface and precise edges, as shown in the microscopic photograph in Figure 7c. The current–voltage (I–V) characteristics of the PD are shown in Figure 7d. The off-state dark current of the device is approximately 1 nA at 5 V. When illuminated by 254 nm of UV light with a power density of 20 μW/cm², the on-state photocurrent is increased by 3 orders of magnitude, reaching approximately 1 μA.

Figure 6. (a,b) Three-dimensional AFM images and (c,d) height profiles along the black dashed lines of the buffered tape and flexible β-Ga2O3-coated tape, including texture, waviness, and roughness.
wavelength-dependent photoresponse is measured on the PD sample by tuning the illuminating light wavelength in the range of 230–300 nm at a fixed bias voltage of 5 V. Based on the measured results, the photoresponsivity of the PD sample is calculated using eq 1:

$$R = \frac{I_{\text{photo}} - I_{\text{dark}}}{D \times S}$$

where $R$, $I_{\text{photo}}$, $I_{\text{dark}}$, $D$, and $S$ are the photoresponsivity, photocurrent, dark current, illuminating power density, and exposure area, respectively.

The calculated photoresponsivity as a function of the illuminating wavelength is presented in Figure 7c. The photoresponsivity of the PD sample is 0.7 A/W at 300 nm, dramatically increasing from 260 nm, eventually reaching 40 A/W at 240 nm. The result corresponds well to the theoretical band gap of $\beta$-Ga$_2$O$_3$. Moreover, on the log scale of the responsivity spectrum, a tail can be observed in the range of 250–300 nm, which could arise from the CeO$_2$ layer, as illustrated in Figure S7a.

Generally, the PDs fabricated based on the $\beta$-Ga$_2$O$_3$-coated Hastelloy tape manifest good photoelectrical properties in terms of the on/off ratio ($I_{\text{photo}}/I_{\text{dark}} = 1000$) and wavelength selectivity in the UV region ($R_j = 240$ nm/$R_j = 300$ nm = 57). In comparison with the reports elsewhere, the critical device characteristics are within the mainstream level of $\beta$-Ga$_2$O$_3$ PDs using the conventional rigid single-crystal substrates.

The flexibility of the PDs on the flexible tape is tested by measuring the photoelectrical properties under various bending conditions, as illustrated in Figure 8a–c. Again, the test is performed under 254 nm UV light with a power density of 20 $\mu$W/cm$^2$. Different bending conditions are achieved by pasting the flexible PD sample on the semicircular cylinder molds with different radii of 8, 10, and 12 mm depicted in the insets of Figure 8a–c. An 8 cm-long PD tape sample can be easily rolled into a “PD ring” on a finger when applying a bending radius of 10 mm, as displayed in Figure 8h. Thus, the bending test in this radius range (8–12 mm) is meaningful for fabricating potential wearable and deformable devices. As evident from Figure 8a–c, the dark current and photocurrent of the PD sample remained at 1 nA and 1 $\mu$A, respectively, under different bending conditions, which are the same as those obtained in the flat state.

Repetitive measurements under the mentioned bending conditions with an on/off interval of 120 s were performed to test the response time and stability of the PD sample, as listed in Figure 8d. The results reveal that the on-state current is largely independent of the bending conditions. The response (rise) and recovery (decay) edges acquired in a single on–off cycle are presented in Figure 8e. The response edges can be fitted with a mono-exponential relaxation equation and have a decay time of $1304 \pm 1314$ ms. Based on the simulation result, the spectral response demonstrates a single peak of only around 250 nm on a linear scale when the beam intensity equals 20 $\mu$W/cm$^2$. Again, a tail can be observed in the range between 250 and 300 nm only on the log scale. In general, the simulation agrees with the experimental results.

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To understand the spectral response of Ga$_2$O$_3$ thin-film PDs grown on CeO$_2$, we also performed the 2D Silvaco Atlas TCAD simulation. The schematic diagram of the simulated Ga$_2$O$_3$ thin-film PD on CeO$_2$ is given in Figure S7c. The thicknesses of the Ga$_2$O$_3$ and CeO$_2$ thin film are set to 300 and 200 nm, respectively. Figure S7d provides the spectral response at a bias of 5 V when the beam intensity equals 20 $\mu$W/cm$^2$. Based on the simulation result, the spectral response demonstrates a single peak of only around 250 nm on a linear scale when the beam intensity equals 20 $\mu$W/cm$^2$. Again, a tail can be observed in the range between 250 and 300 nm only on the log scale. In general, the simulation agrees with the experimental results.
response time of 1.2 s, whereas the recovery edges require fitting with a bi-exponential relaxation equation (eq 2). The average decay times are calculated using eq 3

\[ I = I_0 + A e^{-t/\tau_1} + B e^{-t/\tau_2} \]  

\[ \tau_{ave} = (A\tau_1^2 + B\tau_2^2) / (A\tau_1 + B\tau_2) \]  

where \( I \) is the intensity-modulated photocurrent, \( I_0 \) is the stable state current, and \( A \) and \( B \) are slow and fast component amplitude constants of the fit model, respectively, that establish component dominance. In addition, \( \tau \) denotes the time, and \( \tau_1 \) and \( \tau_2 \) represent the slow and fast components, respectively.

Based on fitting, the recovery edge provides the fast and slow counterparts of 0.05 and 1.12 s, respectively, giving an overall average recovery time of 0.14 s. In general, the fast component is associated with the ultrafast change in the carrier concentration upon on-off cycling of the incident light, whereas the slow component is the reason for the sluggish trapping and releasing processes of the carriers at the oxygen vacancy defects in Ga2O3 thin films. Previous reports have demonstrated that the oxygen vacancy population can be tuned via thermal annealing, plasma etching, and different contact types.

In this work, the PD is based on the PLD-derived fully crystallized epitaxial Ga2O3 thin film using conventional Ti/Au contacts. Thus, the response and the decay times are similar to the PLD-derived PDs reported elsewhere. The only influencing factor is the bending of the flexible substrate that may cause tension and cracks in Ga2O3 thin films. Hence, the photoresponse was also measured after the fatigue test (RTP = 20,000), as presented in Figure S8. The response curve provides a response time and average recovery time of 1.5 and 0.15 s, respectively, suggesting that the photoresponse time is not affected by the bending of the thin films.

Finally, a fatigue test was conducted using a homemade machine to test the mechanical robustness of the PD sample, as illustrated in Figure 8h. First, the sample is fully straightened by pasting on the two arms. Then, the movable arm
grown epitaxial $\beta$-Ga$_2$O$_3$ thin film. The coated tapes were fabricated into flexible, highly crystallized $\beta$-Ga$_2$O$_3$ thin films, such as flexible thin-film transistors, power rectifiers, and gas sensors. Moreover, the described technique paves the way for direct in situ epitaxial growth of other flexible oxide semiconductor devices in the future.

**EXPERIMENTAL SECTION**

Deposition of Stacked Buffer Layers. Reactive sputtering and the IBAD technique were used to deposit Hastelloy/Al$_2$O$_3$/Y$_2$O$_3$/MgO/LaMnO$_3$/CeO$_2$ layers. The details involved in the above procedures are in our previous studies.

Deposition of the $\beta$-Ga$_2$O$_3$ Layer. The $\beta$-Ga$_2$O$_3$ thin films were synthesized via PLD. During the deposition process, the CeO$_2$-buffered tapes were cut into 8 cm in length and fixed by two hollow plungers. The working distance between the $\beta$-Ga$_2$O$_3$ target and the hollow plungers was set at 9.5 cm. Before the deposition started, the temperature of the sample holder and oxygen partial pressure reached 640 °C and 5 mTorr, respectively. During deposition, a KrF excimer laser was operating at a frequency of 5 Hz with an energy per pulse of 300 mJ. The deposition process was finished after 5000 to 30000 pulses.

Cross-Section Characterization. HRTEM was applied to investigate the specimen by operating an FEI Titan ST system at an acceleration voltage of 300 kV. The images were processed using a Gatan Digital Micrograph. The TEM specimens were prepared using an FEI Helios G4 dual-beam focused ion beam (FIB) scanning electron microscopy (SEM) system equipped with an Omni probe and a gallium ion source.

Plane-View Characterization. The TEM-ready samples were prepared using the in situ FIB lift-out technique on FEI Strata G4 HX dual-beam FIB/SEM. The samples were copped with sputtered Ir and e-PI/1–Pt prior to milling. The TEM lamella thickness was ~20 nm. The samples were imaged using FEI Themis Z FEG/scanning transmission electron microscopy (STEM) operated at 200 kV in the bright-field STEM mode, HRSTEM mode, and high-angle annular dark-field STEM mode. The STEM probe size was 1 to 2 nm in nominal diameter.

XRD Measurements. The crystal structure properties of all described samples were measured using a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα ($\lambda = 1.54 Å$) radiation.

Surface Morphology Measurements. The surface morphologies of all samples were measured using Bruker Dimension Icon SPM AFM.

XPS Measurements. The XPS was measured using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source ($\hbar\nu = 1486.6$ eV) operating at 150 W.

Table 1. Comparison of In Situ Grown Epitaxial $\beta$-Ga$_2$O$_3$ Thin-Film PDs with Previously Reported Flexible Ga$_2$O$_3$ PDs

<table>
<thead>
<tr>
<th>type of Ga$_2$O$_3$</th>
<th>substrate materials</th>
<th>bias (V)</th>
<th>photocurrent ($\mu$A)</th>
<th>decay time (s)</th>
<th>responsivity (mA/W)</th>
<th>$I_{\text{photo}}/I_{\text{dark}}$ ratio</th>
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<td>transferred $\beta$-Ga$_2$O$_3$ thin film</td>
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<td>1.18 x 10$^3$</td>
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<td>28</td>
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<tr>
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<td>1 x 10$^5$</td>
<td>32</td>
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<tr>
<td>a-Ga$_2$O$_3$ thin film</td>
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<td>0.01</td>
<td>N/A</td>
<td>8 x 10$^6$</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>a-Ga$_2$O$_3$ thin film</td>
<td>polyimide</td>
<td>20</td>
<td>0.3</td>
<td>N/A</td>
<td>5 x 10$^4$</td>
<td>N/A</td>
<td>47</td>
</tr>
<tr>
<td>transferred a-Ga$_2$O$_3$ thin film</td>
<td>polyimide</td>
<td>5</td>
<td>0.07</td>
<td>N/A</td>
<td>2.75 x 10$^3$</td>
<td>1 x 10$^6$</td>
<td>48</td>
</tr>
<tr>
<td>a-Ga$_2$O$_3$ thin film</td>
<td>polyethylene terephthalate</td>
<td>5</td>
<td>1.1</td>
<td>N/A</td>
<td>49</td>
<td>100</td>
<td>49</td>
</tr>
<tr>
<td>polycrystalline $\beta$-Ga$_2$O$_3$ thin film</td>
<td>mica</td>
<td>10</td>
<td>1</td>
<td>0.05</td>
<td>0.06</td>
<td>1 x 10$^6$</td>
<td>50</td>
</tr>
<tr>
<td>$\beta$-Ga$_2$O$_3$ nanowires</td>
<td>glass fiber fabric</td>
<td>25</td>
<td>3.39</td>
<td>0.19</td>
<td>710</td>
<td>260</td>
<td>51</td>
</tr>
<tr>
<td>epitaxial $\beta$-Ga$_2$O$_3$ thin film</td>
<td>buffered Hastelloy</td>
<td>5</td>
<td>1</td>
<td>0.15</td>
<td>4 x 10$^4$</td>
<td>1 x 10$^6$</td>
<td>this work</td>
</tr>
</tbody>
</table>

Ti/Au contacts. The PDs have good photoelectrical performance and robust flexibility, making them promising for applications in various UV-sensitive wearable devices. In addition, we believe that the described epitaxial technique can also be extended to the fabrication of other technically important devices based on flexible, highly crystallized $\beta$-Ga$_2$O$_3$ thin films, such as flexible thin-film transistors, power rectifiers, and gas sensors. Moreover, the described technique paves the way for direct in situ epitaxial growth of other flexible oxide semiconductor devices in the future.
UV–Vis Measurements. Transmittance was measured using a Thermo Scientific Evolution 160 UV–Vis spectrometer.

PD Device Fabrication. Flexible PDs were constructed following the widely used photolithography standard operation procedures.

Photoelectrical Measurements. All I–V curves and the responsivity spectra were measured under 254 nm DUV light. The responsivity measurements were conducted using a test system from Zolix Instruments Co., Ltd. The system comprises a digital source meter (Keithley 2400), monochromator (TLS1509, Zolix), xenon lamp, and LabVIEW-developed software.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/ doi/10.1021/acsami.1c15560.

Out-of-plane 2θ XRD patterns and 3D AFM images of the Hastelloy tape before and after annealing at 800 °C for 3 h; out-of-plane 2θ XRD patterns and ϕ-scan of the CeO2/Yttria-stabilized zirconia (YSZ) commercial single-crystal substrate (MTI Technology Corporation) with and without β-Ga2O3 coating; XRD patterns measured on Hastelloy tape coated with Al2O3, Al2O3/Y2O3, Al2O3/Y2O3/MgO, and Al2O3/Y2O3/MgO/LaMnO3 buffer layers and RHEED pattern obtained during the deposition of the MgO layer; I–V curves and out-of-plane 2θ XRD patterns measured from the samples with different β-Ga2O3 thicknesses; out-of-plane 2θ XRD patterns measured at various sample positions in Figure 1c; XPS spectrum of the Ga2O3-coated tape sample; wavelength-dependent responsivity on the log scale of the PD, optical transmittance spectra of β-Ga2O3 films grown on the CeO2/YSZ substrate, schematic diagram of the simulated Ga2O3 thin film (300 nm) PD grown on CeO2 (200 nm), and spectral response at a bias of 5 V under the beam intensity of 20 μW/cm²; and photoresponse curve in a single on–off cycle and exponential fittings for response and decay after 20,000 repetitions (RPT) of bending cycles (r = 8 mm) (PDF)

Fatigue test (MP4)

■ AUTHOR INFORMATION

Corresponding Author
Xiaohang Li — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia; orcid.org/0000-0002-4434-365X; Email: xiaohang.li@kaust.edu.sa

Authors
Xiao Tang — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia; orcid.org/0000-0002-0138-7206
Kuang-Hui Li — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia
Yue Zhao — School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, 200240 Shanghai, China; orcid.org/0000-0002-7231-2156
Yanxin Sui — Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
Huili Liang — Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China; orcid.org/0000-0002-5164-4290
Zengxia Mei — Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Huili Liang — Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Wedyan Babatain — King Abdullah University of Science and Technology (KAUST), MMH Labs, Electrical and Computer Engineering, Thuwal 23955–6900, Saudi Arabia
Rongyu Lin — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia
Chuanju Wang — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia
Yi Lu — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia
Feras S. Alqataari — Advanced Semiconductor Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955–6900, Saudi Arabia
Zengxia Mei — Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
Weihua Tang — Laboratory of Information Functional Materials and Devices, School of Science and State Key Laboratory of Information Photonics and Optical Communications, Beijing University of Posts and Telecommunications, Beijing 100876, China

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsami.1c15560

Author Contributions
All authors contributed to the preparation of this paper. X.T. conceived the idea, fabricated the device, performed the tests, and analyzed the data; K-H.L. performed the TEM measurements; Y.Z. performed the IBAD materials growth; Y.S., H.L., Z.L., W.T. and Z.M. helped with photocurrent measurements; C-H.L. performed the AFM measurements; W.B. performed the fatigue measurements; Y.L. performed the UV/Vis measurements; R.L. performed the simulation; C.W. performed the XPS measurements; F.A. revised the manuscript; X.L. supervised the research and corrected the paper.

Notes
The authors declare no competing financial interest. The datasets generated or analyzed during this study are available from the corresponding author on reasonable request.

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