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Enhanced detectivity self-powered (photovoltaic) solar-blind UV-C Sn-doped β -Ga₂O₃-based photodetectors via Sn⁺-implantation with outstanding dark current suppression

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Abstract:

Self-powered solar-blind Ga₂O₃-based photodetectors (PDs) encounter several challenges, including demanding and complex fabrication processes that substantially increase production costs. However, cost-effective simple device structures based on a single Ga₂O₃ layer do not exhibit adequate performance due to high dark current. In this report, these challenges are addressed by employing Sn⁺ implantation and post-implantation annealing of β -Ga₂O₃ epilayers grown by pulsed laser deposition (PLD), enhancing the performance of the resulting metal–semiconductor–metal (MSM) PDs. As-grown β -Ga₂O₃ film-based PDs are characterized by high dark current, a slow photoresponse (several seconds), and a weak on/off ratio (~10). We show that Sn⁺ implantation and post-implantation annealing suppresses the dark current completely as bias increases, yielding an exceptionally superior photocurrent-to-dark current ratio

($\sim 10^9$) and faster photoresponse (< 40 ms). We also demonstrate significant detectivity enhancement by a factor of 10^5 , along with a significant solar-blind rejection ratio ($\sim 10^4$), a sharp cut-off at 265 nm (UV-C region), as well as excellent self-powered characteristics of implantation-based devices. X-ray photoelectron spectroscopy and density functional theory reveal the possible causes of such improvements. This is the first investigation of self-powered solar-blind DUV PDs based solely on a single Sn^+ -implanted $\beta\text{-Ga}_2\text{O}_3$ layer.

Keywords: Deep UV optoelectronics, Visible-blind, Ion implantation, Thermal treatment, Surface passivation, wide bandgap semiconductor, Transparent oxides

1. Introduction

Due to their usage in critical fields, there is a high demand for smart, self-powered solar-blind deep ultra violet (DUV) photodetectors (PDs).¹⁻³ In addition, although DUV PDs are known to have other beneficial applications in environmental monitoring—such as ozone detection, air and water quality monitoring, medical imaging, flame detection, photovoltaic space communications, and missile detection—commercial DUV PDs rely on silicon-based devices. However, these devices face several limitations, such as the need for complex design and fabrication processes that include optical filter layers to avoid visible-light absorption, as they are overly sensitive to low-energy radiation, leading to high dark current.⁴ These drawbacks drive up production costs as well as hinder their scalability in commercial applications. Therefore, to advance the solar-blind DUV-based technology, alternative DUV materials that can be utilized in solar-blind PD applications need to be explored.

To this end, a variety of wide-bandgap and ultra-wide-bandgap semiconductors^{5 6} have been recently studied, whereby Ga_2O_3 has emerged as the most promising candidate.^{1, 4, 7} As the most stable Ga_2O_3 polymorph, monoclinic-structured $\beta\text{-Ga}_2\text{O}_3$ has attracted significant research interest focusing on high-power electronics and solar-blind DUV (mainly in the UV-C range) PDs due to its ultra-wide bandgap (4.5–5 eV) and high breakdown voltage, as well as high chemical, thermal, and radiation resistance, and the availability of high-quality bulk substrates.⁸ Various types of Ga_2O_3 -based PDs with different crystal phases have been reported, including p–n heterojunctions, Schottky and avalanche diodes, and metal–semiconductor–metal (MSM) devices.⁹⁻¹¹ All previous reports confirmed that, to attain the required self-powered characteristics and low dark current (i.e. high detectivity), DUV devices based on Ga_2O_3 should incorporate

heterojunction structures, which necessitates complex fabrication processes, increasing the cost and resource utilization, and preventing their widespread adoption.

Therefore, to facilitate large-scale production, it is essential to develop approaches that simplify the device structure, reduce the complexity of device fabrication, and render the growth methods more cost-effective. All these requirements are met by MSM devices. However, self-powered, single-layer Ga₂O₃ MSM devices have not yet been realized, and existing devices often suffer from high dark current under bias.¹²⁻¹⁴ Such poor performance is ascribed to the surface defects such as dangling bonds and oxygen vacancies at the interface between the film and the metal contacts, since the low formation energy of these defects reduces film quality.¹⁴⁻¹⁷ Such defects cause deep states in the bandgap, which act as traps for the photogenerated carriers, resulting in a low carrier density and a dark current ranging up to 10⁻⁵ A.¹⁸ This high trap density also slows down the device response due to the adverse effects of long persistent photocurrent on the switching behavior which is a crucial parameter for effective light detection.¹⁹ Most importantly, Schottky devices suffer from high dark current and low detectivity. Therefore, these issues must be addressed to achieve high-performance self-powered solar-blind Ga₂O₃-based devices operating in the UV-C range.

To mitigate problems with dangling bonds on the film surface, several techniques have been proposed, such as surface passivation using a capping layer,²⁰ introducing an interlayer between the metal and the semiconductor components,²¹ semiconductor-metal sandwich structures, plasmonic nanostructures, etc.^{12, 13} However, developing PDs with extremely low dark current (in the pA to fA range) and self-powered characteristics is still a challenge. Ion implantation as a strategy for doping β -Ga₂O₃ with a desired impurity has recently gained scholarly interest as it has several advantages over the in-situ doping, given that it allows facile introduction

of different elements into the device structure. It is a powerful way for controlling the impurity density and depth within the host material, while the material quality can be restored or improved by post-implantation annealing.²² In extant studies, annealing was also employed to alter the oxygen vacancies to reduce the dark current.^{23, 24} Sn has been used as an n-type dopant for Ga₂O₃ due to its tetravalency and ability to form shallow donor levels below the conduction band. Moreover, its atomic radius is similar to that of Ga which, compared to other tetravalent elements, minimizes the lattice distortion upon substitution.^{22, 25, 26} However, thus far, Sn-implanted Ga₂O₃ has not been demonstrated as a PD device.

Therefore, the goal of our work on DUV PDs based on Sn⁺-implanted/post-implantation annealed Ga₂O₃ film is not only suppressing the dark current and enhancing the signal-to-noise ratio but also achieving high detectivity and superior switching speeds. This is a significant contribution to the pertinent literature given that band-alignment modifications at the Ga₂O₃–metal interface via Sn⁺ implantation and subsequent annealing to achieve MSM devices with high self-powered photoresponse and fast photoresponse have not yet been studied. Similarly, theoretical investigations have not yet elucidated how the reduction in the intrinsic defects (such as vacancies, interstitials, and point defect complexes) and Sn impurity levels, which modifies the electronic band structure of Ga₂O₃, can enhance Ga₂O₃-based PD performance.

These gaps in extant literature have motivated this work, as a part of which we used the pulsed laser deposition (PLD) technique to grow β -Ga₂O₃ epitaxial films implanted with Sn dopants. This approach is much more cost-effective than other common techniques such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). We also demonstrate an outstanding suppression of the dark current characteristics of Sn implanted β -Ga₂O₃ based devices (with significantly remarkable photocurrent to dark current ratio ($\sim 10^9$)), for

the first time. We conducted advanced experimental and theoretical analyses to elucidate the mechanisms underlying the significantly improved performance of devices based on Sn (IMP-AN) implanted films compared to that based on as grown (AG) films.

2. Results

2.1 *Modification of structural properties of IMP-AN Sn-implanted Ga₂O₃*

All samples were grown by PLD on c-plane sapphire substrates. The implanted β -Ga₂O₃ by Sn⁺ ions were subsequently annealed at 1000 °C under ambient conditions to recover implantation damage. Secondary ion mass spectroscopy (SIMS) measurements revealed the Sn atomic concentration and its distribution as the depth increases, as shown in the Sn concentration profile illustrated in Supplementary Fig.1(a) in Supplementary Information (SI), revealing an atomic concentration of Sn at the film surface is around 7×10^{18} at/cm³. Initially, such as concentration gradually increases and reaches its maximum value of 2×10^{19} at/cm³ at a depth of 50–70 nm from the surface, after which declines gradually to be negligible beyond 250 nm depth.

To understand the structural characteristics of the films, we carried out X-ray diffraction (XRD, as shown in Fig. 1(a) for IMP-AN film compared to that of AG film. Three dominant distinct diffraction peaks centered at approximately 19.14°, 38.55°, and 59.34° were observed in the XRD patterns of the AG film, corresponding to the -201, -402, and -603 reflections of monoclinic (-201)-oriented β -Ga₂O₃, respectively, which shift to a higher 2 θ value compared to typical single-crystalline β -Ga₂O₃ values (18.95°/38.40°/59.1°), indicating compressive strain.²⁷ Other minor peaks observed at 30.59°, 44.59°, and 64.71° in the AG film-related XRD spectrum (disappeared in IMP-AN film) correspond to the 400, -601, and -712 reflections of β -Ga₂O₃, respectively.^{28, 29} No peaks related to the other Ga₂O₃ phases are observed for any of the studied films.

High-resolution scanning transmission mode (HR-STEM) images of the AG film shown in Fig. 1(b) and 1(c) reveal its crystallinity. Fig. 1(b) illustrates polycrystalline nature (composed of small grains) of the region located near the substrate/film interface, as confirmed by the Fast Fourier Transform (FFT) patterns included in the inset. As can be seen in Supplementary Fig.1(b) in SI, these elongated grains were grown almost perpendicularly to the surface of the sapphire substrate. Fig. 1(c) indicates that, as the film thickness increases, these grains coalesce to form a single β -Ga₂O₃ crystal structure.^{30, 31} The corresponding FFT patterns (the inset of Fig. 1(c)) taken from several areas in the top region of the films confirm the single-crystalline properties of these large columnar grains along the (-201) direction. This improved crystallinity contributes to strain relaxation with increasing thickness. Such columnar growth has been reported for different materials,^{30, 31} reflecting a typical epitaxial Volmer-Weber system with domain wall formation contributing to an intrinsic compressive stress,³² which is consistent with the strain discussed in this paper when reporting on the XRD analysis. Such transformation of crystallinity from the substrate interface to the surface has been reported previously.³⁰

The atomic force microscopy (AFM) surface morphology images (Supplementary Fig.1(c) and 1(d) in SI) show that all samples contain island-like structures, typically observed in PLD-grown films,³³ while no nanodroplet formation upon implantation was observed.³⁴ Interestingly, the RMS roughness of the AG film surface, which is estimated to be ~16 nm, improved to be $\approx$ 7 nm after implantation and post-annealing.

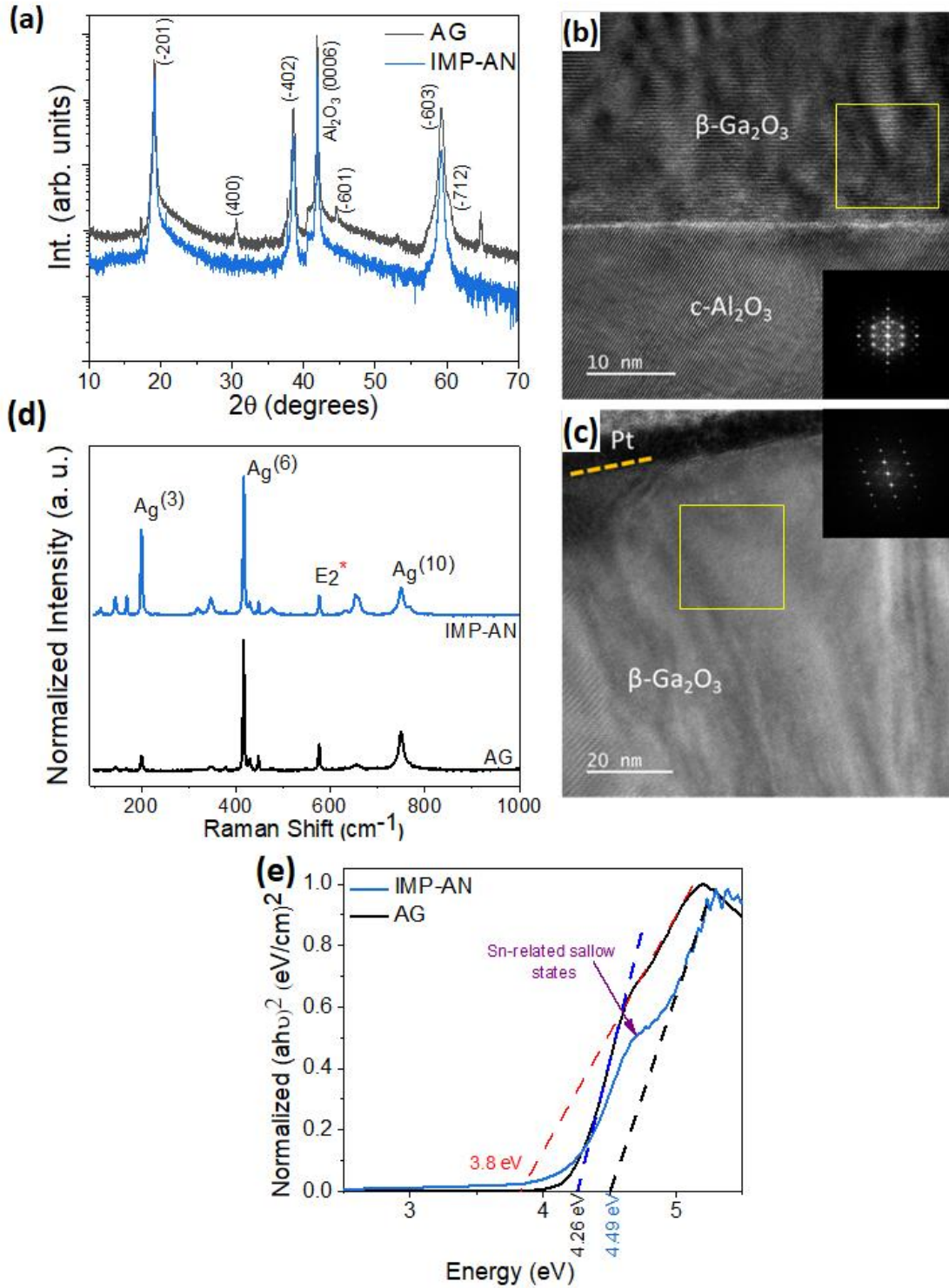


Fig. 1. (a) (log-scale) X-ray diffraction scans AG and IMP-AN β -Ga₂O₃ films. HR-STEM images of the AG β -Ga₂O₃ film (b) near the substrate interface and (c) the top film region. The insets show the FFT patterns taken from the area marked with yellow box on STEM images. (d) Raman spectra and, (e) Tauc plots for both films (dashed lines pointed the bandgap of the materials).

We carried out confocal Raman measurements on all films to understand the effect of Sn^{4+} implantation/post-annealing. As shown in Fig. 1(d), both AG and IMP-AN films are characterized by the presence of the 15 active Raman phonon modes expected for the beta phase of Ga_2O_3 , whereby the low-frequency modes ($<200\text{ cm}^{-1}$) correspond to libration and translation of whole tetrahedral chains, mid-frequency modes ($200\text{--}450\text{ cm}^{-1}$) correspond to the translational motions of Ga_{II} -octahedron, and high-frequency modes ($>450\text{ cm}^{-1}$) correspond to Ga_{I} -tetrahedron stretching and bending.³⁵⁻³⁷ The $\text{A}_g^{(6)}$ mode around 416 cm^{-1} is the most intense and the most dominant mode for all samples, indicating strong presence of octahedron vibrations.

The Raman spectrum of the AG film reveals presence of three dominant phonon modes— $\text{A}_g^{(3)}$ at 200.39 cm^{-1} , $\text{A}_g^{(6)}$ at 416.4 cm^{-1} , and $\text{A}_g^{(10)}$ at 749.68 cm^{-1} . However, no additional peaks associated with local vibrations of Sn were observed. Furthermore, no significant broadening is noticed for any of the peaks generated by the IMP-AN film. The $\text{A}_g^{(3)}$ and $\text{A}_g^{(6)}$ peak positions are consistent with those reported for the single-crystal bulk $\beta\text{-Ga}_2\text{O}_3$.³⁵ On the other hand, the pronounced red shift (by $>13\text{ cm}^{-1}$) of the $\text{A}_g^{(10)}$ peak can be potentially attributed to a significant change in the local oxygen ordering around the tetrahedral Ga_{I} atoms compared to the single-crystal film, resulting in a notable disorder in the Ga–O bonds in tetrahedrons,^{30, 38} which is in good agreement with the X-ray photoelectron spectroscopy (XPS) findings, as will be shown later.

Although the IMP-AN film shows the intensity of the high-frequency $\text{A}_g^{(9)}$ mode increases in Raman spectrum, the $\text{A}_g^{(10)}$ mode is suppressed compared to the AG film. This means that implantation affects the bending and stretching mode of Ga–O_I bonds in the tetrahedral structure since substituting Ga at octahedron sites by Sn^{4+} ions disrupts the tetrahedron sites, creating vacancies and interstitials around the tetrahedron chains, ultimately forming $2\text{V}_{\text{Ga}}^{\text{I}}\text{--Ga}_i$ complexes.³⁹⁻⁴⁰ A considerable increase in the $\text{A}_g^{(3)}$ mode intensity with respect to the $\text{A}_g^{(6)}$ mode

in IMP-AN films, and exhibits stronger $B_g^{(2)}$ and $A_g^{(2)}$ modes at 144.93 and 169.17 cm^{-1} , respectively, compared to the AG film. This behavior can be ascribed to distortions caused by the substitution of Sn^{4+} ions at the octahedral Ga_{II} sites during implantation as well as reorganization during post-implantation annealing. This indicates better crystallinity of the IMP-AN film compared to the AG film.⁴¹

The more pronounced peaks representing the $A_g^{(4)}$ and $A_g^{(5)}$ modes in the IMP-AN film are due to Sn substituting Ga in the octahedrons, thereby enhancing the translational motions of the octahedral chains in addition to improvements in crystal quality. The peak observed in the 470–480 cm^{-1} frequency range corresponds to superposition of the $B_g^{(4)}$ and $A_g^{(7)}$ modes.³⁷ Similar to $B_g^{(2)}$ and $A_g^{(2)}$, these vibrational modes correspond to tetrahedral vibrations, which become slightly pronounced in the IMP-AN film compared to the other two samples as a result of different size of Sn substituting at a Ga site.

Fig. 1(e) shows the Tauc plot of the absorption measurements of both films, revealing a bandgap at ~ 4.26 eV for AG film accompanied by another band at 3.8 eV. After implantation and subsequent post-annealing (the IMP-AN film), the bandgap blueshifted to be ~ 4.49 eV (to the typical Ga_2O_3 bandgap value), indicating an improvement in film quality and a reduction in defects associated with deep states. Additionally, we observe second absorption edge around 4.2 eV (pointed with an arrow), which can be attributed to Sn-related shallow donor states; followed by a minor absorption tail is observed in the implanted film, which was attributed to the doping effect in Ga_2O_3 .⁴²

2.2 Improvement of device performance

The AG and IMP-AN films discussed above were utilized to fabricate MSM $\text{ITO}/\beta\text{-Ga}_2\text{O}_3/\text{Au}$ junction PDs with asymmetric Au and ITO interdigitated electrode (IDE) contacts, as shown in

the schematic cross-section diagram (Fig. 2(a)) and the field-emission scanning electron microscope (SEM) image in Fig. 2(b). No further treatment was carried out after the electrode deposition process.

Fig. 2(c) shows that, under both DUV illumination and dark conditions, the I–V characteristics of the AG β -Ga₂O₃ film-based PD exhibit linear behavior (SI Supplementary Fig.2 shows the I–V curves at different power densities for both devices), suggesting ohmic conduction, while the dark current is high ($\sim 1 \times 10^{-5}$ A). Fig. 2d shows the corresponding transient on/off cycles, indicating that photocurrent increases from 1×10^{-5} A under dark conditions to 1×10^{-4} A under DUV illumination (on/off cycles under different bias voltages are presented in Supplementary Fig.3(a)). Such high dark current results in extremely weak photocurrent-to-dark current (I_P/I_D) ratio (~ 10), which significantly limits the device response time and sensitivity. Supplementary Fig.3(a) indicates that in AG-based devices, the dark current increases significantly as applied bias increases, which can be due to defect-assisted tunneling process. The transient photoresponse signal obtained by fitting a double exponential function to the data shows a slow response time, yielding $\tau_{r1} = 0.19$ s and $\tau_{r2} = 2.59$ s rise times (see Supplementary Fig.3(b)) and $\tau_{d1} = 0.27$ s and $\tau_{d2} = 2.33$ s decay times (see Supplementary Fig.3(c)), as shown in Fig. 2(c).

The I–V curves for the PD based on the IMP-AN film presented in Fig. 2(e) demonstrate a nonlinear behavior unlike the AG film-based PD. A significant increase in photocurrent with increasing bias voltage is observed for such devices as shown in Fig. 2(f), indicating that the transient cycle of the IMP-AN film-based PD is characterized by a high photocurrent up to 3×10^{-5} A, demonstrating the outstanding photoresponse.

Surprisingly, IMP-AN film-based device exhibits a remarkable dark current suppression (to $\sim 10^{-14}$ A) compared to that measured for the AG film-based PD across the entire voltage range,

while there is no increase in the dark current as the voltage increases, as confirmed by the transient cycles illustrated in Supplementary Fig.3(d). This unique characteristic results in a superior I_P/I_D ratio (about 10^9), which is eight orders of magnitude better than that of the AG film-based PD, and has never been reported for devices comprising elements that were subjected to implantation and post-annealing.

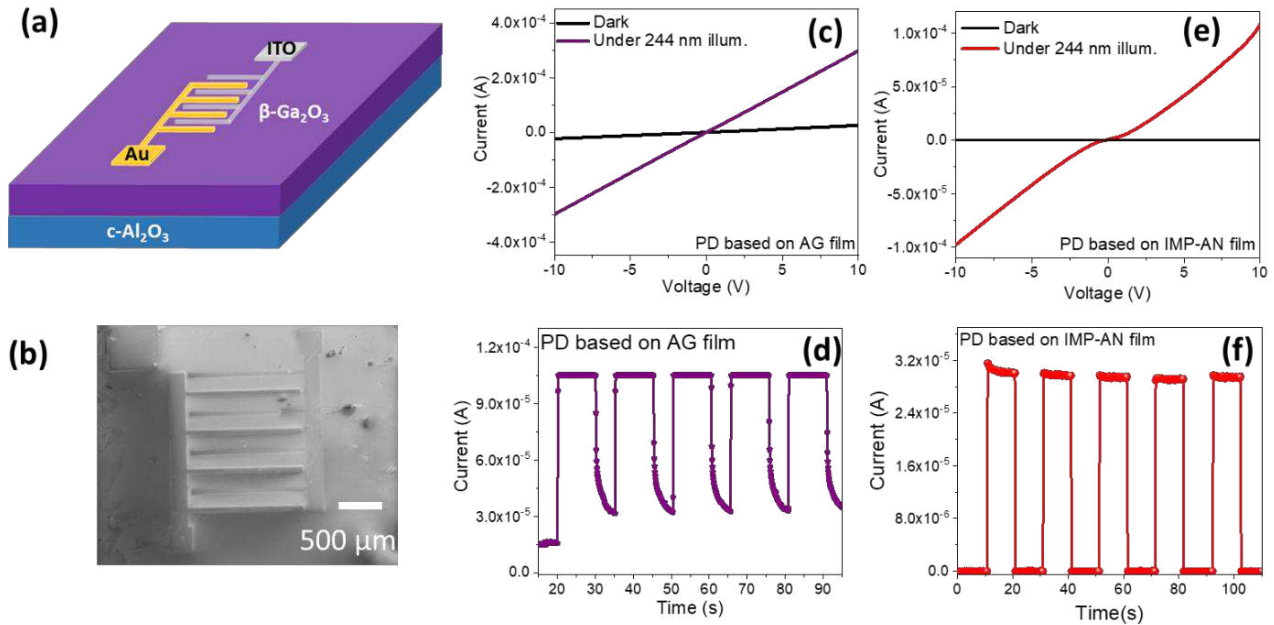


Fig. 2. (a) Schematic cross-section diagram showing the device structure, (b) SEM image of the PD devices showing metal electrodes. I – V curves under dark conditions and DUV illumination at 1.79 W/cm^2 and corresponding time-dependent photoresponse on/off cycles at 10 V and 0.69 W/cm^2 for the PD devices based on (c & d) AG and (e & f) IMP-AN films.

Fig. 2(f) demonstrates that photoresponse of the device improves significantly after implantation/post-implantation annealing, as the rise and fall times decrease significantly compared to the values measured for the AG film-based PD, i.e., from several seconds to $< 40 \text{ ms}$, revealing its potential for fast applications.

The performance of PD devices is defined by their Figure of merit, which are responsivity, detectivity, and the I_P/I_D ratio. Fig. 3(a) and 3(b) show responsivity as a function of different bias

values under different illumination densities for the AG and the IMP-AN film-based device, respectively. The peak responsivity of IMP-AN film-based PD ~ 74 mA/W at 10 V. Interestingly, due to the dark current suppression, as shown in Fig. 3(c), superior detectivity (10^{14} Jones) is achieved in IMP-AN film-based PD, which is five orders of magnitude higher than that of the AG film-based device. On the other hand, the AG film-based device can attain responsivity values up to 219 mA/W, but this improvement is coupled with a substantially lower detectivity ($D^* \sim 10^9$ Jones), largely due to the high dark current, which profoundly constrains the performance of AG film based device.

These findings underscore the substantial advantage of using Sn implantation followed by thermal annealing treatment in enhancing the functionality of PDs based on MSM single-layer β -Ga₂O₃ structure.

We demonstrated outstanding solar-blind characteristics in IMP-AN-based devices as shown in Fig. 3(d). The maximum photocurrent peaks around 244 nm, with a sharp cut-off at 265 nm for the IMP-AN film-based PD, showing an impressive solar-blind rejection ratio ($I_{245\text{nm}}/I_{500\text{nm}}$) of $\sim 10^4$, demonstrating their superior functionality in selective UV-C detection.

To demonstrate the self-powered (photovoltaic) characteristics, the transient photoresponse at 0 V bias voltage (Fig. 3(f)) was carried out, showing superior self-powered behavior for the IMP-AN film-based PD device relative to that based on the AG film. When operating in self-powered (photovoltaic) mode, the AG film-based PD exhibits an I_p/I_D ratio of ~ 10 , which increases by four orders of magnitude (to $\sim 10^5$) for the PD incorporating the IMP-AN film, as shown in the log-scale I–V characteristics illustrated in Supplementary Fig.2(b).

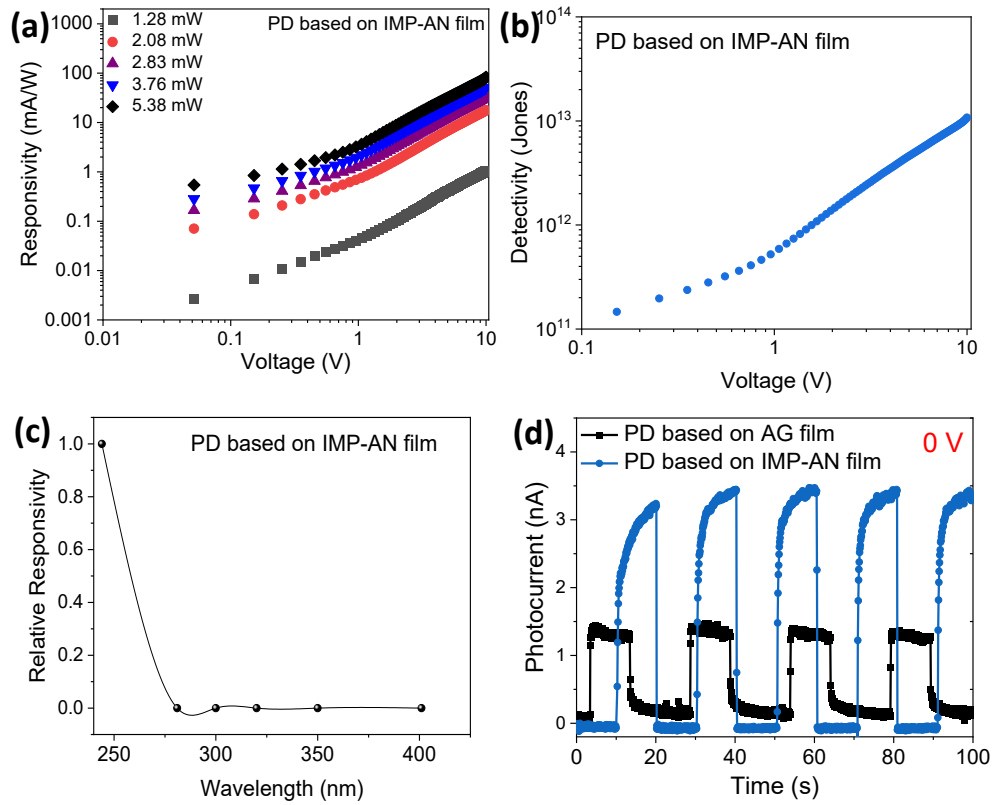


Fig. 3. IMP-AN based PD characteristics: (a) Responsivity as a function of voltage at different illumination power densities and (b) Detectivity vs. voltage as well as (c) Responsivity as a function of incident light wavelengths for IMP-AN based PD. (f) Self-powered characteristics at 0 V for IMP-AN-based PDs compared to that based on AG film.

Table 1. Comparison of our IMP-AN film-based PD device with other implanted Ga_2O_3 -based PD devices reported in literature

Growth	Dopant	Film Annealing conditions	Self-powered	I_p/I_D	Rejection ratio $I_{245\text{nm}}/I_{300\text{nm}}$	D^* (Jones)	Time (s)	Ref
MOCVD	Si	900 °C for 60 s in Ar	No	9.43	-	-	$\tau_{\text{rise}} = 0.58$ $\tau_{\text{fall}} = 1.2$	45
MOCVD	Si	900 °C for 60 s in Ar	No	328	-	-	-	44
Bulk substrate	Mg	950 °C for 30 min in N_2	No	1733	-	3.9×10^{11}	$\tau_{\text{rise}} = 0.157$ $\tau_{\text{fall}} = 0.048$	43
PLD	Sn	1000 °C in air	Yes	$>10^9$	10^4	2×10^{14}	< 0.04	This work

Table 2. Comparison of our IMP-AN film-based PD device performance with that reported for other Sn-doped single-layer MSM PDs

Device	Growth	Self-powered	Dark current (A)	I_p/I_D	Solar-blind rejection ratio I_{245nm}/I_{300nm}	D^* (Jones)	Time (s)
Ti/Au/Sn: β -Ga ₂ O ₃ /Ti/Au ⁴⁶	Sputtering	No	10^{-8} – 10^{-9}	10 ¹	-	-	$\tau_{rise} = 31$ $\tau_{fall} = 22.83$
Ti/Au/Sn: β -Ga ₂ O ₃ /Ti/Au ⁴⁷	Radio Frequency (RF) Sputtering	No	$\sim 10^{-12}$	10 ⁶	-	$\sim 10^{12}$	$\tau_{rise} = 0.39$ $\tau_{fall} = 0.12$
Ag/Sn: β -Ga ₂ O ₃ microwire/Al ⁴⁸	Chemical Vapour Deposition (CVD)	No	10^{-9}	10 ³	--	3.9×10^{11}	$\tau_{rise} = 0.37$ $\tau_{fall} = 0.25$
Ag/Sn: β -Ga ₂ O ₃ /Ag ⁴⁹	RF sputtering	No	$\sim 10^{-6}$ – 10^{-7}	<100	-	10 ¹²	$\tau_{rise} = 0.48$ $\tau_{fall} = 0.59$
Al/Sn: β -Ga ₂ O ₃ /Al ⁵⁰	Sol-gel	No	$\sim 10^{-8}$	$\sim 10^4$	-	10 ¹⁴	$\tau_{fall} > 3000$
Au/Ti/Sn: α -Ga ₂ O ₃ /Au/Ti ⁵¹	Molecular Beam Epitaxy	-	10^{-9}	$\sim 10^2$	-	-	7.3
Au/Sn: β -Ga ₂ O ₃ /ITO (This work)	PLD and Ion implantation	Yes	<10⁻¹²	>10⁹	10⁴	2×10^{14}	< 0.04

To compare superiority of our device, Table 1 presents performance parameters of our IMP-AN film-based PD device compared to PD devices based on ion-implanted β -Ga₂O₃ reported in literature, showing superior performance.^{43–45} Specifically, it exhibits superior detectivity, I_p/I_D ratio, rejection ratio and—most importantly—self-powered characteristics, whereas the other devices have no self-powered characteristics, demonstrating the novelty of our work. Furthermore, our PDs achieved impressive metrics, including exceptionally high I_p/I_D ratio, exceeding eight orders of magnitude, and four-orders-of-magnitude higher detectivity than that reported for other devices.

Furthermore, our IMP-AN Sn-implanted β -Ga₂O₃ device shows significant enhancement compared to other Sn-doped single-layer Ga₂O₃-based MSM photodetectors as shown in Table 2,

demonstrating the superiority of our IMP-AN device.⁴⁶⁻⁵¹ The superior rejection value and UV-C photoresponse of our devices further emphasize the value of our innovative approach. In addition, several previous literature has reported that MSM structure photodetectors based on Ga₂O₃ doped with other dopants lacked self-powered characteristics, such as Ti/Si-doped Ga₂O₃/Au.⁵² Thus, these findings revealed the superior characteristics of our devices.

2.3 Electronic structure examination via XPS measurements

To understand the effect of annealing on the dark current reduction and the photoresponse speed enhancement, XPS measurements were performed, allowing us to identify the changes in surface chemistry through core-level spectral analysis and modified electronic structure using valence band spectra. XPS measurements were performed to elucidate the effect of annealing on the dark current mitigation and the photoresponse speed enhancement, allowing us to understand the changes in surface chemistry through core-level spectral analysis and modified electronic structure using valence band spectra.

As shown in Fig. 4(a), in AG and IMP-AN films, spin-orbital components (Ga-2p_{3/2} and Ga-2p_{1/2}) of the Ga-2p core-level spectra obtained via XPS exhibit single-band nature and their symmetric shapes are typical of oxide compounds, confirming that the metallic gallium component is negligible. The binding energy (BE) positions of Ga-2p_{3/2} and Ga-2p_{1/2} for the AG film are 1117.32 eV and 1144.23 eV, respectively, and shift slightly towards higher values for the IMP-AN film (1117.85 eV and 1144.73 eV, respectively). These values are in between the BE values of Ga metal (1116.5 eV and 1143.3 eV) and bulk Ga₂O₃ (1118.3 eV and 1145.1 eV) suggesting the presence of other GaO_x phases.⁵³ However, we found that the Ga–O bonding in IMP-AN is very close to that of stoichiometric Ga₂O₃ since it is well known that other gallium oxide phases are unstable at the growth temperature employed in this work (850 °C) and under the annealing

conditions (1000 °C) used in our experiments. Thus, it can be surmised that different Ga–O_x ligands (other than the stoichiometric Ga₂O₃), coupled with structural imperfections at the surface, give rise to such shift in the Ga-2*p* core-level spectra.⁵³ On the other hand, Ga-2*p* spectra shift towards higher BE (approaching the value of stoichiometric β-Ga₂O₃) upon annealing, indicating enhanced oxidation and improved β-Ga₂O₃ crystalline quality.

Valence band (VB) spectra (Fig. 4(b)) of both films comprise predominantly O-2*p* states, appearing around 5 eV.⁵³ A linear fit from the lowest part of the VB spectra to the horizontal line of the background signal gives the valence band maximum (VBM) value of 2.85 and 3.35 eV for the AG and IMP-AN film, respectively. These results imply that implantation and post-annealing could modify the band structure properties which might correlate with the enhancement of the transport properties. Thus, the VB edge shifts away from the Fermi level, indicating that the Fermi level moves towards the conduction band in IMP-AN films due to Sn-related shallow donor compared to AG films, which agrees well with absorption measurements.

The O-1*s* core-level spectra for the AG (Fig. 4(c)) and IMP-AN (Fig. 4(d)) films show asymmetric shape, suggesting other contributions apart from the native oxide component. In order to understand this phenomenon, the spectra were deconvoluted using a Voigt line shape obtained by convoluting Gaussian and Lorentzian lines. While the spectrum produced by the AG film exhibits three peaks (at 530.95, 532.36, and 535.98 eV), the spectra for the IMP-AN film includes only two peaks, located at 530.80 eV and 532.22 eV. The peak at 530.95 eV in the spectrum of the AG film corresponds to O–Ga bonds and shifts by 0.15 eV towards lower BE for the IMP-AN film. This finding confirms that implantation and post-annealing improves the O–Ga bonding as it results in the lowering of the O-1*s* binding energy.⁵⁴

The peak located at 532.36 eV observed in the spectrum obtained for the AG film shifts to 532.22 eV for the IMP-AN film, which is attributed to the oxygen sublattice defects commonly observed in heteroepitaxial Ga_2O_3 films grown on *c*-sapphire.^{54, 55} The additional peak at 535.98 eV characterizing the AG film spectrum could be due to surface contamination as it disappeared for IMP-AN film.

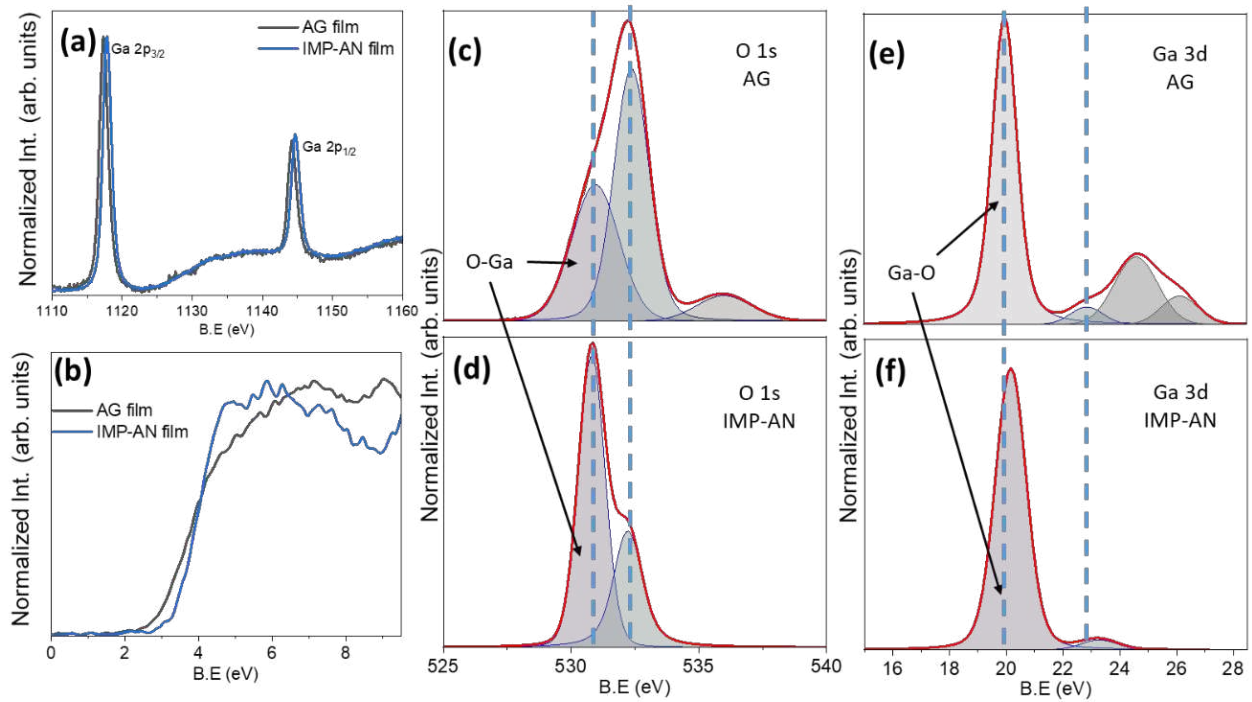


Fig. 4. XPS core-level spectra of (a) Ga-2p, and (b) XPS VB spectra of AG and IMP-AN films. XPS core-level spectra of O-1s for (c) AG and (d) IMP-AN films, and Ga-3d spectra for (e) AG and (f) IMP-AN films.

Ga-3d spectrum produced by the AG film after deconvolution (Fig. 4(e)) shows a peak at 19.51 eV which corresponds to native oxide, indicating presence of Ga–O bonds at the surface.⁵³ This peak shifts by 0.55 eV towards higher BE to 20.16 eV for the IMP-AN film (Fig. 4(f)). This shift reflects enhanced oxidation of the Ga atoms (as observed in the O-1s spectra as well), which is also ascribed to the passivation of dangling bonds by oxygen as well as a reduction in oxygen vacancy density after post-annealing.

Interestingly, the peak observed at 22.8 eV in the AG film spectrum (which corresponds to the O-2s core-level states) shifts to a higher BE value of 23.27 eV for the IMP-AN film, which has a good agreement with reported value of 23.5 eV for crystalline β -Ga₂O₃, further demonstrating significant improvement of the IMP-AN film quality compared to AG films, which agreed well with absorption and Raman findings.

The XPS results reveal that the implantation followed by post-annealing not only improves the bonding between Ga and O but also reduces the oxygen sublattice defects, which thus improves the stoichiometry in Ga₂O₃.

2.4. *Electronic structure modifications using density functional theory (DFT)*

In order to understand the effect Sn doping (-201) Ga₂O₃ on the electronic structure and Fermi level, we calculated the density of states (DOS) for pristine (representing the AG film) and Sn-doped β -Ga₂O₃ (representing the IMP-AN film) structures (see Supplementary Fig.4), along with the partial contributions from individual atomic orbitals.

In pristine β -Ga₂O₃, the valence band edge is primarily composed of O-*p* states, with a minor contribution from Ga-*d* states up to 0.25 eV below the VBM. Above this energy, a small contribution from Ga-*p* states is observed. At the conduction band minimum (CBM), O-*p* and O-*s* states contribute nearly equally. In the conduction band region, the bandgap of pristine β -Ga₂O₃ is filled with O-*p* states, with a minor contribution from O-*s* states.

For Sn-doped β -Ga₂O₃ (representing the IMP-AN film), the VB edge is dominated by O-*p* states with a minor contribution from Ga-*d* states. In addition, we observe a shift in the Fermi level towards the conduction band which is consistent with the previously discussed XPS VB edge shift. No contribution from Sn-related states is observed because Sn doping exhibits negligible effect on Ga sites due to a comparatively low Sn concentration.

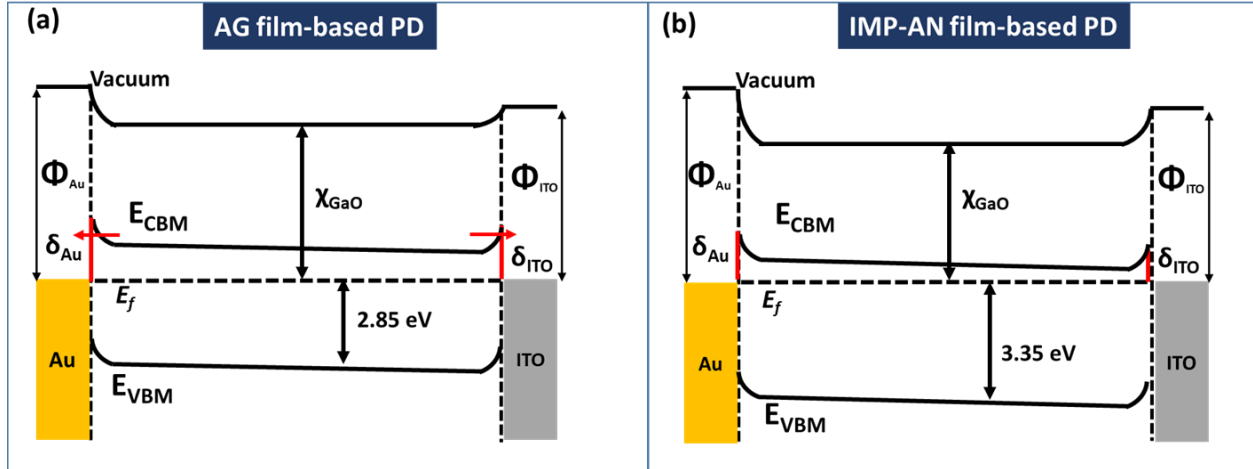


Fig. 5. Schematic band diagram of devices based on (a) AG and (b) IMP-AN films.

3. Discussion

Raman measurements revealed that the AG film contains high density of oxygen vacancies, which is decreased in IMP-AN Sn-implanted films. Annealing such films can passivate the surface dangling bonds as well as reduce the density of such vacancies within the film, affecting the film/contact interface, which in turn modifies the device performance.

Fig. 5(a) and 5(b) show schematic band diagrams of PDs based on AG and IMP-AN films, which were constructed using the VB maxima values obtained by XPS.⁵⁶ The bandgap structure of β -Ga₂O₃ is characterized by its DUV bandgap, which ranges from 4.5 to 4.9 eV, along with additional UV and visible bands resulting from its unique band structure.³⁷ The work functions of ITO and Au are larger than the electron affinity of Ga₂O₃ which results in the formation of a Schottky barrier at the interface.^{57, 58} The presence of high density surface states due to dangling bonds as well as vacancy complexes on bulk of AG film as demonstrated by the Raman and XPS analyses,^{53, 59} significantly influences the barrier height. As negatively-charged oxygen vacancies are formed at its surface during growth, oxygen deficiency introduces state-related defect band within the band gap, which cause the Fermi level pinning.⁶⁰ When the metal and semiconductor come into contact, deep defect-related states that trap carriers are created, causing the formation

of a dipole layer that pins the Fermi level of Ga_2O_3 at the surface.⁵⁸ Such a process reduce the photogenerated carriers in AG films. Furthermore, the high density of traps in AG film, the defect-assisted tunneling paths through the barrier (indicated by red arrows in Fig. 5(a) for the AG film) can promote tunneling current and results in a linear ohmic conduction behavior in the AG-based PD device (Fig. 2(c)).^{57, 61, 62} The slow switching characteristics noted for this AG-based device can be arise from trap states caused by oxygen vacancies or Ga interstitials, trapping the photogenerated carriers, reducing the PD response speed, and increasing the recovery time, as previously reported for $\beta\text{-Ga}_2\text{O}_3$ PDs.^{63, 64} Notably, increasing the bias voltage enhances the photocurrent, but the dark current remains relatively unaffected.

Sn implantation followed by annealing (Fig. 5(b)), reduces such deep defect states and introduces the shallow Sn-related donor states in Ga_2O_3 bandgap^{65, 66} as demonstrated also by absorption measurements, which allow the Fermi level to shift closer to the conduction band (as observed in XPS and DFT analysis, the VB edge shifts to 3.35 eV). Moreover, the affinity of Sn-implanted Ga_2O_3 film is superior to that of the AG film, whereas the substantially reduced tunneling current⁶⁰ increases the photogenerated carrier density, thereby collectively reducing the Schottky barrier height.

This enhancement eliminates the possibility of ohmic conduction observed in the AG-based PD.⁵⁷ Therefore, for IMP-AN-based devices, once the applied voltage is increased, the photo-excited carriers can overcome such a tiny barrier, resulting in the nonlinear behavior observed in Fig. 2(e) and the dark current suppression (by a factor of 10^9).

The self-powered behavior observed for the AG and IMP-AN film-based PDs is primarily due to the built-in electric field caused by different band bending (Fig. 5) at both metal interfaces because of the difference in the work-function of asymmetrical electrodes (Au and ITO).⁶⁷ This

built-in electric field serves as an internal driving force, facilitating the separation of photogenerated electron–hole pairs and thus enabling the self-powered behavior observed in these devices. The superior self-powered transient on/off cycles of the IMP-AN film-based PD (Fig. 3(f)) is attributed to the lowering of the Schottky barrier height due to Sn doping, which is superior to that reported previously, as shown in Table 1 and Table 2.

4. Conclusions

We demonstrated for the first time an enhanced solar-blind self-powered photodetector based on Sn^+ -implanted $\beta\text{-Ga}_2\text{O}_3$ grown by PLD that is characterized by superior detectivity ($\sim 10^{14}$), I_p/I_D ratio ($\sim 10^9$), and rejection ratio ($\sim 10^4$), with a remarkable dark current suppression capacity. The Sn^+ -implanted and post-implantation annealed film-based PD shows $\sim 10^4$ -fold enhancement in the I_p/I_D ratio compared to the as-grown film-based PD. Analysis of Raman, XPS, and DFT data confirms that the reduction in the oxygen vacancies and the improvement in the stoichiometric Ga–O bonds due to implantation and annealing reduces the dark current and improving the overall device speed and responsivity. While this is the first demonstration of Sn^+ -implanted PD device, it is expected to catalyze the development of affordable, high-performance solar-blind DUV self-powered photodetectors suitable for a wide range of applications, such as missile detection, environmental monitoring, medical imaging, and high-speed space communication, unlocking new possibilities across various industries.

5. Methods

Growth, annealing, and implantation

$\beta\text{-Ga}_2\text{O}_3$ films of ~ 650 nm thickness were grown on *c*-plane sapphire substrates by PLD in a chamber under high-vacuum ($<10^{-6}$ Torr) at 800°C , whereby 15,000 KrF excimer laser pulses with 250 mJ energy at 5 Hz frequency were used to ablate a commercial undoped Ga_2O_3 target.

IMP-AN film was implanted with Sn^+ (at $5 \times 10^{15} \text{ cm}^{-2}$ fluence) at 300 keV and room temperature with 7° tilt (to avoid channeled implantation), leading to an expected ion range of 70 nm and a maximum Sn concentration of $7.5 \times 10^{20} \text{ at/cm}^2$ according to Stopping and Range of Ions in Matter (SRIM) simulations.⁶⁸ The sample was then subjected to post-implantation annealing at 1000 °C for 60 minutes in air.

Sample characterizations

SIMS analysis was performed using a Hiden Analytical Dynamic SIMS instrument (Warrington, UK) under ultrahigh vacuum (10^{-9} Torr). A 4 keV continuous Ar^+ beam sputtered the surface, and a MAXIM spectrometer with a quadrupole analyzer collected selected ions. To minimize edge effects, ions were extracted from a $75 \times 75 \text{ }\mu\text{m}^2$ area centered within the larger sputtered area ($750 \times 750 \text{ }\mu\text{m}^2$) using electronic gating. Sputtering time was converted to depth using a constant sputtering rate and crater depth measurements from a Bruker DektakXT stylus profiler. Sn quantification was based on a reference sample with known Sn concentration. The Sn concentration in the IMP-AN film (Supplementary Fig.1(a)) at a depth of 60 nm reached $2 \times 10^{19} \text{ atoms/cm}^3$ while the Sn implantation depth extended up to 200 nm below the surface. The thin lamellas for TEM analysis were fabricated using a Helios G4 Dual Beam system from Thermo Fisher Scientific. The samples were initially covered with approximately 5 nm-thick carbon layer using evaporated carbon. Two Pt protection layers were deposited using 1.6 nA electron beam current and 0.26 nA ion beam current. The bulk milling current was 9.6 nA while 1.2 nA was used for the final milling. The final thinning was performed with 90 pA ion beam current at 30 kV acceleration voltage, followed by a cleaning step performed at 5 kV with 63 pA current. The TEM measurements were carried out using a Themis Z microscope from Thermo Fisher Scientific. For The transmission electron microscopy, 300 kV was used in scanning transmission mode (STEM).

High-resolution imaging was performed in high-angle annular dark field modes with a detector inner angle of around 50 mrad. XRD measurements were conducted using a Bruker D2 Phaser system, equipped with a Cu K-alpha radiation source ($\lambda = 1.54 \text{ \AA}$). The measurements were conducted over a 2θ range of $10\text{--}80^\circ$. The sample surface roughness was characterized by using AFM on a Bruker Dimension Icon SPM system. Absorption measurements were performed on a Perkin Elmer LAMDA 950 UV-Vis absorption spectrometer, scanning the spectral range from 200 to 800 nm. Raman measurements were carried out using a confocal Raman spectrometer (WITec Apyron) with $50\times$ objective attached to a CCD camera, while a solid-state laser emitting at 473 nm wavelength in 180° backscattering mode served as the excitation source with laser power of 25 mW. XPS studies were conducted in Kratos Axis Supra system using an Al K-alpha source.

Device fabrication and measurements

Samples were cleaned with acetone, isopropanol, and deionized water separately for 5 min each before fabricating the IDEs with asymmetric ITO–Au contact (each of 100 nm thickness) combination using a reactive sputtering system. IDEs with $1500 \mu\text{m} \times 50 \mu\text{m}$ interconnected fingers were patterned by photolithography on the $\beta\text{-Ga}_2\text{O}_3$ films. No post-processing was done after the IDE contact deposition on any of the films. Photoconductivity measurements were performed using a DUV 244 nm of the second harmonic of the 488 nm Ar^+ laser line. Keithley SourceMeter 2400, 2460, and 4200-SCS were used for electrical characterizations. All measurements were conducted under ambient conditions. Several laser lines (244, 280, 325, 350 and 400 nm) were used for Wavelength dependent photocurrent measurements. PD photoresponsivity (R) was

calculated using $R = \frac{I_P - I_D}{P * S}$, where I_P , I_D , P , and S denote the photocurrent, dark current, illumination area power density, and sample exposure area, respectively, while detectivity (D^*)

was calculated using $D^* = R \sqrt{\frac{S}{2qI_D}}$, where q is the elementary charge. The active photoconduction area was estimated at $7.32 \times 10^{-4} \text{ cm}^2$.

Theoretical calculations

To investigate the electronic properties of $\beta\text{-Ga}_2\text{O}_3$ along the (-201) direction for all three structures, we employed first-principles DFT calculations using the Vienna Ab initio Simulation Package (VASP)^{69, 70} within the projector augmented wave (PAW) method.⁷¹ The bulk crystal structure parameters of $\beta\text{-Ga}_2\text{O}_3$ were used to construct the (-201) surface slab.⁷² A vacuum layer of 15 Å was introduced along the c -direction to minimize interactions between periodic images. The exchange-correlation potential was treated within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).⁷³ A plane-wave energy cutoff of 600 eV was used, and the Brillouin zone was sampled with a $6 \times 30 \times 1$ Monkhorst-Pack k -point mesh.⁷⁴ All calculations were performed using experimental lattice parameters and converged to an energy tolerance of 10^{-5} eV, and atomic coordinates were relaxed to a force tolerance of 0.01 eV/Å.

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DATA AVAILABILITY

All data supporting the findings of this study are included in the paper and its Supplementary Information files. The corresponding author can also provide additional data upon reasonable request.

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AUTHOR CONTRIBUTIONS

K.U. and I.S.R. devised and planned all experiments as well as wrote the paper, while K.U. carried out PLD growth, device fabrication and characterizations. V.G. conducted theoretical simulation. F.A. carried out XRD measurements, D.M.E., M.P. and K.L. performed ion implantation and post annealing. M.N. performed XPS, while N.W. carried out SIMS characterizations. The results were collectively analyzed and discussed by all authors. K.U. wrote the paper, incorporating input from all co-authors. I.S.R. supervised the project.

COMPETING INTERESTS

The authors declare no competing interests.

SUPPLEMENTARY INFORMATION

STEM images of the cross-section of the entire film, doping profile by SIMS, AFM images, I–V and transient measurements under different bias and illumination density, DOS analyses.

Supplementary Files

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