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ABSTRACT

Acceptor impurity doping is recognized as a functional tool to extend the capabilities and applications of \(\beta\)-Ga\(_2\)O\(_3\). The effect of thermal annealing on photoexcited carriers was characterized by measuring the photocurrent spectra of nitrogen (N)-ion-implanted \(\beta\)-Ga\(_2\)O\(_3\) crystals, where the N was found to cause less crystal damage to the crystal and much lower thermal diffusivity than Mg. The photocurrent intensity at 4.5–5.5 eV showed an increase with an increase in external bias, and the increase was attributed to the photo-generated non-equilibrium electrons and holes. The spectra under a positive external bias showed a distinct onset at 3.0–3.5 eV owing to optical transitions involving deep donor levels formed by the N-implantation. Spectrally integrated responsivity showed a significant change with the annealing temperature.

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Monoclinic \(\beta\)-Ga\(_2\)O\(_3\) has a wide bandgap energy \((E_g)\) of 4.5–4.9 eV\(^{1–4}\) and exhibits a high breakdown electric field of 8 MV/cm and good chemical and thermal stabilities.\(^{5–7}\) It has thus been attracting attention as an alternative material for power electronics such as field-effect transistors (FETs)\(^6\) and Schottky barrier diodes\(^6\) as well as solar-blind deep-UV photodetectors.\(^{10,11}\) The \(n\)-type conductivity in \(\beta\)-Ga\(_2\)O\(_3\) is tunable over an extremely wide range \((\sigma = 10^{-12}–10^5\ \text{S/cm})\) by doping with Si, Ge, or Sn impurities.\(^{5–7}\) While performance is progressing due to using lateral or vertical geometries for \(n\)-type unipolar devices, demand is increasing for \(p\)-type conductivity of \(\beta\)-Ga\(_2\)O\(_3\) in order to extend its capabilities and applications.

Several efforts have been made to realize \(p\)-type conductivity by doping with Mg, Zn, or nitrogen (N) impurities.\(^{12–17}\) However, the acceptor impurity-doped bulk crystals or epitaxial films have mostly shown a semi-insulating behavior with extremely high resistivities \(\rho\) of \(10^{11}–10^{12}\ \Omega\ \text{cm}\). The N-implanted layer nevertheless worked well as a current blocking layer in vertical metal-oxide-semiconductor FETs.\(^{15}\) The fabrication of \(p-n\) homojunctions for nanowires\(^{19,20}\) by doping with Zn has been reported, although only the rectifying behavior of the current–voltage \((I-V)\) characteristics was described. Electronic structure calculations\(^{11,21–25}\) have shown that the valence band maximum is composed of oxygen (O) 2p states. The strong localization nature of the O states induces a relatively flat valence band structure with a large effective hole mass. It also induces spontaneous formation of small polarons for holes; i.e., a hole attracts an O atom, resulting in the self-trapped hole (STH) state. The existence of STHs has been shown by theoretical\(^{26}\) and experimental\(^{11,27–30}\) studies, including ones that measured luminescence,\(^{13,27}\) reflectance,\(^{30}\) absorption,\(^{27}\) and photoluminescence dynamics.\(^{30}\)

Deep acceptor doping of Mg and N by implantation of impurity ions into \(n\)-type bulk substrates was recently demonstrated.\(^{16}\)
The N was found to cause less crystal damage to the substrate and to produce much lower thermal diffusivity than Mg. The \( n^-Ga_2O_3/Ga_2O_3\):N test structures revealed that N works as a deep acceptor, suppressing the leakage current in the I–V characteristics. In this study, the \( n^-Ga_2O_3/Ga_2O_3\):N test structures were further investigated using photocurrent measurement. The effect of thermal annealing on photoexcited carriers was characterized in order to gain a better understanding of their performance.

The schematic cross-sectional diagram of the sample structure is shown in Fig. 1. Nitrogen ions were implanted into (001) unintentionally Si-doped substrates with an energy of 480 keV and a dose of \( 4 \times 10^{18} \) cm\(^{-2}\), leading to a peak N concentration \([N]\) of \( 1.5 \times 10^{17} \) cm\(^{-3}\). This is about ten times higher than the residual Si concentration \([Si]\) of \( 2 \times 10^{17} \) cm\(^{-3}\). Nitrogen activation and crystal recovery were attempted for a series of five samples annealed at different temperatures \( T_a (800, 900, 1000, 1100, \) and \( 1200 ^\circ C) \) in \( N_2 \) ambient for 30 min. The contact layers were fabricated partially on the surface and fully on the backside by implanting Si with \([Si]\) of \( 5 \times 10^{19} \) cm\(^{-3}\), followed by thermal annealing at 800 \( ^\circ C \). Finally, Ti (20 nm)/Au (230 nm) Ohmic electrodes were formed on the contact layers, where the top electrode had a diameter of 100 \( \mu m \). Details of the samples are available elsewhere.\(^{16}\)

Energy-band profiles were calculated by solving the one-dimensional Poisson equation.\(^{11}\) The zero-bias effective Schottky barrier height was set to 0.33 eV by taking the work function of Ti as 4.33 eV\(^{15}\) and the electron affinity of \( \beta^-Ga_2O_3 \) as 4.00 eV\(^{13}\) into account, and a static dielectric permittivity \( \epsilon_s \) of 10.2 was used.\(^{14}\)

The thickness of the heavily Si-doped surface contact layer was set in accordance with the secondary-ion-mass-spectroscopy (SIMS) profile\(^{16}\) to be 10 nm although a 100-nm-deep box profile was designated in the Si-implantation. The parameters for the N-ion-implanted layer were also set in accordance with SIMS profiles,\(^{16}\) dose of \( 2.2 \times 10^{13} \) cm\(^{-2}\), N-ion projected range of 500 nm, and ion straggle range of 400 nm, corresponding to an average \([N]\) of \( 5.5 \times 10^{15} \) cm\(^{-3}\). The calculated dose value is slightly lower than the experimental one, but full activation of the implanted N impurities still induced upward band bending in the N-ion-implanted layer, as shown by the black solid lines in Fig. 2. Application of a positive (negative) bias to the surface electrode should cause the residual free electrons to flow toward the surface (backside) Ohmic electrode as the leakage current.\(^{16}\)

Photocurrent spectra were measured at room temperature (RT) using monochromatic light generated from a 450 W Xe lamp. As shown in Fig. 1, the incident light was irradiated near the edge of the circular surface Ti/Au Ohmic electrode with an excitation spot diameter of 200 \( \mu m \) and an incidence angle of 45\( ^\circ \). The photogeneration of excess carriers is expected to arise mostly from the region circularly surrounding the electrode and partially beneath the surface contact layer. According to the spectroscopic ellipsometry measurements on \( \beta^-Ga_2O_3 \) single crystals,\(^{3} \) the absorption coefficient \( \alpha \) is in a range of \( 10^1-10^3 \) cm\(^{-1}\) for \( E < E_g \), and the value gradually increases up to \( 10^4-10^5 \) cm\(^{-1}\) for \( E > E_g \). The penetration depths of the incident light are, respectively, several hundreds of \( \mu m \) and nm for \( E < E_g \) and \( E > E_g \), and the depths are enough to reach the N-ion-implanted layer. The photocurrents were probed using a pico-ammeter (Keithley 6458) under external bias conditions (\( V_{ext} \) between \(-10 \) and \(+10 \) V). Since the photocurrent is overlapped with the background leakage current and noise, the photocurrent signals were extracted using a lock-in amplifier by modulating the incident light with the optical chopper. Then, to calculate the spectral responsivities, the spectral irradiance of the monochromatic incident light was measured using an optical power meter (Newport 843-R) equipped

![FIG. 1. Schematic cross-sectional diagram of the \( n^-Ga_2O_3/Ga_2O_3\):N test structure. The top electrode had a diameter of 100 \( \mu m \). Incident light was irradiated near the edge of the Ohmic electrode with an excitation spot diameter of 200 \( \mu m \) and an incidence angle of 45\( ^\circ \).](image-url)

![FIG. 2. Numerically simulated energy-band diagram of the \( n^-Ga_2O_3/Ga_2O_3\):N/Ga\(_2O_3\) structure in neutral and charged states. The Fermi level at thermal equilibrium is indicated by the black solid line. The calculated band gap of \( 3.4 \) eV is in agreement with the experimental one. The absorption coefficient \( \alpha \) is in a range of \( 10^1-10^3 \) cm\(^{-1}\) for \( E < E_g \), and the value gradually increases up to \( 10^4-10^5 \) cm\(^{-1}\) for \( E > E_g \). The penetration depths of the incident light are, respectively, several hundreds of \( \mu m \) and nm for \( E < E_g \) and \( E > E_g \), and the depths are enough to reach the N-ion-implanted layer.](image-url)
with a UV-enhanced Si photodetector (918D-UV-OD3R). The overall system was calibrated using a conventional Si PIN photodiode (S2281-04).

Representative photocurrent spectra of samples at $T_a = 800\, ^\circ\mathrm{C}$ and 1000 $^\circ\mathrm{C}$ are shown in Figs. 3(a) and 3(b), respectively. Similar datasets were collected for all the annealed samples. The spectrum for $T_a = 800\, ^\circ\mathrm{C}$ at $V_{\text{ext}} = 0\, \mathrm{V}$ shows the background in the order of $10^{-12} - 10^{-13}$ A in an energy range of $E = 1.8-4.0\, \mathrm{eV}$ followed by a rapid increase for $E > 4.5\, \mathrm{eV}$, shoulders at 4.6 and 4.75 eV, and peaks at 4.85 eV due to the excitation absorption reflecting optical anisotropy of the direct $\Gamma - \Gamma$ transitions.\(^{34}\) The spectrum for $T_a = 1000\, ^\circ\mathrm{C}$ at $V_{\text{ext}} = 0\, \mathrm{V}$ shows a weak but noticeable increase in the energy range of $E = 3.5-4.5\, \mathrm{eV}$ followed again by the rapid increase for $E > 4.5\, \mathrm{eV}$. The photocurrent intensity for $E > 4.5\, \mathrm{eV}$ shows an increase with an increase in $V_{\text{ext}}$ by virtue of increases in the photoexcited excess carriers. The photo-generated minority free holes are considered to be scarcely observable as a photocurrent due to the spontaneous formation of small polarons.\(^{13,26-30}\) However, recent electron beam-induced current experiments\(^{36,37}\) have shown that electron beam-induced non-equilibrium holes are mobile, and low-energy cross-sectional cathodoluminescence (CL) measurement\(^{35}\) has claimed apparent contribution of electron beam-induced minority hole diffusion for the nonradiative surface recombination. The increase in the photocurrent intensity for $E > 4.5\, \mathrm{eV}$ is thus considered to be due to the photo-generated non-equilibrium electrons and holes under positive and negative $V_{\text{ext}}$ conditions on the surface, respectively.

The spectra for $T_a = 800\, ^\circ\mathrm{C}$ at $V_{\text{ext}} = +5$ and $+10\, \mathrm{V}$ begin to exhibit a gradual increase in the energy range of $E = 3.0-4.5\, \mathrm{eV}$. It is noteworthy that the spectrum for $T_a = 1000\, ^\circ\mathrm{C}$ at $V_{\text{ext}} = +5\, \mathrm{V}$ shows a distinct onset at 3.5 eV and that the onset energy position shows a lower energy shift of 0.5 eV for $V_{\text{ext}} = +10\, \mathrm{V}$. On the contrary, the onsets for $E = 3.0-4.5\, \mathrm{eV}$ are hardly observable at $V_{\text{ext}} = -5$ and $-10\, \mathrm{V}$. The results indicate a significant contribution of photocurrent generated by photoexcitation involving deep-level states for N-ion-implanted crystals. According to theoretical studies on acceptor dopants in $\beta$-Ga$_2$O$_3$, N substituting on an O site (N$_O$) exhibits deep acceptor levels having ionization energies of 2.2 and 3.5 eV,\(^{36,40}\) where the three inequivalent O sites have different ionization energies. The latter value falls within the range of onset energies (3.0–3.5 eV), indicating a certain degree of contribution of optical transitions from the valence band to the N$_O$ acceptor levels. However, the photo-generated minority free holes are hardly observable due to the limited diffusion length,\(^{36,37}\) in the range of 330–400 nm. Another possible origin of the onset is the contribution of deep donors formed by the N doping. A theoretical study\(^{40}\) suggests that both N$_O$ compensated by oxygen vacancy (V$_O$) and N$_O$-V$_O$ complex act as deep donors with ionization energies of ~3.5 eV. Although the defect and impurity related optical transitions are analyzed using the configuration coordinate diagram, the thermodynamic ionization energies still give a reasonable estimation for the transition energy. Optical transitions from neutral deep donor levels to the conduction band are thus considered to be the probable cause of the onset observed in the photocurrent spectra under positive $V_{\text{ext}}$ on the surface electrode. Similar but small onsets for $E = 3.0-4.5\, \mathrm{eV}$ are also observed under negative $V_{\text{ext}}$ conditions on the surface, and they are attributed to the photo-generated majority free electrons flowing toward the backside Ohmic electrode.

The responsivity spectra of the samples at $T_a = 800\, ^\circ\mathrm{C}$ and 1000 $^\circ\mathrm{C}$ are shown in Figs. 4(a) and 4(b), respectively. The dataset used in Fig. 3 was divided by the spectral irradiance of the monochromatic incident light to extract the responsivity. To visualize the effect of thermal annealing on the photoexcited carriers, the responsivities were spectrally integrated for energy ranges of $E = 2.0-4.5\, \mathrm{eV}$ and 4.5–5.5 eV. The values are plotted as a function of $T_a$ in Figs. 5(a) and 5(b), respectively. The intensities show a monotonous increase with the increase in $T_a$ followed by a decrease at a high $T_a$. According to the $J-V$ characteristics for the background leakage current,\(^{16}\) the initial increases are attributed to the recovery of crystallinity. The decrease at $T_a = 1100\, ^\circ\mathrm{C}$ for $E = 2.0-4.5\, \mathrm{eV}$ [Fig. 5(a)] is ascribed to the thermal activation of N impurities

![Representative photocurrent spectra at RT for N-implanted $\beta$-Ga$_2$O$_3$ annealed at (a) 800 $^\circ\mathrm{C}$ and (b) 1000 $^\circ\mathrm{C}$. The cross in (a) indicates the spike in background noise.](image)

**FIG. 3.** Representative photocurrent spectra at RT for N-implanted $\beta$-Ga$_2$O$_3$ annealed at (a) 800 $^\circ\mathrm{C}$ and (b) 1000 $^\circ\mathrm{C}$. The cross in (a) indicates the spike in background noise.
since the photo-generated excess free electrons are considered. On the other hand, the decrease at \( T_a = 1000 ^\circ \text{C} \) for \( E = 4.5-5.5 \text{ eV} \) [Fig. 5(b)] indicates formation of additional nonradiative recombination centers (NRCs) by N-implantation since the photo-generated excess free electrons and holes are considered for the band-to-band transitions. A similar tendency was found for N-doped epitaxial films grown by radio-frequency plasma-assisted molecular-beam epitaxy\(^1\) the overall CL intensities decreased due to doping N with \([N] = 1 \times 10^{18} \text{ cm}^{-3}\).\(^2\) According to the rate equation model analysis of the temperature-dependent CL intensities,\(^2\) the decrease was ascribed to an increase in the NRC capture rate. Further studies are necessary to clarify the origin of the NRCs.

In summary, the photocurrent spectra of N-ion-implanted \( \beta\)-Ga\(_2\)O\(_3\) crystals annealed at \( T_a = 800 ^\circ \text{C} - 1200 ^\circ \text{C} \) were measured under \( V_{ext} \) at RT. The photocurrent intensity for \( E > 4.5 \text{ eV} \) showed an increase with an increase in \( V_{ext} \), and the increase was attributed to the photo-generated non-equilibrium electrons and holes under positive and negative \( V_{ext} \) conditions on the surface, respectively. In addition, the photocurrent spectra exhibited the apparent onsets for \( E = 3.0-4.5 \text{ eV} \) under positive \( V_{ext} \) conditions on the surface. The onsets were ascribed to optical transitions involving deep donor levels formed by the N-ion-implantation. The spectrally integrated responsivity showed a monotonical increase with an increase in \( T_a \) followed by a decrease at high \( T_a \). The initial increase was attributed to the recovery of crystallinity. The decrease at \( T_a = 1100 ^\circ \text{C} \) for \( E = 2.0-4.5 \text{ eV} \) was ascribed to the thermal activation of N impurities. The decrease at \( T_a = 1000 ^\circ \text{C} \) for \( E = 4.5-5.5 \text{ eV} \) indicates the formation of additional NRCs due to N-implantation.

**DATA AVAILABILITY**

The data that support the findings of this study are available within the article.
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