Improved External Quantum Efficiency of GaN p-i-n Photodiodes With a TiO_2 Roughened Surface

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***Abstract*—Gallium nitride p-i-n ultraviolet photodiodes (PDs) with a titanium dioxide (TiO_2) nano-particles roughened surface have been fabricated. It was found that the responsivity and external quantum efficiency can be improved 60% on the surface roughened PDs. It was also found that light absorption can be enhanced from various incident angles by the TiO_2 roughened surface. Furthermore, the high detectivity of 9.2×10^{13} cm $\cdot$ Hz$^{1/2}$ $\cdot$ W^{-1} can be achieved from the PD with a rough surface.**

***Index Terms*—Gallium nitride (GaN), p-i-n, photodiodes (PDs), surface roughness, titanium dioxide (TiO_2).**

GALLIUM nitride (GaN)-based semiconductor devices have been developed over 20 years. Commercial products such as light-emitting diodes (LEDs) [1] and laser diodes [2] have been applied in full-color display, illumination, and high-density digital storage. One important issue of LED is how to increase light-emitting efficiency. Surface roughness has been proven to be an effective technique to enhance light extraction efficiency. With a rough surface, photons generated in the active layer will have multiple opportunities to find the escape cone [3]–[6]. Thus, the output intensity of such LEDs is larger than conventional LEDs. The roughened surface by *in situ* growth or etching process, however, usually damages the crystal quality of the p-type top layer to form leakage current paths. The generation of large leakage current is not suitable for devices operated at reverse voltages (photodiodes (PDs), for example). Unlike GaN-based LEDs, no such surface roughness technologies have been applied in GaN-based photodiodes (PDs). Although the GaN-based semiconductor is the best candidate for an ultraviolet (UV) PD, the responsivity of a UV PD is low in theory. Thus, it is very useful for GaN PDs to improve device performance by surface roughness technologies. In this letter, we used titanium dioxide (TiO_2) nano-particles coating on the top surface as a roughness technique to improve the performance of GaN p-i-n PDs. We know that TiO_2 is not expensive and exhibits high resistance to corrosion and photocorrosion in aqueous environments. Due to its stable performance, TiO_2 has been used in many applications, including self-cleaning building materials [7], chemical gas sensors [8], antiseptic coatings [7], and the generation of photovoltaic electricity [9]. Here, we applied TiO_2 nano-particles coating as surface roughness techniques in GaN PDs. The electrical and optical properties of the fabricated PDs will also be discussed.

The device structures of this letter were all grown on c-plane (0 0 0 1) sapphire substrates by a low-pressure metal–organic chemical vapor deposition system. Trimethylgallium (TMGa) and ammonia (NH_3) were used as the source materials of Ga and N, respectively. Silane (SiH_4) and biscyclopentadienyl-magnesium (Cp_2Mg) were used as the n-type and p-type dopant sources. The carrier gas was hydrogen. Prior to the growth, sapphire substrates were first heated to 1120 °C in a stream of hydrogen to clean the substrate surfaces. Then a two-step growth procedure was employed with low-temperature GaN nucleation layer grown at 520 °C and the high-temperature epitaxial layers grown at 1120 °C. The p-i-n PD structure consists of a 25-nm-thick GaN nucleation layer, a 4-μm-thick Si-doped n-GaN layer, a 1-μm-thick undoped GaN absorption layer, and a 100-nm-thick Mg-doped p-GaN layer. All samples were subsequently annealed *in situ* to active Mg in the p-type layer. GaN p-i-n PDs were then fabricated by conventional photolithography and inductively coupled plasma etching. The TiO_2 nano-particles were coated on the p-type layer surface by spin coater, and then covered with indium tin oxide layer alloyed at 600 °C. For comparison, samples without TiO_2-coated layer were also prepared. On the other hand, Cr–Pt–Au contact was subsequently evaporated onto the n-type GaN surface to serve as the n-electrode and bonding pads. After these procedures, we used an HP-4156B semiconductor parameter analyzer to measure current–voltage (I–V) characteristics of the fabricated PDs. Spectral responsivity measurement was also performed by JOBIN-YVON SPEX 1000M System with a xenon arc lamp light source. All the optical systems are calibrated by using a UV-enhanced silicon PD.

Fig. 1 presents the atomic force microscopy (AFM) photograph of the surface morphology of sample with TiO_2 coating. It can be seen that the island-like structures were formed by TiO_2 nano-particles on the sample surface. The diameter and height of TiO_2 islands are around 500 and 400 nm, respectively. It also can be seen that some big islands are made up of several small islands. The density of TiO_2 islands is about

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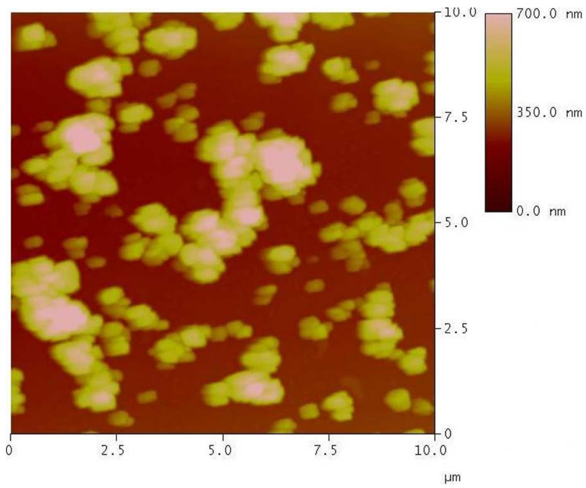

Fig. 1. AFM photograph of the surface morphology of sample with TiO_2 coating.

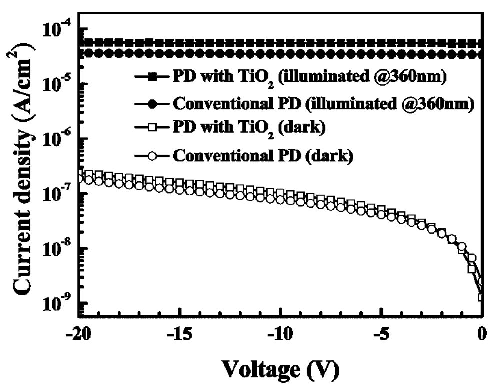

Fig. 2. Room-temperature I–V characteristics of fabricated PDs.

$2.8 \times 10^8 \text{cm}^{-2}$ in our sample. The refractive index of TiO_2, however, is near/or higher than that of GaN [10]–[12]. Therefore, it would be disadvantageous for incident light transmitting through the GaN device if the device surface were entirely covered with TiO_2. Other densities of TiO_2 islands would result in lower responsivities of PDs in our experiments. The responsivity values of 0.09, 0.12, 0.15, 0.13, and 0.13 A/W are corresponding to the TiO_2 island densities of 0, 1.7×10^8, 2.8×10^8, 3.8×10^8, and $4.4 \times 10^8 \text{cm}^{-2}$, respectively. Thus, we only discussed the characteristics of the PD with a TiO_2 island density of $2.8 \times 10^8 \text{cm}^{-2}$ in this letter. Fig. 2 shows the room-temperature I–V characteristics of fabricated PDs taken in the dark and under 360-nm wavelength light illumination. It can be seen that the dark leakage currents were almost identical for these two samples. With a 5-V reverse bias, it was found that the dark current densities were $4 \sim 5 \times 10^{-8} \text{Acm}^{-2}$. The small dark current density observed from our PDs suggests good crystalline quality of our epitaxial layers and good interfacial properties of our contacts. The measured photocurrent densities of these two samples are also shown in Fig. 2. It was found that photocurrent from a PD with a TiO_2-coated layer was larger than that from a conventional PD. The large photocurrent generated from the PD with a TiO_2-coated layer can be attributed to the fact that more incident photons reach the absorption layer of PD by the roughened surface.

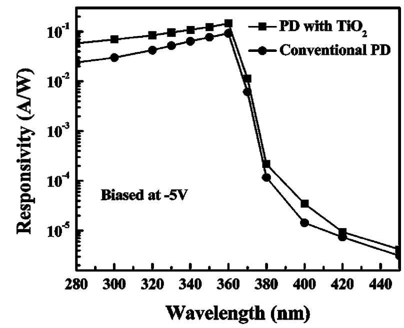

Fig. 3. Spectral responsivities of fabricated PDs under 5-V reverse bias.

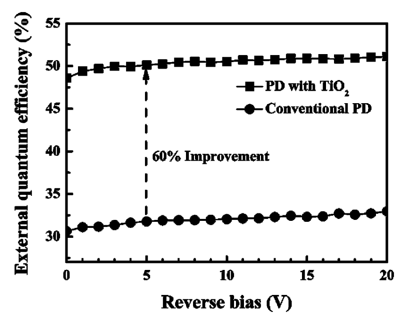

Fig. 4. External quantum efficiency of fabricated PDs measured at different reverse biases and under 360-nm wavelength light illumination.

Fig. 3 shows the spectral responses of fabricated PDs biased at 5 V. It can be seen clearly that the peak responsivity occurred at 360 nm for all samples. With 5-V applied reverse bias and an incident light wavelength of 360 nm, it was found that the measured responsivities were 0.15 and 0.09 A/W for PD with and without a TiO_2-coated layer, respectively. The rejection ratio from UV to visible can be defined as the responsivity measured at 360 nm divided by the responsivity measured at 450 nm. With such a definition, we found that UV-to-visible rejection ratio were 3.6×10^4 and 2.8×10^4 for PD with and without TiO_2 coating, respectively. Fig. 4 shows external quantum efficiencies of both samples with different applied biases. Obviously the external quantum efficiency of PD with a TiO_2-coated layer is always higher than that of conventional PD in the entire measurement range. It can be seen that 60% improvement of external quantum efficiency can be achieved by TiO_2 nanoparticles surface roughness technique. We believe such an enhancement should be attributed to the very rough surface of the TiO_2-coated PD. Furthermore, in order to clarify the influence of the TiO_2 roughened surface on PD performance, the responsivitity experiments with different incident light angles were carried out to find the relation between responsivity and incident angles. The responsivitity experiments with different incident light angles were carried out to find the relation between responsivity and incident angles. Although the maximum responsivity was found in both samples when the incident light was perpendicular to the surface of the PD, the responsivity of a PD with TiO_2-coated layer is always higher than that of a conventional PD at every various incident angle. Fig. 5 shows the zero bias responsivity ratio of a PD with a TiO_2-coated layer

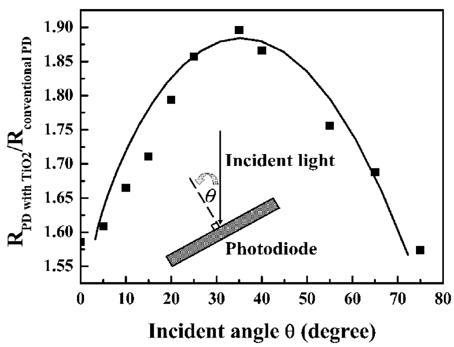

Fig. 5. Responsivity ratio of PD with a TiO_2-coated layer to conventional PD measured at different incident angles of light (the solid line is an eye-guiding line). The inset shows the schematic illustration of experiment with different incident angles.

to a conventional PD at different incident angles of light. We found that the value of ratio is over 1.55 from 0° to 75° incident angle and the maximum value of 1.9 happens to the incident angle of 35°. Although the origin shape of TiO_2 nano-particles is sphere-like, the shapes of TiO_2 islands are quit different. A randomly textured surface should be formed by these TiO_2 islands, which enhances the light absorption. The increment of absorption with different incident angles would depend on the surface geometry and the refractive index of the medium [13]. The largest incremental ratio of light absorption was found at the incident angle of 35° from the TiO_2 roughened PD. Such a result clearly indicates that the light absorption can be enhanced from various incident angles by the TiO_2 roughened surface.

For a PD, detectivity $(D*)$ is an important parameter to examine its performance. Assuming the primary noise source is thermal noise [14], then the detectivity can be calculated by $D* = R_\lambda (R_0 A/4\ \mathrm{kT})^{1/2}$, where R_λ is the zero bias responsivity of PD, R_0 is the differential resistance, A is the device area, k is the Boltzmann constant, and T is the absolute temperature. The differential resistance R_0 can be calculated by fitting the dark current data of PD with a curve fitting method [15]. By taking the derivative (dV/dI) of the fitted curve at zero bias, we obtained the differential resistance $R_0 = 1.6 \times 10^{13}$ and $1.3 \times 10^{13}\ \Omega$ for PD with and without TiO_2 coating, respectively. Then the detectivities of PD with TiO_2-coated layer and conventional PD that can be calculated from the above equation are 9.2×10^{13} and $6.5 \times 10^{13}\ \mathrm{cm \cdot Hz^{1/2} \cdot W^{-1}}$, respectively. The high external quantum efficiency should result in high responsivity. Thus, the high detectivity of the PD with TiO_2-coated layer originates from the high responsivity and high external quantum efficiency by the rough surface of the device.

In summary, GaN p-i-n UV PDs with TiO_2 nano-particle roughened surfaces have been fabricated. It was found that the responsivity and external quantum efficiency can be improved 60% on the surface roughened PDs. It was also found that light absorption can be enhanced from various incident angles by the TiO_2 roughened surface. Furthermore, the high detectivity of $9.2 \times 10^{13}\ \mathrm{cm \cdot Hz^{1/2} \cdot W^{-1}}$ can be achieved from the PD with a rough surface.

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