Article

AlGa_N Ultraviolet Metal–Semiconductor–Metal Photodetectors with Reduced Graphene Oxide Contacts

Bhishma Pandit and Jaehee Cho *

School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju 54896, Korea;
bhishmapandit2046@gmail.com

* Correspondence: jcho@chonbuk.ac.kr

Received: 24 September 2018; Accepted: 27 October 2018; Published: 1 November 2018

Abstract: AlGa_N semiconductors are promising materials in the field of ultraviolet (UV) detection. We fabricated AlGa_N/Ga_N UV metal–semiconductor–metal (MSM) photodiodes with two back-to-back interdigitated finger electrodes comprising reduced graphene oxide (rGO). The rGO showed high transparency below the wavelength of 380 nm, which is necessary for a visible-blind photodetector, and showed outstanding Schottky behavior on AlGa_N. As the photocurrent, dark current, photoresponsivity, detectivity, and cut-off wavelength were investigated with the rGO/AlGa_N MSM photodiodes with various Al mole fractions, systematic variations in the device characteristics with the Al mole fraction were confirmed, proving the potential utility of the device architecture combining two-dimensional materials, rGO, and nitride semiconductors.

Keywords: ultraviolet photodiode; AlGa_N; graphene oxide; MSM photodiode; visible-blind

1. Introduction

The III-nitride semiconductors and alloys thereof have been studied extensively because of their wide and direct bandgaps, high breakdown voltages, high mechanical and chemical stabilities, and low reverse leakage currents. These promising properties have inspired the use of III-nitride semiconductors for many applications such as light-emitting diodes, laser diodes, photodetectors, high electron mobility transistors, field-effect transistors, Schottky diodes, and solar cells [1–5]. Among these applications, ultraviolet (UV) photodetectors that are usable in visible- to solar-blind conditions have drawn significant attention for use in missile plume detection, flame engine sensors, ozone layer monitoring, and secure intersatellite communication systems [6,7]. With a bandgap between those of Ga_N (3.4 eV) and Al_N (6.2 eV) [8], AlGa_N can be used in both visible- and solar-blind UV photodetectors without bulky filter systems or heavy cooling systems such as those required for Si-based photodetectors, thus reducing the footprint and the production cost of the devices [7]. Regarding the photodetector device architecture, the easy and cost-effective fabrication of metal–semiconductor–metal (MSM) photodiodes with two interdigitated Schottky electrode contacts on their planar semiconductor surfaces has attracted significant attention. Such devices present low dark currents, low noise, high response speeds, and no doped layers [9,10].

Another important factor of planar UV MSM photodiodes is the transparent conducting electrode [11]. The transparency of existing metals and metal oxides declines sharply with decreasing illumination wavelength [12]. Therefore, high transparency in the UV spectral region, high material conductivity, and linear Ohmic contact properties are essential for electrodes in UV photodetectors [7]. Graphene oxide (GO), a derivative of graphene, possesses significant potential as a conductive electrode material with UV transparency [13]. GO can be fabricated via inexpensive and facile

processes while retaining graphene's properties. Furthermore, by adding thermal or chemical reduction processing [14,15], so-called reduced GO (rGO) can be obtained, which presents variable optical and electrical properties depending on the degree of the oxygen functional groups contained on the basal plane of the rGO. Recently, Zhu et al. and Li et al. demonstrated the potential of rGO electrodes in the Si photodiodes [16,17]. Pandit et al. studied rGO Schottky contacts on a GaN layer, presenting the dependency of the Schottky barrier height on the GO reduction temperature [18]. Hence, the combination of AlGaIn and GO-based materials for UV-enhanced optical sensors seems to be an interesting and attractive topic for exploration. An rGO/AlGaIn-based photodiode may provide an enhanced photo-to-dark current ratio and tunable cut-off wavelength depending on the Al mole fraction. Here, we investigated rGO/Al_xGa_{1-x}N MSM photodiodes with various Al mole fractions, x . Measurements of the dark current, photocurrent, and photoresponsivity of the fabricated devices showed systematic correlations of these properties with the Al mole fraction in the AlGaIn layer.

2. Materials and Methods

Three Al_xGa_{1-x}N/GaN (300 nm/1.5 μ m) samples with different Al mole fractions were grown on (0001) sapphire substrates by metalorganic chemical vapor deposition. Before device fabrication, the samples were cleaned by ultrasonication in acetone, methanol, isopropyl alcohol, and deionized (DI) water. Then, the samples were cleaned with buffered oxide etchant (BOE), piranha solution (H₂SO₄:H₂O₂), and, lastly, DI water. As shown in Figure 1, for device fabrication, first, the aqueous GO solution prepared by the modified Hummers method [19] is sprayed over the sample, which is laid on a hot plate with a temperature of 180 °C. The GO/AlGaIn/GaN samples are quickly transferred to a furnace chamber for the thermal reduction of the GO films by heating at 800 °C for 10 min. Next, a probing metal pad of Ti/Au is deposited by an electron beam (E-beam) evaporation system, assisted by a lift-off process. An etch mask of 100 nm thick SiO₂ for rGO etching is deposited by E-beam evaporation and patterned as an interdigitated shape by conventional photolithographic techniques and BOE treatment. Finally, the rGO film is etched out by O₂ plasma treatment before the remaining SiO₂ is dissolved using BOE.

Figure 1. Schematic fabrication process for reduced graphene oxide (rGO)/AlGaIn/GaN metal–semiconductor–metal (MSM) photodiodes.

High-resolution X-ray diffraction (XRD) measurement was performed to determine the lattice parameters of the AlGaIn films and thus obtain the Al mole fractions. The measurements of the photodetection properties were performed using a dark-room probe station system equipped with a

Keithley 2400 source meter, a Bentham SSM150Xe switching monochromator, and a calibrated optical power sensor.

3. Results and Discussion

Figure 2 shows the high-resolution XRD measurements of the three AlGaIn/GaN samples that were used to obtain the accurate Al mole fraction. Peaks corresponding to the lattice parameters of GaN and AlGaIn are clearly shown in the figure. An enlarged view of the AlGaIn peaks is shown in the inset of Figure 2. The lattice parameters (c) of the samples were calculated by the Bragg relation, $c = \frac{\lambda l}{2 \sin \theta_B}$, where λ is the wavelength of the X-ray radiation used for the measurement, θ_B is the Bragg angle, and l is the Miller index. The Al mole fractions (x) of the samples were then calculated by Vegard's rule: $C_{AlGaIn}(x) = xC_{AlN} + (1-x)C_{GaN} - \delta_c x(1-x)$, where C_{AlN} (4.9792 Å) and C_{GaN} (5.1855 Å) are the bulk lattice constants of AlN and GaN, respectively, and δ_c is the bowing parameter available from previous studies [20–22]. The Al mole fractions of the three samples were thus confirmed as 9.5%, 13.4%, and 17.9% (henceforth given in decimal form as 0.095, 0.134, and 0.179, respectively).

Figure 2. High-resolution XRD measurements of the (0002) planes of AlGaIn samples with various Al mole fractions (inset: enlarged view of the AlGaIn peaks).

The GO film shows a very high transmittance over a broad wavelength range, as shown in Figure 3. A slight decrease in transmittance occurs after thermal reduction at 800 °C, and a gradual decrease occurs as the wavelength decreases from 350 nm, which is well matched with the previous report in the literature [23]. Regardless, the transmittances of GO and rGO are >90% even for wavelengths <300 nm. The Raman spectral investigation of the GO film on the AlGaIn/GaN substrate showed clearly the primary in-plane vibrational mode of sp^2 -bonded carbon atoms (G peak) and the defect-induced breathing mode (D peak) [23]. The samples showed I_D/I_G peak intensity ratios of <0.8, indicating that the GO layers were successfully formed on the substrates and that defect generation was well suppressed, even during the reduction process. In addition, the sheet resistance of rGO in our study was in the range of $6 \times 10^3 \Omega/\text{sq}$ [24].

Figure 3. Transmittance spectra of the as-sprayed GO and rGO reduced at 800 °C.

Figure 4 shows the current–voltage (I – V) characteristics of the rGO/AlGa_N MSM photodiodes under dark and under illumination at 330 nm. The measurements are done on MSM photodiodes (the total area of $350 \times 450 \mu\text{m}^2$) with the finger length of 200 μm , width of 10 μm , and spacing of 10 μm . Noise-like dark currents of less than 10 pA are measured, indicating that the dark current is below the measurement limit of our measurement system. Under the 330-nm illumination and the bias voltage of -5.5 V, the photocurrent increases to 24 nA, 58 nA, and 70 nA for the samples with the Al mole fractions of 0.179, 0.134, and 0.095, respectively. The increase of more than three orders of magnitude between the dark current and photocurrent implies a high photo/dark current contrast ratio of the devices. Slight increases in photocurrent with the increase of bias are observed in Figure 4. When defects in the active layer are involved, the trapping of photoexcited carriers might be influenced by the induced bias. The photocurrent under illumination is lower for samples with higher Al mole fractions, namely, in samples with higher energy bandgaps, which is caused by the lower excited carrier concentrations in the samples with higher Al mole fractions.

Figure 4. Current–voltage (I – V) characteristics of the rGO/AlGa_N MSM photodiodes under dark and under 330 nm of illumination.

Figure 5 shows the spectral photoresponses of the samples with three different Al mole fractions from 300 nm to 410 nm. The spectral photoresponsivity (R) is calculated with the ratio of the measured output current for a given input optical power as follows [25]:

$$R = (I_{photo} - I_{dark}) / P_{inc}$$

where I_{photo} is the photocurrent, I_{dark} is the dark current, and P_{inc} is the incident optical power. The peak in photoresponsivity is shifted to lower wavelengths (i.e., higher energies) for the rGO/AlGa_N samples with higher Al mole fractions. The samples show the peak photoresponses of 0.176, 0.143, and 0.111 A/W at the wavelengths of 335 nm, 325 nm, and 315 nm, respectively. Note that the difference in the peak wavelengths can be associated with the difference in the energy bandgaps of Al_xGa_{1-x}N. The energy bandgap of AlGa_N can be calculated by linear interpolation between the theoretical bandgap values of GaN (3.43 eV) and AlN (6.2 eV) [26,27]. Energy bandgaps of 3.69 eV, 3.8 eV, and 3.93 eV are obtained for the samples with $x = 0.095$, 0.134, and 0.179, respectively. These values show high correspondence with the peak photoresponsivity wavelengths in Figure 5. The photoresponsivity curves show gradual decreases for further decreasing wavelengths, which is because the photoresponsivity is proportional to the wavelength [5]. All of the experimental results in Figure 5 agree with the theoretical prediction that is expected for the AlGa_N UV MSM photodiodes with various Al mole fractions. Small kinks (only visible in a logarithmic-scale plot of Figure 5) in the photoresponsivity curves were also observed near the wavelengths corresponding to the energy bandgap of GaN, which is possibly because of absorption by the underlying GaN layer, as in the previous report by Kumar et al. with a graphene/AlGa_N Schottky diode [28]. As another figure of merit of photodetectors, the detectivity (D^*) shows how much minimum signal can be detected by the photodetector. The detectivity is calculated by using the simplified equation [29]:

$$D \sim \frac{A^{\frac{1}{2}} R}{(2qI_{dark})^{\frac{1}{2}}} \quad (1)$$

where A is the junction area and q is the elementary charge. At the peaks in photoresponsivity, the MSM photodiodes with the Al mole fractions of 0.095, 0.134, and 0.179 showed the detectivity of 3.9×10^{12} , 3.17×10^{12} , and 2.46×10^{12} cmHz^{1/2}W⁻¹, respectively, which are values that are comparable to the literature [29].

Figure 5. Spectral photoresponses of the rGO/AlGa_N MSM photodiodes with various Al mole fractions.

4. Conclusions

In summary, we successfully fabricated and analyzed rGO/AlGa_N MSM photodiodes. After a facile fabrication of highly transparent rGO layers, excellent rectifying properties were obtained from the rGO/AlGa_N MSM structures. When the photoresponsivity was investigated along with the various Al mole fractions, high photo/dark current ratios and sharp cut-off wavelengths were observed, which were systematically associated with the energy bandgaps of the three different AlGa_N samples with Al mole fractions $x = 0.95$, 0.134 , and 0.179 . The results suggested that the rGO as a transparent Schottky electrode has potential applicability for visible-blind optical sensors when combined with AlGa_N semiconductors.

Author Contributions: Original draft preparation with experiment and analysis, B.P.; Supervision and writing-review, J.C.

Funding: This research was funded by the basic science research program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education (No. 2017R1D1A1A09000684) and by the research funds of Chonbuk National University in 2018.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Khan, A.; Balalrishnan, K.; Katona, T. Ultraviolet light-emitting diodes based on group three nitrides. *Nat. Photonics* **2008**, *2*, 77–84. [[CrossRef](#)]
2. Khan, A.M.; Shatalov, M.; Maruska, H.P.; Wang, H.M.; Kuokstis, E. III–Nitride UV Device. *Jpn. J. Appl. Phys.* **2005**, *44*, 7191–7206. [[CrossRef](#)]
3. Mishra, U.K.; Parikh, P.; Wu, Y.F. AlGa_N/Ga_N HEMTs—An Overview of Device Operation and Applications. *IEEE Trans. Electron. Devices* **2002**, *90*, 1022–1031. [[CrossRef](#)]
4. Sang, L.; Liao, M.; Sumiya, M.A. Comprehensive Review of Semiconductor Ultraviolet Photodetectors: From Thin Film to One-Dimensional Nanostructures. *Sensor* **2013**, *13*, 10482–10518. [[CrossRef](#)] [[PubMed](#)]
5. Monroy, E.; Omnès, F.; Calle, F. Wide-bandgap semiconductor ultraviolet photodetectors. *Semicond. Sci. Technol.* **2003**, *18*, R33–R51. [[CrossRef](#)]
6. Schreiber, P.; Dang, T.; Pickenpaugh, T.; Smith, G.; Gehred, P.; Litton, P. Solar blind UV region and UV detector development objectives. *Proc. SPIE* **1999**, 3629, 230–248.
7. Razeghi, M.; Rogalski, A. Semiconductor ultraviolet detectors. *J. Appl. Phys.* **1996**, *79*, 7433–7473. [[CrossRef](#)]
8. Walker, D.; Zhang, X.; Saxler, A.; Kung, P.; Xu, J.; Razeghi, M. Al_xGa_{1-x}N ($0 \leq x \leq 1$) ultraviolet photodetectors grown on sapphire by metal-organic chemical-vapor deposition. *Appl. Phys. Lett.* **1997**, *70*, 949–951. [[CrossRef](#)]
9. Carrano, J.C.; Grudowski, P.A.; Eiting, C.J.; Dupuis, R.D.; Campbell, J.C. Very low dark current metal–semiconductor–metal ultraviolet photodetectors fabricated on single-crystal Ga_N epitaxial layers. *Appl. Phys. Lett.* **1997**, *70*, 1992–1994. [[CrossRef](#)]
10. Qi, L.; Mok, K.R.C.; Aminian, M.; Charbon, E.; Nanver, L.K. UV-sensitive low dark-count pureB single-photon avalanche diode. *IEEE Trans. Electron. Devices* **2014**, *61*, 3768–3774. [[CrossRef](#)]
11. Berger, P.R. Metal-semiconductor-metal photodetectors. *Proc. SPIE* **2001**, 4285, 198–207.
12. Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A.C. Graphene photonics and optoelectronics. *Nat. Photonics* **2010**, *4*, 611–622. [[CrossRef](#)]
13. Becerril, H.A.; Mao, J.; Liu, Z.; Stoltenberg, R.M.; Bao, Z.; Chen, Y. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano* **2008**, *2*, 463–470. [[CrossRef](#)] [[PubMed](#)]
14. Pei, S.; Cheng, H.M. The reduction of graphene oxide. *Carbon* **2012**, *50*, 3210–3228. [[CrossRef](#)]
15. Tu, N.D.K.; Choi, J.; Park, C.R.; Kim, H. Remarkable Conversion between n- and p-Type Reduced Graphene Oxide on Varying the Thermal Annealing Temperature. *Chem. Mater.* **2015**, *27*, 7362–7369. [[CrossRef](#)]
16. Zhu, M.; Li, X.; Guo, Y.; Li, X.; Sun, P.; Zang, X.; Wang, K.; Zhong, M.; Wu, D.; Zhu, H. Vertical junction photodetectors based on reduced graphene oxide/silicon Schottky diodes. *Nanoscale* **2014**, *6*, 4909–4914. [[CrossRef](#)] [[PubMed](#)]

17. Li, G.; Liu, L.; Wu, G.; Chen, W.; Qin, S.; Wang, Y.; Zhang, T. Self-Powered UV–Near Infrared Photodetector Based on Reduced Graphene Oxide/n-Si Vertical Heterojunction. *Small* **2016**, *12*, 5019–5026. [[CrossRef](#)] [[PubMed](#)]
18. Pandit, B.; Cho, J. Metal–semiconductor–metal ultraviolet photodiodes based on reduced graphene oxide/GaN Schottky contacts. *Thin Solid Films* **2018**, *660*, 824–827. [[CrossRef](#)]
19. Hummers, W.S., Jr.; Offeman, R.E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339. [[CrossRef](#)]
20. Vegard, L. Die konstitution der mischkristalle und die raumfüllung der atome. *Z. Phys.* **1921**, *5*, 17–26. [[CrossRef](#)]
21. Liou, B.T.; Yen, S.H.; Kuob, Y.K. Vegard’s law deviation in band gaps and bowing parameters of the wurtzite III-nitride ternary alloys. *Proc. SPIE* **2005**, *5628*, 296–305.
22. Mahata, M.K.; Ghosh, S.; Jana, S.K.; Chakraborty, A.; Bag, A.; Mukhopadhyay, P.; Kumar, R.; Biswas, D. Comprehensive strain and band gap analysis of PA-MBE grown AlGaIn/GaN heterostructures on sapphire with ultrathin buffer. *AIP Adv.* **2014**, *4*, 117120. [[CrossRef](#)]
23. Pandit, B.; Jo, C.H.; Joo, K.S.; Cho, J. Changes in physical properties of graphene oxide with thermal reduction. *J. Korean Phys. Soc.* **2017**, *71*, 156–160. [[CrossRef](#)]
24. Ryu, B.D.; Hyung, J.H.; Han, M.; Kim, G.S.; Han, N.; Ko, K.B.; Kang, K.K.; Cuong, T.V.; Hong, C.H. Long-term stability of Si-organic hybrid solar cells with a thermally tunable graphene oxide platform. *RSC Adv.* **2016**, *6*, 73242–73250. [[CrossRef](#)]
25. Ravikiran, L.; Radhakrishnan, K.; Dharmarasu, N.; Agrawal, M.; Wang, Z.; Bruno, A.; Soci, C.; Lihuang, T.; Ang, K.S. GaN schottky metal–semiconductor–metal UV photodetectors on Si (111) grown by ammonia-MBE. *IEEE Sens. J.* **2017**, *17*, 72–77. [[CrossRef](#)]
26. Wickenden, D.K.; Barger, C.B.; Bryden, W.A.; Miragliotta, J.; Christenmacher, T. High quality self-nucleated Al_xGa_{1-x}N layers on (00.1) sapphire by low-pressure metalorganic chemical vapor deposition. *Appl. Phys. Lett.* **1994**, *65*, 2024–2026. [[CrossRef](#)]
27. Ochalski, T.J.; Gil, B.; Lefebvre, P.; Grandjean, N.; Leroux, M.; Massies, J.; Nakamura, S.; Morkoç, H. Photorefectance investigations of the bowing parameter in AlGaIn alloys lattice-matched to GaN. *Appl. Phys. Lett.* **1999**, *74*, 3353–3355. [[CrossRef](#)]
28. Kumar, M.; Jenong, H.; Polat, K.; Okyay, A.K.; Lee, D. Fabrication and characterization of graphene/AlGaIn/GaN ultraviolet Schottky photodetector. *J. Phys. D Appl. Phys.* **2016**, *49*, 275105. [[CrossRef](#)]
29. Xu, K.; Xu, C.; Xie, Y.; Deng, J.; Zhu, Y.; Guo, W.; Xun, M.; Teo, K.B.K.; Chen, H.; Sun, J. Graphene GaN-based schottky ultraviolet detectors. *IEEE Trans. Electron. Devices* **2015**, *62*, 2802–2808. [[CrossRef](#)]