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Use of graphene for forming Al-based p-type reflectors for near ultraviolet InGaN/AlGaN-based light-emitting diode

Dae-Hyun Kim [a], Jaecheon Han [b], Tae-Yeon Seong [a,*]

[a] Department of Materials Science and Engineering, Korea University, Seoul 136-713, Republic of Korea
[b] LED Division, LG Innotek Co., Ltd, Paju-City 413-901, Republic of Korea

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ABSTRACT

We demonstrated the improved performance of near UV (365 nm) InGaN/AlGaN-based LEDs using highly reflective Al-based p-type reflectors with graphene sheets as a diffusion barrier. The use of graphene sheets did not degrade the reflectance of ITO/Al contacts, viz. ~81% at 365 nm. The ITO/graphene/Al contacts annealed at 300 °C exhibited better ohmic behavior with a specific contact resistance of 1.5×10^{-3} Ωcm^2 than the ITO/Al contact (with 9.5×10^{-3} Ωcm^2). Near UV LEDs fabricated with the ITO/graphene/Al contact annealed at 300 °C showed a 7.2% higher light output (at 0.1 W) than LEDs with the ITO/Al reflector annealed at 300 °C. The SIMS results exhibited that, unlike the ITO/graphene/Al, the ITO/Al contacts undergo a significant indiffusion of Al atoms toward the GaN after annealing. Furthermore, both Ga and Mg atoms were also more extensively outdiffused in the ITO/Al contacts after annealing. On the basis of the SIMS and electrical results, the possible explanations for the annealing-induced degradation of the ITO/Al contacts are described and discussed.

1. Introduction

InGaN/AlGaN-based ultraviolet (UV) light-emitting diodes (LEDs) are of considerable interest because of their applications in water purification and solid-state lighting [1–3]. However, UV LEDs suffer from significantly low external quantum efficiency (EQE), which is partially due to low light extraction efficiency and high contact resistivity. In order to increase the light extraction efficiency, different approaches, such as patterning of substrates [4], surface texturing [5], and photonic crystals (PCs) [6], have been adopted. For example, Khizar et al.[4], investigating the effect of dome-shape-patterned substrate on the performance of flip-chip 280 nm UV LEDs, showed that the use of the integrated microlens array caused a 55% enhancement in the output power at 20 mA compared to the same LEDs without microlens. Oder et al. [6], investigating the effect of PCs on the performance of 340 nm UV LEDs (a chip of 300 × 300 μm^2), exhibited that triangular arrays of the PCs (300 nm in diameter and 700 nm in periodicity) resulted in a 95% increase in the output power at 20 mA compared to LEDs without PCs. In addition, attempts were made to enhance the light extraction efficiency using highly reflective electrodes [7], such as Ag [8], oxide-based distributed Bragg reflector [9], nanopixel contact with Al [10], and tin-doped indium oxide (ITO)/Al reflectors [11]. For instance, Lobo et al.[10], investigating the effect of nanopixel contacts with Al reflector on the light extraction in UV LEDs, showed that the light output increased with decreasing the nanopixel size and spacing. The nanopixel LEDs (with a nanopixel size of 1 × 1 μm^2) exhibited a 90% higher light-output power than LEDs with square Pd contact (150 × 150 μm^2). Takehara et al.[11] showed that ITO/Al electrode had high reflectance in the UV region and good contact properties. 350 nm UV LEDs with the ITO (10 nm)/Al (150 nm) contacts exhibited an operating voltage similar to that of a conventional Ni/Au (10 nm/40 nm) and a high light output power comparable to that of non-alloyed Al only (150 nm) contacts. These results indicate that the use of optimized electrodes with low contact resistance and high reflectance in the UV region is crucial to the fabrication of high EQE UV LEDs. In this study, we investigated the electrical and optical properties of Al-based reflectors for UV LEDs, because Al has high reflectance in the UV region. However, since Al is n-type contact scheme, graphene sheets were used as a barrier to prevent the indiffusion of Al toward the GaN [12,13]. The interfacial mixing in the ITO/Al-based contacts is investigated by X-ray photoemission spectroscopy (XPS) and secondary ion mass spectrometry (SIMS).

* Corresponding author. Tel.: +82 2 3290 3288; fax: +82 2 928 3584.
E-mail address: tyseong@korea.ac.kr (T.-Y. Seong).

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2. Experimental procedure

Near UV (365 nm) InGaN/AlGaN multiple quantum-well (MQW) LED structures were grown on (0001) sapphire substrates by a metalorganic chemical vapor deposition system. The LED structures consisted of a 2-nm-thick p-GaN:Mg layer, a 0.1-μm-thick p-type AlGaN:Mg ($n_a = 5 \times 10^{17}$ cm^{-3}) layer, a 20-nm-thick AlGaN electron blocking layer, a 100-nm-thick active layer, and a 200-nm-thick spreading layer, a 2.0-μm-thick n-type AlGaN:Si ($n_d = 5 \times 10^{18}$ cm^{-3}) layer, and a 2.0-μm-thick undoped GaN layer on the sapphire substrate. Prior to electrode deposition, the samples were cleaned by a HCl:DI water solution (1:2) for 1 min and then rinsed by DI water for 5 min. Graphene sheets were grown on a Cu foil by chemical vapor deposition. After poly[methyl methacrylate] (PMMA) was coated on top of the graphene sheets, the PMMA/graphene/Cu foil was immersed in a dilute ammonium persulfate solution for 6 h to selectively remove the Cu-foil. To remove the PMMA, the samples were dipped in acetone and then washed by DI water. The graphene was characterized by Raman spectroscopy, showing 'G' and '2D' peaks at ~1592 and ~2696 cm^{-1}, respectively [Fig. 1(a)], showing the synthesis of graphene sheets [14]. The ratio of G/2D peak implies that the graphene sheets were very thin, namely, a few layers [12–15]. A 10-nm-thick ITO layer was first electron-beam-evaporated on the p-GaN, which was annealed at 600 °C for 1 min in vacuum. Then, the graphene sheets (which were believed to be two sheets by the Raman results) were transferred to the GaN sample, after which a 150-nm-thick Al layer was finally deposited. For comparison purposes, ITO (10 nm)/Al (150 nm) scheme was also electron-beam-evaporated. The specific contact resistances were measured by means of circular transfer length method. Some of the samples were rapid-thermal-annealed at 300 °C for 1 min in vacuum. This temperature was chosen because LED chips go through an annealing process at ~300 °C during a soldering process. An electrode structure with the graphene sheets is schematically illustrated in Fig. 1(b). For LED chips, Cr/Ni/Au (25 nm/25 nm/50 nm) layers were deposited as an n-type ohmic electrode. Current–voltage (*I–V*) measurements were carried out by a high-current source-measuring unit (Keithley 238). The optical outputs of LED chips were examined by means of a Newport dual channel powermeter. X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) were performed to characterize the surface characteristics before and after annealing and to understand ohmic mechanisms.

3. Results and discussion

Fig. 2 shows the reflectances of ITO/Al contacts with and without graphene sheets before and after annealing at 300 °C. Irrespective of annealing, all of the reflectors exhibit similar reflectances. In addition, use of the graphene sheets does not degrade the reflectances of the ITO/Al-based contacts. For instance, the ITO/Al contacts exhibit reflectances of 81.7 and 81.5% at 365 nm before and after annealing, respectively, whereas the ITO/graphene/Al contacts show reflectances of 81.6 and 81.1%, respectively. It is noteworthy that both of the ITO/Al and ITO/graphene/Al contacts produce higher reflectances than the Al-based contacts previously investigated by other groups [16–18], but comparable to the sputtered ITO (10 nm)/Al (150 nm) contacts [11], where the ITO was annealed at 600 °C for 5 min in a N_2 atmosphere.

Fig. 3 exhibits the *I–V* characteristics of ITO/Al and ITO/graphene/Al contacts before and after annealing at 300 °C. Before annealing, both of the samples exhibit ohmic behavior. After annealing, their electrical properties were degraded, although the ITO/graphene/Al contacts showed better electrical properties than the ITO/Al contacts. The measurements showed that the specific contact resistances of the ITO/Al contacts were 1.7×10^{-4} and 9.5×10^{-3} Ωcm^2 before and after annealing, respectively. The specific contact resistances of the ITO/graphene/Al contacts were 3.1×10^{-4} and 1.5×10^{-3} Ωcm^2 before and after annealing, respectively.

Fig. 4 illustrates the typical *I–V* characteristics of near UV (365 nm) InGaN/AlGaN MQW LEDs fabricated with ITO/Al and ITO/graphene/Al reflectors before and after annealing at 300 °C. The LEDs with the non-alloyed ITO/Al and ITO/graphene/Al reflectors show lower forward-bias voltages at 20 mA than the LEDs with the annealed reflectors. It is noted that the LEDs with the annealed ITO/Al reflectors exhibit a 0.14 V higher forward voltage than the LEDs with the annealed ITO/graphene/Al reflectors. The series resistances of the LEDs with the ITO/Al and ITO/graphene/Al reflectors before and after annealing were 6.4 and 7.5 Ω, and 12.7 and 10.0 Ω, respectively. The forward voltages and series resistances are proportional to the specific contact resistances (Fig. 3).

Fig. 5 illustrates the light output-power characteristics of near UV LEDs fabricated with ITO/Al and ITO/graphene/Al reflectors before and after annealing at 300 °C. The LEDs with the non-alloyed ITO/Al and ITO/graphene/Al reflectors produce 11.7 and 10.8% higher light outputs (at 0.1 W), respectively, than the LEDs with the annealed ITO/Al reflector. On the one hand, the LEDs with the annealed ITO/graphene/Al reflector produce a 7.2% higher light output (at 0.1 W) than the LEDs with the as-deposited ITO/Al reflector. However, considering the fact that LEDs go through an annealing process at ~300 °C because of the packaging and soldering processes, the electrical and optical properties of the reflectors annealed at ~300 °C are more important than the non-alloyed samples.

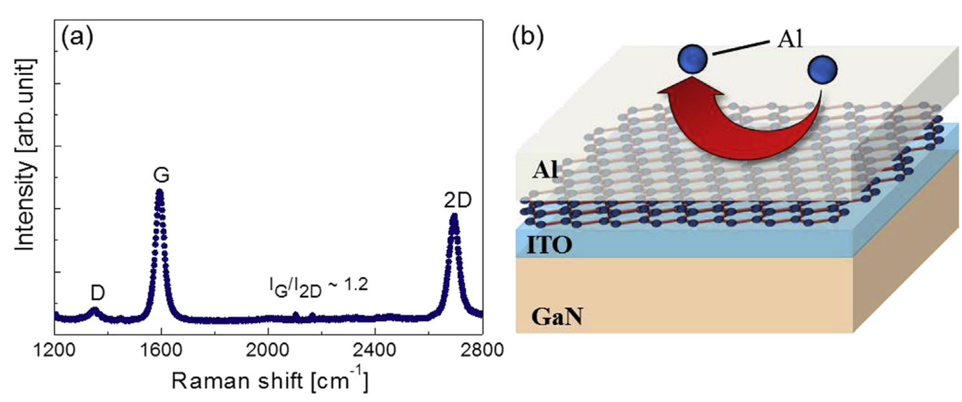

Fig. 1. Raman spectrum obtained from graphene sheets grown by CVD and schematic diagram of an electrode structure with graphene sheets.