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## **Optics Letters**

## Plasmonic-enhanced efficiency of AlGaN-based deep ultraviolet LED by graphene/Al nanoparticles/graphene hybrid structure

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The AlGaN-based deep ultraviolet light-emitting diode (DUV LED) has advantages of environmentally friendly materials, tunable emission wavelength, and easy miniaturization. However, the light extraction efficiency (LEE) of an AlGaN-based DUV LED is low, which hinders its applications. Here, we design a graphene/Al nanoparticles/graphene (Gra/Al NPs/Gra) hybrid plasmonic structure, where the strong resonant coupling of local surface plasmons (LSPs) induces a 2.9-times enhancement for the LEE of the DUV LED according to the photoluminescence (PL). The dewetting of Al NPs on a graphene layer by annealing is optimized, resulting in better formation and uniform distribution. The near-field coupling of Gra/Al NPs/Gra is enhanced via charge transfer among graphene and Al NPs. In addition, the skin depth increment results in more excitons being coupled out of multiple quantum wells (MQWs). An enhanced mechanism is proposed, revealing that the Gra/metal NPs/Gra offers a reliable strategy for improving the optoelectronic device performance, which might trigger the advances of LEDs and lasers with high brightness and power density. © 2023 Optica Publishing Group

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The AlGaN-based deep ultraviolet light-emitting diode (DUV LED) has the unique advantages of easy miniaturization and pure chromatography, thus it shows great potential for handheld air/water purification and sterilization applications [1,2]. To date, the DUV LED is mainly limited by a low light extraction efficiency (LEE) due to the total internal reflection at the interface of AlGaN epilayer/air [3]. Sun *et al.* used the sidewall angle design [4] and micro-cavity [5] to improve the LEE, providing novel strategies for the fabrication of efficient DUV LED. In addition, local surface plasmons (LSPs) resonant coupling is an effective method [6], which is achieved by matching with the exciton energy. Hence, the extracted exciton recombination

among the AlGaN and LSPs could enhance the LEE. The metallic LSPs structure has the advantages of easy fabrication [7], excellent applicability [8–10], and flexibility in resonant wavelength [11]. The Al NPs have LSPs resonant coupling at the DUV region, which is promising to enhance the LEE of DUV LEDs. However, the fabrication of Al NPs on an LED wafer by annealing can cause an interfacial reaction or atom diffusion. At the same time, the diffusion barrier of an Al atom on the dielectric substrate is high, making it difficult to form uniform NPs. In addition, the Al NPs are easily oxidized in ambient air, which degrades the LSPs resonant coupling efficiency and stability. Meanwhile, the resonant coupling of bare Al NPs LSPs is relatively low, and the enhanced LEE is usually limited to ~15% [12].

Graphene exhibits the favorable properties of high electrical conductivity, excellent thermal/chemical stability, and low absorption [13]. The metal NPs and graphene composite is reported to enhance the light-matter interaction, which is promising for serving as a novel LSP structure to enhance the LEE [14]. Apart from the enhanced resonant coupling, the graphene could serve as a passivation layer to prevent Al oxidation, making the LSPs resonant coupling effect stable. Although metal NPs with a top-covered graphene layer are fabricated, the uniform formation of metal NPs by annealing is still difficult.

In this Letter, we realized a largely enhanced PL emission from the MQWs of the DUV LED wafer by integrating it with a Gra/Al NPs/Gra hybrid plasmonic structure. Both the experimental and simulated results confirm the strong LSPs' near-field coupling of Gra/Al NPs/Gra. It achieves a 2.9 times PL enhancement in contrast to the bare LED wafer, revealing an optimized LEE. The designed Gra/metal NPs/Gra hybrid structure could be extended into numerous nitride-based optoelectronic devices by controlling the metal species and nanostructure parameters.

Figures 1(a)-1(f) show the fabrication process of Gra/Al NPs/Gra, the details of which are provided in Supplement 1. The samples are defined as: 10-nm Al on graphene layer (Gra/Al)

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**Fig. 1.** (a)–(f) Schematic diagrams for the fabrication processes of Gra/Al NPs/Gra hybrid plasmonic structure. AFM images of (g) Gra/Al, (h) Gra/Al NPs, and (i) Gra/Al NPs/Gra.

[see Fig. 1(c)]; after the dewetting by annealing (Gra/Al NPs) [see Fig. 1(d)]; and after transferring another graphene layer on Gra/Al NPs (Gra/Al NPs/Gra) [see Fig. 1(e)]. The atomic force microscopy (AFM) images of these samples are shown in Figs. 1(g)-1(i). The Gra/Al has high-density particles with an average diameter of  $\sim$ 35 nm. This morphology of the asdeposited Al is induced by the Volmer-Weber growth mode, which tends to be isolated islands at the initial deposition, especially for that with a thin film thickness. After the annealing, the diameter of Al NPs increases to ~54 nm with a standard deviation of  $\sim 4.8$  nm, showing the uniformity in size and distribution. For the Gra/Al NPs/Gra, although the surface of Al NPs becomes blurred, the Al NPs underneath the graphene layer could be observed, which possess a comparable height of 5.5 nm as to that of Gra/Al NPs, implying that the Al NPs are tightly encapsulated by the top graphene layer.

To verify the function of the underneath graphene layer on the deformation of Al NPs, the annealing of Al on bare sapphire is carried out, as shown in Fig. S1, Supplement 1. The particle size of the as-deposited Al is ~10 nm, which is smaller than that on a graphene layer, and the particle size varies [see Fig. S1(a), Supplement 1]. Similar results appear for the Al NPs after annealing, where the size becomes bigger while showing a more disordered distribution [see Fig. S1(b), Supplement 1], which is inferior to that on the graphene. The height profiles for Al and Al NPs on bare sapphire and graphene layer are shown in Figs. S2(a)–2(d), Supplement 1. The standard deviation of Al NPs on bare sapphire reaches ~18.4 nm, and it is much higher than that of Al NPs on graphene.

The deformation of Al into Al NPs on bare sapphire and graphene are schematically shown in Figs. S2(e) and S2(f), Supplement 1. It is known that a nano-thickness metal film is thermodynamically unstable and spontaneously deforms into NPs by annealing, which is recognized as the dewetting effect [15]. This process could happen at an annealing temperature lower than the melting point of metal film, which is named as solid-state dewetting. Therefore, although the Al annealed at 500°C is lower than its melting point of  $660^{\circ}$ C, Al NPs are successfully prepared. We have proved the diffusion barrier of Al atoms on graphene (0.07 eV) is lower than that on bare sapphire (0.21 eV) [16]. Thus, the diffusion of Al atoms on graphene is





**Fig. 2.** (a) Schematic diagrams of cross sectional Al NPs, Al NPs/Gra, Gra/Al NPs, and Gra/Al NPs/Gra. (b) Experimental absorption spectra of the structures in panel (a), and (d) the hybrid plasmonic structure with different top graphene layers. (c) Variation of the absorption peak position and intensity extracted from panel (b).

easier, so they readily diffuse to a stable position and form Al NPs. The stable position for Al NPs formation initiates from a defect on the substrate surface, and we consider that the original defects in graphene provide the sites for the Al NPs formation. Since the annealing process provides the activation energy for Al atoms diffusion, we prove that the geometrical parameters of Al NPs could be controlled by the annealing temperature (see Fig. S3, Supplement 1). The structural properties of graphene are evaluated by Raman spectroscopy, as shown in Fig. S4, Supplement 1. The pristine graphene on sapphire exhibits a defect-related D band, revealing that there are defects in the graphene. In addition, the intensity ratio of the 2D to G band ( $I_{2D}/I_G$ ) is ~2, demonstrating its monolayer nature [17].

The LSPs resonant coupling of Gra/Al NPs/Gra is evaluated by experimental absorption spectroscopy, as shown in Fig. 2(b), where the other structures of Al NPs, Al NPs/Gra, and Gra/Al NPs are measured as references, and the cross sectional structures' view is shown in Fig. 2(a). For Al NPs on bare sapphire (green plot), no obvious resonant absorption peak emerges, while it appears at ~270 nm for Gra/NPs (red plot), which belongs to the resonant coupling of Al NPs-induced LSPs. We consider that the absent resonant absorption peak of Al NPs on bare sapphire is attributed to the large difference in NPs size and irregular distribution. As for Gra/Al NPs/Gra (blue plot), the resonant absorption intensity is enhanced to the highest. It is known that charge transfer would contribute to the enhanced LSPs resonant coupling. Since the work function of Al metal (4.28 eV) is smaller than that of graphene (4.5 eV) [18], to maintain the Fermi level continuity, holes transfer from the graphene into Al NPs as they come into contact with each other [see Fig. S5, Supplement 1]. Compared with Al NPs on bare sapphire, the Gra/Al NPs/Gra resonant absorption peak position redshifts, as shown by the summarized absorption peak intensity and position in Fig. 2(c). The reason for the redshift of the resonant absorption peak is that an antiparallel image dipole generates in the graphene, then reduces the internal electric field of Al NPs as the LSPs are excited [19]. Moreover, the absorption spectra of Gra/Al NPs/Gra with the top graphene with different numbers of layers are measured in Fig. 2(d), revealing that the increased



**Fig. 3.** Electric field distribution of (a) Al NP, (b) Al NP/Gra, (c) Gra/Al NP, and (d) Gra/Al NP/Gra. (e) Electric field intensity extracted from panels (a)–(d) along the red dashed line (from interior to surface). (f) Simulated absorption spectra of Gra/Al NPs/Gra with the top graphene in different layers.

number of graphene layers could efficiently enhance the LSPs resonant coupling effect.

Figures 3(a)-3(d) show the electric field distributions of Al NP, Al NP/Gra, Gra/Al NP, and Gra/Al NP/Gra simulated by the finite-difference time-domain method, the details are shown in Supplement 1. The maximum electric field intensity  $(|E|^2)$ appears at the bottom corners of the Al NP induced by the LSPs resonant coupling. After inserting a graphene layer under the Al NP, the light confinement effect at their interfacial corners is enhanced [see Figs. 3(c)]. Furthermore, the Gra/Al NP/Gra also results in the stronger electric field confinement effect on the surface [see Fig. 3(d)]. The electric field variation from the Al NP interior to the surface is extracted in Fig. 3(e), it sharply increases at the surface while exponentially decays in the interior, directly showing that the Gra/Al NP/Gra has largely enhanced the LSPs resonant coupling by ~3.1 times. We further compare the simulated absorption spectra of Gra/Al NP/Gra with the top graphene having different numbers of layers (0-2L), as shown in Fig. 3(f). The resonant absorption intensity enhances and the position redshifts with the increment in the number of graphene layers, which is consistent with the experimental absorption spectra. The enhanced resonant absorption is also confirmed by the electric field distribution shown in Fig. S6, Supplement 1.

As shown in Fig. S7, Supplement 1, the absorption spectra of Al NP with different diameters are simulated, showing the variation in absorption intensity and position. The redshift of the resonant absorption peak is explained by

$$C_{abs} = k \times Im[\alpha] = 4\pi \times k \times a^{3} \times Im\left[\frac{\varepsilon_{m} - \varepsilon_{d}}{\varepsilon_{m} + 2\varepsilon_{d}}\right], \quad (1)$$

where  $C_{abs}$  is absorption cross section,  $\alpha$  is polarizability, a is the diameter of Al NP,  $\varepsilon_d$  and  $\varepsilon_m$  are dielectric constants of AlGaN medium and Al NP, and k is the vacuum wave vector. The



**Fig. 4.** (a) Schematic diagram of as-grown DUV LED structure. (b) XRD  $2\theta$  scan of the DUV LED wafer. (c) PL spectra of a bare DUV LED wafer and integrated with different LSP structures. (d) Schematic models of the enhanced light emission mechanism for a DUV LED with the Gra/Al NPs/Gra hybrid plasmonic structure.

Al NP diameter increment leads to the larger polarizability and absorption cross section, thus the resonant wavelength redshifts, showing the resonant coupling could be adjusted by geometrical parameters. In addition, we prove that the metal species (e.g., Ag) could also control the properties of the resonant coupling effect, as shown in Fig. S8, Supplement 1.

The Gra/Al NPs/Gra hybrid plasmonic structure is used in a DUV LED wafer to evaluate its effect for enhancing the LEE. The epitaxial AlGaN MQWs is schematically shown in Fig. 4(a). The x ray diffraction  $2\theta$  scan of the DUV LED wafer is measured, as shown in Fig. 4(b), where multi-level diffraction peaks of MQWs appear, and the satellite peaks from -3 to +1 indicates that the MQWs have excellent periodicity and steep interface. The PL spectra of a bare DUV LED and integrated with different LSPs structures are measured in Fig. 4(c). The main PL emission of a bare DUV LED locates at ~268 nm (orange plot), which is the radiative recombination in MQWs. A weaker shoulder peak at 250 nm also emerges, arising from the n-AlGaN layer with an Al content of 0.6. By integrating with Al NPs (green plot), the PL intensity slightly increases. After that, the introduction of graphene at the top and bottom of the Al NPs both result in a stronger PL emission. The PL emission of the DUV LED with the Gra/Al NPs/Gra is largely enhanced by ~2.9 times.

As for the bare DUV LED, part of photons generation via exciton radiation recombination in MOWs can be restrained inside the device due to the total reflection at the interface of AlGaN/air. In contrast, the introduction of Al NPs with a diameter far smaller than the wavelength of the excited-state energy could serve as a Rayleigh scattering center, which changes the photon propagation direction. In addition, the near-field coupling of LSPs with the excitons in the MQWs has provided additional exciton recombination paths. Therefore, the DUV LED integrated with Al NPs induces two additional processes for the photon generation and extraction, as shown in Fig. 4(d). One is photon generation via near-field coupling of LSPs with excitons on the Al NPs surface, which happens before the exciton recombination in MQWs. The other is photon extraction in MQWs by the scattering effect of Al NPs after recombination. Different from the near-field coupling, the scattering of photons is independent of the wavelength, thus it has both contributions to the PL emission

from the AlGaN electron injection layer ( $\sim$ 250 nm) and MQWs ( $\sim$ 268 nm).

Apart from momentum matching, the near-field coupling effect between LSPs and excitons is also related to the skin depth, which depends on the coupling ability for the excitons in MQWs. The skin depth ( $\delta_d$ ) and effective dielectric constant ( $\epsilon_{eff}$ ) of LSPs structures are expressed as

$$\delta_{\rm d} = \frac{\lambda}{2\pi} \times \left| \frac{\varepsilon_{\rm d} + \varepsilon_{\rm eff}}{\varepsilon_{\rm d}^2} \right|^{1/2},\tag{2}$$

$$\varepsilon_{\rm eff} = \frac{1}{3} \times (\varepsilon_{\rm g} + \varepsilon_{\rm m} + \varepsilon_{\rm g}),$$
 (3)

where  $\lambda$  is the light emission wavelength of 268 nm,  $\varepsilon_d$ ,  $\varepsilon_m$ , and  $\varepsilon_g$  are the dielectric constant real parts of the AlGaN medium, Al NPs, and graphene, corresponding to the values of 6.3, -9.6, and 2.08, respectively. As for Al NPs, the  $\varepsilon_{\text{eff}}$  in Eq. (2) is equal to the  $\varepsilon_m$ . However, for Gra/Al NPs/Gra, the  $\varepsilon_{\text{eff}}$  is calculated from Eq. (3) [20]. Therefore, the skin depth of near-field coupling for Al NPs and Gra/Al NPs/Gra on the MQWs is calculated as 12.2 nm and 14.34 nm, respectively. The increased skin depth of Gra/Al NPs/Gra contributes to the deeper coupling of excitons, which enhances the PL emission and LEE of the DUV LED compared with that with bare Al NPs [see the right part of Fig. 4(d)].

In conclusion, we design a hybrid plasmonic structure with sandwiched Gra/Al NPs/Gra, and the integration with a DUV LED wafer achieves a 2.9-times enhancement of the PL emission, revealing a well optimized LEE. The size and distribution of annealed Al NPs on a graphene layer are uniform and orderly due to the better dewetting effect, and the standard deviation of Al NPs diameter is only ~4.8 nm. The Al NPs integrated with graphene have enhanced the LSPs resonant coupling, verified by both the experimental and simulated results. The largely enhanced near-field coupling of Gra/Al NPs/Gra is attributed to the charge transfer between graphene and Al NPs. Meanwhile, the skin depth increment also contributes to the light extraction. This work provides a reliable strategy for largely enhancing the LEE of DUV LED, which might expand into other spectral ranges and device types.

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**Data availability.** The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supplemental document. See Supplement 1 for supporting content.

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