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TITLE:

Graphene-Assisted Quasi-van der Waals Epitaxy of AlN Film on Nano-Patterned Sapphire Substrate for Ultraviolet Light Emitting Diodes

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KEYWORDS:

graphene, MOCVD, AlN, ultraviolet light emitting diodes, van der Waals epitaxy, nano-patterned sapphire substrate

SUMMARY:

A protocol for graphene-assisted growth of high-quality AlN films on nano-patterned sapphire substrate is presented.

ABSTRACT:

This protocol demonstrates a method for graphene-assisted quick growth and coalescence of AlN

on nano-pattened sapphire substrate (NPSS). Graphene layers are directly grown on NPSS using catalyst-free atmospheric-pressure chemical vapor deposition (APCVD). By applying nitrogen reactive ion etching (RIE) plasma treatment, defects are introduced into the graphene film to enhance chemical reactivity. During metal-organic chemical vapor deposition (MOCVD) growth of AlN, this N-plasma treated graphene buffer enables AlN quick growth, and coalescence on NPSS is confirmed by cross-sectional scanning electron microscopy (SEM). The high quality of AlN on graphene-NPSS is then evaluated by X-ray rocking curves (XRCs) with narrow (0002) and (10-12) full width at half-maximum (FWHM) as 267.2 arcsec and 503.4 arcsec, respectively. Compared to bare NPSS, AlN growth on graphene-NPSS shows significant reduction of residual stress from 0.87 GPa to 0.25 Gpa, based on Raman measurements. Followed by AlGaN multiple quantum wells (MQWS) growth on graphene-NPSS, AlGaN-based deep ultraviolet light-emitting-diodes (DUV LEDs) are fabricated. The fabricated DUV-LEDs also demonstrate obvious, enhanced luminescence performance. This work provides a new solution for the growth of high quality AlN and fabrication of high performance DUV-LEDs using a shorter process and less costs.

INTRODUCTION:

AlN and AlGaN are the most essential materials in DUV-LEDs[1,2], which have been widely used in various fields such as sterilization, polymer curing, biochemical detection, non-line-of-sight communication, and special lighting[3]. Due to the lack of intrinsic substrates, AlN heteroepitaxy on sapphire substrates by MOCVD has become the most common technical route[4]. However, the large lattice mismatch between AlN and sapphire substrate leads to stress accumulation[5,6], high density dislocations, and stacking faults[7]. Thus, the internal quantum efficiency of LEDs are reduced[8]. In recent decades, using patterned sapphire as substrates (PSS) to induce AlN epitaxial lateral overgrowth (ELO) has been proposed to solve this problem. In addition, great progress has been made in the growth of AlN templates[9-11]. However, with a high surface adhesion coefficient and bonding energy (2.88 eV for AlN), Al atoms have low atomic surface mobility, and the growth of AlN tends to have a three-dimensional island growth mode[12]. Thus, the epitaxial growth of AlN films on NPSS is difficult and requires higher coalescence thickness (over 3 μm) than that on flat sapphire substrates, which causes longer growth time and requires high costs[9].

Recently, graphene shows great potential for use as a buffer layer for AlN growth due to its hexagonal arrangement of sp^2 hybridized carbon atoms[13]. In addition, the quasi-van der Waals epitaxy (QvdWE) of AlN on graphene may reduce the mismatch effect and has paved a new way for AlN growth[14.15]. To increase the chemical reactivity of graphene, Chen et al. used N_2-plasma treated graphene as a buffer layer and determined the QvdWE of high quality AlN and GaN films[8], which demonstrates the utilization of graphene as a buffer layer.

Combining the N_2-plasma treated graphene technic with commercial NPSS substrates, this protocol presents a new method for quick growth and coalescence of AlN on a graphene-NPSS substrate. The completely coalesce thickness of AlN on graphene-NPSS is confirmed to be less than 1 μm, and the epitaxial AlN layers are of high quality and stress-released. This method paves a new way for AlN template mass production and shows great potential in the application of AlGaN-based DUV-LEDs.

PROTOCOL:

CAUTION: Several of the chemicals used in these methods are acutely toxic and carcinogenic. Please consult all relevant material safety data sheets (MSDS) before use.

1. Preparation of NPSS by nanoimprint lithography (NIL)

1.1) Deposition of SiO_2 film

1.1.1) Wash the 2" c-plane flat sapphire substrate with ethanol followed by deionized water three times.

1.1.2) Dry the substrate with a nitrogen gun.

1.1.3) Deposit 200 nm SiO_2 film on the flat sapphire substrate by plasma-enhanced chemical vapor deposition (PECVD) under 300 °C. The deposition rate is 100 nm/min.

1.2) Spinning nanoimprint resist

1.2.1) Wash the sapphire substrate with ethanol followed by deionized water 3x.

1.2.2) Dry the substrate with a nitrogen gun.

1.2.3) Spin a 200 nm nanoimprint resist (NIR) TU-2 on the flat sapphire substrate at 3000 r/min for 60 s.

1.3) Thermoplastic imprinting

1.3.1) Place a patterned mold onto the nanoimprint resist polymer film.

1.3.2) Apply high pressure as 30 bar at 60 °C to heat the sapphire substrate to above the glass transition temperature of the polymer.

1.3.3) Expose to ultraviolet irradiation for 60 s and maintain for 120 s after turning off the UV source to solidify the NPR TU-2.

1.3.4) Cool down the sapphire substrate and mold to room temperature (RT).

1.3.5) Release the mold.

1.4) Pattern transfer

1.4.1) Etch the sapphire substrate exposed from the nano-holes on the NIR by inductive coupled plasma reactive ion etching (ICP-RIE) with BCl_3 to transfer the pattern onto the sapphire substrate.

The etching power is 700 W and etching time is 3 min.

1.4.2) Remove the residual NPR TU-2 by O_2 plasma etching in a RIE system for 20 s. The etching pressure is 5 mTorr and etching power is 100 W. Finally, the width of the unetched regions is 300 nm and the depth is 400 nm. The period of pattern is 1 μm.

NOTE: NIL is not the only way to get NPSS. The NPSS are commercialized and could be bought elsewhere.

2. APCVD growth of graphene on NPSS

2.1) Rinse the NPSS with acetone, ethanol, and deionized water 3x.

2.2) Dry the NPSS with a nitrogen gun.

2.3) Load the NPSS into a three-zone high temperature furnace for long, flat temperature zone. Heat the furnace to 1050 °C and stabilize for 10 min under 500 sccm Ar and 300 sccm H_2

2.4) Introduce 30 sccm CH_4 into the reaction chamber for the growth of graphene on NPSS for 3 h. After the growth of graphene, switch off the CH_4 and naturally cool.

3. N_2-plasma treatment

3.1) Rinse the graphene-NPSS with deionized water.

3.2) Dry the NPSS with a nitrogen gun.

3.3) Etch the graphene-NPSS by N_2-plasma with a N_2 flow rate of 300 sccm for 30 s and power of 50 W in a reactive ion etching (RIE) chamber.

4. MOCVD growth of AlN on graphene-NPSS

4.1) Edit the MOCVD recipe for AlN growth and load the graphene-NPSS and its NPSS counterpart into the homemade MOCVD chamber.

4.2) After heating for 12 min, the temperature is stabilized at 1200 °C. Introduce 7000 sccm H_2 as ambient, 70 sccm trimethylaluminum (TMAl), and 500 sccm NH_3 for the growth of AlN for 2 h.

5. MOCVD growth of AlGaN MQWs

5.1) Lower the temperature of MOCVD chamber to 1130 °C to grow 20-period AlN (2 nm)/$Al_{0.6}Ga_{0.4}N$ (2 nm) layer superlattice (SL) with periodic changes in TMAl flow to adjust the deposition component. The ambient gas is H_2. The mole flow rates of TMAl, TMGa, and NH_3 for AlN are 50 sccm, 0 sccm, and 1000 sccm; and for AlGaN are 32 sccm, 7 sccm, and 2,500 sccm,

respectively.

5.2) Lower the temperature of MOCVD chamber to 1002 °C and introduce a silicane flow for the growth of a 1.8 µm n-$Al_{0.55}Ga_{0.45}N$ layer. The ambient gas is H_2 and concentration of n-type AlGaN is 5 x 10^{18} cm^{-3}.

5.3) Grow 5-period $Al_{0.6}Ga_{0.4}N$ (3 nm)/$Al_{0.5}Ga_{0.5}N$ (12 nm) MQWs by switching the TMAl from 24 sccm to 14 sccm, and TMGa from 7 sccm to 8 sccm, for each period at 1002 °C. The ambient gas is H_2.

5.4) Deposit 50 nm Mg-doped p- $Al_{0.65}Ga_{0.35}N$ electron blocking layer (EBL) at 1002 °C. The mole flow rates of TMAl, TMGa, and NH_3 are 40 sccm, 6 sccm, and 2500 sccm. The ambient gas is H_2.

5.5) Deposit 30 nm p-$Al_{0.5}Ga_{0.5}N$ cladding layer with NH_3 flow of 2500 sccm. The ambient gas is H_2.

5.6) Deposit 150 nm p-GaN contact layer with an NH_3 flow of 2500 sccm. The ambient gas is H_2. The mole flow rates of TMGa and NH_3 are 8 sccm and 2500 sccm. The hole concentration of p-AlGaN is 5.4 x 10^{17} cm^{-3}.

5.7) Lower the temperature of MOCVD chamber to 800 °C and anneal the p-type layers with N_2 for 20 min. The ambient gas is N_2.

6. Fabrication of AlGaN-based DUV-LEDs

6.1) Spinning photoresist 4620 on the wafers and lithography. The UV exposure time, developing time, and rinsing time are 8 s, 30 s, and 2 min, respectively.

6.2) ICP etching of p-GaN. The etching power, etching pressure, and etching rate of GaN are 450 W, 4 m Torr, and 5.6 nm/s, respectively.

6.3) Put the sample into acetone at 80 °C for 15 min followed by washing the sample with ethanol and deionized water 3x.

6.4) Spinning negative photoresist NR9 and lithography. The UV exposure time, developing time, and rinsing time are 12 s, 20 s, and 2 min, respectively.

6.5) Wash the sample with acetone, ethanol, and deionized water 3x.

6.6) Deposit Ti/Al/Ti/Au by electron beam (EB) evaporation.

6.7) Spin negative photoresist NR9 and lithography. The UV exposure time, developing time, and rinsing time are 12 s, 20 s, and 2 min, respectively.

6.8) Wash the sample with acetone, ethanol, and deionized water 3x without ultrasonication.

6.9) Deposit Ni/Au by EB evaporation.

6.10) Wash the sample with ethanol and deionized water 3x to clean the sample.

6.11) Deposit 300 nm SiO_2 by plasma enhanced chemical vapor deposition (PECVD). The deposition temperature is 300 °C and deposition rate is 100 nm/min.

6.12) Spin photoresist 304 and lithography. The UV exposure time, developing time, and rinsing time are 8 s, 1 min, and 2 min, respectively.

6.13) Immerse the wafers into 23% HF solution for 15 s.

6.14) Wash the sample with ethanol and deionized water 3x and dry with a nitrogen gun.

6.15) Deposit Al/Ti/Au by EB evaporation after photolithography. The photolithography process is the same as that performed in steps 6.4–6.7.

6.16) Wash the sample with ethanol and deionized water 3x.

6.17) Grind and polish the sapphire to 130 µm by mechanical polishing.

6.18) Wash the sample with dewaxing solution and deionized water.

6.19) Cut the whole wafer into pieces of 0.5 mm x 0.5 mm devices with a laser and cut it into chips using a mechanical dicer.

REPRESENTATIVE RESULTS:

Scanning electron microscopy (SEM) images, X-ray diffraction rocking curves (XRC), Raman spectra, transmission electron microscopy (TEM) images, and electroluminescence (EL) spectrum were collected for the epitaxial AlN film (**Figure 1, Figure 2**) and AlGaN-based DUV-LEDs (**Figure 3**).The SEM and TEM are used to determine the morphology of the AlN on graphene-NPSS. XRD and Raman are used to calculate the dislocation densities and the residual stress. EL is used to illustrate the illumination of the fabricated DUV-LEDs.

FIGURE AND TABLE LEGENDS:

Figure 1: Growth of AlN film on N_2 plasma-treated graphene-NPSS substrate. (**A**) SEM image of the bare NPSS. The inset shows the line profile of the patterns of NPSS by AFM. (**B**) SEM image of the as-grown graphene films on NPSS. (**C**) Raman spectra of graphene film before N2 plasma treatment (black) and after N2 plasma treatment (red). (**D, F**) are the SEM images of the initial 10 min and 2 h growth of AlN films on NPSS without graphene interlayer. (E and G) are the SEM images of the initial 10 min and 2 h growth AlN films on NPSS with graphene interlayer. (**H, I**) are the cross-sectional SEM images of AlN films on NPSS without and with graphene interlayer. This

figure has been modified from Chang et al.[20].

Figure 2: **The characterization of AlN grown on N_2 plasma-treated graphene-NPSS substrate**. XRC of (**A**) (0002) and (**B**) $(10\bar{1}2)$ for AlN films grown on NPSS with and without graphene interlayer. (**C**) Raman spectra of AlN layers grown on NPSS with and without graphene interlayer. (**D**) HRTEM image of the AlN/ graphene/NPSS interface. (**E, F**) are the SAED patterns taken from the AlN layer and interface between AlN and graphene/NPSS. (**G**) Bright-field cross-sectional TEM images of AlN grown on graphene/NPSS with g = $[0\bar{1}10]$. This figure has been modified from Chang et al.[20].

Figure 3: The performance of as-fabricated DUV-LED. (**A**) Schematic diagram of the AlGaN-based DUV-LED structure. (**B**) EL spectra of the DUV-LEDs with and without graphene interlayer. This figure has been modified from Chang et al.[20]

DISCUSSION:

As shown in **Figure 1A**, the NPSS prepared by the NIL technique illustrates the nano-concave cone patterns with 400 nm depth, 1 µm period of pattern, and 300 nm width of the unetched regions. After the APCVD growth of graphene layer, the graphene-NPSS is shown in **Figure 1B**. The significant increased D peak of N-plasma treated graphene in Raman spectra **Figure 1C** demonstrates the increase of dangling bonds generated during the RIE process[16]. After directly MOCVD growth of AlN for 10 min, **Figure 1D** shows 3D growth of irregular AlN islands on bare NPSS while **Figure 1E** shows a lateral 2D manner and rapid coalescence of AlN on graphene-NPSS. After 2 h of growth, the surface of AlN film on graphene-NPSS becomes continuous and flat (**Figure 1G**) due to the quick lateral growth and rapid coalescesence of AlN on graphene. On the contrary, **Figure 1F** shows the rough surface of AlN directly grown on bare NPSS. Also, from the cross-sectional SEM images of the as-grown AlN on NPSS and graphene-NPSS shown in **Figure 1H,I,** it is clear that with the assist of the graphene interlayer, AlN displays quick coalescence on graphene-NPSS.

The (0002) and $(10\bar{1}2)$ XRC of AlN films shown in **Figure 2A,B** confirms the high quality of the AlN grown on graphene-NPSS, with significantly reductions in FWHM XRC from 455.4 arcsec to 267.2 arcsec and 689.2 arcsec to 503.4 arcsec, respectively, compared to AlN grown on bare NPSS. Thus, the estimated densities of screw dislocations of AlN on bare NPSS is 4.51 x 10^8 cm^{-2}, which is reduced to 1.55 × 10^8 cm^{-2} with the assistance of graphene. These results show improvement quality of AlN on NPSS with a graphene buffer, which is more suitable for DUV-LEDs[17].

The Raman spectrum of E_2 phonon mode of AlN (**Figure 2C**), which is sensitive to the biaxial stress[18], demonstrates stress-released AlN on graphene-NPSS with the E_2 peak located at 658.3 cm^{-1}, closer to the stress-free AlN (657.4 cm^{-1}), compared to AlN on the bare NPSS (660.6 cm^{-1}). The residual stress estimated based on Raman spectra shows significantly reduced from 0.87 GPa to 0.25 GPa with the assistance of graphene.[19]

Figure 2D shows an HRTEM image of the AlN/graphene/NPSS interface with smooth epitaxy of AlN on NPSS with the assistance of graphene, indicating quasi-van der Waals epitaxy of AlN.

Figure 2E shows the selected area electron diffraction (SAED) pattern of the AlN, demonstrating that the as-grown AlN on graphene-NPSS is wurtzite structure. The crystal orientation is along the c-axis. As shown in **Figure 2F**, the orientation relationship of AlN and Al_2O_3 is as follows: (0002) AlN/(0006) Al_2O_3 and $(0\bar{1}10)$ AlN/$(\bar{1}\bar{1}20)$ Al_2O_3. **Figure 2G** shows the forming of air void over the cones during the lateral growth of AlN. Some dislocations near the void bend and annihilate at the climax of void; thus, the threading dislocation density of AlN is reduced. The TEM measurements explain the released stress and reduced dislocation density of AlN on graphene due to QvdWE growth.

EL spectrum (**Figure 3B**) of AlGaN-based DUV-LEDS on graphene-NPSS shows 2.6x stronger luminescence at a peak wavelength of 280 nm and current of 40 mA, compared to that of bare NPSS. The protocol demonstrates a method for the growth of high quality stress-released AlN films on NPSS with the assistance of CVD-growth graphene interlayer by MOCVD. N_2 plasma treatment enhances the chemical reactivity of graphene and realizes QvdWE growth of AlN. However, the selective growth of graphene on NPSS still warrants in-depth studies. Using this method, the growth and coalescence rates of AlN on NPSS are also increased, which is essential for mass production with lower cost and shortened time requirements. The AlN template grown on graphene-NPSS shows great potential in the application of AlGaN-based DUV-LEDs.

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DISCLOSURES:

The authors have nothing to disclose.

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Figure

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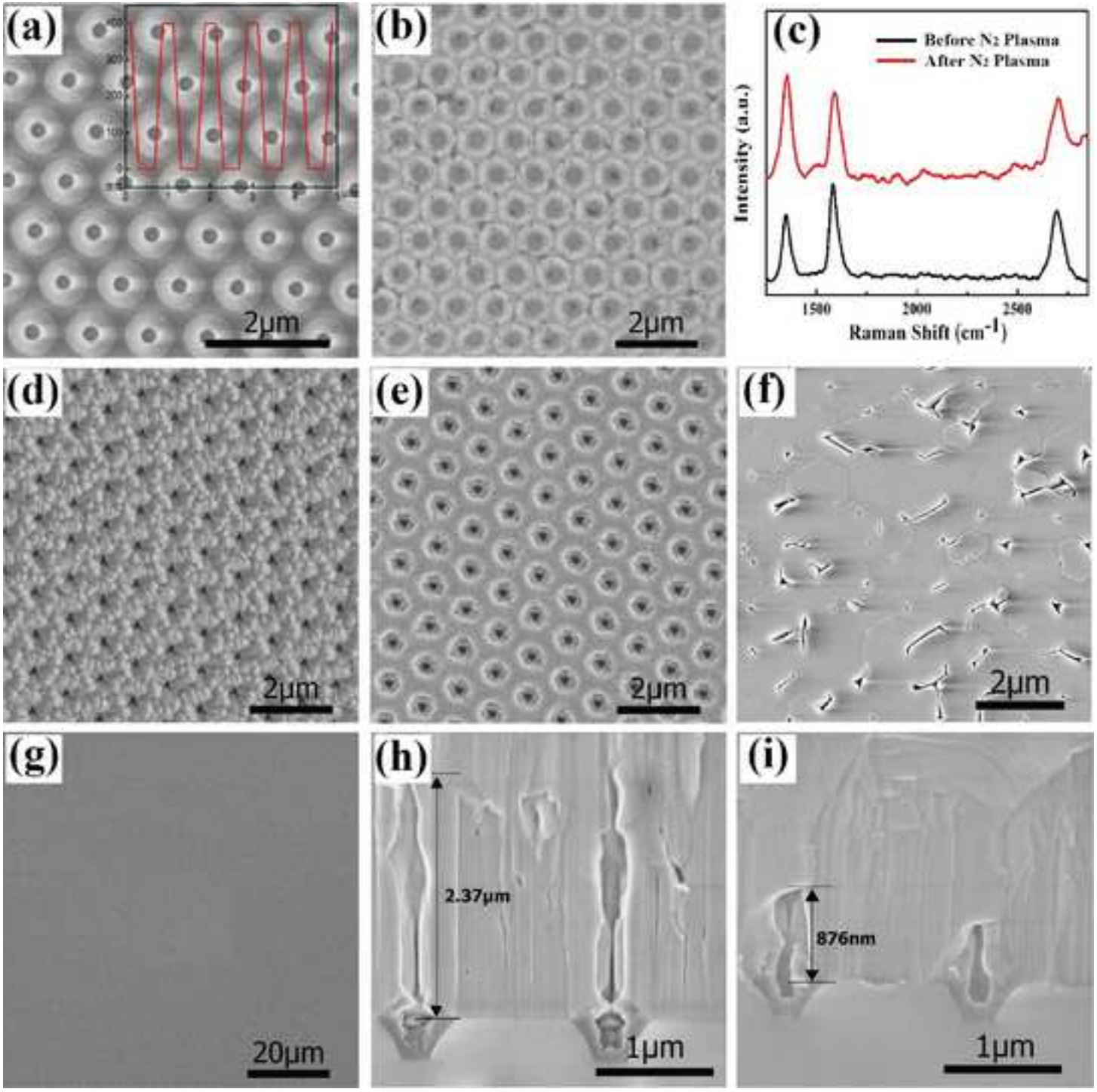

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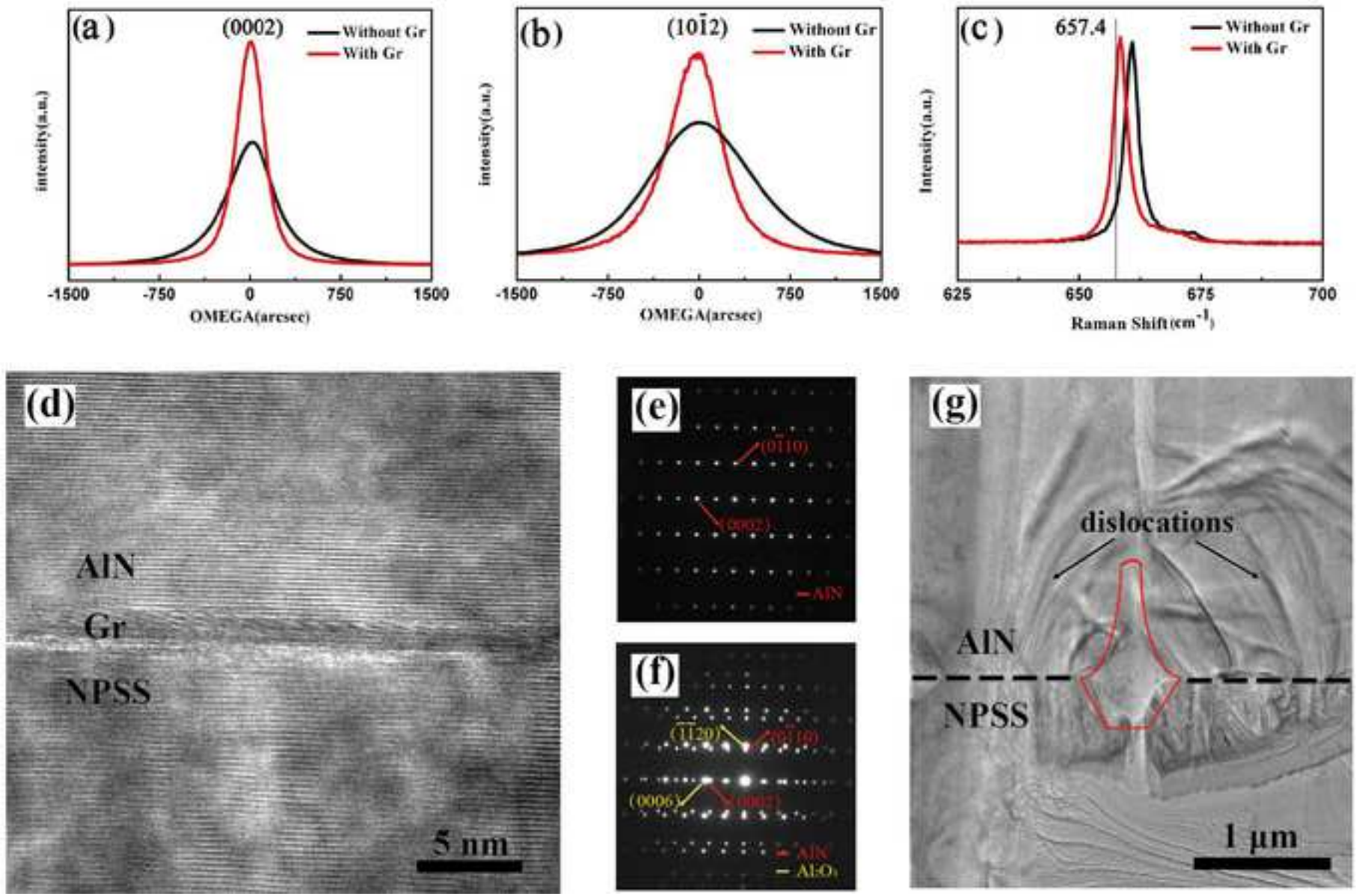

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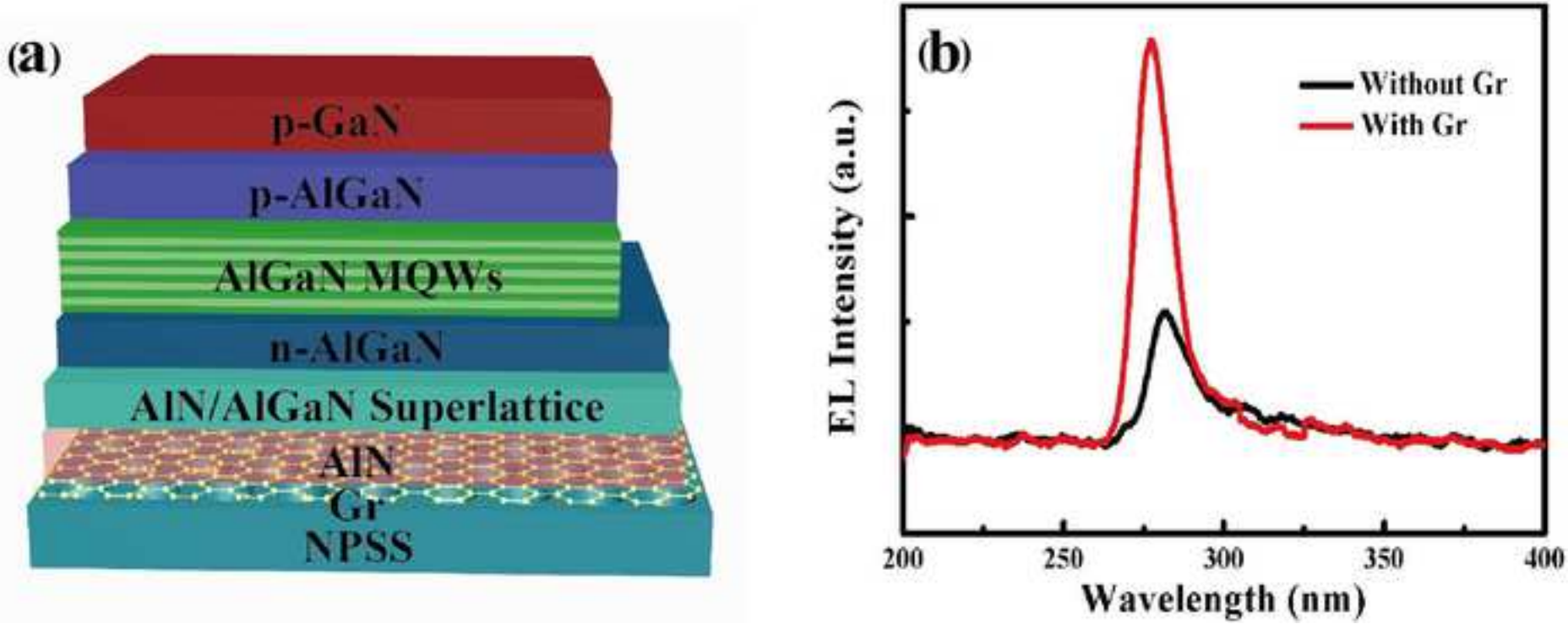

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Dear Editor and reviewers,

Thank you so much for processing and reviewing our manuscript entitled "**Quasi-van der Waals Epitaxy of AlN Film on Nano-patterned Sapphire Substrate with Graphene-assisted for Ultraviolet Light Emitting Diodes**" submitted to Journal of Visualized Experiments (**EMID:51ec02e102d9c34b**). I greatly appreciate both your help and that of the reviewers concerning improvement to this manuscript. We have studied their comments carefully and added the measurement and analysis. Furthermore, we have made the major revisions which we hope to meet with their approval. All the changes have been incorporated into the revised manuscript and marked in red. The detailed changes and the answers to comments are listed below point by point.

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Response: According to editor's suggestion, we have thoroughly proofread our manuscript.

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Response: Thanks for editor's suggestion, we have obtained the explicit copyright permission from Applied Physics Letters. And the copyright permission has been upload to the Editorial Manager account. Also, the Figure has been cited appropriately in the Figure Legend.

3. For in-text referencing, please put the reference numbers before a comma or period.

Response: We have put the reference numbers before a comma or period.

4. Please add a one-line space between each of your protocol steps.

Response: We have added a one-line space between each protocol steps.

5. Please combine some of the shorter Protocol steps so that individual steps contain 2-3 actions and maximum of 4 sentences per step.

Response: We have combined some of the shorter Protocol steps.

6. There is a 2.75 page limit for filmable content. Please highlight 2.75 pages or less of the Protocol steps (including headings and spacing) in yellow that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.

Response: We have highlight the essential steps.

7. Figure 1: Please add a title for the whole figure in Figure Legend.

Response: We have add the Figure legend for Figure 1.

8. Figure 2: Please add a title for the whole figure in Figure Legend.

Response: We have add the Figure legend for Figure2.

9. Figure 3: Please add a title for the whole figure in Figure Legend.
Response: We have add the Figure legend for Figure 3.

10. Please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and trouble shooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique
Response: Thanks for editor's suggestion, we have revise the Discussion.

11. Please do not abbreviate journal titles for references.
Response: We have rewritten the references.

12. Please remove the embedded figure(s) from the manuscript. All figures should be uploaded separately to your Editorial Manager account.
Response: Thanks for editor's suggestion, we have removed the embedded figure(s) from the manuscript and uploaded separately to the Editorial Manager account.

13. Unfortunately, there are a few sections of the manuscript that show significant overlap with previously published work. Though there may be a limited number of ways to describe a technique, please use original language throughout the manuscript. Please rewrite lines 119-122, 129-132, 323-326, 331-333, 341-348.
Response: Thanks for editor's suggestion, we have rewritten lines 119-122, 129-132, 323-326, 331-333, 341-348.

Reviewer 1:

An interesting work on the van der Waals epitaxy of high-quality AlN film on nano-patterned sapphire substrates with assistance of graphene buffer layer. The as-fabricated DUV-LEDs are also demonstrate obviously enhanced luminescence. These results of the work are impressive and should be valuable for the researchers in this field. Therefore, I recommend accepting this work for publication after a minor revision. Below is some information:

Response: We are very grateful for your help in improving this manuscript. We have studied your comments carefully and have made the major revisions so that we hope meet with your approval.

Comment 1: Great improvement in coalescence thickness, but why still so thick? Is there a means to further reduce this coalescence thickness?

Response: Graphene can assist the rapid lateral coalescence of AlN on the nano-patterned sapphire substrate, so that the AlN film can be completely coalesce and cover the Gr/NPSS when the thickness is less than 1μm. However, it was necessary to further grow the thickness of 1-2 μm, because thicker film can further help improve the crystal quality of the AlN film and reduce the surface roughness. Under the premise of ensuring high crystal quality and low surface roughness, the method of reducing the thickness of AlN film is still under study, but we believe that it is promising to achieve this goal by optimizing the growth conditions using the presence of graphene interlayer.

Comment 2: Why do the authors say their growth method is quasi vdWE? Because of N2 plasma treatment?

Response: As we mentioned in the manuscript, the reactivity of graphene is greatly enhanced by introducing defects after plasma treatment, which would be beneficial for the AlN nucleation (Surf. Sci. 634, 81 (2015)). A covalent bond is formed between Al atom and defect sites during the nucleation, while the lateral growth is very fast with low growth-axis bond energies (Adv. Funct. Mater. 24, 6629 (2014)). Therefore, we concluded this growth method is quasi vdWE, combining with the reference.

The above-mentioned references are incorporated in the revised manuscript.

Comment 3: Solid demonstration of reduction in dislocation density, but is it sufficient for target application? If not, can it be further reduced and how?

Response: In our experiment, the estimated densities of screw and edge dislocations of as-grown AlN are reduced to 1.55×10^8 and 2.60×10^9 cm−2 with the assist of Gr. Based on the current material dislocation density level, it can basically meet the application of deep ultraviolet LEDs, but there is still large space for further improvement, and we also need to further reduce the dislocation density.

There are two aspects on how to further improve the growth quality of the material. On the one hand, the distribution of the pattern on the nano-pattern substrate can be adjusted. For example, by reducing the size of the unetched region, thereby increase the tendency of the epitaxial lateral overgrowth and increase the degree of dislocation bending which can further reduce the dislocation density. On the other hand, the dislocation density of the grown AlN material can be further reduced by optimizing the growth parameters and the growth conditions.

Reviewer 2:

Authors fabricated AlGaN LEDs on patterned sapphire substrate with and without graphene interlayer, suggesting the enhanced device performance by using the graphene. The experimental results and methods are not enough to support the suggestions. The experimental protocol was roughly described with lack of key parameters. Also, there are lots of experimental steps without mentioning their necessity. More importantly, there is a missing of scientific evidence to show the role of graphene interlayer in this paper. For the publication JoVE, major revision is required.

Response: Thanks a lot for your suggestions in improving this manuscript.

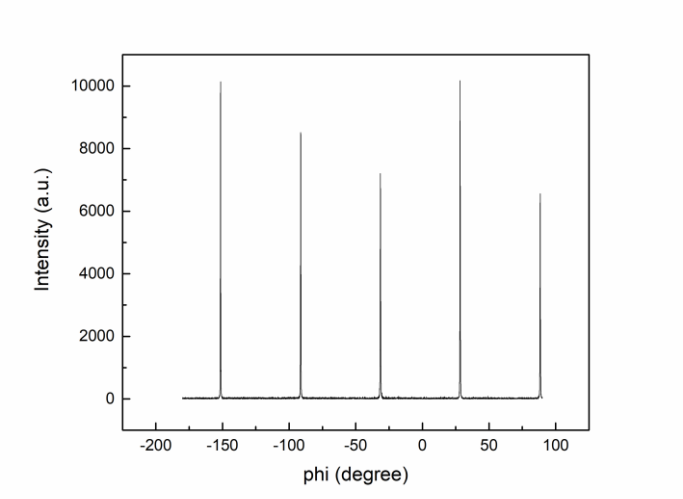
Major Concerns:

- 1.AlN films were grown on graphene/NPPS with N_2 plasma treatments and showed higher lateral growth behavior compared to those grown on NPSS without N_2 plasma treatments. Reviewers think N_2 plasma treatment will form a thin AlN buffer layer on NPPS which can also improve the lateral growth of AlN layers. The authors should provide additional experimental results of AlN layers grown on N_2 plasma-treated NPPS to determine the enhanced lateral growth of AlN films are due to the graphene intermediate layer or due to the N_2 plasma treatment.

Response: Thanks for your suggestion. Here, plasma-treatment power is 50 W under the room temperature. Thus, the effects of plasma-treatment on NPSS is negligible due to the high stability of sapphire.

- 2.Dislocation density is critical to determine LED performances. Authors estimated the dislocation densities using XRD rocking curve results, suggesting the lower dislocation density for AlN films grown on graphene coated NPSS compared to those for AlN films grown NPSS without graphene interlayers. However, it is unclear that both AlN films grown on NPSS with and without graphene interlayer are single crystalline. Because a huge number of dislocations are bounded at large-angle and/or low-angle grain boundaries, it is important to investigate in-plane orientations of the AlN films. TEM results showed only a limited area of the AlN layer crystallinity within few-micrometer-size square. Authors should provide an in-plane orientation pole figure and/or phi-scan using XRD.

Response: Thanks for your suggestion. We provide an AlN (101) phi-scan from -180 degree to 80 degree show as follow. From the phi-scan, there are five peak and the position spacing is 60 degree, showing good quality of AlN.



AlN (102) phi-scan from -180 degree to 80 degree

-3."The HRTEM image of the AlN/Gr/NPSS interface shows the presence of an approximately 0.7-nm-thick Gr layer (dark area in Fig. 2(d)) and a smooth epitaxial interface, indicating quasi-van der Waals epitaxy of AlN on NPSS with Gr-assisted."
The resolution of cross-sectional TEM is not as high as to determine well-ordered lattice arrays at the AlN/graphene/Al2O3 interface. There are no diffraction patterns of graphene in the SAED results. Is there any additional evidence to indicate quasi-van der Waals epitaxy of AlN on graphene-coated NPSS.

Response: Thanks for your valuable comment. Because the graphene interlayer is too thin to get the diffraction patterns of graphene in the SAED results. While in our previous work, the existence of graphene has been proved by Raman results (Chen Z, Liu Z, Wei T, et al. Improved Epitaxy of AlN Film for Deep‐Ultraviolet Light‐Emitting Diodes Enabled by graphene. Advanced Materials, https://doi.org/10.1002/adma.201807345). Also, we have provided the Raman results of AlN grown with and without graphene. With the Gr interlayer, the E_2 peak of AlN is located at 658.3 cm^{-1}, which is very close to the stress-free AlN (657.4 cm^{-1}) as shown in Fig. 2(c), while AlN grown on the bare NPSS shows a higher frequency (660.6 cm^{-1}) due to the high compressive strain. The release of stain also indicates the quasi-van der Waals epitaxy of AlN on graphene-coated NPSS.

-4."Some of the dislocations near the void bend and annihilate at the climax of void thus the threading dislocation density of AlN has been reduced. The TEM measurements explained the released stress and the reduced dislocation density of AlN on Gr due to QvdWE"
Authors suggested the reduced dislocation for AlN film grown on graphene-coated NPSS is due to the lateral growth of AlN layers. Meanwhile, the lateral growths are occurred both on NPSSs with and without graphene interlayer. Authors should investigate dislocation density at the growth region where AlN layers were directly grown on sapphire with and without graphene.

Response: The dislocation density of AlN layers on sapphire with and without graphene has been investigated in the previous work of our group's (Chen Z, Liu Z, Wei T, et al. Improved Epitaxy of AlN Film for Deep‐Ultraviolet Light‐Emitting Diodes Enabled by graphene. Advanced Materials, https://doi.org/10.1002/adma.201807345). It had been shown that graphene helps to reduce the dislocation compared to that directly grown on sapphire.

- 5.In Fig. 3b, the dominant EL peak for the AlGaN LED with graphene was slightly blue shifted compared to that for the AlGaN LED without graphene. One of the main reason of this blue shift is due to a screening effect of the piezoelectric field in the QW with increasing current injections. To avoid the misunderstanding, authors need to provide EL intensity as a function of applied currents for both AlGaN LEDs with and without graphene. Also, authors need to show current-voltage characteristics curves because EL intensity can be affected by the electrical characteristics of the device.

Response: Thank you for your valuable comments. It should be noted that the EL spectra of AlGaN LED with/without graphene shown in Fig. 3b were tested under the same injection current, not increasing current injections. And with the same injection current, the slightly blue shift of EL peak for the AlGaN LED with graphene indicated strain release compared to AlGaN LED without graphene. This conclusion is consistent with Raman results shown in Fig. 2(c). Here, the EL is only the measurement on wafer. Especially, detailed device results will

be published in another paper in near future.

-6.Reviewers also want to know the EL and electrical characteristics of the AlGaN LED fabricated on N_2 plasma treated on NPSS without graphene interlayer.
Since the N_2 plasma treatment of NPSS without graphene interlayer has no effects on growth of AlN film. The EL and electrical characteristics of the AlGaN LED fabricated on N2 plasma treated on NPSS without graphene interlayer should be the same as that fabricated device on NPSS without graphene interlayer.

-The experimental protocol should be revised which enough to reproduce their work elsewhere.
[Protocol]
- 1.1.3) Provide experimental details for SiO2 deposition, such as pre-running, deposition temperature, deposition rate.

Response: The deposition temperature is 300℃. The deposition rate is 100 nm/min. And the answer is incorporated in the text.

- 1.2.3) Change the abbreviation from nano-imprint resist (NPR) to nano-imprint resist (NIR).
Response: Thank you for your detailed instruction. The answer is incorporated in the text.

- 1.3.1) Describe the nano-imprint pattern more in detail in terms of pattern size, pitch, height and/or depth, the material of the mold, total area of the pattern.
Response: Thank you for your detailed instruction. The width of the unetched regions is 300 nm and the depth is 400 nm. The period of pattern is 1μm. The answer is incorporated in the text.

- 1.4.1) Provide experimental details for ICP-RIE, such as etching pressure, power, etching temperature, all gases with flow rates, etching rates, etching time, etching depth, pre-running.
Response: Thank you for your detailed instruction. The answer is incorporated in the text.

- 1.4.2) Required experimental details for O2 plasma treatments such as etching pressure, etching power, etching temperature, etching rates, etching depth, treatment time, pre-running.
Response: Thank you for your detailed instruction. The answer is incorporated in the text.

- 2.1) "Wash the NPSS with acetone, ethanol, and deionized water for three times." Do you use sonication or do you just rinse the sample? Do you put your sample in a mixture of acetone, ethanol, and deionized water and then wash it? What is the size of the NPSS?
Response: Thank you for your detailed instruction. We are sorry for the misleading description. We rinse the sample in acetone, followed by rinsing the sample in ethanol. Finally, we wash the sample with deionized water. The answer is incorporated in the text.

- 2.3) What is a three-zone high-temperature furnace. Describe your apparatus precisely. Also, provide the reason why you use three-zone furnace instead of using, for example, one-zone furnace.

Response: A three-zone high-temperature furnace has three zone at the same temperature to keep the constant temperature. We use three-zone furnace to ensure the dissociation of methane.

- 2.4) You mentioned three-zone high-temperature furnace. What zone do you heated? Where do you load the sample? What is the increasing rate of temperature?
Response: Thank you for your detailed instruction. We put the sample in the second zone and the increasing rate of temperature is 20℃/min.

-2.5) What is the chamber volume? The growth time of graphene is 3-5 hours. What determines the growth time. What is the growth rate? After the graphene growth, how did you cool down your chamber? Describe the cooling process in terms of decreasing temperature rates, gases, and their flow rates, and so on.
Response: Thank you for your detailed instruction. The chamber volume is one inch and the growth time is dependent on carbon source. We cool down the chamber by natural cooling under Ar/H2.

- What are the crystallinity and thickness of the graphene layer? Also, describe the coverage of the graphene layers on the patterned sapphire substrate.
Response: The thickness of the graphene is 0.7 nm. The coverage of the graphene layers on the patterned sapphire substrate is shown in fig.1 (b).

-3.1) Why do you need to wash the as-grown graphene/NPSS before N2 plasma treatment.
Response: To keep the cleaness of graphene surface before N2 plasma treatment.

-3.3) What are you etching using N2 plasma. If N2 plasma etches specific material, what is the etching rate?
Response: Just etching graphene using N2 plasma.

-4.1) What is the MOCVD recipe for AlN growth. Also, there are many different types of MOCVD in the market. What MOCVD did you use? Describe the chamber schematically.
Response: The MOCVD recipe for AlN growth is actually the growth condition for AlN which is shown in 4.2. The MOCVD system was home-made in our experiments. The answer is incorporated in the text.

-4.2) How did you prepare the NPSS counterpart sample. Did you also perform N2 plasma treatment on the NPSS counterpart sample?
Response: The NPSS counterpart sample is without N2 plasma treatment.

-4.3) What is the speed of increasing temperature to reach 1200°C. How long does it take to stabilize the growth temperature? What is the growth pressure? What is the mole flow rate of TMAl? What is the chamber volume of MOCVD? What is the growth rate of AlN? In addition to TMAl and NH3, what gases are used for the ambient? What are the flow rates of ambient gases?
Response: The speed of increasing temperature to reach 1200°C is 100°C/min. It takes 12 min

to stabilize the growth temperature. The growth pressure is 50 torr. The growth rate of AlN is about 1μm/h. And H2 is used for the ambient. The answer is incorporated in the text.

-5.1) Requires information of speed of decreasing temperature, growth pressure, mole flow rates of TMAl and TMGa for each AlN growth and AlGaN growth, NH3 flow rates, growth rates for each AlN growth and AlGaN growth, ambient gases, and their flow rates, and modulation time. Reviewers also wonder why the periodic change of TMAl flow to adjust the deposition components. To obtain AlN/AlGaN heterostructure, TMGa flows may need to be changed.

Response: The speed of decreasing temperature is 10 °C/min. The ambient gases is H2 during the growth process. The mole flow rates of TMAl, TMGa and NH3 for AlN are 50, 0 and 1000 sccm, and for AlGaN are 32, 7 and 2500 sccm respectively. The answer is incorporated in the text.

-5.2) Requires information of speed of decreasing temperature, growth pressure, ambient gases, and their flow rates, mole flow rates of TMAl and TMGa, NH3 and silicane flow rates, growth rates and carrier concentrations of n-type AlGaN.

Response: The speed of decreasing temperature is 10°C/min. The ambient gases is H2. The concentrations of n-type AlGaN is $5\times10^{18}cm^{-3}$.The answer is incorporated in the text.

- 5.3) Requires information of growth temperature, growth pressure, ambient gases, and their flow rates, mole flow rates of TMAl and TMGa, NH3 and silicane flow rates

Response: The growth temperature is 1002℃.The ambient gases is H2. The mole flow rates of TMAl, TMGa and NH3 for $Al_{0.6}Ga_{0.4}N$ are 24, 7 and 2500 sccm and for $Al_{0.5}Ga_{0.5}N$ are 14,8 and 2500 sccm. The answer is incorporated in the text.

- 5.4) Requires information of growth temperature, growth pressure, ambient gases, and their flow rates, mole flow rates of TMAl and TMGa and the doping precursor, NH3 flow rates, hole concentration of p-AlGaN.

Response: The growth temperature is 1002℃.The ambient gases is H2. The mole flow rates of TMAl, TMGa and NH3 are 40, 6 and 2500 sccm. The ambient gases is H2. The answer is incorporated in the text.

-5.5) How Si-dopant make p-type AlGaN? Requires information about growth temperature, growth pressure, ambient gases, and their flow rates, mole flow rates of TMAl and TMGa, hole concentration of p-AlGaN.

Response: The p-type AlGaN is doping with Mg. The answer is incorporated in the text.

-5.6) How Si-dopant make p-type GaN? Requires information about growth temperature, growth pressure, ambient gases, and their flow rates, mole flow rates of TMGa, hole concentration of p-AlGaN.

Response: The p-type AlGaN is doping with Mg. The ambient gases is H2. The mole flow rates of TMGa and NH3 are 8 and 2500 sccm. The hole concentration of p-AlGaN is $5.4\times10^{17}cm^{-}$

[3].The answer is incorporated in the text.

-5.7) Provide information for decreasing temperature time, chamber pressure, N2 flow rates.
-What process did you do between p-GaN annealing and complete cool-down of the growth chamber?
Response: The answer is incorporated in the text.

-6.1) Prior to doing the spin-coating did you clean the sample as you did before. Provide information about the photolithography process including photo-resist name, thickness, UV-exposure power and time, developer, developing and rinsing time, pattern design and dimension, and so on.
Response: The photo-resist name is 4620. The UV-exposure time, developing time and the rinsing time are 8s, 30s and 2 min, respectively. The answer is incorporated in the text.

-6.2) What is ICP-etching. Do you only etch the p-GaN layer? More information requires such as etching power, etching pressure, the etching rate of GaN (or AlGaN) and photo-resist, etching depth, gases, and their flow rates.
Response: ICP-etching is abbreviation for inductively couple plasma-etching. The etching power, etching pressure and the etching rate of GaN are 450W, 4 m Torr and 5.6 nm/s. The answer is incorporated in the text.

-6.3) Some photoresist cannot be removed only by using acetone. How did you wash the sample? Did you use ultra-sonication? More experimental details are required.
Response: We washed the sample by put it into acetone at 80℃ for 15 min followed by washing it with ethanol, and deionized water. The answer is incorporated in the text.

-6.4) Provide information of the photolithography process including photoresist name, thickness, UV-exposure power and time, developer, developing and rinsing time, pattern design and dimension, and so on.
Response: The answer is incorporated in the text.

-6.5) Some photoresist cannot be removed only by using acetone. How did you wash the sample? Did you use ultra-sonication? More experimental details are required.
Response: The answer is incorporated in the text.

-6.6) What metal and thickness did you use for the n-contact. What the size of the n-pad. Where is the n-pad located at your sample?
Response: The answer is incorporated in the text.

-6.7) Provide information of the photolithography process including photo-resist name, thickness, UV-exposure power and time, developer, developing and rinsing time, pattern design and dimension, and so on.
Response: The answer is incorporated in the text.

-6.8) How did you wash the sample. Did you use ultra-sonication? More experimental details are

required.
Response: The answer is incorporated in the text.

-6.9) What metal and thickness did you use for the p-contact. What the size of the p-pad. Where is the p-pad located at your sample? It is not easy to make good Ohmic metal contacts with p-GaN. What is your method?
Response: The answer is incorporated in the text.

-6.10) Repeating sample cleaning processes are required to remove the photoresist. But, the protocol did not provide any reason for washing the sample. Every protocol must be reasonable and has its reason. Also, how did you wash the sample? Did you use ultra-sonication? More experimental details are required.
Response: We wash the sample to make it clean. The answer is incorporated in the text.

-6.11) Provide experimental details for SiO2 deposition, such as pre-running, deposition temperature, deposition rate, deposition thickness.
Response: The answer is incorporated in the text.

-6.12) Provide information of the photolithography process including photo-resist name, thickness, UV-exposure power and time, developer, developing and rinsing time, pattern design and dimension, and so on.
Response: The answer is incorporated in the text.

-6.13) Why do you immerse the sample into an HF solution. What is the concentration rate of HF? What is the etching material and what is the etching rate? How long did you immerse the sample in HF? Did you rinse the sample before drying it?
Response: We immerse the sample into an HF solution to etch SiO2 for 15s. The concentration rate of HF is 23%. The answer is incorporated in the text.

-6.14) What material did you wash out. Did you use ultra-sonication? More experimental details are required.
Response: We wash the whole wafer without ultra-sonication.

-6.15) What is the thick n/p-pad. Describe the materials and the device structure precisely. What metal did you use for the thick n/p-pad? Where did form the thick n/p-pad? Without photolithography, the thick n/p-pad will deposit the entire substrate. Did you pattern the substrate prior to form the thick n/p-pad?
Response: The thick n/p-pad is used for lining. The material here is Al/Ti /Au. The thick n/p-pad is overlapped on the n/p contact. The photolithography is same as before. The answer is incorporated in the text.

-6.16) What material did you wash out. You already washed out the sample prior to form the thick n/p-pad.
Response: We wash the whole wafer to make it clean.

-6.17) Provide a method to grind and polish the sapphire substrate. Why you need to grind the sapphire substrate. Why you etch 130 micrometers.
Response: The method to grind and polish the sapphire substrate is mechanical polishing. We grind the sapphire substrate to cut them into devices. 130 micrometers is an optimized parameter.

-6.18) Why you wash the sample with the dewaxing solution. What chemicals were composed in the dewaxing solution?
Response: We wash the sample with the dewaxing solution to get rid of paraffin.

-6.19) How did you cut the sample. What devices are in each piece samples. What do you mean the sample is packaged.
Response: We first scribe the sample by laser and then cut it into chips by mechanical dicer. The device size is 0.5 mm × 0.5 mm. The answer is incorporated in the text.

Minor Concerns:
[Abstract & Introduction]
-1. Authors mentioned the advantage of graphene-assisted quick growth. Discuss clearly experiment time for growing an AlN film only and for growing a graphene/AlN heterostructure.
Response: After growth for the same time, figure1 shows different surface topography of AlN on NPSS with and without graphene. These results clearly proofed the advantage of graphene-assisted quick growth.

- 2.There is no reason to abbreviate graphene, and Gr is not a chemical symbol of graphene.
Response: We have changed "Gr" into graphene.

- 3.What is N-plasma
Response: Nitrogen is used as gas source for plasma generation.

- 4.You mentioned quick AlN growth. What is quick for AlN growth.
Response: The coalescence thickness is less than 1 um showing quick growth of AlN on Graphene-NPSS substrate.

- 5.What is Gr-NPSS? Describe precisely about your growth substrate.
Response: After CVD growth of graphene on NPSS substrate, the combined graphene and NPSS substrate is graphene-NPSS.

- 6.Provide your LED emission wavelength instead of writing your LED has a DUV emission.
Response: We have give the emission wavelength of LED in the manuscript. Line 354-356 "EL spectrum (Figure 3b) of AlGaN-based DUV-LEDS on GrGraphene-NPSS shows 2.6 times stronger luminescence at a peak wavelength of 280 nm"

- 7.Authors claimed a new method to fabricate AlGaN LEDs with shortening the process and less

cost. However, there are no comparisons with conventional AlGaN LEDs in terms of shortening process and less cost. The new method requires additional graphene growth resulting in a longer process. Also, it is hard to know the cost-effectiveness of using graphene layer.

Response: The graphene synthesis system is much cheaper than MOCVD. And the gas source for graphene growth is also cheaper than AlN source.

-8. Instead of using an expression "gives us a lot of inspiration", describe logically the relation between Z. Chen's work with this manuscript.

Response: We change it into "shows the way for utilization of graphene as buffer layer."

[Figures and discussion]

-9.Revised the inset of Fig. 1a with bigger font sizes. What's the scale for x and y-axes.

Response: The scale for x-axes is 5 μm and the scale for y-axes is 400 nm.

-10.How can we recognize the graphene layer in Fig.1(b).

Response: The bright area is graphene.

-11.In Fig. 1(c), what evidence supports the increase of dangling bonds. More explanation is required.

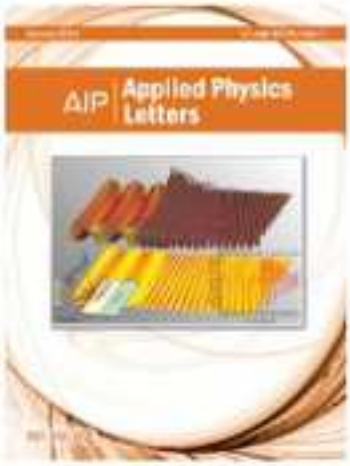
Response: The increase of D peak of graphene shows the increase of dangling bonds.

- 12.What is the FWHM of (0002) and (10-12)GaN XRD rocking curves for GaN films grown on N2 plasma treated NPSS without graphene interlayer.

Response: The (0002) and ($10\bar{1}2$) XRC of AlN films shown in Figures 2a and 2b confirms the high-quality of the AlN grown on Gr-NPSS, with significantly reduced of FWHM XRC from 455.4 to 267.2 arcsec and 689.2 to 503.4 arcsec, respectively, compared to AlN grown on bare NPSS. Thus, the estimated densities of screw and edge dislocations of AlN on bare NPSS are 4.51×10^8 and 4.40×10^9 cm−2, and are reduced to 1.55×10^8 and 2.60×10^9 cm^{-2} with the assist of graphene.

- 13.In Fig. 3a, where the p- and n- metal electrodes were formed in the device schematic.

Response: On the surface of p-GaN and n-AlGaN respectively.



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