Metal-assisted Direct Growth of CVD Graphene on GaN as Transparent Electrodes

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ABSTRACT

This paper reports a metal assisted process for the direct growth of CVD graphene on GaN LED epiwafers. The metal layer was introduced as both the mask and catalyst, which was subsequently removed in a penetration etching process. This provides a solution for the integration of graphene and GaN devices.

1 Introduction

With the continuous development of lighting and display technology, light-emitting diodes (LEDs) have attracted more and more attention. Isamu Akasaki, Hiroshi Amano and Shuji Nakamura, the inventors of the blue LEDs, won the Nobel Prize in physics in 2014. Recently, GaN-based LEDs have been developing rapidly at an unprecedented speed. However, it is difficult to achieve very effective p-type heavy doping of GaN, which seriously hinders the current in p-GaN, thereby affecting the performance of LEDs. Therefore, transparent electrodes are generally introduced into GaN-based LEDs to improve the current spreading and current injection [1-3]. Indium tin oxide (ITO) is the most common transparent electrode material [4], but the scarcity of In reduces its sustainability. As a result, graphene, which is ultra-thin, highly stable, environmentally friendly and has excellent electrical and thermal conductivity, has the potential to be an ideal material for transparent electrodes [5].

Nevertheless, graphene also has problems in the device processing. In the existing reports, high-quality and high-yield graphene is mostly grown on metal substrates [6-8]. However, graphene attached to the metal catalyst surface is difficult to be directly applied to most electronic devices such as LEDs, and generally requires some techniques to transfer it to the target substrates. More or less impurities and defects will inevitably be introduced during the transfer process whether it is dry transfer or wet transfer, thus reducing the contact quality between graphene and target substrates. Therefore, the direct growth of graphene on GaN is highly desired, and can avoid contamination and damage to LEDs caused by the transfer process [9], which greatly promotes the development of graphene transparent electrodes.

In this paper, we propose a metal-assisted direct growth process of chemical vapor deposition (CVD) graphene on GaN. The patterned growth of graphene can be realized by the catalysis of patterned metal layer (fabricated by photolithography). At the same time, the metal layer can also be used as a mask to etch the LED mesas. They are subsequently removed by the process of penetration etching, so that graphene and GaN are in direct contact. With the simple process and high repeatability, this method effectively avoids the transfer process of graphene. It could be used as a guideline for the development of graphene transparent electrodes in the future.

2 Experiments

Fig. 1 shows the process flow diagram of the LEDs in this paper. Commercial GaN LED epitaxial wafers grown on sapphire (Xiangneng Hualei Optoelectronic Corporation) were used as-received. In this paper, LEDs were fabricated with Co or Ni as the metal catalyst layer, and other optional metals include but are not limited to copper, copper-nickel alloys. First, photolithography and sputtering were performed on the epitaxial wafer to obtain a patterned metal layer with a thickness of 200 nm, as shown in Fig. 1a. Using this as a mask, the p-GaN and multiple quantum well (MQW) were etched by inductively coupled plasma (ICP) to form the 260 × 515 μm^2 LED mesas (Fig. 1b). Next, the growth of graphene was performed using cold-wall plasma enhanced CVD

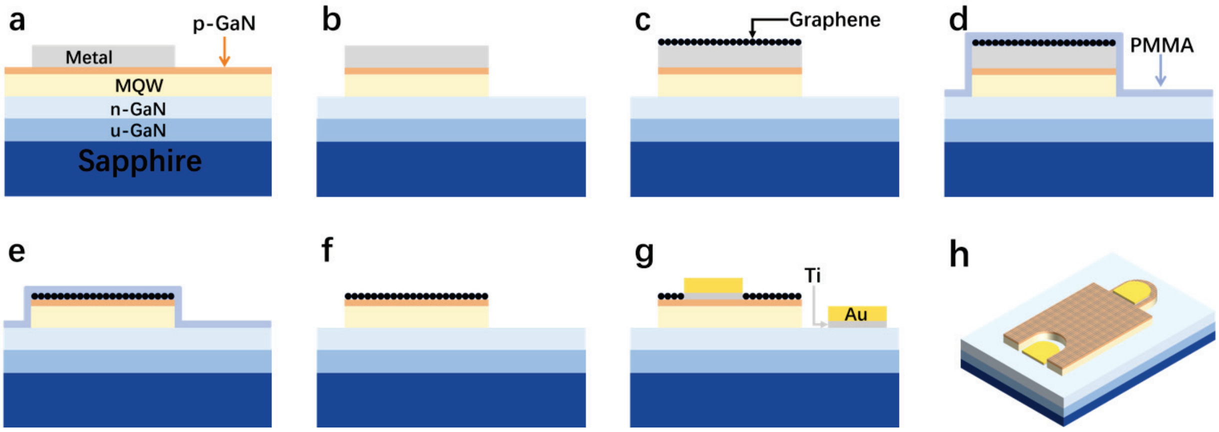

Fig. 1 Schematic diagram of the process flow of LEDs with the directly grown graphene as transparent electrodes. (a) After photolithography, a metal layer is sputtered on the GaN LED epitaxial wafer. (b) The LED mesas are formed by dry etching. (c) Under the catalysis of metal, graphene is generated in PECVD. (d) A PMMA layer is spin coated to protect graphene. (e) Metal is removed by wet etching. (f) The PMMA layer is removed. (g) The metal electrodes are sputtered. (h) Schematic diagram of the 3D structure of LEDs. MQW represents multiple quantum well.

(PECVD). Taking the growth on Co as an example, the samples were grown at 600 °C and 6 mbar for ten minutes under a $CH_4/H_2/Ar$ (5/20/960 sccm) atmosphere. Due to the catalysis of the metal, graphene was only formed on Co, realizing the patterned growth of graphene. Since the catalytic mechanisms of Co and Ni in graphene growth are basically the same, their device characterizations and test results are relatively similar. Fig. 2 shows the optical microscope photos of graphene grown on Ni and the Raman spectrum of the graphene.

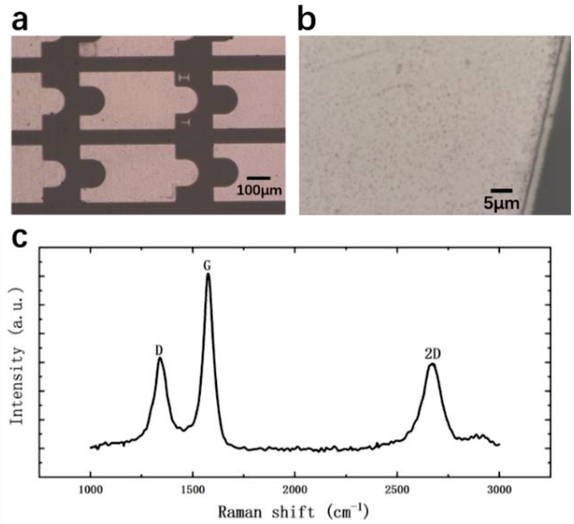

Fig. 2 (a) 50x (b) 1000x optical images of graphene grown on Ni. (c) Raman spectrum of graphene grown on Ni.

After the growth of graphene, a PMMA (poly(methyl-methacrylate)) layer was spin-coated onto the sample and baked at 150 °C for 15 min. The PMMA layer was firmly attached to both graphene and p-GaN, and then the sample was put into the metal etching solution. Since the thickness of the PMMA layer is only 150~200 nm, water, etchants and products can pass through it. After the metal layer is etched away, due to the protection of PMMA, the graphene lands on the p-GaN surface instead of floating away in the solution (Fig. 1e). The PMMA layer was then removed using acetone and isopropanol. The electrode pattern was photo-lithographed and 300 nm Au and 15 nm Ti were sputtered, as shown in Fig. 1g. For better contact among the metal electrodes, graphene, and p- or n-GaN, the sample was annealed in vacuum at 450 °C for 5 min. Fig. 1h presents the 3D structure diagram of the LEDs.

3 Result and Discussion

In order to explore whether the graphene indeed plays the role of current spreading, LEDs without graphene transparent electrodes were fabricated from the same GaN LED epiwafers. Fig. 4 is a comparison of the I-V characteristics of LEDs with and without graphene. The turn-on voltages of graphene-coated GaN LEDs and graphene-free GaN LEDs are abouct 3.9 V and 5 V, respectively, and the working voltages at 20 mA are about 6.4 V and 7.3 V, respectively. It can be concluded that graphene transparent electrodes improve the electrical properties of GaN LEDs.

The scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) characterizations of the LEDs fabricated with Co as the metal layer were performed (Fig. 4). It can be seen from the EDS results that the Co element is absent, and it can be concluded that the Co layer has been etched away.

Figure 5 presents the electroluminescence photographs of the LEDs. It can be clearly seen that the LED with graphene emits uniformly and brightly over the entire mesa. In contrast, the LED without graphene only emits near the metal electrodes. It can be used as the direct evidence to confirm that the as-grown graphene has a good current spreading effect in GaN LEDs.

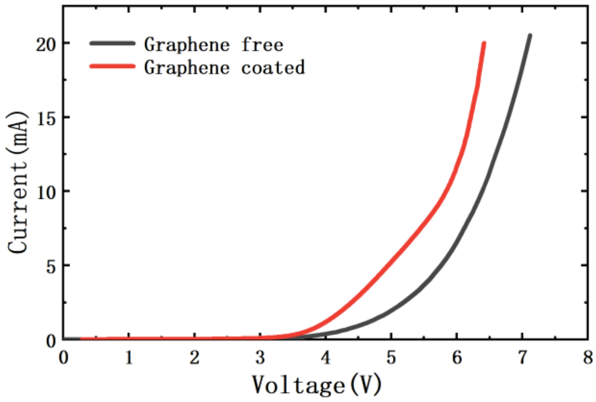

Fig. 3 IV characteristics of LEDs with and without graphene.

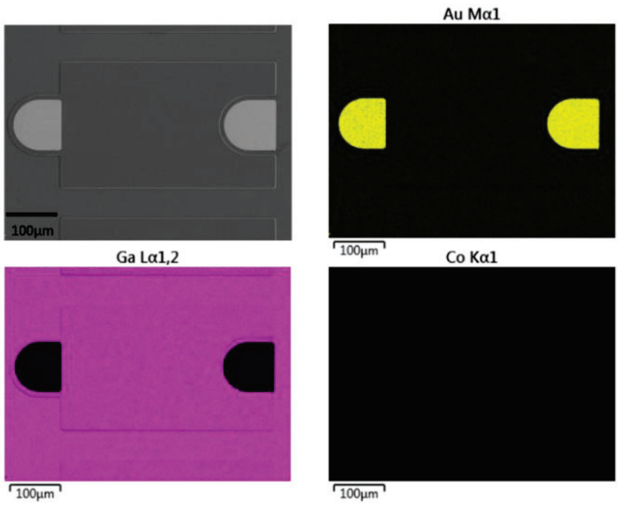

Fig. 4 SEM and EDS images of the LEDs fabricated with Co as the metal layer.

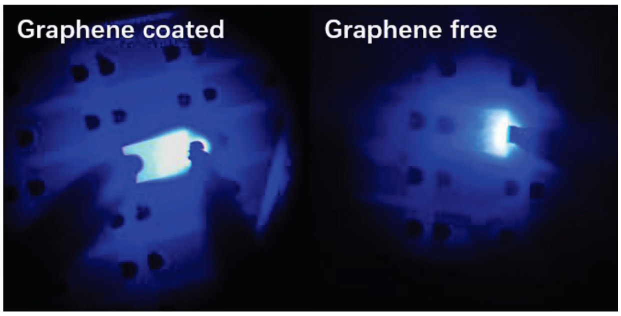

Fig. 5 Electroluminescence optical images of the LEDs with and without graphene at 20 mA.

4 Conclusions

In this paper, some recent progress in the application of graphene in GaN LED transparent electrodes is introduced. As a transfer-free method for graphene, this direct growth scheme achieves good contact between the graphene and GaN, thereby significantly improving the performance of LEDs. The metal layer plays an indispensable role as both the mask and catalyst, which significantly simplifies the process flow. This method is not only suitable for the application of graphene in transparent electrodes, but also provides an idea for the integration of graphene with other GaN devices.

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