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Nickel-Assisted Transfer-Free Technology of Graphene Chemical Vapor Deposition on GaN for Improving the Electrical Performance of Light-Emitting Diodes

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Abstract: With the rapid development of graphene technology, today graphene performs well in the application of light-emitting diode (LED) transparent electrodes. Naturally, high-quality contact between the graphene and the GaN underneath is very important. This paper reports a process for nickel-assisted transfer-free technology of graphene chemical vapor deposition on GaN. The nickel film plays the dual role of etching mask and growth catalyst, and is removed by the subsequent "penetration etching" process, achieving good direct contact between the graphene and GaN. The results show that the graphene effectively improves the current spreading of GaN-based LEDs and enhances their electrical performance. This scheme avoids the wrinkles and cracks of graphene from the transfer process, and is not only suitable for the combination of graphene and GaN-based LEDs, but also provides a solution for the integration of graphene and other materials.

Keywords: GaN; LEDs; graphene; transparent electrode; CVD; transfer-free

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1. Introduction

With the development of science and technology, light-emitting diodes (LEDs) play an increasingly important role in our daily life. Since the birth of gallium nitride (GaN)-based LEDs, they have greatly promoted the development of lighting and display fields. However, there are still problems in the development, such as the difficulty of heavy doping of p-type GaN. This means that the conductivity of p-type GaN is relatively poor, so that the current is difficult to spread to achieve sufficient current injection. For this reason, transparent electrodes came into being. Indium tin oxide (ITO) is the most representative transparent electrode material, which has excellent electrical conductivity and high transparency in the visible band [1–4]. Nevertheless, from the perspective of sustainable development, ITO is inferior to graphene because of the scarcity of indium [5,6]. In addition, graphene performs better than ITO on flexible substrates. These factors make graphene one of the most viable potential transparent electrode materials [7].

In the growth of graphene, metals play a crucial catalytic role. The catalytic mechanism is mainly divided into two types [8]: one is the carbon segregation and precipitation mechanism represented by nickel, under which more layers of graphene are grown; the other is the surface adsorption mechanism represented by copper, under which the number of graphene layers grown is lesser. Both of these mechanisms are widely used in the growth of graphene.

However, the vital role played by metal catalysts in graphene growth means that the growth of high-quality graphene is often inseparable from metals. As a result, as-grown graphene is always attached to the surface of metal substrates [9–11], which is difficult to use in electronic devices directly. There are some solutions to this problem: for example, graphene can be transferred from the metal substrates to the target substrates, but in this process greater or lesser contamination and defects will inevitably be introduced. In addition, graphene can be directly grown on the target substrates, but without metal catalysis the growth of graphene is often more difficult [12,13].

To solve this problem, in this paper we propose a nickel-assisted transfer-free technology of CVD graphene on GaN. In this method, nickel film is used to catalyze the growth of high-quality graphene, and it is removed by the penetration etching process to realize the contact of graphene with the target substrates, so as to avoid the transfer process. In addition, nickel is not only used as a catalyst, but also as a mask to etch the LED mesas. The measurement results show that the as-grown graphene film effectively improves the electrical performance of LEDs. The effects of different growth time on the performance of LEDs are compared as well. The process is simple, efficient and highly repeatable, which directly realizes good, tight contact between graphene and GaN, providing a solution for the integration of graphene and GaN devices.

2. Materials and Methods

Since lift-off photolithography of metal electrodes after graphene growth may cause some damage to graphene, in order to pursue more stable and excellent electrical performance nickel is selected as the catalyst to grow graphene with more layers, reducing the impact of subsequent processes on the continuity of graphene.

Figure 1 shows a schematic diagram of the process flow of the LEDs in this paper. The epitaxial wafers used were provided by Xiangneng Hualei Optoelectronics Company. First, a 300 nm nickel film was photolithographically sputtered on the epitaxial wafer as the subsequent etching mask and growth catalyst. The 260 × 515 μm^2 LED mesas were etched with inductively coupled plasma (ICP) at an etching ratio of approximately 1:80 for nickel and GaN, as shown in Figure 1b. The samples were subsequently grown in cold-wall plasma-enhanced chemical vapor deposition (PECVD) at 600 °C and 6 mbar, under an atmosphere of $CH_4/H_2/Ar$ (5/20/960 sccm) and at a plasma power of 40 W. As shown in Figure 1d, after the growth of graphene, PMMA (poly(methyl-methacrylate)) was spin-coated on the sample (3000 rpm for 30 s) and baked at 150 °C for 10 min. It is approximately 150 nm thick. Then the sample was put into the etching solution for more than four hours ($CuSO_4$:HCl:H_2O = 10 g:50 mL:50 mL). The etching solution can pass through the PMMA and graphene to slowly etch Ni film. Since PMMA is in close contact with graphene and n-GaN, after the metal is etched, PMMA and graphene will fall onto the surface of the sample instead of floating away in the solution. Then PMMA was removed by acetone and isopropyl alcohol (Figure 1f). Due to the weak van der Waals force on the surface of graphene, it is necessary to remove the graphene on the electrode area with oxygen plasma etching to prevent metal electrodes from falling off, as shown in Figure 1g. Finally, 15 nm Ti and 300 nm Au were sputtered as electrodes and annealed in a 450 °C vacuum for five minutes (Figure 1h).

Figure 2a shows the structure of the LEDs. Figure 2b shows the scanning electron microscope (SEM) image of the LED arrays (SE2 mode). An area of intentionally broken graphene has a higher contrast for better observation of graphene film, which is characterized by SEM (in-lens mode), as shown in Figure 2c. Since the in-lens mode has higher resolution, which is more suitable for observing the microscopic morphology, the graphene layer can be clearly seen in Figure 2c. The white boundary line in the image is the edge of the LED mesa, below which is the p-GaN and graphene on the mesa, and above which is the n-GaN beside the mesa. The dark film is graphene, and p-GaN is exposed in the broken area of graphene, corresponding to the white area in the image. It can be clearly seen that the graphene film has been broken and folded in this area, and even some graphene falls on n-GaN.

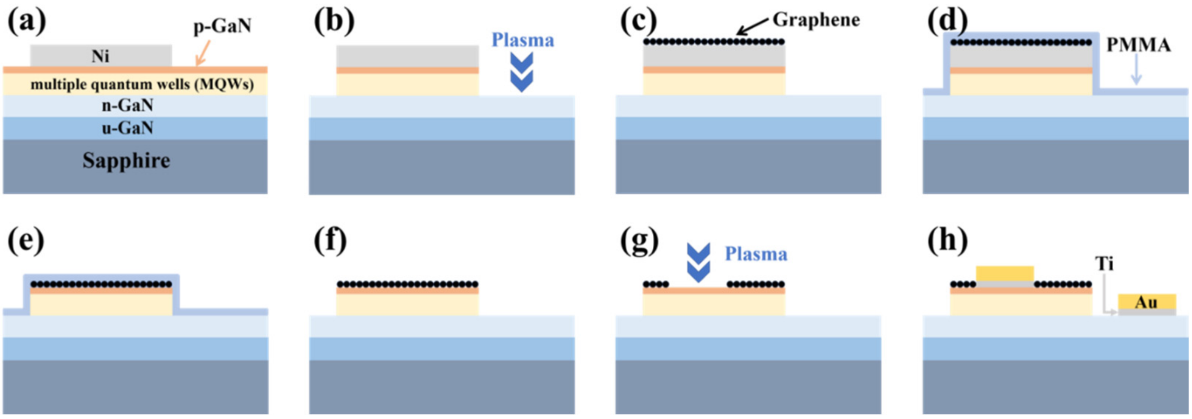

Figure 1. Process flow diagram of growth of graphene and fabrication of LEDs. (**a**) Sputter Ni film. (**b**) Etch the mesas. (**c**) Grow graphene. (**d**) Spin-coat PMMA. (**e**) Etch Ni film. (**f**) Remove the PMMA. (**g**) Remove some graphene. (**h**) Sputter metal electrodes.

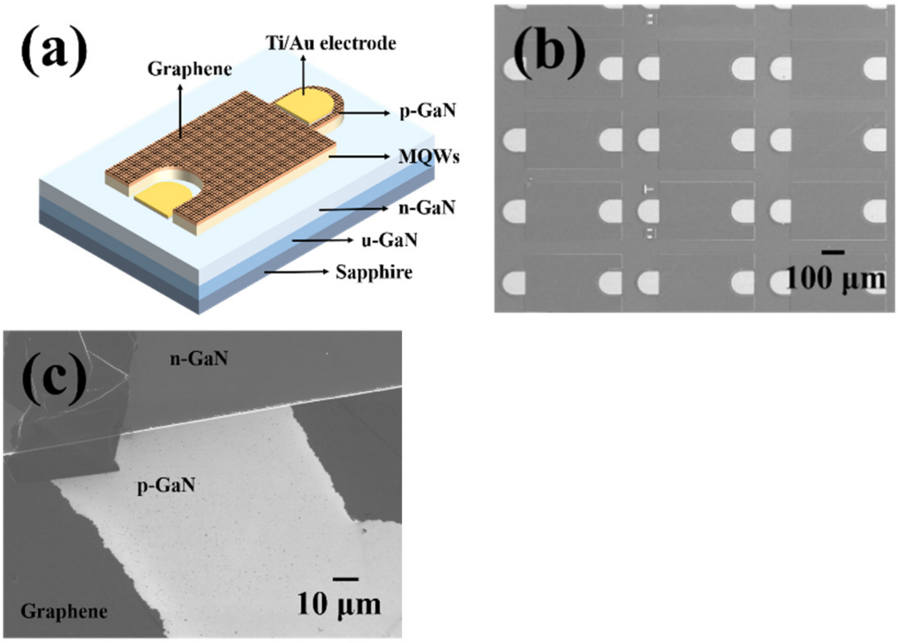

Figure 2. (**a**) Structure diagram of LEDs. (**b**) SEM image of LED arrays in SE2 mode. (**c**) SEM image of graphene on the mesa in in-lens mode.

3. Results and Discussion

In order to study the effect of graphene of different qualities on LED performance, LEDs with different graphene growth time were fabricated. Figure 3 shows the Raman characterization of graphene with different growth time after the fabrication of LEDs. The number of graphene layers is usually estimated in terms of the 2D/G ratio and the shape of the peaks [14]. It can be seen that with the increase of growth time, the 2D/G ratio gradually decreases, indicating that the number of graphene layers gradually increases. The graphene is estimated to be about 5–10 layers thick, based on both the Raman spectra [15] and our previous atomic force microscopy (AFM) measurement [12]. In addition, the Raman characterization was performed after the LEDs were fabricated, indicating that the graphene still maintains good quality after the lift-off photolithography of the metal electrodes.

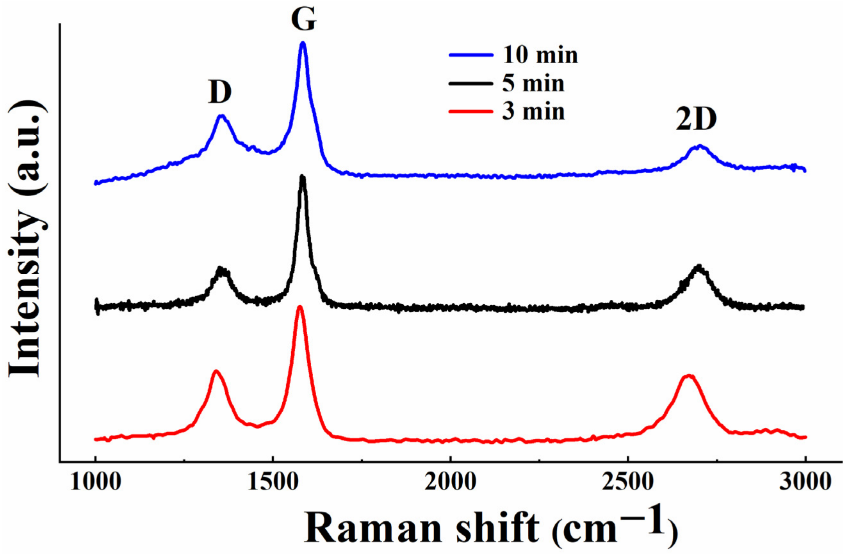

Figure 3. Raman characterization of graphene grown for 3 min, 5 min and 10 min, respectively.

Figure 4 is the energy dispersive spectroscopy (EDS) surface scanning result, inset is the characterized area and the characterized elements are Ni, Ga and Au. Among them, the molecular ratio of Ni is 0.01%, and the weight ratio is 0.02%. This indicates that the Ni film has been substantially etched away.

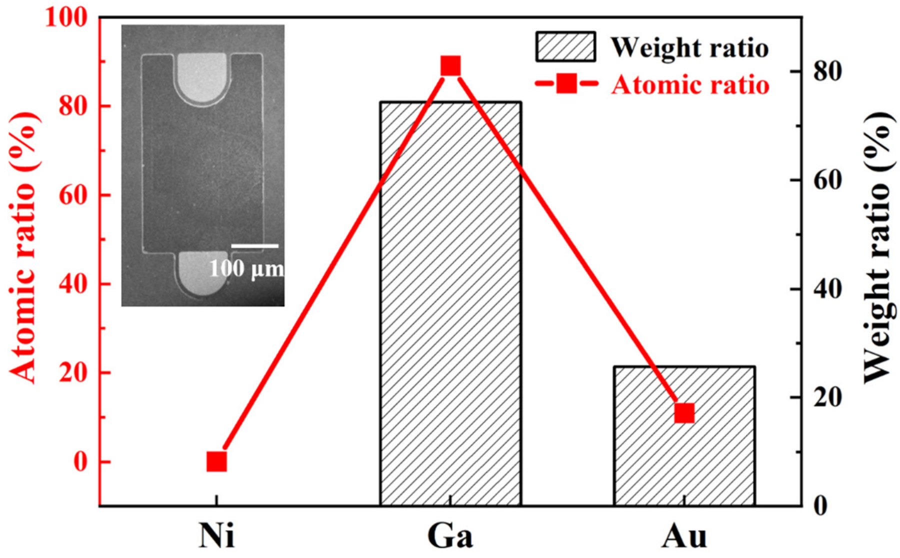

Figure 4. EDS characterization of the LED. Characterized elements are Ni, Ga and Au. The inset is the characterized area.

In addition to the fabrication of LEDs with graphene, graphene-free LEDs were also fabricated for comparison using basically the same process, and their current–voltage characteristics are shown in Figure 5. The inset is the current–voltage characteristics in semi-log scale. The dotted auxiliary lines are the reverse extension lines of the nearly linear part of the current–voltage characteristic curves, and their intersections with the abscissa represent the turn-on voltages of LEDs. The turn-on voltages of LEDs with growth time of 10 min, 5 min, 3 min and without graphene are about 3.2 V, 3.5 V, 3.7 V and 4 V, respectively; the operating voltages at 20 mA are about 3.5 V, 4.2 V, 4.4 V and 4.7 V, respectively. The slopes (k_1–k_4) of these auxiliary lines, which are mainly related to the LED series resistance, are also shown in Figure 5. Compared with graphene-free LEDs, the current spreading effect of graphene will reduce the series resistance of graphene-coated LEDs. Therefore, with the increase of growth time, the slope increases and the series resistance decreases. It can be inferred that graphene improves electrical performance of LEDs, and the thicker the graphene the greater the improvement, which may be attributed to its better continuity. From the inset, it is clear that these LEDs have a certain degree of leakage current before reaching their respective turn-on voltage, which may be related to the recombination current in the barrier area. Compared with graphene-free LEDs, the leakage current of LEDs with a growth time of 3 min and 5 min is not much different. However, the LEDs with graphene grown for 10 min have serious leakage current. This may be due to the fact that many carbon atoms are adsorbed on the sidewalls of the mesas because the growth time is too long, even though graphene is not formed because there is no metal catalyst on the sidewalls. Therefore, properly increasing the growth time can effectively improve the electrical performance of LEDs.

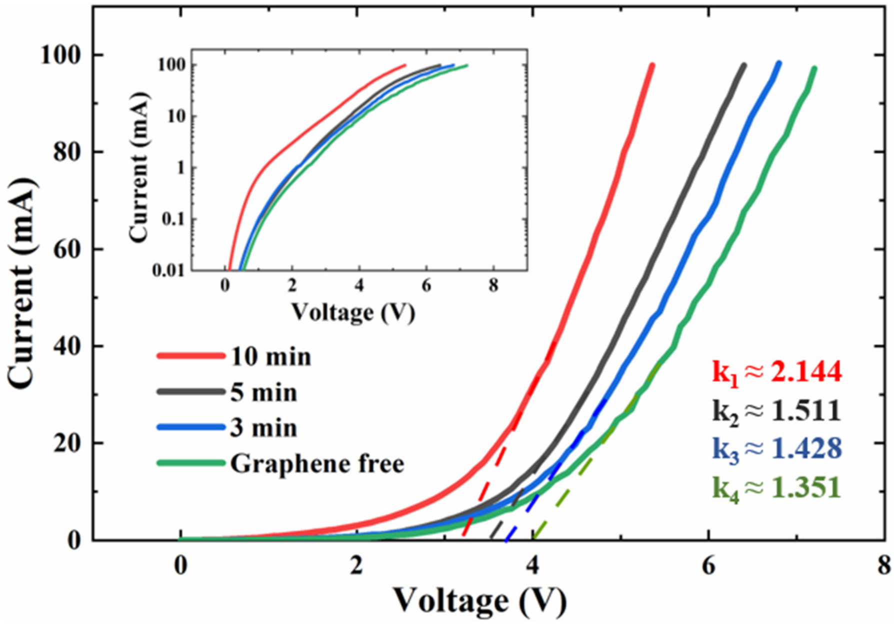

Figure 5. Current–voltage characteristics of LEDs with and without graphene. The dotted auxiliary lines are the reverse extension lines of the nearly linear part of the current–voltage characteristic curves, and k1–k4 represent their slopes. The inset is the current–voltage characteristics in semi-log scale.

Figure 6 is the optical microscope luminescence images of LEDs with and without graphene at 20 mA. Even though thicker graphene theoretically blocks more light [10], the difference in luminescence of LEDs coated with different graphene is still small when observed under an optical microscope, so only a representative graphene-coated LED is shown. It can be seen that the graphene-free LED only emits light near the metal electrodes, while the graphene-coated LED emits light evenly on the entire mesa. This shows that graphene plays a good role in current expansion, which indicates that graphene plays a good role in current spreading.

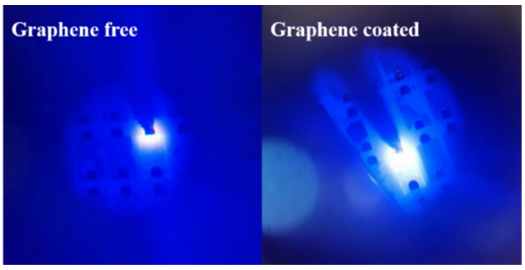

Figure 6. Images of LEDs without and with graphene at 20 mA.

4. Conclusions

In this paper, a method of growing transfer-free graphene on GaN by PECVD is introduced. LEDs with different thickness of graphene are fabricated by controlling the growth time. In the whole process, the Ni film is not only used as the mask for mesa etching but also as the catalyst for graphene growth, which is subsequently removed to achieve direct contact between graphene and GaN. When the growth time is less than ten minutes, the thickness of graphene increases with the growth time. The measurement results show that graphene realizes current spreading and effectively improves the electrical performance of LEDs, although excessive growth time may lead to current leakage of LEDs. This method makes CVD graphene achieve good contact with GaN substrate, avoiding the defects and impurities introduced in the transfer process.

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