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RESEARCH ARTICLE

Direct growth of graphene on gallium nitride using C_2H_2 as carbon source

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Growing graphene on gallium nitride (GaN) at temperatures greater than 900°C is a challenge that must be overcome to obtain high quality of GaN epi-layers. We successfully met this challenge using C_2H_2 as the carbon source. We demonstrated that graphene can be grown both on copper and directly on GaN epi-layers. The Raman spectra indicated that the graphene films were about 4–5 layers thick. Meanwhile, the effects of the growth temperature on the growth of the graphene films were systematically studied, and 830°C was found to be the optimum growth temperature. We successfully grew high-quality graphene films directly on gallium nitride.

Keywords graphene, C_2H_2, gallium nitride, chemical vapor deposition, Raman spectroscopy

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1 Introduction

As a representative nitride semiconductor material, gallium nitride (GaN) has attracted remarkable attention as an important material for applications in optoelectronic and electronic devices such as light-emitting diodes (LEDs) [1], laser diodes (LDs) [2], solar cells (SCs) [3], and high-electron-mobility transistors (HEMTs) [4]. LEDs have already reached high power and brightness levels, with the exception of the problems experienced with transparent and conductive electrodes (TCEs). Indium tin oxide (ITO) films, which are the most commonly used materials for TCEs, have low thermal conductivity. This reduces the diffusion efficiency of the heat generated during the operation of LEDs. Moreover, ITO is a brittle material, easily cracks, and becomes increasingly expensive with usage.

Graphene consists of a film with one or a few layers of carbon atoms arranged in a two-dimensional hexagonal lattice, which is chemically inert and mechanically strong. Its unique electrical properties have generated exciting possibilities for this material as are placement for silicon [5–12]. The unique electronic, optical, and thermal properties of graphene make it a competitive candidate to replace ITO for future applications in photovoltaics and optoelectronics [13], especially in the green energy industry, such as for LEDs and solar cells [14–18]. In addition, it has application prospects in the energy storage field [19–21].

For practical applications, large area grapheme films on insulating substrates are required. Several techniques have been developed to address this need, with the primary method involving chemical vapor deposition (CVD) on transition metals [22–28]. As is well known, the CVD processes that have been reported to date have utilized transition metal surfaces for the growth of graphene, using either methane or ethylene gases as precursors at deposition temperatures of about 1000°C. However, this temperature is too high for the direct growth of graphene on a GaN LED. Previous efforts and progress have been made by our group [29]. It has been demonstrated that 950°C is the optimum temperature for growing graphene on GaN using methane [29]. Here, we report the use of acetylene (C_2H_2) for the CVD growth of graphene on a GaN/sapphire substrate without the assistance of any metal catalysts. By controlling the process parameters, a few layers of graphene can be grown on certain semi-conductive surfaces at 830°C under atmospheric pressure without the extra catalyst. We examined such a growth process when the substrate and carbon source were gallium nitride (GaN) and acetylene, respectively.

2 Experimental

In our previous work [29], GaN epi-layers grown on c-plane (0001) sapphire substrates via metal-organic chemical vapor deposition (MOCVD) were used. The GaN epitaxial structure consists of a 50-nm-thick low-temperature-grown GaN buffer layer, a 2-μm-thick undoped GaN layer, a 2-μm-thick n-type GaN layer, five pairs of InGaN (3 nm)/GaN (12 nm) multiple quantum wells (MQWs), and a 100-nm-thick p-type GaN layer.

We used a CVD system manufactured by a domestic manufacturer from Fujian Province. It is a quartz tube with several gases flowing through a thermal field. In addition to the acetylene used as the carbon source, two other gases are used in the reaction: argon (Ar) and hydrogen (H_2). Prior to the graphene growth, an annealing process was carried out at the growth temperature for 20 min in the same atmosphere for surface activating. After the thermal annealing process for the GaN substrates, while the Ar continued to flow for the atmospheric pressure or was turned off for barometric depression, the C_2H_2 was introduced into the quartz tube. The graphene films were basically grown in a flow of 100-sccm Ar, 100-sccm H_2, and 10-sccm C_2H_2 for 35 min, followed by natural cooling to room temperature. All of the processes occurred under atmospheric pressure. We demonstrated several different conditions to obtain efficient graphene film growth on the GaN epi-layers. We compared the uses of C_2H_2 and CH_4 as carbon sources, changing the growth temperature to confirm the damage to the GaN epi-layer. The gas flow rate and growth were optimized to control the layers and quality of the graphene films. We used high-resolution X-ray diffraction (HRXRD) to characterize the crystal quality of the GaN substrates, the photoluminescence (PL) spectra to represent the optical enhancement effect of the graphene films on the LEDs, a scanning electron microscope (SEM)to observe the surface morphology after graphene growth, and the Raman spectra to comprehensively understand the graphene films.

3 Results and discussion

Before discussing the direct growth of graphene films, we are glad to present a series of interesting temperature phenomena. We know that acetylene (C_2H_2) has a lower thermal decomposition temperature than methane (CH_4). CH_4 need 900°C to decompose into carbon and hydrogen atoms [30, 31] , whereas C_2H_2 need just 700°C. The epitaxial temperature of GaN is higher than 1000°C, whereas the growth of InGaN MQWs occurs between 700 and 800°C. GaN decomposes and produces ammonia under a hydrogen atmosphere when the temperature is higher than 600°C [32]. Thus, it can be concluded that 700–800°C is the ideal temperature for growing graphene films directly on the epi-GaN. Here, we provide a further discussion of this subject.

Figure 1 shows top-view SEM images of pristine GaN, GaN after the growth of graphene films using CH_4, sapphire after the growth of graphene films using C_2H_2, and GaN after the growth of graphene films using C_2H_2. Here, we compare several forms. The graphene films grown using CH_4 were grown at 1030°C, whereas those grown using C_2H_2 were grown at 830°C. Compared with pristine GaN [Fig. 1(a)], rough and rugged metal balls can be observed at the GaN surface after the growth of graphene films using CH_4 [Fig. 1(b)]. These balls are the result of the warping of GaN flakes from the serious decomposition of GaN at temperatures higher than 900°C. However, such metal balls are absent in the graphene films grown using C_2H_2 [Fig. 1(d)], revealing little decomposition of this film. In addition, obvious sharp flakes can be seen in the images in Fig. 1(b) and Fig. 1(d). These graphene films are a few layers thick, which can be confirmed in the Raman spectra shown below. However, we can only see the smooth surface of the sapphire in Fig. 1(c), with nothing grown on it. Only several black spots emerge on it. This means graphene films can only grow on special substrates, which are not limited to the metals Ni and Cu, but include polar substrates like GaN.

Raman spectroscopy [33] is commonly used for characterizing carbon materials [34, 35] and identifying graphene films. It is especially useful for determining

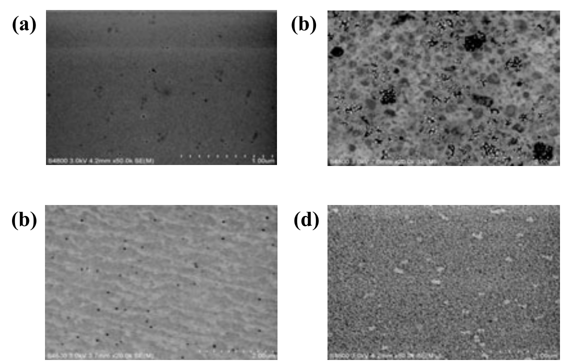

Fig. 1 A typical top-view SEM image of **(a)** GaN epi-wafer; **(b)** GaN after the growth of graphene films by CH_4; **(c)** sapphire after the growth of graphene films by C_2H_2; **(d)** GaN after the growth of graphene films by C_2H_2. The scale bar of SEM images is 50 μm.

the crystalline quality and counting the number of graphene layers [36, 37]. Here, we used Raman spectroscopy to characterize the graphene films grown on the GaN using C_2H_2. Figure 2 shows the Raman spectra of graphene films grown under different conditions, including graphene films grown on sapphire using C_2H_2, graphene films grown on GaN using CH_4, and graphene films grown on GaN using C_2H_2. We do not provide the Raman spectra for pristine sapphire, because, as can be seen, there is no carbon signal for the sapphire in Fig. 2 after the growth of graphene films using C_2H_2. We previously provided the theory for graphene films grown on GaN [29]. In contrast to the sapphire substrate, we confirmed the theory by growing graphene films on GaN using. The decomposition of GaN catalyzes amorphous carbon, which changes to graphene. We found two small peaks at 2100 cm^{-1} and 2164 cm^{-1}. There has been no clear evidence or report alleging that these are graphene-like or carbon-like until now. Primarily, in Fig. 2, we compare the graphene films grown on GaN using C_2H_2 and CH_4. We can see distinct G and 2D peaks, located at 1596.9 cm^{-1} (1598.4 cm^{-1}) and 2711.5 cm^{-1} (2701.2 cm^{-1}), respectively, when using C_2H_2 (CH_4), and the intensity ratio I(G)/I(2D) has values of about 1.38 and 2.08, respectively. We can say that we succeeded in growing graphene films on GaN using C_2H_2. The graphene films were about 4–5 layers thick. The quality of the graphene films grown on GaN using C_2H_2 was better than those grown on GaN using CH_4. Because GaN decomposes at high temperatures, there were still a large number of defects as indicated by the D band. Further improvements should focus on smoothing the surface and increasing the graphene quality.

In order to optimize the graphene films grown on GaN using C_2H_2, we optimized the temperature, pressure, and length of time used to grow the graphene films. In relation to the thermal degradation, we examined the XRD spectra to detect the degree of damage to the MQWs at different temperatures. In relation to the optical properties, photoluminescence (PL) measurements at room temperature were performed to evaluate the effects of the graphene films on a GaN LED. In relation to the growing time, the Raman spectra were obtained to characterize the graphene films. The former two conditions were also examined using the Raman spectra.

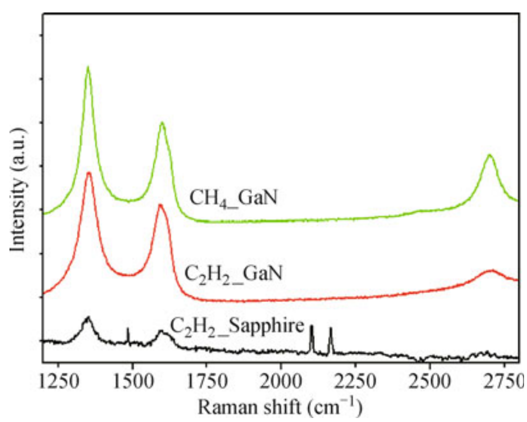

Fig. 2 Raman spectra at different growth condition. From the top to the bottom there are Raman for graphene films grown on sapphire by C_2H_2, graphene films grown on GaN by CH_4 and graphene films grown on GaN by C_2H_2.

Figure 3(a) shows HRXRD curves of the InGaN/GaN MQWs under the ω–2θ model around the GaN (0002) peaks for different temperatures. The temperature gradient is 100°C. We show the result for a graphene film grown on GaN using CH_4 with a growth temperature higher than 1000°C. The zero peak is GaN (0002), which has a diffraction angle of about 34.55°C. The nearest left and right peaks are the InGaN and AlGaN peaks, respectively. We can obviously observe forth-order InGaN satellite peaks, indicating that the good crystal structure of the InGaN/GaN MQWs is maintained during the growth process for the graphene films. There was almost no change between the curves for the pristine GaN and

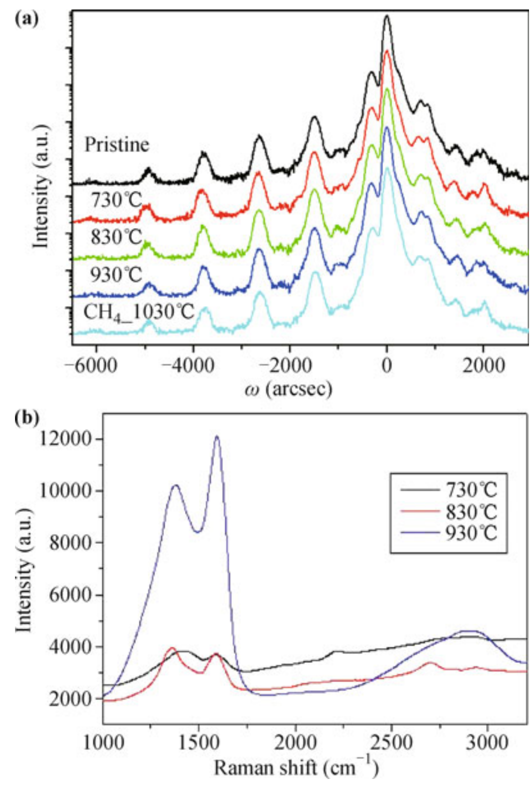

Fig. 3 **(a)** HRXRD curves of the InGaN/GaN MQWs under ω–2θ model around GaN (0002) peaks. There was almost no change between the curve pristine GaN and GaN grown graphene films by C_2H_2 at temperature 730°C, 830°C, and 930 °C. **(b)** Raman spectra at different growth temperatures. The plot 830°C shows the two distinct peaks are at 1580 cm^{-1} (G peak) and 2690 cm^{-1} (2D peak), the intensity ratio I(G)/I(2D) is about 1.15.

the GaN-grown graphene films using C_2H_2 at temperatures of 730°C, 830°C, and 930°C. However, in the curve for CH_4_1030°C, there are certain decreases in the InGaN and satellite peaks, which indicate that the temperature had a more serious effect on the crystal quality compared to the former graphene films.

The quality of the graphene films can be observed in Fig. 4. Obvious differences can be seen in the Raman spectra for the different temperatures. When the growth temperature was lowered to 730°C, no grapheme signal (2D peak) could be found. This may have been caused by the low decomposition efficiency of C_2H_2 at this temperature. When using nickel film substrates, CVD can be used to grow graphene at 650°C [38]. Here, using the GaN substrate, we proved that the lowest temperature needed to be higher than 830°C. We found that graphene films could be grown at 830°C. The plot shows two distinct peaks at 1580 cm^{-1} (G peak) and 2690 cm^{-1} (2D peak), with an intensity ratio $I(G)/I(2D)$ of about 1.15. The peak occurring at about 1354 cm^{-1} (D band), which indicated phonon scattering at defect sites and impurities, was higher than the G band. The curve of the graphene films grown at 930°C was interesting, because it had a much higher intensity in the area of the short wave numbers (D band and G band), but no apparent 2D band. The peak of the latter was about 2859 cm^{-1}, while the full width at half maximum (FWHM) was expanded to larger than 1000. This can be attributed to non-graphitic carbon [39].

Figure 4(a) shows the typical PL spectra of GaN before and after the growth of graphene films at different modes. We attempted to grow graphene on GaN as a function of the pressure. The CVD synthesis of graphene on Cu has long been considered to be surface-mediated and self-limiting as a result of its extremely low carbon solubility in Cu, leading to the formation of monolayer films [40]. Some feel that atmospheric pressure CVD (APCVD) would obviously be more suited to the large-scale production than low-pressure CVD [41]. Here, we present research on the use of different pressures for the growth of graphene on GaN. We can see that growing graphene under both growth conditions improves the optical properties of a GaN LED. The peaks of the AP and LP modes are 1.1 and 1.45 times greater than that of pristine GaN, respectively. We attribute these to the effect of light extraction. Without affecting the material quality of GaN, the direct growth of graphene can implement a surface enhancement. In addition to increasing the roughness, the GaN decomposition improves the graphene transmission.

We also compare the Raman spectra of the two growth modes in Fig. 4(b). The plot shows that the G bands of graphene grown at the AP mode and LP mode are centered at 1598.4 cm^{-1} and 1592.0 cm^{-1}, with distinct G bands located at 2712.8 cm^{-1} and 2670.1 cm^{-1}, respectively. The AP mode had an up shift in both bands compared to the LP mode. This was consistent with theories for growth on Cu. However, we did not obtain a monolayer under the LP mode. This may have been because of the different growth conditions for GaN and Cu. The intensity ratio $I(G)/I(2D)$ values of these were 2.08 and 1.5, respectively, indicating that graphene films grown in the AP mode were thicker.

4 Conclusions

We have demonstrated that graphene can be grown directly on GaN epi-layers using C_2H_2 as a carbon source. The Raman spectra indicated that the graphene films were about 4–5 layers in thickness. Meanwhile, the effects of the growth temperature on the growth of graphene films were systematically studied, and 830°C was found to be the optimum growth temperature. The

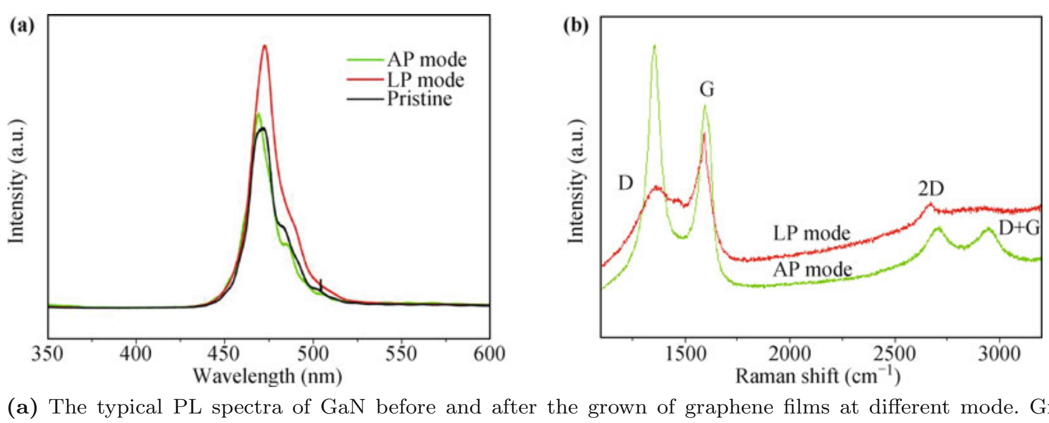

Fig. 4 **(a)** The typical PL spectra of GaN before and after the grown of graphene films at different mode. Graphene grown in both growth conditions increase the optical properties of GaN LED. **(b)** The typical Raman spectra of graphene grown at different mode. The intensity ratio $I(G)/I(2D)$ of each were 2.08 and 1.5, indicating that graphene films grown at AP mode was thicker.

PL spectra showed that growing graphene on GaN could enhance the optical properties of a GaN LED. High-quality graphene films were successfully grown directly on GaN.

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