Direct growth of graphene on gallium nitride by using chemical vapor deposition without extra catalyst*

Zhao Yun(赵 云)[a)b)c)†], Wang Gang(王 钢)[b)c)†], Yang Huai-Chao(杨怀超)[b)c)], An Tie-Lei(安铁雷)[a)b)], Chen Min-Jiang(陈闽江)[b)c)], Yu Fang(余 芳)[b)c)], Tao Li(陶 立)[b)c)], Yang Jian-Kun(羊建坤)[a)], Wei Tong-Bo(魏同波)[a)], Duan Rui-Fei(段瑞飞)[a)‡], and Sun Lian-Feng(孙连峰)[b)§]

[a)] *Semiconductor Lighting Technology Research and Development Center, Institute of Semiconductors, Chinese Academy of Sciences, Beijing* 100083, *China*

[b)] *National Center for Nanoscience and Technology, Beijing* 100190, *China*

[c)] *University of Chinese Academy of Sciences, Beijing* 100049, *China*

(Received 29 December 2013; revised manuscript received 21 March 2014; published online 16 July 2014)

Graphene on gallium nitride (GaN) will be quite useful when the graphene is used as transparent electrodes to improve the performance of gallium nitride devices. In this work, we report the direct synthesis of graphene on GaN without an extra catalyst by chemical vapor deposition. Raman spectra indicate that the graphene films are uniform and about 5–6 layers in thickness. Meanwhile, the effects of growth temperatures on the growth of graphene films are systematically studied, of which 950 °C is found to be the optimum growth temperature. The sheet resistance of the grown graphene is 41.1 Ω/square, which is close to the lowest sheet resistance of transferred graphene reported. The mechanism of graphene growth on GaN is proposed and discussed in detail. XRD spectra and photoluminescence spectra indicate that the quality of GaN epi-layers will not be affected after the growth of graphene.

Keywords: graphene, photoluminescence, gallium nitride, chemical vapor deposition, Raman spectroscopy

PACS: 68.65.Pq, 78.55.Cr, 81.05.ue, 81.15.Kk **DOI:** 10.1088/1674-1056/23/9/096802

1. Introduction

As the representative of nitride semiconductors, 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] GaN-based materials form a continuous alloy system with direct band gaps,[5] ranging from about 0.7 (InN) to 6.2 eV (AlN) with 3.4 eV for GaN.[6] Because of the p-doping problem with GaN material, in some GaN-based electronic devices, including GaN-based LEDs and SCs transparent conductive electrodes (TCEs) are conventionally used to improve the current injection and light extraction efficiency simultaneously.[7] Indium tin oxide (ITO) films are the most commonly used material as the TCE in industrial applications today, owing to its high transparency ($>$ 90% at a wavelength of 550 nm), low sheet resistances (10–30 Ω/square) and high work function ($>$ 4.3 eV). However, ITO is a brittle material and easy to crack, which greatly limits its applications in the flexible electronic devices. Moreover, ITO is becoming more and more expensive and is very sensitive to both acidic and alkaline environments.[8] All these disadvantages call for new kinds of TCEs with more reliable and stable chemical characteristics and superior physical properties.

Monolayer graphene, where sp^2-bonded carbon atoms are arranged in a regular hexagonal pattern, has a high transmittance of 97.7% in the range of visible light and conductance values of 31 Ω/square in theory.[9] Therefore, graphene's high electron mobility, outstanding optical properties,[10] and chemical and mechanical stability[11] make it an ideal alternative transparent conductor for ITO.[12] Recently, much attention has been paid to the graphene TCEs that are applied in the GaN-based LEDs.[13] In all previous research, the graphene films are grown on Cu/Ni foil using a chemical vapor deposition (CVD) method and transferred on the target LED devices.[14] However, the graphene films will be damaged in the transfer process. Meanwhile, wrinkles and overlaps inevitably appear on transferred graphene. Therefore, its electrical properties will also be influenced. In addition, because of the large mismatch between p-GaN (about 7.5 eV) and graphene (about 4.8 eV), it is very hard for the transferred graphene film to form a very good ohmic contact with p-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 61274040 and 51102226), the National Basic Research Program of China (Grant No. 2011CB301904), the National High Technology Program of China (Grant Nos. 2011AA03A103 and 2011AA03A105), the National Science Foundation of China (Grant Nos. 10774032 and 90921001), and the Key Knowledge Innovation Project of the Chinese Academy of Sciences on Water Science Research, Instrument Developing Project of the Chinese Academy of Sciences (Grant No. Y2010031).

†These authors contributed equally to this work.

‡Corresponding author. E-mail: duanrf@semi.ac.cn

§Corresponding author. E-mail: slf@nanoctr.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

GaN, resulting in a bad injection of electrons into the multiple quantum wells. Although some insertion layers have been introduced to improve the electrical contacts of graphene/p-GaN,[15] it still urges us to find a better way to avoid the damages to graphene in the transfer process to improve the electrical contacts with p-GaN. In order to overcome these limitations of previous methods, in this study, we have developed a direct growth of large-scale graphene on GaN without the extra catalyst. These transfer-free graphene films were directly grown on GaN at 950 °C and under atmospheric pressure without the extra catalyst. The graphene film has been confirmed by the distinct G peak and 2D peak in the Raman spectra. We have also investigated the impact of the growth temperature on the graphene quality and the growth mechanism as well.

2. Experimental

The substrates used herein are GaN epi-layers grown on *c*-plane (0001) sapphire substrates via metal–organic chemical vapor deposition (MOCVD). 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. All the substrates were sonicated in acetone and alcohol and then cleaned with deionized water before being sealed in a quartz tube. Then, the GaN wafers were heated to a series of growth temperatures at a rate of about 10 °C·min^{-1} in 90 min in a flow of 100-sccm Ar and 100-sccm H_2. Prior to graphene growth, an annealing process was carried out at the growth temperature for 20 min in the same atmosphere for the surface activation. After the thermal annealing process for the GaN substrates, the Ar was stopped and the CH_4 was introduced into the quartz tube. The graphene films were grown in a flow of 100-sccm H_2 and 20-sccm CH_4 for 20 min, followed with natural cooling to the room temperature. All processes took place under atmospheric pressure. In order to investigate the impact of the growth temperature on the graphene quality, in this work, we prepared three pieces of GaN wafers that were grown under 900 °C, 950 °C, and 1000 °C, respectively. A common CVD system was used to grow the graphene films in our experiment. The crystal quality of the GaN substrates was characterized by high resolution X-ray diffraction (HRXRD). The HRXRD rocking curves of GaN were obtained using an X-ray diffractometer (Bede D1) using Cu $K\alpha$ as the X-ray source ($\lambda = 1.54056$ Å). The surface morphologies and roughness of the GaN substrates were observed using an atomic force microscope (AFM, Veeco D3100). The Raman spectra of our samples with graphene films were collected using a 514-nm laser, which was excited from an argon ion laser. The surface morphology after graphene growth was observed using a scanning electron microscope (SEM) at an acceleration voltage of 10 kV. The damage of the substrate, which was grown under 950 °C, was characterized by photoluminescence (PL) spectra.

High resolution X-ray diffraction (HRXRD) and atomic force microscopy (AFM) measurements were performed in order to check the structural quality and the surface morphology and roughness (not shown).[16] The full width at half maximum (FWHM) of HRXRD rocking curves of the GaN substrate before the growth of graphene is 383.4 and 258.8 arcsec at the $(10\bar{1}2)$ and (0002) reflex, respectively. The XRD FWHM for the (0002) plane is only up to the screw threading dislocation density. The FWHM for the $(10\bar{1}2)$ plane is related to the edge and screw threading dislocation densities. The root mean square (RMS) surface roughness of the GaN substrate over a 10 μm×10 μm area was 1.064 nm, revealing a flat and smooth morphology of the GaN substrates grown via MOCVD. These results indicated that the GaN substrates used to grow graphene had a good crystalline quality and a smooth surface.

3. Results and discussion

To date, the basic strategy for graphene films used as TCEs for optoelectronic devices[17] is transferred graphene films, which need to be separated from metal substrates and transferred to the target substrates[18] for further electronic processing.[19] We directly synthesize large-scale graphene films on GaN by CVD without a further transfer process.

Figure 1 shows the optical photographs and top-view SEM images of pristine GaN and GaN after the growth of graphene films. Different annealing and growth temperatures were used for the growth of graphene on GaN by CVD. Figures 1(b)–1(d) show respective optical microscope images of graphene films on GaN substrates under the hydrogen atmosphere at 900 °C, 950 °C, and 1000 °C, respectively. Compared with pristine GaN (Fig. 1(a)) on an optical microscope image, GaN after the growth of graphene at 900 °C had no difference. When the temperature is up to 950 °C, some metal dots can be found under the microscope. A mount of metal appears and the surface of GaN becomes rough and rugged at 1000 °C. Inserts show the corresponding top-view SEM images of GaN substrates. It is found that the GaN substrate has been covered with warping GaN flakes when the growth temperature was 1000 °C, while less warpage was observed at 950 °C and smooth GaN at 900 °C. Figure 1(e), from left to right, shows the pristine substrate and graphene films on GaN epi-layers/sapphire, which were grown under 900 °C, 950 °C, and 1000 °C. From these images, we can conclude that GaN

decompose and buckle more and more seriously with the increase of the growth temperature. Decomposition of GaN usually begins with a dislocation, so we need to use GaN substrates with a better crystalline quality to grow graphene to further improve the quality of graphene.

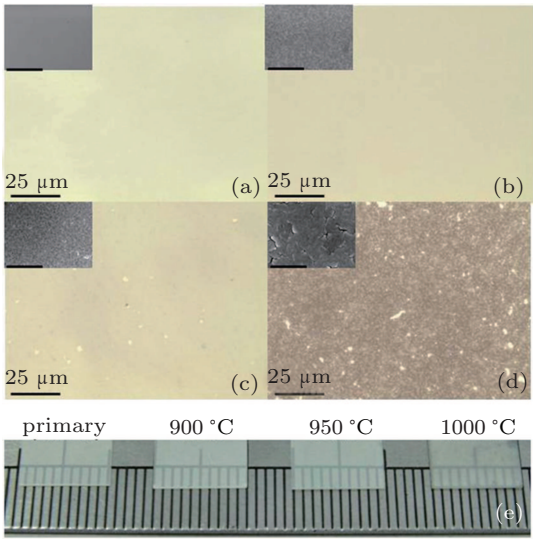


Fig. 1. (a) A typical optical microscope image of GaN substrate before the growth of graphene. (b)–(d) The Optical microscope images of graphene films on GaN substrates. The growth temperatures are 900 °C (b), 950 °C (c), and 1000 °C (d), respectively. Insets show the corresponding top-view SEM images and the scale bar is 50 μm. (e) Four samples of graphene on GaN /sapphire substrates. The samples correspond to pristine GaN /sapphire, graphene on the substrate grown at 900 °C, 950 °C, and 1000 °C from left to right, respectively.

Raman spectroscopy[20] is commonly used for the characterization of carbon materials[21,22] and graphene identification and counting the number of graphene layers.[23] The transfer-free graphene films, which were directly grown on GaN without an extra catalyst, were characterized by Raman. Figure 2 shows the Raman spectra of graphene films on GaN grown at different temperatures. Raman spectra of graphene films were excited by a 514-nm laser. It is demonstrated that the lower limit of the temperature for methane-derived graphene growth on GaN is about 950 °C. When the growth temperature was lowered to 900 °C, little signal of graphene could be found. Distinct G peak and 2D peak, located at 1598.8 cm^{-1} (1591.4 cm^{-1}) and 2694.8 cm^{-1} (2696.0 cm^{-1}) at 950 °C (1000 °C), prove graphene films have been successfully deposited on GaN under atmospheric pressure. In spite of graphene that could have a smaller D peak if warping GaN does not contribute to enlarge the D peak, the graphene obtained at 1000 °C had a relatively small D peak, because the methane decomposition rate increases at higher temperatures. Meanwhile, GaN releases NH_3 in hydrogen atmosphere, leading to graphene doped with nitrogen. When N is doping into graphene, the existence of heteroatoms will break the symmetry of the graphene lattice and enlarge the intensity of the D band.[24] The D bands of graphene at 1000 °C and 950 °C centered at 1349.0 cm^{-1} and 1352.0 cm^{-1}, respectively, whose intensity is affected by the graphene quality. Compared with that of 950 °C, a downshift of the G band and upshift of the 2D band affirm that graphene films grown at 1000 °C are thicker.[25,26] The bigger intensity ratio I(G)/I(2D), 2.34(1000 °C)> 2.17(950 °C), also confirms that graphene films grown at 1000 °C are thicker. Considering that GaN would be buckled at high temperature, further improvement would be focused on reducing the temperature and the time of annealing and deposition.

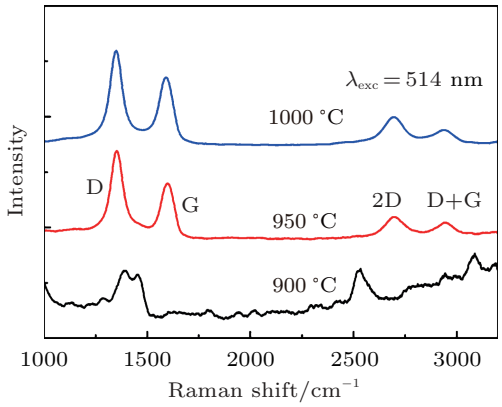


Fig. 2. Raman spectra at different growth temperatures. At a temperature of 950 °C, the characteristic peaks of graphene of the D peak, G peak, and 2D peak can be clearly observed at 1352.0 cm^{-1}, 1598.8 cm^{-1}, and 2694.8 cm^{-1}, respectively. The intensity ratio I(G)/I(2D) is 2.17, suggesting the multilayer graphene has 5–6 graphene layers.

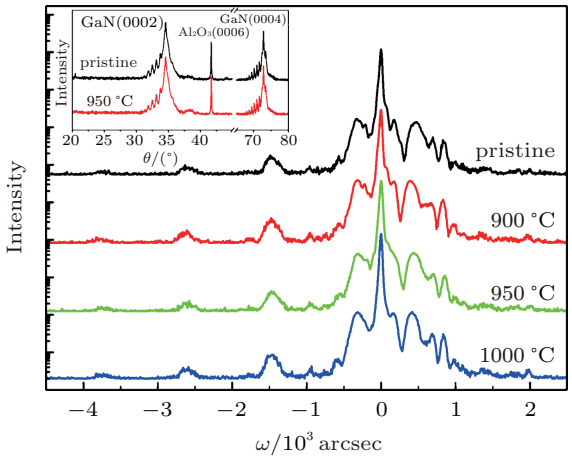


Fig. 3. HRXRD curves of the InGaN/GaN MQWs under ω–2θ model around GaN (0002) peaks before and after different growth temperature treatments. GaN (0002) satellite peaks are observed up to the third orders, indicating that the thermal degradation of the MQWs layer is negligible. The inset shows wide angle X-ray curves of a pristine GaN substrate and after the growth of graphene films at 950 °C, which is from 20 degrees to 80 degrees under the 2θ–ω model.

To investigate thermal degradation of GaN epi-layers, XRD spectra was examined, and photoluminescence (PL)

measurements were perform at room temperature for samples which were grown at 950 °C. Figure 3 shows HRXRD curves of the InGaN/GaN MQWs under ω–2θ model around GaN (0002) peaks before and after different growth temperature treatment. GaN (0002) satellite peaks are observed obviously up to the third orders, which are originated from the periodicity of the InGaN/GaN multi-quantum well (MQWs) layers, indicating that the thermal degradation of the MQWs layer is negligible. The inset shows wide angle X-ray curves of a pristine GaN substrate and after the growth of graphene films at 950 °C, which is from 20 to 80 degrees under 2θ–ω model. GaN (0002), GaN (0004), and Al_2O_3(0006) peaks are observed, suggesting that the preferred orientation of the substrate is very good and the growth progress will not affect the orientation.

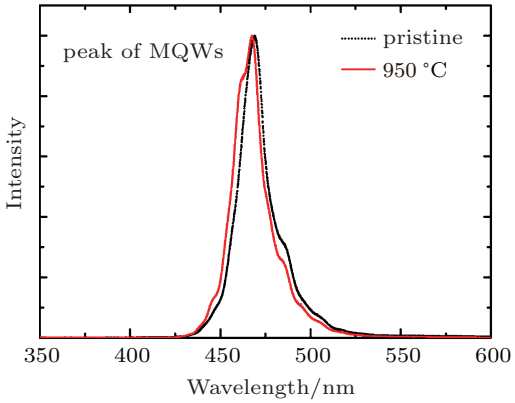


Fig. 4. PL spectra of pristine GaN substrate (black dot) and after the growth of graphene films at 950 °C (red line). Almost the same peak of MQWs indicates that GaN remains undamaged after the high temperature growth of graphene.

Typical PL spectra of a substrate before and after the growth of graphene films at 950 °C are shown in Fig. 4. An He–Cd laser (325 nm) was used as an excitation source. The PL peak of the pristine substrate locates at 469.5 nm and the PL peak position is 467.5 nm after the growth of graphene films at 950 °C. The intensity is not weakened and a slight blue shift can be found after the growth progress. This is attributed to the interdiffusion of In and Ga in InGaN/GaN quantum wells, and the indium content in the quantum well decreasing.[27] Meanwhile, it indicates that the top quantum well is intact. If the number of quantum wells decreases, a red shift appears in the PL peak position.[28] According to this, it can be found that there is little damage to the main structure of GaN epi-layers in the high-temperature graphene growth process. The sheet resistance of grapheme (R_G) on a GaN substrate is tested by using a four-point probe method. For comparison, we also deposit 100-nm ITO on glass and GaN epi-layers, and test the sheet resistance of ITO on glass (R_I) and the sheet resistance of ITO on GaN epi-layers (R_e). Experimental data obtained by using the four-point probe method are summarized in Table 1. Here, contact resistance of graphene/GaN is small enough and can be ignored.[29] Furthermore, we test different places on the wafer, namely, 1, 2, 3, 4 in Table 1, to fully reveal the conductivity of graphene films on GaN. Finally, the sheet resistances of graphene (R_G) are evaluated to be 41.1 Ω/square and 53.2 Ω/square corresponding to growth temperatures 950 °C and 1000 °C. This value is close to the lowest sheet resistance reported.[30]

Table 1. The sheet resistances of 100-nm ITO on GaN (R_I) and on glass (R_e), and graphene on GaN substrate (R_t), which were grown at 950 °C and 1000 °C.

	1	2	3	4	Average
R_e	32.82	32.86	33.00	32.98	32.93
R_I	36.59	35.54	34.52	34.21	35.22
R_t(950 °C)	39.54	40.70	40.69	43.43	41.09
R_t(1000 °C)	50.74	51.58	53.06	57.30	53.17

It is known that GaN substrate would be decomposed and buckled during the graphene films growth process at high temperature, especially under the hydrogen atmosphere. Nevertheless, there are two reasons for the use of hydrogen during the growth process. Firstly, grown graphene needs an active surface for deposition, which means that the surface of GaN needs to decompose to catalyze amorphous carbon to change to graphene. The chemical equation decomposition of GaN under the hydrogen atmosphere at high temperature is

$$\mathrm{GaN} + \frac{3}{2}\mathrm{H_2} \Leftrightarrow \mathrm{Ga} + \mathrm{NH_3}.$$

Secondly, hydrogen could etch away amorphous carbon on graphene films. Meanwhile, hydrogen can prevent the leakage of oxygen in the normal pressure reaction device. There is a balanced relationship between the decomposition of GaN and the formation of graphene. Figure 5 illustrates the mechanisms of the direct growth of the graphene film on GaN by using CVD without an extra catalyst. As mentioned in the experimental part, before graphene was grown, an annealing treatment with the substrate was carried out. The purpose of annealing is to produce an active surface for the deposition in the next growth procedure. In the annealing treatment, GaN decomposes and releases ammonia under the hydrogen when the temperature is higher than 600 °C.[31] Therefore, a layer of Ga atoms will be exposed when the upper N atoms are gone in the decomposition. Methane as the carbon source for graphene growth also provides a portion of the hydrogen. Under the catalysis of the exposed Ga atoms, carbon atoms will be gradual graphitized.[32] After the growth, the samples were naturally cooled to room temperature. Finally, graphene

films were directly grown on GaN substrates. Based on this work and the growth temperature optimization, we can predict that a better grown graphene on GaN can be obtained when acetylene is used as the carbon source at 650 °C because acetylene has a lower thermal decomposition temperature compared with CH_4.[33]

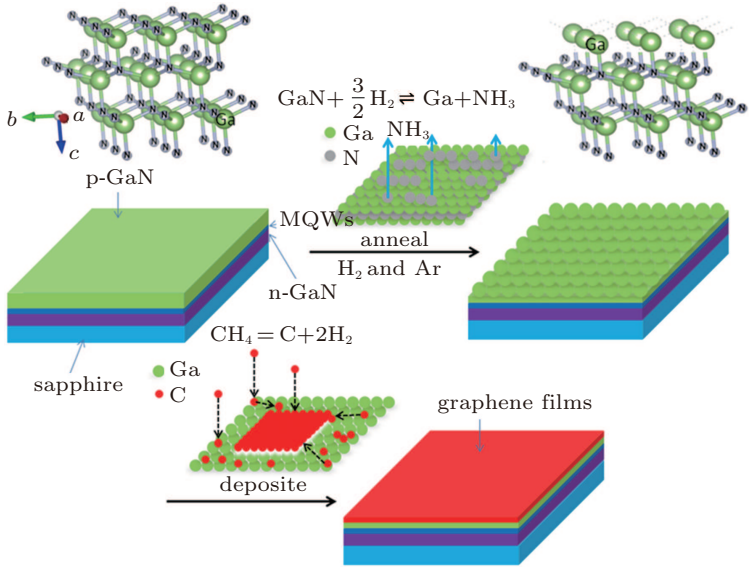


Fig. 5. Proposed mechanism of the growth of graphene film on GaN. The substrates are GaN epi-layers grown on *c*-plane (0001) sapphire substrates and the GaN epitaxial structure consists of an n-type GaN layer, multiple quantum wells (MQWs), and a p-type GaN layer. The crystal structure of GaN is shown: blue balls are Ga atoms and gray balls are nitrogen atoms; *a*, *b*, *c* represent the space coordinate direction. When annealing, GaN decomposes and releases ammonia under the hydrogen if the temperature is higher than 600 °C. Thus, a layer of Ga atoms will be exposed. The exposed Ga atoms can catalyze the growth of the graphenes films using methane as the carbon source.

4. Conclusions

In conclusion, we have demonstrated a direct synthesis of graphene on GaN by using CVD without an extra catalyst. Using methane as the carbon source, the transfer-free graphene film can be directly grown on GaN and under atmospheric pressure without other catalysts, which is confirmed by the distinct G peak and the 2D peak. Meanwhile, the effects of the growth temperature on the growth of graphene were also studied. The optimum growth temperature is 950 °C. After the growth of graphene, XRD and photoluminescence spectra indicate that the quality of gallium nitride substrate is not affected by the growth temperature and the sheet resistance of 5–6 layers of uniform graphene is 41.1 Ω/square. The growth model of the graphene film is given to explain the mechanisms of graphene growth on GaN. This method may be a suitable method for synthesis large-scale and high-quality graphene film for TCEs on GaN for optoelectronic devices.

References

[1] Chichibu S F, Uedono A, Onuma T, Haskell B A, Chakraborty A, Koyama T, Fini P T, Keller S, Denbaars S P, Speck J S, Mishra U K, Nakamura S, Yamaguchi S, Kamiyama S, Amano H, Akasaki I, Han J and Sota T 2006 *Nat. Mater.* **5** 810

[2] Nakamura S 1998 *Science* **281** 956

[3] Horng R H, Lin S T, Tsai Y L, Chu M T, Liao W Y, Wu M H, Lin R M and Lu Y C 2009 *IEEE Electron Dev. Lett.* **30** 724

[4] Mishra U K, Parikh P and Wu Y F 2002 *Proc. IEEE* **90** 1022

[5] Wang W L, Yang H C and Li G Q 2013 *J. Mater. Chem. C* **1** 4070

[6] Yam F K and Hassan Z 2008 *Superlattices and Microstructures* **43** 1

[7] Wu K, Wei T B, Lan D, Zheng H Y, Wang J X, Luo Y and Li J M 2014 *Chin. Phys. B* **23** 028504

[8] Ellmer K 2012 *Nat. Photonics* **6** 809

[9] Katsnelson M I 2007 *Mater. Today* **10** 20

[10] Kaner J K and Wa R B 2010 *Mater. Today* **3** 52

[11] Edwards R S and Coleman K S 2013 *Nanoscale* **5** 38

[12] Koh W S, Gan C H, Phua W K, Akimov Y A and Bai P 2014 *IEEE J. Sel. Top. Quantum Electron.* **20** 4000107

[13] Lee M S, Lee K, Kim S Y, Lee H, Park J, Choi K H, Kim H K, Kim D G, Lee D Y, Nam S and Park J U 2013 *Nano Lett.* **13** 2814

[14] Wang L C, Zhang Y Y, Li X, Liu Z Q, Guo E Q, Yi X Y, Wang J X, Zhu H W and Wang G H 2012 *Appl. Phys. Lett.* **101** 061102

[15] Zhang Y, Li X, Wang L, Yi X, Wu D, Zhu H and Wang G 2012 *Nanoscale* **4** 5852

[16] Zhang Y T, Dong X, Li G X, Li W C, Zhang B L and Du G T 2013 *J. Cryst. Growth* **366** 35

[17] Kuila T, Bose S, Mishra A K, Khanra P, Kim N H and Lee J H 2012 *Prog. Mater.* **57** 1061

[18] Bae S, Kim S J, Shin D, Ahn J H and Hong B H 2012 *Phys. Scr.* **T146** 014024

[19] Zhang Y Y, Wang L C, Li X, Yi X Y, Zhang N, Li J, Zhu H W and Wang G H 2012 *J. Appl. Phys.* **111** 114501

[20] Ferrari A C, Meyer J C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S and Geim A K 2006 *Phys. Rev. Lett.* **97** 187401

[21] Tao L, Qiu C Y, Yu F, Yang H C, Chen M J, Wang G and Sun L F 2013 *J. Phys. Chem. C* **117** 10079

[22] Qin M M, Ji W, Feng Y Y and Feng W 2014 *Chin. Phys. B* **23** 028103

[23] Calizo I, Bejenari I, Rahman M, Liu G X and Balandin A A 2009 *J. Appl. Phys.* **106** 043509

[24] Gao H, Song L, Guo W, Huang L, Yang D, Wang F, Zuo Y, Fan X, Liu Z, Gao W, Vajtai R, Hackenberg K and Ajayan P M 2012 *Carbon* **50** 4476

[25] Zhou H Q, Qiu C Y, Liu Z, Yang H C, Hu L J, Liu J, Yang H F, Gu C Z and Sun L F 2010 *J. Am. Chem. Soc.* **132** 944

[26] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 *Nano Lett.* **9** 30

[27] Chuo C C, Lee C M and Chyi J I 2001 *Appl. Phys. Lett.* **78** 314

[28] Chang S J 2012 *IEEE J. Sel. Top. Quantum Electron.* **8** 278
[29] Wang L, Zhang Y, Li X, Liu Z, Guo E, Yi X, Wang J, Zhu H and Wang G 2012 *J. Phys. D* **45** 505102
[30] Bae S, Kim H, Lee Y, Xu X and Park J S 2010 *Nat. Nano* **5** 574
[31] Furtado M and Jacob G 1983 *J. Cryst. Growth* **64** 257
[32] Ding G Q, Zhu Y, Wang S S, Gong Q, Sun L, Wu T R, Xie X M and Jiang M H 2013 *Carbon* **53** 321
[33] Nandamuri G, Roumimov S and Solanki R 2010 *Nanotechnology* **21** 145604