Controlled construction of nanostructures in graphene*

Li Zhong-Jun(李忠军), Li Qiang(李 强), Cheng Zeng-Guang(程增光),
Li Hong-Bian(李红变), and Fang Ying(方 英)†

National Center for Nanoscience and Technology, Beijing 100190, *China*

(Received 4 May 2013; revised manuscript received 5 August 2013; published online 10 December 2013)

We report on the laser-assisted fabrications of nanostructures in graphene membranes supported on polymer films. By using a laser beam to deposit heat locally, irradiated polymer instantaneously melts and vaporizes. During laser drilling of the polymer, the single-layer graphene membrane adheres to the polymer surface and consequently forms tens of nanometer deep wells. Due to the short time scale of laser irradiation, heat diffusion in the polymer is negligible, and the excitation energy is highly confined in the polymer. As a result, graphene nanowells of hundreds of nanometers in diameter can be patterned with high fidelity. With the increasing of nanowell density, we observe the spontaneous formation of nanowrinkles connecting pairs of nanowells in the graphene membranes. Importantly, Raman spectra confirm that no defects are introduced in graphene membranes by laser irradiation under our experimental conditions. Our results highlight the possibility to construct nanostructures and to design novel devices based on graphene.

Keywords: graphene, nanowrinkles, laser ablation, polymer drilling

PACS: 81.05.ue, 61.48.Gh **DOI:** 10.1088/1674-1056/23/2/028102

1. Introduction

Graphene is a single-layer honeycomb crystal of densely packed carbon atoms.[1] It exhibits unique electrical, thermal, and mechanical properties,[2–5] and inspires a variety of applications.[6–12] In particular, graphene-based nanoelectronics has been attracting tremendous attention due to its high carrier mobility.[13,14] Unfortunately, graphene is a zero-gap semiconductor whose conduction and valence bands touch at the Dirac point. Thus, graphene field effect transistor (FET) cannot be turned off due to the absence of a bandgap, which results in a low current on/off ratio and poses serious obstacles towards further applications of graphene FET. To solve this problem, a number of theoretical and experimental investigations have been carried out to open a band-gap in graphene. For example, plasma assisted oxidation was applied to pattern graphene nano-dots and nano-ribbons. Geometrical quantum confinement in these nanostructures was shown to create a band-gap up to a few hundred meV in graphene.[15–17] However, plasma-assisted oxidation is prone to induce edge-disorders and edge-defects in graphene,[15,18] and thus this method seriously degrades the carrier mobility in graphene.[19] Recently, anisotropic etching of graphene by hydrogen plasma was successfully demonstrated to create graphene nano-ribbons with zigzag edges (Z-GNRs), and the values of carrier mobility of FETs fabricated on Z-GNRs were in a range from ~ 3500 cm$^2\cdot$V$^{-1}\cdot$s^{-1} to ~ 1000 cm$^2\cdot$V$^{-1}\cdot$s^{-1}. However, the Z-GNR FET exhibited a quasi-metallic transport behavior with a low on/off ratio of ~ 3 at room temperature.[20] Therefore, there is still a need to open a band-gap with little/no degradation of the crystalline structure of graphene.

The single-layer nature of the graphene membrane makes it amenable to external deformation, offering the possibility to manipulate graphene's geometry and physical properties by strain forces. Consequently, methods based on strain engineering have been proposed to modulate the electronic properties of graphene.[21–25] For example, strain was proven to induce the shift of the Dirac point in graphene and a band-gap can be introduced by creating a pseudo-magnetic field in graphene.[23,25–28] When a strain with triangular symmetry was introduced, the resulting periodic pseudo-magnetic field with triangular symmetry could lead to a Landau-level-like energy spectrum with multiple energy gaps in graphene.[25] Recently, a pseudo-magnetic field was measured to be above 300 T in graphene nano-bubbles formed by strain.[29] In addition, wrinkles in graphene membranes have been proposed to effectively modulate the electronic properties of graphene by changing local potential and inducing effective magnetic field,[21,29,30] which, for example, can be applied to band-gap engineering in graphene.[30] On the other hand, some new physical phenomena have been observed in wrinkled graphene, and novel wrinkle-based nano-systems could be built up.[31–33] For example, the wrinkled graphene membrane has recently been shown to be a good candidate for field emitters and thermal motors.[33,34] Until now, several efforts have been made to construct nanowrinkles in graphene membranes.[35–38] For example, a previous study induced tension forces in suspended graphene by thermal effects, and periodic wrinkles were formed in the direction parallel to the

*Project supported by the National Natural Science Foundation of China (Grant Nos. 21173055 and 21161120321).
†Corresponding author. E-mail: fangy@nanoctr.cn
© 2014 Chinese Physical Society and IOP Publishing Ltd

tension force.[37] The amplitudes of the wrinkles were in a range from 0.7 nm to 30 nm and the wavelengths were from 370 nm to 5 μm. Our previous study investigated thermally induced structure changes of graphene membranes supported on polymer substrates.[38] Strain forces were induced due to the mismatch in thermal expansion coefficients between the polymer and graphene. We found that the movements of polymer chains at elevated temperatures could assist the dynamical behaviors of graphene on the polymer surface, which resulted in the formation of nanometer-scale wrinkles at graphene edges. Besides this, a systematic study was recently conducted on the wrinkling of graphene supported on SiO_2/Si substrate with randomly distributed SiO_2 nanoparticles.[39] After being annealed, single-layer graphene was found to adhere to the substrate at low nanoparticle density, except for regions near the SiO_2 nanoparticles. As the nanoparticle density was increased, nanowrinkles in the graphene membranes were gradually formed between two nanoparticles. However, it should be noted that all the methods mentioned above lack precise position control of graphene nanostructures, and practical methods to introduce local strain forces at defined positions in graphene membranes are still lacking. Here, we report on the controlled construction of nanowells and nanowrinkles in graphene membranes supported on polymer. A laser is able to heat local regions effectively because of its focused nature and high energy. Therefore, we utilize a focused laser beam to ablate the polymer at defined positions. Subsequent atomic force microscopy (AFM) studies show that after polymer ablation, single-layer graphene membranes adhere to the underlying polymer and form wells of tens of nanometers in depth and hundreds of nanometers in diameter. Both positions and sizes of the nanowells can be well-defined by laser irradiation. Moreover, at increased nanowell density, nanowrinkles are formed spontaneously to connect neighboring nanowells in the graphene membranes, therefore the positions of the nanowrinkles are also defined between the nanowells.

2. Experiments

A 230-nm thick polystyrene (PS, molecular weight, 200 K∼300 K) layer was spin-coated on a silicon wafer. The thickness of the PS layer was set at such a value that the contrast of single-layer graphene on it is maximized (Fig. 1(a)). The sample was then baked at 180 °C for 30 min to completely remove the solvent toluene. Graphene flakes were then deposited on the top of the polymer substrate by mechanical exfoliation of natural graphite. The sample was then placed under a micro-Raman microscope equipped with a high precision motorized XY stage (Renishaw inVia Raman spectroscope). A focused laser beam (514 nm) of the Raman spectroscope was used to ablate the polymer at defined locations. The laser beam was focused with a 100 X objective lens (N.A. = 0.90) and the corresponding laser spot was about 1.0 micrometer in size. We note that in typical Raman spectrum characterization, in order to avoid thermal effects, the laser density is generally set at no more than 10%, while the corresponding laser power is less than 1 mW. However, in our study, in order to transfer enough heat to the polymer substrate, the laser was set at a 50% density, and the corresponding laser power was measured to be about 4.5 mW. Single-layer graphene was irradiated for 72 s, while few-layer graphene was irradiated for 92 s. The distances between the irradiated spots were controlled by the XY stage with a sub-micrometer resolution, and the values of the distances were varied from hundreds of nanometers to several micrometers. We then carried out AFM (Dimension 3100 Veeco) measurements on the laser-irradiated samples to illustrate the structure changes of graphene membranes. AFM measurements were performed in tapping mode with a silicon tapping tip under ambient conditions.

3. Results and discussion

Typical optical images of single-layer and few-layer graphene membranes before and after laser irradiation were shown in Figs. 1(a) and 1(b), respectively. A series of bright yellow spots can be identified in the laser-irradiated areas. We first compare the Raman spectra[40,41] recorded at the same position of the single-layer graphene membranes with 10% laser density and 50% laser density (Fig. 1(c)). The survival of the graphene flake after polymer ablation can be confirmed by the G and 2D bands in Raman spectra in Fig. 1(c).[42] The increased laser density leads to a red-shift of the G band, which indicates a rise in the local temperature of graphene at a higher laser density.[5] The increased Raman baseline intensity at 50% laser density may be caused by a fluorescence effect after polymer ablation.[43] Small molecules are produced by the decomposition of PS during laser irradiation,[44] which causes a fluorescence effect in the Raman spectrum. Importantly, the integrity of the graphene crystalline structure was supported by the absence of the D band around 1350 cm^{-1}, since the D band is generally observed in defects and disorder regions of graphene.[45] These results demonstrate that the laser irradiation does not result in any damage to the crystalline structure of graphene under our experimental conditions.

AFM measurements were further carried out to illustrate the details of laser-irradiated areas in single-layer and few-layer graphene. As shown by AFM topographic images in Figs. 2(a) and 2(b), shallow nanowells were formed in single-layer and few-layer graphene after laser irradiation. The corresponding AFM height profiles (Figs. 2(c) and 2(d)) confirm that the nanowells are about ten nanometers in depth and several hundred nanometers in diameter. As mentioned above, the nanowells were formed due to the ablation of PS during laser irradiation, and the top graphene membranes adhere tightly

to the polymer substrate by van der Waals interactions. It should be noted that the edges of the nanowells are quite sharp (Fig. 2(a)), which indicates that the excitation energy by laser is highly confined and heat diffusion in the polymer is negligible. Importantly, the laser beam can be positioned by the XY stage with a submicrometer resolution, and therefore, the positions of the nanowells in graphene membranes are precisely determined in our study. Moreover, the sizes of the nanowells can also be controlled via changing the irradiation time (Fig. 2(b)).

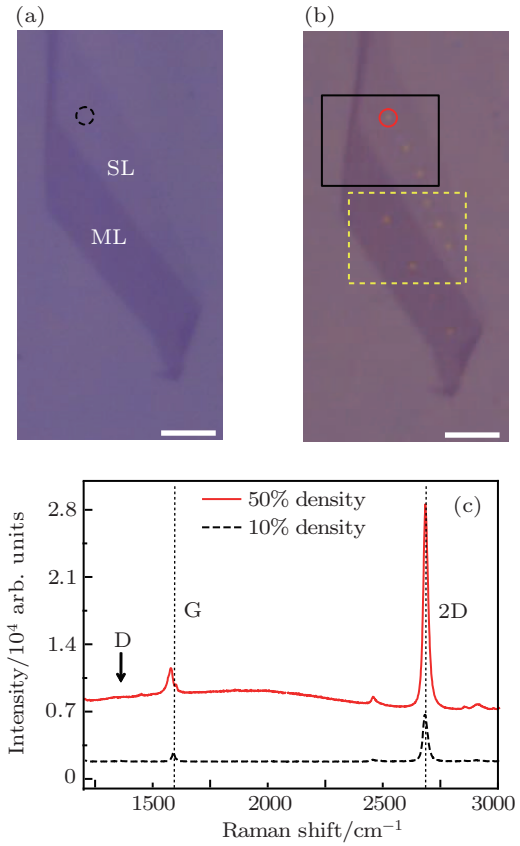


Fig. 1. (color online) (a) Optical image of graphene on PS substrate before laser irradiation. Single-layer and few-layer graphene of the sample are indicated with SL and FL. (b) Optical image of the same graphene sample after laser irradiation with a 50% density. The laser-irradiated spots can be identified as bright spots in single-layer and few-layer graphene. Scale bars in panels (a) and (b) are both 5 μm. (c) Raman spectra recorded in the laser-irradiated single-layer graphene with laser densities of 10% (dashed curve) and 50% (solid curve). The total time for the collection of a typical Raman spectrum of single-layer graphene is 72 s. The spectra are offset for clarity, and the positions of G band and 2D band are indicated with vertical dashed lines.

Wrinkles (indicated with dashed line) with heights of ∼ 1.5 nm are sometimes observed around the nanowells in single-layer graphene after irradiation (Fig. 2(b)). The phenomenon indicates that the surrounding graphene of a nanowell is under strain after irradiation. As mentioned above, graphene adheres tightly to the ablated PS substrate to form nanowells. As a result, the sagged graphene nanowells will generate stretching strains in the flat surrounding regions due to the elasticity of graphene.[39,46] It has been reported that a material under strain is inclined to generate out-of-plane deformation (bending) other than in-plane deformation (stretching), as its thickness is reduced.[39,47] Graphene is the thinnest two-dimensional material, and the sp^2 carbon bond of graphene exhibits an inextensible but bendable nature.[48] Therefore, to release the in-plane elastic stretching strains in the surrounding regions, the graphene membrane may wrinkle through out-of-plane buckling. In this study, the nanowrinkles are only deposited around the nanowells, other than in other regions, indicating that the positions of nanowrinkles could be determined by the nanowells.

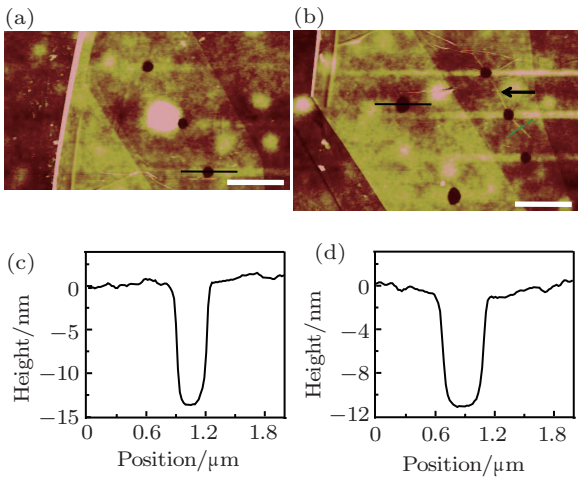


Fig. 2. (color online) (a) and (b) AFM height images of selected areas indicated with solid line box and dashed line box, respectively, in Fig. 1(b). (c) and (d) The corresponding height profiles of the black lines in panels (a) and (b), the respectively. Scale bars are both 2 μm in panels (a) and (b).

Moreover, as indicated by an arrow in Fig. 2(b), one of the nanowrinkles even connects two neighboring nanowells. Herein we suggest that with the further careful design of the nanowell density, nanowrinkles may be constructed with high fidelity to connect neighboring nanowells in graphene. We then construct nanowells with various distances in the single-layer graphene membrane (bright spot arrays in Fig. 3(b)). The distances between every two neighboring nanowells range from several hundred nanometers to several micrometers, and the nanowell density increases as the distance decreases. As evidenced in Fig. 3(c), no connective nanowrinkle can be detected between any two neighboring nanowells when the distance was set as 2 μm. It indicates that there is a critical nanowell density for the successful construction of connective nanowrinkles between nanowells, because the stretching strains induced by the nanowells are localized. Therefore, if the nanowells are deposited too far from each other, it is not possible to create connective nanowrinkles between the nanowells. When the distances between the nanowells decrease (the nanowell density increases correspondingly), nanowrinkles may be constructed between every two neighboring nanowells to connect them, and a network of nanow-

ells and nanowrinkles can be formed. As shown in Fig. 3(d), nanowrinkles (as indicated with arrows) spontaneously form in the graphene membrane when the distances between every two neighboring nanowells decrease to less than 1.5 μm. However, it should be noted that some nanowells are still not connected by the nanowrinkles in this image. Here, we anticipate that the distribution of the stretching strains generated by the sagged nanowells is inhomogeneous around the nanowells in graphene membrane. Therefore, some surrounding areas of the nanowells are not strained efficiently to induce the wrinkling of graphene in these areas.

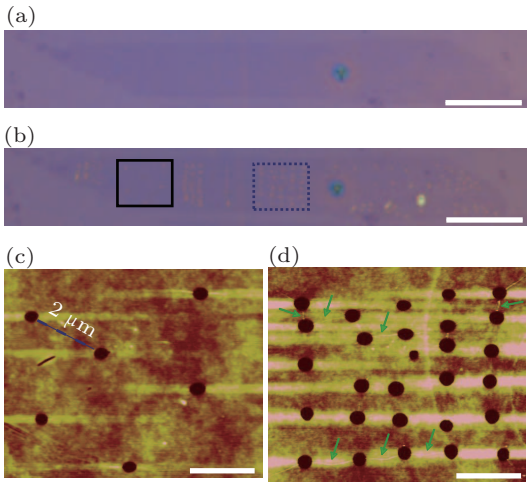


Fig. 3. (color online) Optical images of graphene on PS substrate before (a) and after (b) irradiation, with scale bars being both 10 μm. (c) and (d) Selected AFM images of graphene areas marked with solid line and dashed line boxes in panel (b), with scale bars being both 2 μm.

Therefore, besides the careful design of the nanowell density, it is also necessary to confine the stretching strains to improve the productivity of nanowrinkles in graphene membranes. Here, as shown in Figs. 4(a) and 4(b), we construct separated nanowells along the longitudinal direction of a narrow graphene ribbon. We suggest that, owing to the high length/width ratio of the graphene ribbon, the stretching strains induced by the nanowells will be mainly placed along the longitudinal direction of graphene ribbon in the narrow graphene ribbon. As a result, nanowrinkles will be generated in the ribbon with high fidelity if the nanowells are deposited closely enough. As evidenced in Figs. 4(c) and 4(d), it is apparent that nanowrinkles are successfully constructed between any two neighboring nanowells. Besides this, the lengths of the nanowrinkles are smaller than 1.5 μm and the numbers of nanowrinkles between every two neighboring nanowells are less than 3. As shown in Fig. 4(e), the heights of the nanowrinkles are around 1.5 nm and the widths are around 30 nm. Therefore, a network of nanowells and nanowrinkles is reliably constructed in the graphene ribbon. The nanowells and nanowrinkles will change the electron-hopping amplitude between carbon atoms, which is expected to affect the band-gap, wave-function, and Fermi-velocity in graphene. The isolated nanowell or nanowrinkle acts as a random scattering center and our well-controlled method offers a good opportunity to construct the strained superlattices and thus realize a significant transport gap in graphene.

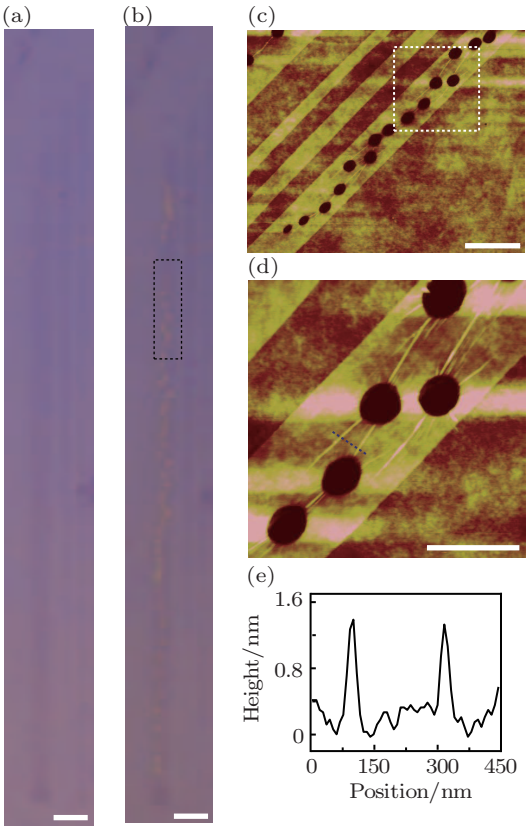


Fig. 4. (color online) Optical images of graphene ribbon on PS substrate before (a) and after (b) irradiation, with scale bars being both 2.5 μm. (c) Selected AFM images of the irradiated area marked with dashed box in panel (b), with scale bar being 2 μm. (d) Zoom-in analysis of the area marked with white dashed box in panel (c), with scaled bar being 1 μm. (e) Height profile of the dashed line marked in panel (d).

4. Conclusions

In the present paper, we demonstrated laser-assisted construction of nanostructures in graphene membranes supported on PS substrates. Detailed analyses show that the PS polymer in laser irradiated areas is ablated by heat. Because the graphene membrane adheres strongly to the polymer substrate, nanowells form with sharp edges in the graphene membranes. At an increased nanowell density, nanowrinkles spontaneously form in graphene membranes to connect two neighboring nanowells. Importantly, both the positions and the sizes of the nanowells can be precisely defined by the laser beam, and consequently the positions of the nanowrinkles can also be defined. Thus, we demonstrate the first study of controlled fabrication of nanowells, nanowrinkles, and their networks in graphene. Moreover, Raman spectra demonstrated that the laser ablation under our experimental conditions causes no damage to the integrity of graphene membranes. Our method

represents a novel approach to fabricating the diverse nanostructures that are based on graphene.

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666

[2] Du X, Skachko I, Barker A and Andrei E Y 2008 *Nat. Nanotechnol.* **3** 491

[3] Miller D L, Kubista K D, Rutter G M, Ruan M, de Heer W A, First P N and Stroscio J A 2009 *Science* **324** 924

[4] Lee C, Wei X D, Kysar J W and Hone J 2008 *Science* **321** 385

[5] Balandin A A, Ghosh S, Bao W Z, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 *Nano Lett.* **8** 902

[6] Ramanathan T, Abdala A A, Stankovich S, Dikin D A, Herrera-Alonso M, Piner R D, Adamson D H, Schniepp H C, Chen X, Ruoff R S, Nguyen S T, Aksay I A, Prud'homme R K and Brinson L C 2008 *Nat. Nanotechnol.* **3** 327

[7] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 *Nature* **442** 282

[8] Wang X, Zhi L J and Mullen K 2008 *Nano Lett.* **8** 323

[9] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y and Hong B H 2009 *Nature* **457** 706

[10] Zhao J, Zhang G Y and Shi D X 2013 *Chin. Phys. B* **22** 057701

[11] Ouyang F P, Peng S L, Zhang H, Weng L B and Xu H 2011 *Chin. Phys. B* **20** 058504

[12] Li P J, Chen K, Chen Y F, Wang Z G, Hao X, Liu J B, He J R and Zhang W L 2012 *Chin. Phys. B* **21** 118101

[13] Cheng Z G, Li Q, Li Z J, Zhou Q Y and Fang Y 2010 *Nano Lett.* **10** 1864

[14] Dean C R, Young A F, Meric I, Lee C, Wang L, Sorgenfrei S, Watanabe K, Taniguchi T, Kim P, Shepard K L and Hone J 2010 *Nat. Nanotechnol.* **5** 722

[15] Jiao L Y, Zhang L, Wang X R, Diankov G and Dai H J 2009 *Nature* **458** 877

[16] Son Y W, Cohen M L and Louie S G 2006 *Phys. Rev. Lett.* **97** 216803

[17] Ponomarenko L A, Schedin F, Katsnelson M I, Yang R, Hill E W, Novoselov K S and Geim A K 2008 *Science* **320** 356

[18] Sols F, Guinea F and Neto A H C 2007 *Phys. Rev. Lett.* **99** 166803

[19] Mucciolo E R, Neto A H C and Lewenkopf C H 2009 *Phys. Rev. B* **79** 075407

[20] Shi Z W, Yang R, Zhang L C, Wang Y, Liu D H, Shi D X, Wang E G and Zhang G Y 2011 *Adv. Mater.* **23** 3061

[21] Pereira V M and Neto A H C 2009 *Phys. Rev. Lett.* **103** 046801

[22] Sun J T, Du S X, Xiao W D, Hu H, Zhang Y Y, Li G and Gao H J 2009 *Chin. Phys. B* **18** 3008

[23] Yang H T 2011 *J. Phys.: Condens. Matter* **23** 505502

[24] Yang M, Cui Y, Wang R Q and Zhao H B 2012 *J. Appl. Phys.* **112** 073710

[25] Guinea F, Katsnelson M I and Geim A K 2010 *Nat. Phys.* **6** 30

[26] Morozov S V, Novoselov K S, Katsnelson M I, Schedin F, Ponomarenko L A, Jiang D and Geim A K 2006 *Phys. Rev. Lett.* **97** 016801

[27] Neto A H C, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 *Rev. Mod. Phys.* **81** 109

[28] Gui G, Li J and Zhong J X 2008 *Phys. Rev. B* **78** 075435

[29] Levy N, Burke S A, Meaker K L, Panlasigui M, Zettl A, Guinea F, Neto A H C and Crommie M F 2010 *Science* **329** 544

[30] Xu K, Cao P and Heath J R 2009 *Nano Lett.* **9** 4446

[31] Wang Y, Yang R, Shi Z W, Zhang L C, Shi D X, Wang E G and Zhang G Y 2011 *ACS Nano* **5** 3645

[32] Zhu W, Low T, Perebeinos V, Bol A A, Zhu Y, Yan H, Tersoff J and Avouris P 2012 *Nano Lett.* **12** 3431

[33] Guo Y F and Guo W L 2013 *J. Phys. Chem. C* **117** 692

[34] Guo Y F and Guo W L 2013 *Nanoscale* **5** 318

[35] Pereira V M, Neto A H C and Peres N M R 2009 *Phys. Rev. B* **80** 045401

[36] Ni Z H, Yu T, Lu Y H, Wang Y Y, Feng Y P and Shen Z X 2008 *ACS Nano* **2** 2301

[37] Bao W Z, Miao F, Chen Z, Zhang H, Jang W Y, Dames C and Lau C N 2009 *Nat. Nanotechnol.* **4** 562

[38] Li Z J, Cheng Z G, Wang R, Li Q and Fang Y 2009 *Nano Lett.* **9** 3599

[39] Yamamoto M, Pierre-Louis O, Huang J, Fuhrer M S, Einstein T L and Cullen W G 2012 *Phys. Rev. X* **2** 041018

[40] 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

[41] Wang D C, Zhang Y M, Zhang Y M, Lei T M, Guo H, Wang Y H, Tang X Y and Wang H 2011 *Chin. Phys. B* **20** 128101

[42] Das A P S, Chakraborty B, Piscanec S, Saha S K, Waghmare U V, Novoselov K S, Krishnamurthy H R, Geim A K, Ferrari A C and Sood A K 2008 *Nat. Nanotechnol.* **3** 210

[43] Matousek P, Towrie M and Parker A W 2002 *J. Raman Spectrosc.* **33** 238

[44] Gurman J L, Baier L and Levin B C 1987 *Fire Mater.* **11** 109

[45] Jorio A, Ferreira E H M, Moutinho M V O, Stavale F, Achete C A and Capaz R B 2010 *Phys. Status Solidi B* **247** 2980

[46] Lobkovsky A, Gentges S, Li H, Morse D and Witten T A 1995 *Science* **270** 1482

[47] Bowden N, Brittain S, Evans A G, Hutchinson J W and Whitesides G M 1998 *Nature* **393** 146

[48] Huang Y, Wu J and Hwang K C 2006 *Phys. Rev. B* **74** 245413