

Direct growth of graphene on SiC(0001) by KrF-excimer-laser irradiation

Masakazu Hattori,^{1,a)} Hiroshi Ikenoue,^{1,a)} Daisuke Nakamura,¹ Kazuaki Furukawa,² Makoto Takamura,² Hiroki Hibino,^{2,3} and Tatsuo Okada¹

¹*Department of Electrical Engineering, Graduate School of Information Science and Electrical Engineering, Kyushu University, 744 Motoooka, Fukuoka 819-0395, Japan*

²*NTT Basic Research Labs., 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan*

³*Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan*

(Received 3 January 2016; accepted 20 February 2016; published online 2 March 2016)

In this report, we propose a direct patterning method of graphene on the SiC(0001) surface by KrF-excimer-laser irradiation. In this method, Si atoms are locally sublimated from the SiC surface in the laser-irradiated area, and direct graphene growth is induced by the rearrangement of surplus carbon on the SiC surface. Using Raman microscopy, we demonstrated the formation of graphene by laser irradiation and observed the growth process by transmission electron microscopy and conductive atomic force microscopy. When SiC was irradiated by 5000 shots of the laser beam with a fluence of 1.2 J/cm^2 , two layers of graphene were synthesized on the SiC(0001) surface. The number of graphene layers increased from 2 to 5–7 with an increase in the number of laser shots. Based on the results of conductive-atomic force microscopy measurements, we conclude that graphene formation was initiated from the step area, after which the graphene grew towards the terrace area by further Si evaporation and C recombination with increasing laser irradiation. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943142>]

Graphene is a two-dimensional allotrope of carbon that has a ultrahigh electron mobility, an excellent electrical and thermal conductivity, optical transparency, and a gapless band structure.^{1–3} Because of these unique characteristics, graphene is expected to be an important material in next-generation optoelectronic devices.^{4–6} A number of processes such as mechanical exfoliation,⁷ chemical vapor deposition (CVD),⁸ and thermal evaporation of SiC have already been developed for graphene fabrication.^{9,10} CVD is generally the most popular technique because of its ability to fabricate high-quality graphene over a large area, but it requires a catalytic metal film for graphene growth, conventional transfer to insulating substrates, and lithography processes. These processes can contaminate and mechanically damage the graphene. In this work, we propose a method of graphene growth on SiC(0001) surfaces using KrF-excimer-laser irradiation. This is based on the premise that localized laser heating of the SiC(0001) surface will result in a rapid increase in temperature and sublimation of Si, inducing graphene growth through a rearrangement of surplus carbon. This method eliminates the need for a metal catalyst, thereby allowing graphene to be formed directly on an insulating substrate without the lower performance associated with the conventional transfer process. Furthermore, in this method, graphene is produced only at a laser-irradiated area on the SiC substrate. In other words, because graphene synthesis and graphene patterning can be completed simultaneously, the loss in performance associated with lithography processes is also eliminated. In addition, our method was used to demonstrate the formation of a line-and-space (L&S) graphene pattern.

Localized heating of the SiC(0001) substrates used in this study was achieved in a stainless steel vacuum chamber evacuated to a base pressure of 10^{-4} Pa with a turbomolecular pump. After piranha etching and HF etching, the SiC(0001) substrate was loaded into the vacuum chamber. A KrF-excimer-laser (wavelength: 248 nm, pulse duration: 55 ns, and repetition rate: 100 Hz) from Gigaphoton, Inc., Japan, was used. The ambient gas was Ar, the partial pressure of which was kept at 500 Pa during the experiment. The laser beam was focused onto the SiC(0001) surface, and the shape of the irradiated area was controlled by an x–y slit to obtain a uniform fluence. L&S graphene patterning was achieved through step-and-repeat scanning and irradiation, during which the substrate was moved using a motorized stage. The properties of the laser-irradiated area were analyzed by Raman microscopy, Auger electron spectroscopy (AES), and high-resolution transmission electron microscopy (HR-TEM); the surface morphology was also surveyed using atomic force microscopy (AFM) and conductive AFM.

Figure 1(a) shows the Raman spectrum of the SiC(0001) surface after 3000 shots, 10 000 shots, and 20 000 shots of laser irradiation at 1.2 J/cm^2 . These spectra were calculated by subtracting the spectrum of the SiC(0001) surface from each of the spectra of the laser-irradiated area. The 2D peak (at $\sim 2700 \text{ cm}^{-1}$) and G peak (at $\sim 1580 \text{ cm}^{-1}$) can be clearly observed in these spectra, confirming the presence of the sp^2 bonds of graphene^{11–13} and the sublimation of Si-induced graphene growth through a rearrangement of surplus carbon atoms. We surveyed the dependence of the G and 2D peak intensities on the number of laser shots. Almost no increase was observed when the number of shots was less than 5000, which indicates that hardly any graphene was synthesized under these conditions. A rapid increase in the intensity of both peaks was clearly observed at more than 5000 shots, which indicates that the sp^2 bonds of graphene began to

^{a)} Authors to whom correspondence should be addressed. Electronic addresses: hattori@laserlab.ees.kyushu-u.ac.jp and ikenoue@ees.kyushu-u.ac.jp.

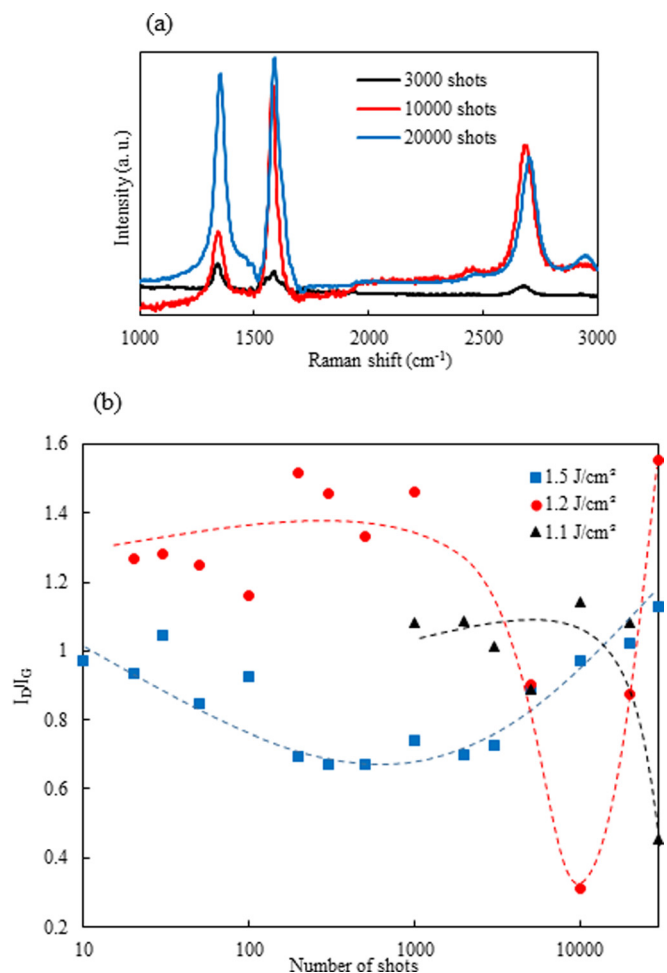


FIG. 1. (a) Raman spectrum of laser-irradiated area (1.2 J/cm², 10 000 and 20 000 shots). (b) Dependence of I_D/I_G ratio on the number of laser pulses (shots).

form. The D peak (at $\sim 1350\text{ cm}^{-1}$) is also visible in the spectrum, indicating that there were some defects in the graphene. The ratio of the intensity of this D peak to the G peak (I_D/I_G) provides an indication of the number of defects, and it was also used to estimate the grain size¹⁴ of 61.3 nm ($I_D/I_G = 0.31$) after 10 000 shots of laser irradiation. In the spectrum obtained after 20 000 shots of laser irradiation, I_D/I_G is clearly reduced, suggesting that the quality of graphene varied with the condition of laser irradiation. Figure 1(b) shows the dependence of I_D/I_G on the number of shots at different fluences. The ratio gradually decreased and increased again with increasing number of laser shots when the fluence was 1.5 J/cm²; the minimum ratio was about 0.7 at 500 shots. On the other hand, it showed a rapid change at lower fluences of

1.2 and 1.1 J/cm², and the minimum ratio was less than 0.5. In addition, the number of shots required to minimize the ratio increased with decreasing laser fluence. Figure 2 shows the cross-sectional TEM images of the laser-irradiated SiC substrate at several fluences. Figure 2(a) shows the multilayered graphene formed in an area irradiated with 200 shots at a laser fluence of 1.5 J/cm²; Figure 2(b) shows the graphene formed in the area irradiated with 5000 shots at a laser fluence of 1.2 J/cm², revealing two uniform layers of graphene as a dark line contrast. When the number of shots was increased to 10 000 shots at the same laser fluence of 1.2 J/cm², 5–7 layers of graphene were synthesized on the SiC(0001) surface, as shown in Fig. 2(c). We thus conclude that laser irradiation with a higher number of laser shots increased the number of graphene layers by increasing the amount of surplus carbon on the SiC(0001) surface.

Figure 3 shows the dependence of the surface concentration of C, Si, and O on the number of laser shots measured in the area irradiated with a laser fluence of 1.2 J/cm². The atomic concentration was calculated from the peak intensity of the micro-AES spectra. The presence of oxygen indicates that SiC was oxidized on the surface. Figure 3 reveals a decline of C concentration between 1000 and 5000 shots, indicating that the surface contamination was eliminated by laser irradiation. The carbon KLL (CKLL) AES spectra reveal a downward shift in the peak position of impure carbon between 5000 and 20 000 shots, which is consistent with the formation of graphene.¹⁵ After more than 20 000 shots, however, the increase in C concentration is indicative of the segregation of excess C.

Taking all of these results into consideration, it would appear that the surface contamination, comprising mainly carbon from the surrounding atmosphere, probably prevented graphene formation. This contamination was eliminated once the number of shots exceeded 5000, resulting in an increasing number of graphene layers being formed as the number of shots was increased. The C concentration that resulted from the laser irradiation between 5000 and 20 000 shots was suitable for graphene formation. With excessive laser irradiation, however, the crystallinity of the graphene layers became poor because of excess C. The condition of graphene was not varied by increasing the frequency of laser irradiation from 100 to 1000 Hz. Therefore, we can neglect the effect of heat accumulation resulting from laser irradiation on the SiC substrate.

Figure 4 shows the Raman spectrum obtained from the L&S patterned area created on the SiC(0001) substrate with 5000 shots of irradiation at a fluence of 1.2 J/cm². The

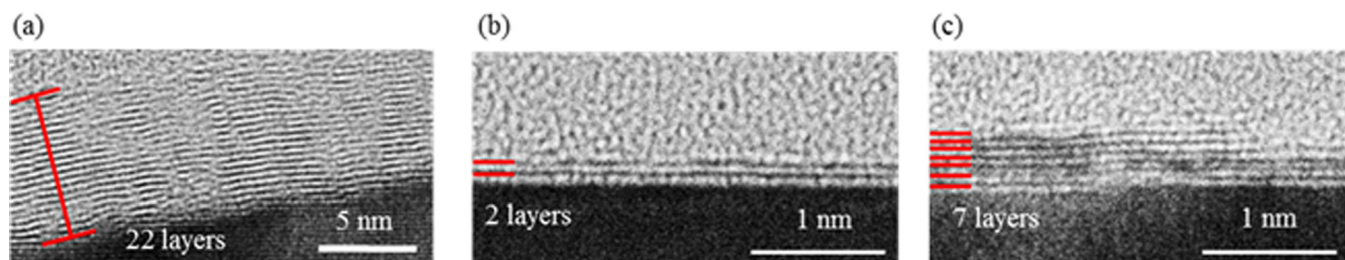


FIG. 2. TEM images of graphene formed with (a) 1.5 J/cm² and 200 shots, (b) 1.2 J/cm² and 5000 shots, and (c) 1.2 J/cm² and 10 000 shots of laser irradiation.

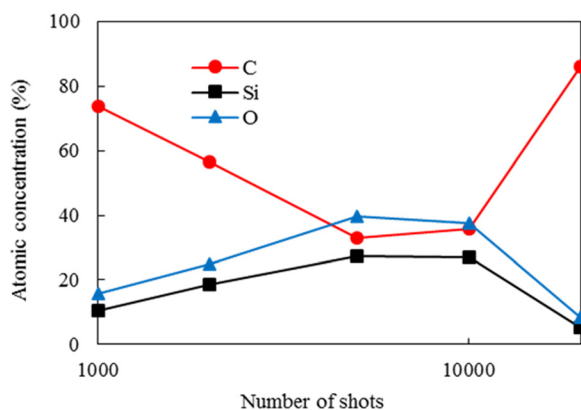


FIG. 3. Dependence of surface atomic concentration on the number of laser shots.

accompanying 2D peak intensity map clearly shows the regions in which graphene was formed by KrF-excimer-laser irradiation.

The surface morphology of the area irradiated with 5000 shots at a fluence of 1.2 J/cm^2 was studied by AFM. We used n-type SiC(0001) with a 4° cut-off because the substrate should be conductive for observation of the current image. Initially, the substrate had a (11 $\bar{2}$ n)-faced step area and a (0001)-faced terrace area.¹⁶ The ablated area on the SiC(0001) substrate surface was about $5 \mu\text{m}$ in width, and it was eroded to a depth of about 20 nm, while its original step-and-terrace structure was preserved. According to this result, the ablation rate was calculated to be 0.004 nm/shot , which reveals that the laser fluence was set at the threshold energy of SiC evaporation. Under this condition, carbon contamination could be removed without irradiation damage of the SiC surface. The current signal from the same region was observed using conductive AFM (sample voltage: -0.3 V), and a current signal of about 15 pA was obtained in an area that was $4 \mu\text{m}$ wide. From the Raman map of the 2D peak intensity, it was concluded that this signal represents an area of graphene formation. In our laser irradiation setup, we could achieve patterning at a width of approximately $1 \mu\text{m}$ by using a KrF-excimer-laser. Therefore, we obtained the $4\text{-}\mu\text{m}$ width of graphene patterning against the $5\text{-}\mu\text{m}$ width of the ablation region. A narrower area, consisting of aggregates of graphene measuring 20–30 nm in size, was also observed (Fig. 5(a)). The size of these current spots agrees with the grain size estimated from the Raman spectrum, and the spots are

thus believed to represent individual graphene grains. Figure 5(b) shows a conductive AFM image obtained using the same fluence but with 3000 shots of laser irradiation. A comparison of Figs. 5(a) and 5(b) shows that the area of graphene increased with laser irradiation. Furthermore, aggregates of graphene were formed at intervals of 150 nm under both irradiation conditions. The surface morphology determined from AFM measurements revealed that the original SiC(0001) substrate with 4° cut-off had a step-and-terrace structure at intervals of 150 nm. Given this result, we think that the graphene growth area corresponded with the step-and-terrace structure of SiC(0001). Figures 5(c) and 5(d) show the profiles along the A–B line in Figs. 5(a) and 5(b). After 5000 shots of the laser beam, the current signal was detected from both step and terrace areas. With 3000 shots of irradiation, however, the current signal of graphene was only detected from the step area. Based on all of these results, we conclude that graphene formation after Si evaporation was initiated from the step area, after which the graphene grew towards the terrace area by further Si evaporation and C recombination with increasing laser irradiation.

In conclusion, layers of graphene were formed on SiC(0001) by KrF-excimer-laser irradiation. The number of graphene layers increased from 2 to 5–7 with an increase in the number of laser shots, which was clearly confirmed by TEM observations together with Raman spectroscopy. The graphene contains some defects and the grain size was smaller than the graphene fabricated through general CVD and SiC evaporation methods. Carbon contamination on SiC(0001) surface was assumed to be the reason for preventing graphene formation. Therefore, we can fabricate graphene with less laser irradiation under more appropriate conditions by eliminating surface contamination. As such, we suggest surface cleaning methods such as flash annealing to improve graphene crystallinity. Furthermore, from the results of conductive AFM measurement, we believe that the terrace length of SiC(0001) affects graphene grain size in our methods. Therefore, crystallinity may be improved by using a lower off cut semi-insulating SiC(0001) substrate with a wide terrace.¹⁷

It was found that the graphene began to grow rapidly after a certain number of laser shots. The growth mechanism is understood as follows: the elimination of the surface contamination proceeded at the initial stage; thereafter, graphene was formed on the terrace of the SiC(0001) surface.

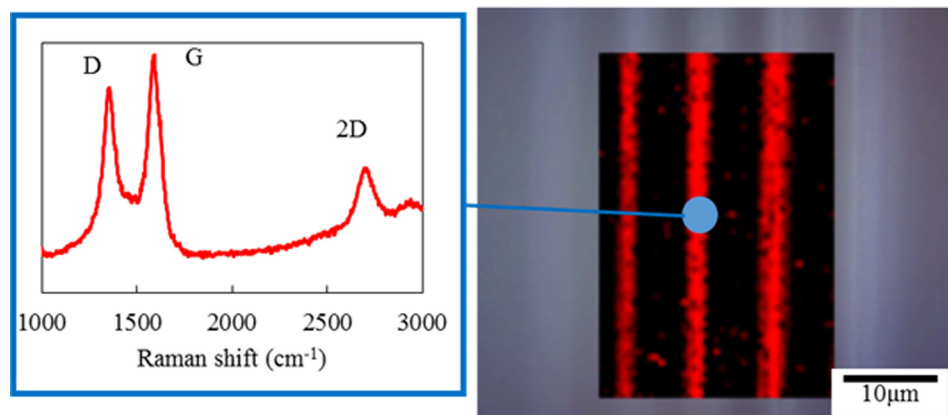


FIG. 4. Raman spectrum and map of the 2D peak intensity.

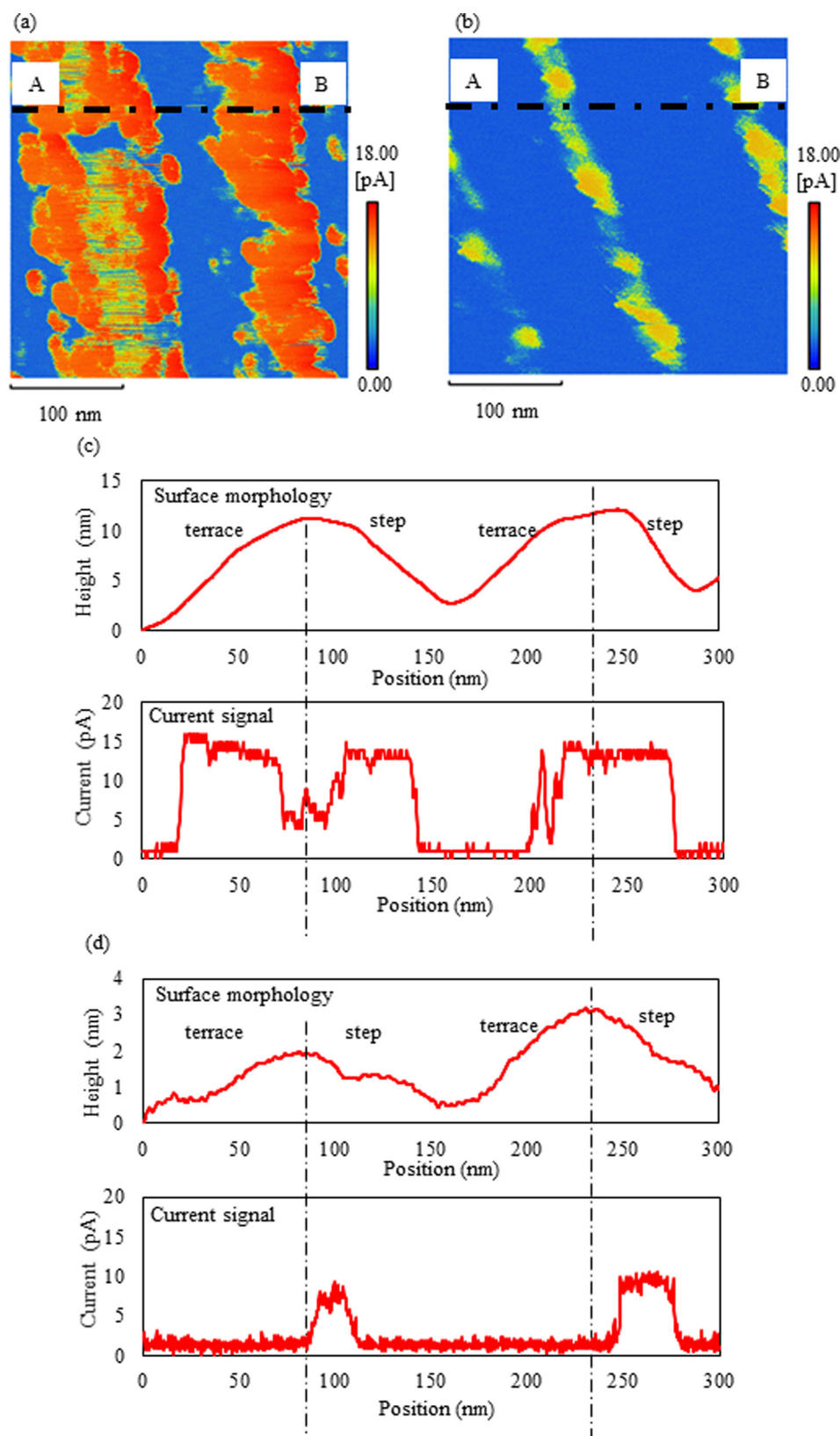


FIG. 5. Conductive AFM image of an area irradiated with (a) 5000 shots (sample voltage: -0.3 V vs. grounded cantilever) and (b) 3000 shots. (c) A–B line profile in Fig. 5(a). (d) A–B line profile in Fig. 5(b).

Using this knowledge, a line-and-space graphene pattern with a pitch of $8\ \mu\text{m}$ and a line width of $4\ \mu\text{m}$ was fabricated on the surface of SiC(0001) by direct laser patterning. The graphene growth process on the SiC(0001) surface was observed with AFM and conductive AFM measurements. Our method is completely different from the conventional resist processes for patterning graphene and thus can be a technology for graphene device fabrication.

¹A. K. Geim and K. S. Novoselov, *Nat. Mater.* **6**, 183 (2007).

²K. I. Bolotin, K. J. Sikes, Z. Jang, Z. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer, *Solid State Commun.* **146**, 351 (2008).

³Y. Q. Wu, P. D. Ye, M. A. Capano, Y. Xuan, Y. Sui, M. Qi, J. A. Cooper, T. Shen, D. Pandey, G. Prakash, and R. Reifengerger, *Appl. Phys. Lett.* **92**, 092102 (2008).

⁴Y. Ohno, K. Maehashi, Y. Yamashiro, and K. Matsumoto, *Nano Lett.* **9**, 3318 (2009).

⁵J. Yan, M. H. Kim, J. A. Elle, A. B. Sushkov, G. S. Jenkins, H. M. Milchberg, M. S. Fuhrer, and H. D. Drew, *Nat. Nanotechnol.* **7**, 472 (2012).

- ⁶V. Ryzhii, M. Ryzhii, and T. Otsuji, *J. Appl. Phys.* **101**, 083114 (2007).
- ⁷K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666–669 (2004).
- ⁸X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, *Science* **324**(5932), 1312 (2009).
- ⁹W. Norimatsu, J. Takada, and M. Kusunoki, *Phys. Rev. B: Condens. Matter* **84**(3), 035424 (2011).
- ¹⁰W. Norimatsu and M. Kusunoki, *Phys. E* **42**, 691–694 (2010).
- ¹¹A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, *Phys. Rev. Lett.* **97**, 187401 (2006).
- ¹²Z. H. Ni, W. Chen, X. F. Fan, J. L. Kuo, T. Yu, A. T. S. Wee, and Z. X. Shen, *Phys. Rev. B* **77**, 115416 (2008).
- ¹³J. Röhl, M. Hundhausen, K. V. Emtsev, Th. Seyller, R. Graupner, and L. Ley, *Appl. Phys. Lett.* **92**, 201918 (2008).
- ¹⁴L. G. Cançado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio, L. N. Coelho, R. Magalhães-Paniago, and M. A. Pimenta, *Appl. Phys. Lett.* **88**, 163106 (2006).
- ¹⁵Z. Li, F. Zhou, D. Parobek, G. J. Shenoy, P. Muldoon, and H. Liu, *J. Solid State Chem.* **224**, 14 (2015).
- ¹⁶H. Nakagawa, S. Tanaka, and I. Suemune, *Phys. Rev. Lett.* **91**, 226107 (2003).
- ¹⁷C. Dimitrakopoulos, A. Grill, T. J. McArdle, Z. Liu, R. Wisnieff, and D. A. Antoniadis, *Appl. Phys. Lett.* **98**, 222105 (2011).