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978-1-107-40666-7 - Fundamentals of Low-Dimensional Carbon Nanomaterials:

Materials Research Society Symposium Proceedings: Volume 1284

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Growth of Graphene/Substrate Structures

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Graphene growth on SiC and other substrates using carbon sources

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ABSTRACT

Direct deposition of graphene from carbon sources on foreign substrates without the use of metal catalysts is shown to be an effective process with several advantages over other growth techniques. Carbon source molecular beam epitaxy (CMBE) in particular provides an additional control parameter in carbon flux and enables growth on substrates other than SiC, including oxidized Si and sapphire. CMBE using thermally evaporated C₆₀ and a heated graphite filament on SiC is reported here. The graphene films were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy and Hall effect. Graphene films on Si-face SiC grown using the C₆₀ source have Bernal-like stacking and n-type conduction while those grown using the graphite filament have turbostratic stacking and p-type conduction. The sheet concentration for both n- and p-type doping is linearly dependent on film thickness.

INTRODUCTION

Since the isolation of single layer graphene was reported by Novoselov et al. in 2004 [1] a variety of techniques have been used to grow or fabricated this material. Novoselov et al. used mechanical exfoliation from natural or artificial graphite. The technique for removing a few layers from the top of a graphite sample with tape was well known in the scanning tunneling microscopy community for some time but the graphene was always discarded with the tape. Mechanical exfoliation still produces the highest electrical quality graphene but the largest areas exfoliated to date are about 100 μm x 100 μm and no one has yet developed a reliable process for precisely depositing graphene at specific locations on the substrate by this approach. Perhaps the oldest approach for producing graphene is chemical vapor deposition on metal films. Karu and Beer [2] reported growth of "crystalline films of graphite by pyrolysis of methane on hot single crystal nickel" in 1966. However, this technique did not become a viable means of producing electronic grade graphene until the work of Kim et al. [3] and Li et al. [4]. Growth on both Ni [3] and Cu [4] foils has produced high quality graphene. However, the technique requires somewhat elaborate processes to transfer the graphene from the conductive metal foils to more useful substrates such as oxidized Si and damage can result. Chemical exfoliation of graphene oxide from graphite and subsequent deposition and reduction back to graphene has been reported [5]. This technique is inexpensive and useful for applications that do not require high mobility, such as transparent conductors and interconnects. It was long known in the SiC community that annealing SiC at high temperatures resulted in the sublimation of Si and the formation of a graphite-like carbon layer on the SiC surface [6], but it took Berger et al. [7] to use the decomposition of SiC in ultra high vacuum (UHV) to produce a useful form of graphene.

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Emtsev et al. [8] later demonstrated high quality growth of graphene by decomposition of SiC in an atmospheric pressure argon ambient but at the cost of higher annealing temperatures.

Recently several groups have investigated the direct deposition of graphene on foreign substrates without the use of catalysts in UHV using a variety of carbon sources. Hackley et al. [9] reported growth of graphitic films directly on Si(111) in a molecular beam epitaxy (MBE) chamber. Their carbon source was an electron beam evaporated graphite target. They reported X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy measurements but not resistivity or Hall effect measurements. The disorder based Raman D band was more intense than the G band and the Raman spectra did not go out far enough to show the 2D band. Al-Temimy et al. [10] used a commercial resistively heated graphite filament as their carbon source. They used low energy electron diffraction to demonstrate graphene like surface reconstructions as well as angle resolved ultraviolet photoelectron spectroscopy and atomic force microscopy (AFM) to demonstrate the presence of graphene. Moreau et al. [11] used the same carbon source as Al-Temimy to grow graphene on SiC. Both Al-Temimy et al. and Moreau et al. first prepared the SiC surface as for UHV SiC decomposition but then turned on their carbon source rather than continuing heating the substrate for Si sublimation. Neither reported Raman spectroscopy or electrical measurements. Hwang et al. [12] reported graphene growth directly on SiC and sapphire substrates by chemical vapor deposition growth using propane at temperatures from 1350 to 1650°C. Raman measurements showed strong G and 2D bands and a weak D band for both substrates. Synchrotron X-ray measurements indicated that the stacking sequence in multilayer graphene depended on the substrate. Also using CVD but with acetylene Usachov et al. recently reported direct growth of graphene on BN films [13]. The present authors [14] reported growth in a UHV MBE chamber using both thermally evaporated C₆₀ and a resistively heated graphite filament carbon sources. We report here further experiments on carbon source MBE (CMBE) of graphene using these two sources including resistivity and Hall effect measurements in addition to AFM, XPS and Raman spectroscopy measurements. We demonstrate that both the graphene layer stacking for multilayer films and the carrier type depend on the carbon source used. We also demonstrate graphene growth on SiO₂ on Si using the C₆₀ source.

EXPERIMENTAL DETAILS

The growth process has been described elsewhere [14, 15]. All growths were on Si-face semi-insulating 4H SiC. Two carbon sources were used, thermally evaporated C₆₀ and a resistively heated graphite filament. The C₆₀ powder is heated in a conventional shuttered MBE cell to around 500°C. This is well below the decomposition temperature of around 800°C [16]. Kolodney, Tsipinyuk and Budrevich [17] report that C₆₀ decomposes as $C_{60}^+ \rightarrow C_{58}^+ + C_2$ with an activation energy of about 4 eV. C₆₀ has been used as carbon source in MBE growth of SiC on Si [18], SiC on SiC [19] and SiC on sapphire [20]. The graphite filament in these experiments serves the dual purpose of both substrate heater and carbon source. The back side of the substrate holder was cut open to enable higher growth temperature but also exposed the back side of the substrate to the carbon flux emitted from the heater. The heater was used as a carbon source by mounting the substrate with the surface of interest facing the heater. Resistively heated graphite has been used for some time as carbon sources for p-type doping of III-V semiconductors in MBE experiments [21]. The flux from such filaments consists mainly of C₃ molecules with C₁ and C₂ also prominent [22].

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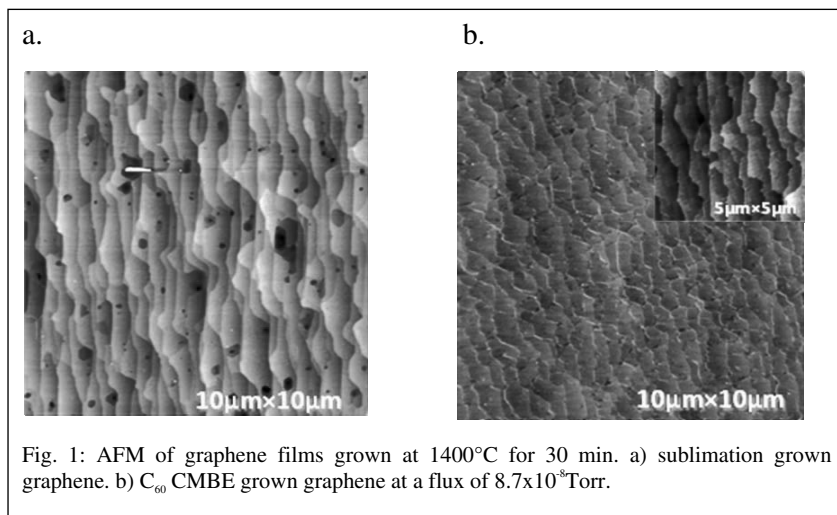
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Fig. 1: AFM of graphene films grown at 1400°C for 30 min. a) sublimation grown graphene. b) C₆₀ CMBE grown graphene at a flux of 8.7×10^{-8} Torr.

Prior to growth for both sources a tantalum film was deposited on the back of all samples for thermal management. After growth the samples were evaluated with Raman spectroscopy measurements. The thickness was estimated from X-ray photoelectron spectroscopy (XPS) measurements of the C1s peak intensity for graphene and SiC using the attenuation model of Seyller et al. [23]. Surfaces were studied with atomic force microscopy (AFM). Electrical measurements were made at room temperature on macroscopic indium contacted van der Pauw squares.

RESULTS AND DISCUSSION

Growth on Si-Face SiC

Raman measurements of CMBE grown films showed both the G and 2D bands in films grown at 1200°C with both sources [15] indicating the presence of graphene. It is usually assumed that temperatures above 1250°C are required for graphene growth by UHV sublimation on Si-face SiC [24] so this demonstrates lower temperature growth with CMBE. The disorder induced D band was weak or nonexistent in CMBE samples grown at 1400°C. Fitting of the 2D bands to multiple Lorentzians indicated multiple components for multilayer C₆₀ material but only a single Lorentzian for multilayer GF material. This suggests that C₆₀ material has Bernal stacking but GF material has random or turbostratic stacking. Figure 1 shows AFM images of graphene films grown by conventional sublimation and C₆₀ CMBE at 1400°C for 30 min. The sublimation grown film is typical of graphene grown in UHV. The pit density is high and steps are irregular. The C₆₀ CMBE sample is smoother with significantly lower pit density. The wrinkles common in multilayer films are clearly visible. GF CMBE films grown at 1200°C showed AFM similar to the 1400°C C₆₀ CMBE shown in the figure. The AFM in ref. 10 also suggested a reduction in pit density.

Table I: Electrical Properties of sublimation grown and CMBE grown graphene films with typical growth conditions. T_{growth} and t_{growth} are the substrate temperature and growth time respectively.

Source	n/p (cm^{-2})	μ (cm^2/Vs)	Type	T_{Growth} ($^{\circ}\text{C}$)	t_{Growth} (min)
Sublimation	4.5×10^{12}	256	n	1400	30
C_{60}	9×10^{12}	235	n	1400	30
GF	2×10^{12}	265	p	1200	60

Like Si-face sublimation grown material all C_{60} grown films showed n-type conduction. However, the GF material was consistently p-type, similar many to exfoliated and free standing graphene films. Typical sheet concentration and mobility values are given in Table I. In general the mobilities are low for the growth chamber used in these experiments.

As seen in fig. 2, the charge carrier sheet density for both sources depends linearly on film thickness, suggesting the doping coming from the source rather than the background pressure in the chamber. Experiments are underway to identify the source of the doping in both types of films.

Raman measurements have already

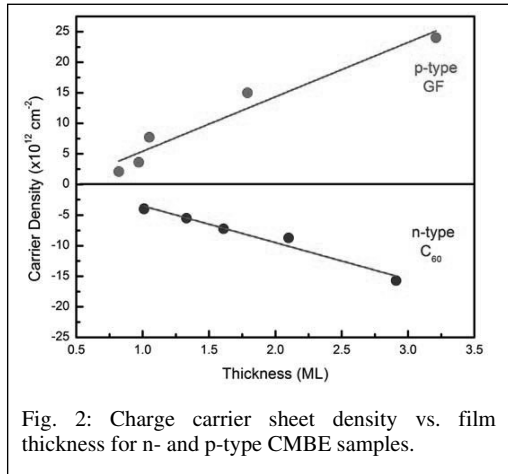


Fig. 2: Charge carrier sheet density vs. film thickness for n- and p-type CMBE samples.

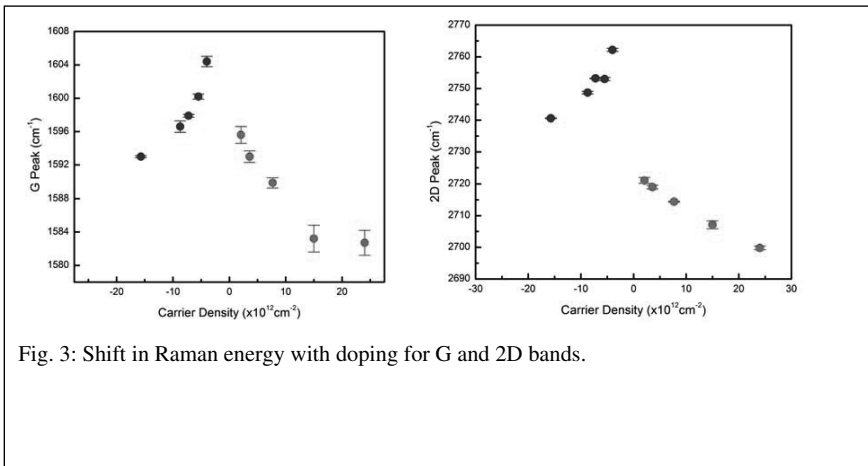


Fig. 3: Shift in Raman energy with doping for G and 2D bands.

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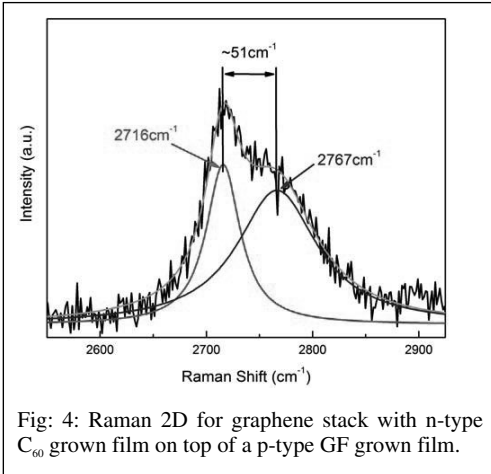
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Fig. 4: Raman 2D for graphene stack with n-type C_{60} grown film on top of a p-type GF grown film.

(fig. 2) they do suggest that with further refinement *in-situ* control of doping concentration and even type may be possible.

In addition to single carrier type growth, stacks of p doped and n doped graphene layers were made by first growing a film with the GF source then removing the sample, turning it over and then growing on top of the GF film with the C_{60} source. Figure 4 shows the Raman 2D for such a p-n stack. A high energy shoulder is clearly visible and fits show two peaks separated by

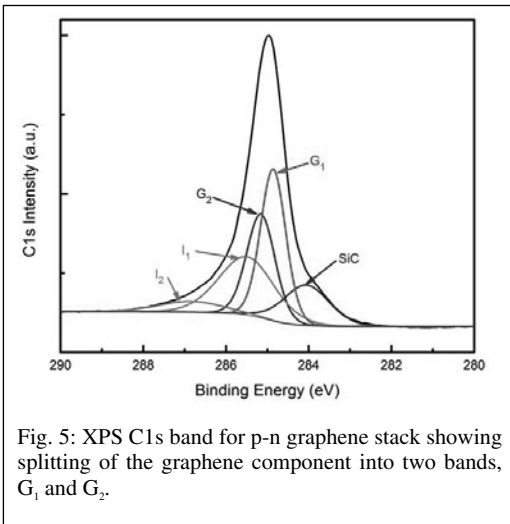


Fig. 5: XPS C1s band for p-n graphene stack showing splitting of the graphene component into two bands, G_1 and G_2 .

been reported for both types of sources [15]. The SiC spectrum was subtracted in all spectra reported here. The D band was typically weak or not observable. There was a noticeable shift in peak position for the Raman G and 2D bands show a phonon softening with increasing carrier density. This can be seen in fig. 3 where G and 2D peak positions are plotted as a function of sheet carrier density. A similar dependence of G band peak position versus charge density for gated graphene has been reported by Yan et al. [25].

While the doping effects reported here are accompanied with corresponding changes in thickness (fig. 2) they do suggest that with further refinement *in-situ* control of doping concentration and even type may be possible. In addition to single carrier type growth, stacks of p doped and n doped graphene layers were made by first growing a film with the GF source then removing the sample, turning it over and then growing on top of the GF film with the C_{60} source. Figure 4 shows the Raman 2D for such a p-n stack. A high energy shoulder is clearly visible and fits show two peaks separated by 51 cm^{-1} . The individual components in Fig. 4 are similar to others reported in the literature so we therefore speculate that Fig. 4 represents two isolated layers of graphene with different doping. Fitting to the XPS C1s band (fig. 5) also indicates two separate films suggested by two graphene peaks. The splitting observed in both the Raman and XPS experiments is most likely due to different strain induced by two carbon sources. The GF growth rate is much faster than the C_{60} source and so the film might not be coupled to the SiC substrate in the same manner although interface layers are observed in the low energy regions of the XPS spectra for both types of material. Schmidt et al. [26] did report that the individual layers of folded exfoliated graphene

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monolayers were decoupled from each other and that even acted as separate conduction channels for electrical transport. The process of removing the sample to flip it may have caused the decoupling or it may be due to the different strain layers in the films with turbstratic graphene under Bernal stacked graphene.

Growth on Foreign Substrates

The ability to grow graphene directly on substrates other than SiC without transfer from other sources would be very beneficial though increasing the application space for graphene while reducing processing time and cost. There have been several reports of direct deposition of graphene on substrates other than SiC without the use of metal catalyst films. Hackley et al. [9] grew graphene like carbon on Si(111) substrates in an MBE chamber using e-beam evaporated graphite source. The confirmed the presence of graphene with XPS and Raman measurements. However, they did not show the region around the Raman 2D band and their D band was more intense than their G band. In addition to growth on C-face SiC Hwang et al. [12]

recently demonstrated growth on sapphire substrates using a propane source but without metal catalysts. They too used Raman measurements but they had a strong well defined 2D peak and a low intensity ratio, I_D/I_G , indicating a low defect density and a quality similar to their material grown on C-face SiC. Synchrotron X-ray measurements indicated that the stacking order for multilayer films was predominantly rhombohedral rather than Bernal.

We report here the preliminary results of our studies of C_{60} CMBE growth on alternate substrates. The most successful experiments involved growth on oxidized Si wafers, directly onto the SiO_2 . Here the C_{60} was deposited at 850°C for 30 min. then annealed at 1100°C for 30 min to form the graphene without evaporating the SiO_2 . Figure 6 shows the Raman spectrum. A weak 2D band is present as well as the D and G bands. I_D/I_G is less than but close to one indicating significant defects and disorder. Very preliminary results suggest growth of graphene-like carbon films on GaN and sapphire substrates. The Raman results are similar to fig. 6 but with weaker 2D bands. Both G and D bands are strong.

CONCLUSIONS

Growth of graphene on SiC and other substrates by direct deposition of carbon without metallic catalysts has been demonstrated now by several laboratories. This is a viable process that provided several benefits over conventional SiC decomposition such as reduced pit density and lower growth temperatures. The technique eliminates the need for transfer of graphene from metal films to usable substrates as with CVD graphene. We have demonstrated CMBE growth

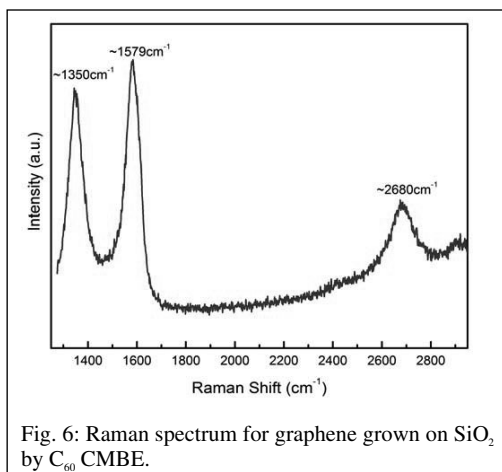


Fig. 6: Raman spectrum for graphene grown on SiO_2 by C_{60} CMBE.

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of graphene in UHV from two different solid carbon sources, thermally evaporated C₆₀ and a heated graphite filament. The carrier concentration, mobility and carrier type of the graphene films have been reported. GF grown films are consistently p-type while C₆₀ grown films are n-type. Fitting of the Raman 2D bands suggests that the n-type C₆₀ films have Bernal stacking while the p-type GF films are turbostratic. Growth of n-type on p-type stacks using both carbon sources was demonstrated. Raman and XPS measurements suggest that these stacks consist of two decoupled layers of graphene. We also report the growth of graphene-like carbon films on SiO/Si, sapphire and GaN substrates using C₆₀ CMBE.

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REFERENCES

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I. V. Grigorieva, and A.A. Firov, *Science* **306**, 666 (2004).
2. A. E. Karu and M. Beer, *J. Appl. Phys.* **37**, 2179 (1966).
3. K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, and B. H. Kim, *Nature* **457**, 706 (2009).
4. X. Li, Y. Zhu, 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**, 1312 (2009).
5. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, **45**, 1558 (2007).
6. A. J. van Bommel, J. E. Crombeen, and A. van Tooren, *Surf. Sci.* **48**, 463 (1975).
7. C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, *Science* **312**, 1191 (2006).
8. K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellog, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, and Th. Seyller, *Naturer Mater.* **8**, 203 (2009).
9. J. Hackley, D. Ali, J. DiPasquale, J. D. Demaree, and C. J. K. Richardson, *Appl. Phys. Lett.* **95**, 133114 (2009).
10. A. Al-Temimy, C. Riedl, and U. Starke, *Appl. Phys. Lett.* **95**, 231907 (2009).
11. E. Moreau, F. J. Ferrer, D. Vignaud, S. Godey, and X. Wallart, *Phys. Status Solidi A* **207**, 300 (2010).
12. J. Hwang, V. B. Shields, C. I. Thomas, S. Shivaraman, D. Hao, M. Kim, A. R. Woll, G. S. Tompa, and M. G. Spencer, *J. Cryst. Growth* **312**, 3219 (2010).
13. D. Usachov, V. K. Adamchuk, D. Haberer, A. Grüneis, H. Sachdev, A. B. Preobrajenski, C. Laubschat, and D. V. Vyalikh, *Phys. Rev.* **82**, 075415 (2010).
14. J. Park, W. C. Mitchel, L. Grazulis, H. E. Smith, K. G. Eyink, J. J. Boeckl, D. H. Tomich, S. D. Paclay, and J. E. Hoelscher, *Adv. Mater.* **22**, 4140 (2010).
14. W. C. Mitchel, J. H. Park, H. E. Smith, L. Grazulis, and K. Eyink, *Mater. Res. Soc. Symp. Proc.* **1246**, B10-02 (2010).
15. D. Chen, R. K. Workman, and D. Sarid, *J. Vac. Sci. Technol. B* **14**, 979 (1996).
16. E. Kolodney, B. Tspinyuk and A. Budrevich, *J. Chem. Phys.* **100**, 8542 (1994).

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17. A. V. Hamza, M. Balooch, and M. Moalem, *Surf. Sci.* **317**, L1129 (1994).
18. W. V. Lampert, C. J. Eiting, S. A. Smith, K. Mahalingham, L. Grazulis, and T. W. Haas, *J. Cryst. Growth* **234**, 369 (2002).
19. J. Li, P. Batoni, and R. Tsu, *Thin Solid Films* **518**, 1658 (2010).
20. R. J. Malik, R.N. Nottenberg, E. F. Schubert, J. F. Walker, and R. W. Ryan, *Appl. Phys. Lett.* **56**, 2651 (1988).
21. M. Joseph, N. Sivakumar, and P. Manoravi, *Carbon* **40**, 2031 (2002).
22. Th. Seyller, K. V. Emtsev, K. Gao, F. Speck, L. Ley, A. Tadlich, L. Broekman, J. D. Riley, R. C. C. Lackey, O. Rader, A. Varykhalov, and A. M. Shikhin, *Surf. Sci.* **600**, 3906 (2006).
23. J. Hass, W. A. de Heer and E. H. Conrad, *J. Phys.: Condens. Matter* **20**, 1 (2008).
24. J. Yan, Y. Zhang, P. Kim, and A. Pinczuk, *Phys. Rev. Lett.* **98**, 166802 (2007).
25. H. Schmidt, T. Lüdtkke, P. Barthold, E. McCann, V. I. Fal'ko, and R. J. Haug, *Appl. Phys. Lett.* **93**, 172108 (2008).