

## Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates

Alfonso Reina,<sup>†</sup> Hyungbin Son,<sup>‡</sup> Liying Jiao,<sup>§</sup> Ben Fan,<sup>§</sup> Mildred S. Dresselhaus,<sup>‡,||</sup> ZhongFan Liu,<sup>\*,§</sup> and Jing Kong<sup>\*,‡</sup>

*Department of Materials Science, Department of Electrical Engineering and Computer Sciences, and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Centre for Nanoscale Science and Technology (CNST), Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China*

*Received: August 18, 2008; Revised Manuscript Received: September 23, 2008*

The transferring and identification of single- and few-layer graphene sheets from SiO<sub>2</sub>/Si substrates to other types of substrates is presented. Features across large areas ( $\sim\text{cm}^2$ ) having single and few-layer graphene flakes, obtained by the microcleaving of highly oriented pyrolytic graphite (HOPG), can be transferred reliably. This method enables the fast localization of graphene sheets on substrates on which optical microscopy does not allow direct and fast visualization of the thin graphene sheets. No major morphological deformations, corrugations, or defects are induced on the graphene films when transferred to the target surface. Moreover, the differentiation between single and bilayer graphene via the  $G'$  ( $\sim 2700\text{ cm}^{-1}$ ) Raman peak is demonstrated on various substrates. This approach opens up possibilities for the fabrication of graphene devices on a substrate material other than SiO<sub>2</sub>/Si.

The possibility of depositing and recognizing single- and few-layer graphene sheets on silicon with a specific oxide thickness<sup>1</sup> has allowed and promoted fundamental investigations of these graphitic systems.<sup>2–7</sup> As a consequence, the remarkable electronic properties of graphene have been revealed and many exciting potential applications have been proposed.<sup>2,8,9</sup> The deposition of graphene sheets on a SiO<sub>2</sub>/Si substrate is carried out by microcleaving HOPG without control of the locations of the sheets on the substrate. As the density of single- to few-layer graphene sheets on a given sample is significantly low for this method, an efficient identification of graphene sheets relies on optical microscopy imaging which gives a wide field of view. The identification of graphene sheets, down to one layer in thickness, with optical microscopy is possible via the color contrast caused by the light interference effect on the SiO<sub>2</sub> which is modulated by the graphene layer.<sup>10,11</sup> This makes the preparation of graphene samples and devices not only possible but also efficient. However, the observation of a clear color contrast requires Si substrates with a specific SiO<sub>2</sub> thickness,<sup>10,11</sup> thus limiting the fabrication of graphene devices to these substrates. The fabrication of samples and devices on other types of substrates is relevant for fundamental studies or the optimization of graphene's performance.<sup>12</sup> Therefore, it is necessary to develop methods which can integrate graphene sheets with a wider variety of substrate materials while also allowing an

efficient identification of the graphene sheets once they are placed on the substrates. In this letter, we report the transfer of graphene pieces, including single- and few-layer sheets that are predeposited on SiO<sub>2</sub>/Si across large areas ( $\sim\text{cm}^2$ ), to a nonspecific substrate and the fast localization of the graphene pieces once placed on these target substrates. This approach is very useful for experimental studies of the same graphene piece on different substrates, and it could also be used for the controlled placement of graphene pieces derived from the microcleaving of HOPG on specific locations.

Single- and few-layer graphene sheets were deposited on SiO<sub>2</sub>/Si substrates as received from Silicon Quest Inc. (300 nm SiO<sub>2</sub>, p-type doped, one side polished) by the microcleaving of HOPG. The location of each graphene sheet, its morphology, and its number of layers were determined using optical microscopy, atomic force microscopy (AFM), and Raman spectroscopy. The transferring of the graphene deposited on a SiO<sub>2</sub>/Si substrate was carried out similarly to a method previously reported on the transfer of carbon nanotubes.<sup>13</sup> Figure 1 summarizes the steps of the transfer process. A layer of poly(methyl methacrylate) (PMMA) (MicroChem, 950,000 MW, 9–6 wt. % in anisole) is spin coated on the substrate prior to the transfer. Afterwards the detachment of the PMMA/graphene layer from the initial surface is done by partially etching the surface of the SiO<sub>2</sub> with a 1 M NaOH aqueous solution. The 300 nm SiO<sub>2</sub> does not etch completely, and only a minor etching of the SiO<sub>2</sub> surface is enough to release the PMMA/graphene layer. When the release begins, the substrate is usually put in water at room temperature where manual peeling can be used to detach completely the PMMA/graphene membrane from the substrate. As a result, a PMMA membrane with all of the

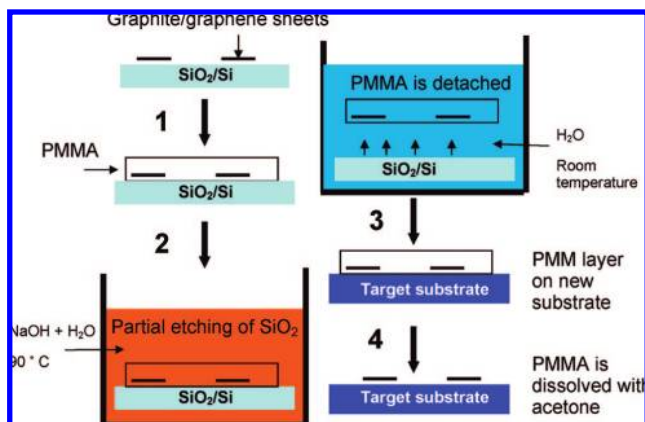
\* To whom correspondence should be addressed. E-mail: zfliu@pku.edu.cn; jingkong@mit.edu.

<sup>†</sup> Department of Materials Science, MIT.

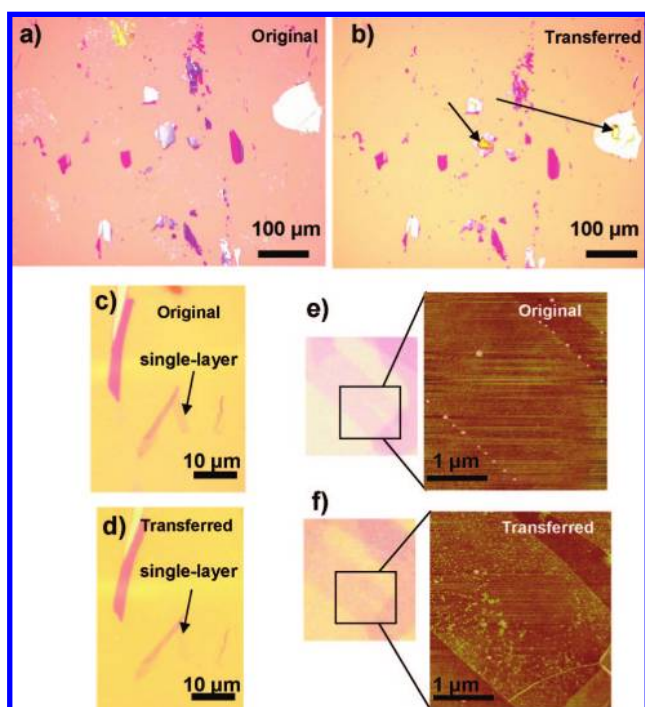
<sup>‡</sup> Department of Electrical Engineering and Computer Sciences, MIT.

<sup>§</sup> Peking University.

<sup>||</sup> Department of Physics, MIT.



**Figure 1.** Schematic diagram of the transferring process. The graphene sheets are deposited on SiO<sub>2</sub>/Si substrates (300nm thermal oxide) via HOPG microcleaving and are finally transferred to a nonspecific substrate.



**Figure 2.** Optical and AFM images of graphite and graphene pieces on SiO<sub>2</sub>/Si on the original and transferred substrates. (a and b) Optical images of macroscopic regions having graphite and graphene flakes on the original (a) and the transferred (b) SiO<sub>2</sub>/Si substrates. Another SiO<sub>2</sub>/Si substrate is used in (b) as the target substrate for illustration purposes. Arrows point to PMMA residues. (c and d) Optical images of single- and few- layer graphene on an original (c) and transferred substrate. The single-layer graphene is pointed out by an arrow in the two images respectively. (e and f) AFM and optical images of a single layer graphene piece before (e) and after (f) being transferred to a target SiO<sub>2</sub>/Si substrate.

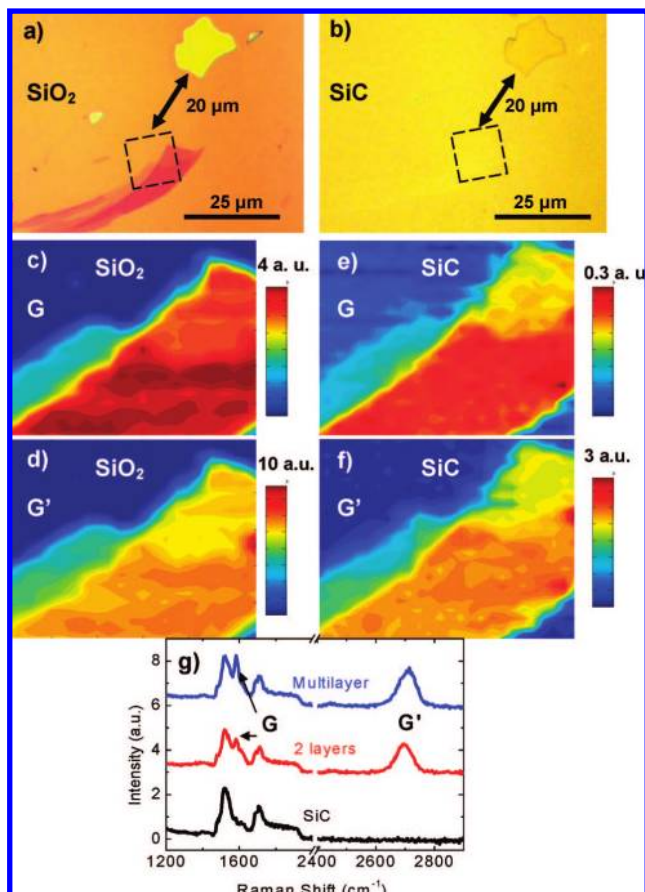
graphite/graphene sheets attached to it is obtained. Finally, this membrane is laid over the target substrate and the PMMA is dissolved carefully with a slow acetone flow.

The transferring of macroscopic regions containing multiple graphite/graphene pieces can be accomplished (Figure 2, panels a and b). The location of the pieces with respect to each other is preserved as shown by the two optical images. This permits the quick localization of pieces identified in the original deposition substrate as discussed below. Figure 2c–f shows optical and AFM images of graphene flakes

transferred from a SiO<sub>2</sub>/Si substrate to a second substrate. Another SiO<sub>2</sub>/Si substrate is used as a target for visualization purposes. Both single- and few-layer graphene sheets are successfully transferred. Our AFM analysis suggests that no morphological changes and most importantly, no major folds on the thin films are induced by the transfer process. The latter is a major advantage since the graphene sheets' tendency to corrugate complicates their manipulation. Furthermore, the graphite pieces originally present in each region preserve their relative distance and location when transferred. We also observe by AFM that the number of layers in few-layer graphene structures (relative color contrast) is preserved when transferred to a second substrate.

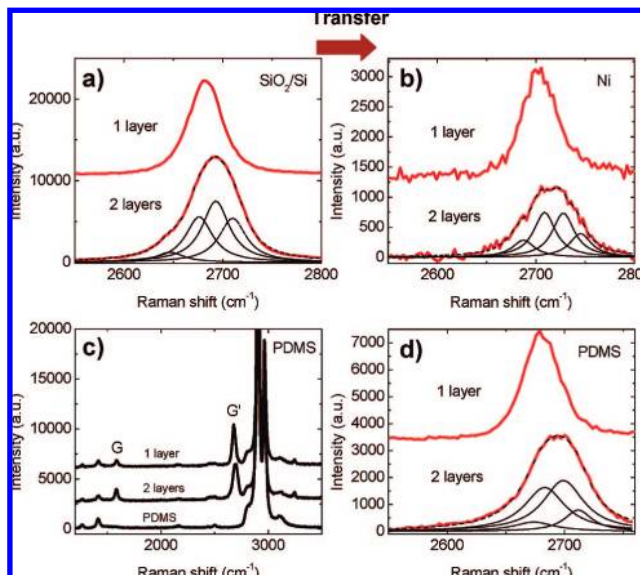
This technique allows the fast identification and localization of graphene sheets on substrates for which a quick optical recognition is not feasible. This is done by recording the optical microscopy images of the regions containing pieces of interest before transferring. In this way, the relative coordinates between the thin graphene sheets and thicker graphite flakes around them are tracked when they are predeposited on a SiO<sub>2</sub>/Si substrate. By performing a second optical microscopy scan on the target substrate, it is possible to find the regions and graphene pieces previously recorded. As an example, Figure 3a shows the identification of a graphene sheet previously deposited on SiO<sub>2</sub>/Si with a thick graphite piece next to it (upper right corner). The relative distance between the two pieces is recorded (20 μm as shown in Figure 3a) when they are still on SiO<sub>2</sub>. Once this arrangement is transferred to a SiC substrate by the process described above, it is possible to quickly localize the thick graphite piece (Figure 3b, upper right corner). Since the relative distance between the single- and few- layer graphene pieces and the visible graphite piece does not change after the transfer process, it is possible to find the position of the graphene pieces on the SiC although the contrast between graphene and SiC is poor under the optical microscope. This localization can be confirmed by either Raman spectroscopy or AFM inspection. Figure 3, panels c and d, shows (respectively) *G* band and *G'* band intensity maps of the region enclosed by the black square in Figure 3a (before transferring). Figure 3, panels e and f, shows intensity maps of the two Raman peaks of the same graphene region after transferring (region corresponding to the black square in Figure 3b). The *G* band intensity maps in Figure 3, panels e and f, show the presence of the thin graphene sheets which are invisible with an optical microscope (Figure 3b). Figure 3g shows the Raman spectra of double- and multilayer graphene regions identified in Figure 3b. The *G* band overlaps with the modes of SiC<sup>14,15</sup> but it can still be observed, while the *G'* band is isolated from the SiC features. The difference in the *G'* line shape between pieces with different number of graphene layers is still preserved. Indeed, the differentiation between single layer and multilayer graphene<sup>6,16,17</sup> is also possible in the target substrates.

In order to confirm the possibility of distinguishing between single and bilayer graphene transferred to different substrates using this technique, we have transferred single and bilayer pieces identified on SiO<sub>2</sub>/Si to other substrates such as transition metals, semiconductors and plastics. Afterwards, their *G'* band lineshapes obtained on the new target substrate were compared to those observed when the same pieces were on SiO<sub>2</sub>/Si. The *G'* band is a double resonance Raman process which involves the scattering of two phonons with opposite momentum around the high



**Figure 3.** Transferring and identification of graphene on non-SiO<sub>2</sub> substrates. (a) Optical image of single- and few-layer graphene pieces on SiO<sub>2</sub>/Si with 300 nm SiO<sub>2</sub>. (b) Optical image of the same pieces after being transferred to SiC. The rough positioning of the single- to few-layer pieces are made by identifying the thicker pieces (upper right corner) on SiC. The black squares enclose the same region of a few-layer graphene piece before (a) and after (b) transferring to SiC (b). Exact identification of the thin regions can be made by Raman mapping. (c) *G* band and (d) *G'* band intensity maps of the region enclosed by the black square in (a) before transferring. (e) *G* band and (f) *G'* band intensity maps of the same region after being transferred to SiC. Note the presence of the Raman signal while in (b) no graphene pieces can be distinguished from the optical image. Note that the shape of the regions where the Raman signal is observed resembles the graphene area enclosed by the black square in (a). (g) Raman spectra of pieces consisting of 2 and multiple graphene layers identified on SiC in the area enclosed by the black square in (b). The Raman spectrum of SiC is also shown for reference.

symmetry *K* point in the first Brillouin zone of graphene.<sup>18,19</sup> The wavevector **q** of the phonons participating in this process is dependent on the wavevector, **k**, of the electrons involved in the process by the relation  $\mathbf{q} \sim 2\mathbf{k}$ .<sup>20,21</sup> Therefore, the phonon energies and the Raman shift observed for this peak depend on the electronic structure of the graphene films. The *G'* line shape of single layer graphene is composed of one Lorentzian peak. For bilayer graphene, the interaction between the two layers splits the degenerate electronic conduction (and valence) bands, giving rise to four Lorentzian components in the *G'* peak.<sup>6</sup> This enables the direct differentiation between single and few-layer graphene. Figure 4a shows the *G'* spectra of one and two graphene layers on SiO<sub>2</sub>/Si and Figure 4b shows the *G'* spectra of the same pieces after they were transferred to a Ni substrate. On both substrates, the *G'* spectra of single layer graphene is found



**Figure 4.** (a) *G'* spectra of single and double layer graphene on SiO<sub>2</sub>/Si with 300 nm SiO<sub>2</sub>. (b) *G'* spectra of the same single and bilayer graphene pieces shown in (a) on a Ni substrate. The differentiation between single and bilayer graphene is possible on the Ni substrate after the transfer. (c) Raman spectra of single- and bilayer graphene pieces on PDMS, transferred from another SiO<sub>2</sub>/Si substrate. (d) *G'* spectra of single- and bilayer graphene pieces on PDMS.

to be composed of a single Lorentzian centered around 2690–2700 cm<sup>-1</sup> (with 532 nm excitation), and for double layer graphene the *G'* is found to be composed of four Lorentzian peaks centered around 2700–2720 cm<sup>-1</sup>. The differentiation between single and bilayer graphene is still possible on the new substrates. The lineshapes are qualitatively preserved and their full-width half-maximum (FWHM) remain constant (~35 cm<sup>-1</sup> for 1 layer and ~54 cm<sup>-1</sup> for 2 layers) after the transferring process. Figure 4, panels c and d, shows the Raman spectra of graphene pieces transferred to poly(dimethylsiloxane) (PDMS) substrates. Similarly, single and bilayer graphenes can also be differentiated from their Raman spectra when they are on the PDMS substrates. This is very important for fabricating graphene devices on plastic substrates for flexible electronics applications. These results indicate that the interaction of the different substrates and the transfer process are not significantly modifying the electronic structure of the graphene pieces analyzed. This is an important observation for future device fabrication and it is consistent with recent Raman studies of microcleaved graphene on different substrates.<sup>22</sup>

In summary, we have shown the large scale transfer and quick identification of single- and few-layer graphene sheets deposited on SiO<sub>2</sub>/Si, to potentially any type of substrate material. No morphological changes or corrugations are induced on the transferred pieces. The transferring of all sheets deposited across macroscopic regions is possible and our transfer method preserves the relative distances of each graphitic film. The method transfers the few-layer graphene structures without reducing the number of its constituent layers. Finally, the identification of graphene on the final substrate is enabled and simplified by this approach. This could enable simpler and more efficient fabrication of graphene-based devices on substrates other than SiO<sub>2</sub>/Si.

**Acknowledgment.** The authors thank the support of the Lincoln Laboratory Advanced Concept committee for the

initiation of the work and Intel Higher Education Program. H.S. acknowledges the support of a Xerox fellowship. Raman measurements were carried out in the George R. Harrison Spectroscopy Laboratory supported by NSF-CHE 0111370 and NIH-RR02594 grants.

## References and Notes

- (1) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci.* **2005**, *102*, 10451–10453.
- (2) Berger, C.; Song, Z. M.; Li, X. B.; Wu, X. S.; Brown, N.; Naud, C.; Mayo, D.; Li, T. B.; Hass, J.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. Electronic confinement and coherence in patterned epitaxial graphene. *Science* **2006**, *312*, 1191–1196.
- (3) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **2005**, *438*, 197–200.
- (4) Ohta, T.; Bostwick, A.; Seyller, T.; Horn, K.; Rotenberg, E. Controlling the electronic structure of bilayer graphene. *Science* **2006**, *313*, 951–954.
- (5) Zhang, Y. B.; Tan, Y. W.; Stormer, H. L.; Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **2005**, *438*, 201–204.
- (6) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, *97*, 187401–4.
- (7) Han, M. Y.; Ozyilmaz, B.; Zhang, Y.; Kim, P. Energy Band-Gap Engineering of Graphene Nanoribbons. *Phys. Rev. Lett.* **2007**, *98*, 206805–4.
- (8) Li, X.; Wang, X.; Zhang, L.; Lee, S.; Dai, H. Chemically Derived, Ultrasoft Graphene Nanoribbon Semiconductors. *Science* **2008**, *319*, 1229–1232.
- (9) Morozov, S. V.; Novoselov, K. S.; Katsnelson, M. I.; Schedin, F.; Elias, D. C.; Jaszczak, J. A.; Geim, A. K. Giant Intrinsic Carrier Mobilities in Graphene and Its Bilayer. *Phys. Rev. Lett.* **2008**, *100*, 016602–4.
- (10) Roddaro, S.; Pingue, P.; Piazza, V.; Pellegrini, V.; Beltram, F. The Optical Visibility of Graphene: Interference Colors of Ultrathin Graphite on SiO<sub>2</sub>. *Nano Lett.* **2007**, *7*, 2707–2710.
- (11) Blake, P.; Hill, E. W.; Neto, A. H. C.; Novoselov, K. S.; Jiang, D.; Yang, R.; Booth, T. J.; Geim, A. K. Making graphene visible. *Appl. Phys. Lett.* **2007**, *91*, 063124–3.
- (12) Chen, J.-H.; Jang, C.; Xiao, S.; Ishigami, M.; Fuhrer, M. S. Intrinsic and extrinsic performance limits of graphene devices on SiO<sub>2</sub>. *Nat. Nano* **2008**, *3*, 206–209.
- (13) Jiao, L.; Fan, B.; Xian, X.; Wu, Z.; Zhang, J.; Liu, Z. Creation of Nanostructures with Poly(methyl methacrylate)-Mediated Nanotransfer Printing. *J. Am. Chem. Soc.* **2008**, *130*, 12612–12613.
- (14) Faugeras, C.; Nerriere, A.; Potemski, M.; Mahmood, A.; Dujardin, E.; Berger, C.; de Heer, W. A. Few-layer graphene on SiC, pyrolytic graphite, and graphene: A Raman scattering study. *Appl. Phys. Lett.* **2008**, *92*, 011914–3.
- (15) Ni, Z. H.; Chen, W.; Fan, X. F.; Kuo, J. L.; Yu, T.; Wee, A. T. S.; Shen, Z. X. Raman spectroscopy of epitaxial graphene on a SiC substrate. *Phys. Rev. B* **2008**, *77*, 115416–6.
- (16) Graf, D.; Molitor, F.; Ensslin, K.; Stampfer, C.; Jungen, A.; Hierold, C.; Wirtz, L. Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene. *Nano Lett.* **2007**, *7*, 238–242.
- (17) Gupta, A.; Chen, G.; Joshi, P.; Tadigadapa, S.; Eklund, P. C. Raman scattering from high-frequency phonons in supported n-graphene layer films. *Nano Lett.* **2006**, *6*, 2667–2673.
- (18) Thomsen, C.; Reich, S. Double Resonant Raman Scattering in Graphite. *Phys. Rev. Lett.* **2000**, *85*, 5214.
- (19) Saito, R.; Jorio, A.; Souza Filho, A. G.; Dresselhaus, G.; Dresselhaus, M. S.; Pimenta, M. A. Probing Phonon Dispersion Relations of Graphite by Double Resonance Raman Scattering. *Phys. Rev. Lett.* **2001**, *88*, 027401.
- (20) Malard, L. M.; Nilsson, J.; Elias, D. C.; Brant, J. C.; Plentz, F.; Alves, E. S.; Castro, A. H.; Pimenta, M. A. Probing the electronic structure of bilayer graphene by Raman scattering. *Phys. Rev. B* **2007**, *76*, 201401.
- (21) Mafra, D. L.; Samsonidze, G.; Malard, L. M.; Elias, D. C.; Brant, J. C.; Plentz, F.; Alves, E. S.; Pimenta, M. A. Determination of LA and TO phonon dispersion relations of graphene near the Dirac point by double resonance Raman scattering. *Phys. Rev. B* **2007**, *76*, 233407.
- (22) Wang, Y. y.; Ni, Z. h.; Yu, T.; Shen, Z. X.; Wang, H. m.; Wu, Y. h.; Chen, W.; Shen Wee, A. T. Raman Studies of Monolayer Graphene: The Substrate Effect. *J. Phys. Chem. C* **2008**, *112*, 10637–10640.

JP807380S