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Published in:
Small

DOI:
[10.1002/sml.201101908](https://doi.org/10.1002/sml.201101908)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2012

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Castellanos-Gomez, A., Wojtaszek, M., Arramel, N. V., Tombros, N., & van Wees, B. J. (2012). Reversible Hydrogenation and Bandgap Opening of Graphene and Graphite Surfaces Probed by Scanning Tunneling Spectroscopy. *Small*, 8(10), 1607-1613. <https://doi.org/10.1002/sml.201101908>

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Reversible Hydrogenation and Bandgap Opening of Graphene and Graphite Surfaces Probed by Scanning Tunneling Spectroscopy

Andres Castellanos-Gomez,^{*} Magdalena Wojtaszek, Arramel, Nikolaos Tombros, and Bart J. van Wees^{*}

The effects of hydrogenation on the topography and electronic properties of graphene and graphite surfaces are studied by scanning tunneling microscopy and spectroscopy. The surfaces are chemically modified using an Ar/H₂ plasma. By analyzing thousands of scanning tunneling spectroscopy measurements it is determined that the hydrogen chemisorption on the surface of graphite/graphene opens on average an energy bandgap of 0.4 eV around the Fermi level. Although the plasma treatment modifies the surface topography in an irreversible way, the change in the electronic properties can be reversed by moderate thermal annealing and the samples can be hydrogenated again to yield a similar, but slightly reduced, semiconducting behavior after the second hydrogenation.

1. Introduction

Since its first experimental realization by mechanical exfoliation of graphite on SiO₂ surfaces,^[1] graphene has attracted a lot of attention because of its unique electronic properties.^[2–6] Graphene is a zero-gap semiconductor with a linear energy–momentum dispersion relation, which implies that the charge carriers behave as massless Dirac fermions.^[7] This fact made possible the experimental observation of very

unusual effects such as the fractional quantum Hall effect,^[8] Klein tunneling,^[9] and bipolar supercurrent.^[10] However, the application of graphene in microelectronic devices is hampered by the lack of a bandgap around the Fermi level. Such an energy bandgap is mandatory to fabricate electrically switchable devices with large on/off ratio based on graphene. To date, several strategies have been developed to open a bandgap in graphene. Among them, chemical functionalization of the graphene surface can be very attractive for industrial applications because it is compatible with large-scale production of semiconducting graphene. In particular, the exposure of the graphene surface to hydrogen plasma^[11–13] or hot atomic hydrogen^[14,15] leads to the chemisorption of hydrogen atoms, which produces sp³ hybridization of the carbon network, reduces the number of delocalized sp² electrons, and consequently opens a bandgap. The value of the bandgap E depends on the level of hydrogenation—for instance for graphone,^[16] a graphene layer with only one side of the surface fully hydrogenated, the calculated value is $E = 0.45$ eV—and it is respectively lower for partially hydrogenated graphene surfaces.^[17] This property provides a degree of freedom to tailor the graphene transport properties according to the required semiconducting behavior.

Herein, we report studies of the effect of hydrogenation on graphene by its exposure to hydrogen plasma in a reactive

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DOI: 10.1002/sml.201101908

ion etching (RIE) system, as described in Reference [18]. Hydrogenation using plasma, next to hot atomic hydrogen exposure, is the most common technique to induce H chemisorption in graphene. Its advantages are the high reactivity of incident hydrogen ions and compatibility with standard wafer-scale microfabrication techniques. The acceleration voltage used for feeding the plasma, when too high, can cause graphene etching and its irreversible damage. Although in Reference [18] it was shown through electronic transport measurements that at properly chosen plasma conditions there is no sputtering of graphene, the microscopic confirmation of this hydrogen plasma effect on graphene is missing so far. We have studied the topographic and electronic changes produced by the chemisorption of hydrogen on top of graphene and graphite surfaces by means of scanning tunneling microscopy (STM) and spectroscopy (STS). From a statistical analysis of thousands of STS spectra, acquired at 50–100 different positions on the surface of both materials, we determined that chemisorption of hydrogen induces the opening of an energy bandgap of 0.4 eV around the Fermi level. We also found that moderate thermal annealing of the crystals is enough to close this bandgap and, more interestingly, the samples can be hydrogenated again to yield a similar semiconducting behavior.

2. Results and Discussion

2.1. Topographic Changes Due to Hydrogenation

We first studied the structural changes of the topography induced by the hydrogenation of the surface with an Ar/H₂ plasma treatment (see Reference [18] and the Experimental Section for more details). Although the presence of Ar gas in the mixture is not strictly necessary for the hydrogenation process, it was used due to safety considerations. Both highly oriented pyrolytic graphite (HOPG) and graphene/few-layer graphene grown on nickel by chemical vapor deposition (CVD) were studied. Graphite samples were cleaved before starting the study whereas CVD graphene samples were used as received.^[19] According to the manufacturer, the CVD graphene samples present patches 3–10 μm in size with a thickness that ranges from one to four layers.

Figure 1 shows $8 \times 8 \text{ nm}^2$ topographic images acquired in the constant-current STM mode of the surface of HOPG and graphene grown on nickel by CVD. Before the plasma treatment, both samples exhibited a highly crystalline surface. In the case of graphite, the typical triangular lattice can be resolved in most of the surface regions (Figure 1a).^[20] For the CVD graphene one can see a Moiré pattern superimposed

Figure 1. a–f) Topography images acquired in the constant-current STM mode: a–c) HOPG, d–f) graphene grown by CVD on top of a nickel surface at different steps of the hydrogenation/dehydrogenation process. a,d) Topography of the surface before the hydrogen plasma treatment. For the HOPG, the typical triangular lattice can be resolved all over the surface. For the CVD graphene, a Moiré pattern, due to the lattice mismatch between the graphene and the nickel lattices, superimposed onto the honeycomb lattice is observed. b,e) After 40 min of H₂/Ar plasma treatment, the roughness of the surfaces increases. The surfaces are covered with bright spots where the atomic resolution is lost or strongly distorted. c,f) Graphene surface after 10 min of moderate annealing; the topography of both the HOPG and CVD graphene surfaces does not fully recover its original crystallinity. g) Current–voltage traces measured for a CVD graphene sample in several regions with pristine atomic resolution, such as the one marked with the red square in (e). h) The same as (g) but measured in several bright regions, such as the one marked with the blue circle in (e), where the atomic resolution is distorted.

on the honeycomb lattice of graphene (Figure 1d).^[21–27] This Moiré pattern, which is the most commonly observed in our samples, corresponds to that reported for a graphene monolayer grown on a nickel (111) surface, and is due to the mismatch between the graphene and the nickel lattices.^[28] During the experiments reported herein we studied several tens of locations on the CVD graphene samples, observing occasionally other Moiré patterns associated with few-layer graphene. Therefore, in the CVD graphene samples we sometimes probed regions 2–4 layers in thickness.

Both graphite and CVD graphene samples were then exposed for 40 min to an Ar/H₂ plasma to hydrogenate their surfaces. Previous electronic transport measurements indicate a large increase of scattering cross section for exposure times >1 h both in single-layer and bilayer graphene,^[18] which suggests the coalescence of hydrogen defects. Moreover, Raman spectroscopy measurements have shown that 40 min of plasma treatment does not introduce a noticeable number of defects on graphene.^[18] Therefore we chose an exposure time of 40 min, which yielded moderate hydrogen coverage, thus allowing local resolution of the underneath graphene surface. The hydrogen coverage was estimated from the ratio of the regions showing pristine atomic resolution and the bright regions in which the atomic resolution is strongly distorted due to chemisorbed hydrogen. From the analysis of tens of STM topography images, acquired at different locations on the sample, we estimate that the hydrogen absorption modifies about 30–40% of the surface of the sample for both graphite and CVD-grown graphene samples.

The expected structural changes due to hydrogenation are twofold. First, the chemisorption of hydrogen atoms will change the sp² hybridization of carbon atoms to tetragonal sp³ hybridization, thereby modifying the surface geometry.^[29,30] Second, the impacts of heavy Ar ions, present in the plasma, could also modify the surface by inducing geometrical displacement of carbon atoms (rippling the graphene surface) or creating vacancies and other defects. Figure 1b and e show the topographic images of the surfaces of graphite and CVD graphene after the extended plasma treatment. The corrugation increases for both of them after the treatment and there are brighter regions in which the atomic resolution is lost or strongly distorted. This increase of corrugation can be explained by the change of hybridization induced by the chemisorption of hydrogen.^[29,30] We also found that these bright regions present a semiconducting behavior while the rest of the surface remains conducting (see Figure 1g,h). The room-temperature thermal drift, however, makes it challenging to spatially resolve the electronic properties of the samples by STS with atomic accuracy, and thus in the presented approach we focus on the statistical properties of the graphene surface. Both the strong distortion of the pristine atomic resolution and the semiconducting behavior can be explained by the accumulation of hydrogen atoms in these bright regions to form clusters. For the CVD graphene samples, the graphene–substrate interaction may play an important role in the spatial distribution of the hydrogen chemisorption for low coverages.^[14] Nevertheless, we did not observe any preferential distribution of hydrogen in the CVD graphene samples, which is in agreement with previous

work on graphene on SiC where it was reported that for large hydrogen coverage the chemisorption does not show any preferential position on the graphene lattice.^[15]

To confirm whether the hydrogenation or the Ar-ion impact is the main source of these structural changes, we annealed our samples at moderate temperature. Previous work on similar graphene-based systems^[31,32] indicates that annealing the samples for 10 min at 280 °C largely removes the chemisorbed hydrogen from the surface, while it cannot cure possible graphene voids. It is thus interesting to study the topographic changes produced after annealing. As shown in Figure 1c and f, the topography of the samples after annealing is similar to that after plasma treatment. There are regions in which the graphite/graphene lattice can be well resolved but there are also a few brighter regions, which indicates that the recovery was not complete. However, after the thermal treatment the brighter regions show horizontal lines and elongated features in the STM topography images, which are typical of samples with movable atoms on the surface. These movable atoms can be carbon atoms or atmospheric adsorbates on the surface. As the samples have been annealed, we ruled out that these movable atoms are remaining hydrogen atoms on the surface. We also observed that the STS spectra from all over the surface are rather homogeneous, and show a marked conducting behavior.

2.2. Study of the Electronic Changes Due to Hydrogenation

It is interesting to study the changes in the electronic properties of both graphite and graphene after hydrogen plasma treatment to verify whether a bandgap is opened. In a previous work, electronic transport measurements showed a dramatic increase in the resistance of graphene after hydrogenation.^[18] The absence of a systematic study as a function of the temperature, however, hampered the estimation of the bandgap in those measurements. Herein, we use STS, which is well known as an extraordinarily sensitive technique, to probe the electronic properties of the samples before and after the H₂/Ar plasma treatments.

The measured STS spectra, however, typically depend on the exact atomic arrangement of the atoms involved in the tunneling process. Therefore, under ambient conditions the atomic diffusion and the thermal drift yield fluctuations between different measured spectra. To overcome these trace-to-trace variations, we introduced a procedure to statistically analyze thousands of STS spectra acquired at several tens of different, randomly selected spots in the sample for each step of the hydrogenation/dehydrogenation cycle (see Experimental Section for a more detailed description of the STS measurement procedure).

The data corresponding to each step of the hydrogenation/dehydrogenation cycle are represented together, without any selection of the traces, in a two-dimensional histogram (Figure 2). This kind of representation has been previously used to determine the most probable STS spectra of a single molecule in a break junction experiment^[33] where the configuration of the molecule can change during the experiment. We can use this method to determine the most

Figure 2. Two-dimensional histograms of the differential conductance as a function of the tip bias voltage measured for HOPG (a–e) and CVD graphene (f–j) at different steps of the hydrogenation/dehydrogenation process. The samples were hydrogenated/dehydrogenated several times and the changes in their electronic properties were probed after each process step, by measuring 2000 STS spectra at 50–100 different positions on the surface. The hydrogenation step was carried out by 40 min of exposure to an Ar/H_2 plasma and the dehydrogenation was performed by annealing for 10 min at 280 °C. For both the HOPG and CVD graphene samples it was observed that after the Ar/H_2 treatment, the 2D histograms show a semiconducting behavior (accumulation of data points around zero differential conductance value). This behavior disappears after the annealing of the samples, which recover a metallic behavior.

probable differential conductance versus voltage (dI/dV vs. V hereafter) trace on the surface after each step of the plasma/annealing treatment. A general feature of the measured dI/dV vs. V curves is their parabolic shape for voltages larger than 0.5–0.6 V. This parabolic shape of the tunneling differential conductance can be accounted for with the Simmons model when the tip–sample voltage is comparable to the apparent tunneling barrier height. At low tip–sample voltages, however, the tunneling differential conductance is proportional to the local density of states, thus giving information about the electronic properties of the sample. For instance, for freshly cleaved graphite (Figure 2a) the dI/dV vs. V curve has a nonzero minimum value of 35 ± 11 pS, while the value for the CVD graphene sample is 45 ± 10 pS. The high value of differential conductance measured in CVD graphene samples is in agreement with the metallic behavior observed by Murata et al. in graphene over nickel.^[28] Additionally, in Reference [28] the authors perform density functional calculations demonstrating that, despite the bandgap opening at the K point of the Brillouin zone,^[34] the hybridization of the Ni and C

orbitals renders the graphene metallic, thus explaining the observed increase of the differential conductance at low bias with respect to the graphite.^[28] After the plasma treatment, this dI/dV vs. V curve presents a clear accumulation of points with zero differential conductance (Figure 2b), as expected for a semiconducting material. After moderate annealing, the samples recover their original conducting behavior; the differential conductance minimum value for the graphite sample is 31 ± 15 pS and for the CVD graphene it is 44 ± 20 pS. It is important to note, however, that the increased corrugation of the surface after these treatments causes an inhomogeneous distribution of the electronic properties on the sample, which shows up as more blurry histograms (see Figure 2c). After that, the sample is treated again with Ar/H_2 plasma and the semiconducting behavior is again observed (Figure 2d). A final annealing was used to check that the sample recovers the metallic behavior (Figure 2e).

The case of CVD graphene is remarkably similar to that of graphite. One main difference, however, can be pointed out. After the second plasma treatment the semiconducting

behavior of the CVD graphene is less marked, with a lower density of zero dI/dV counts in the STS 2D histogram. Based on our STM images and previous Raman spectroscopy measurements in similar systems, we rule out the possible breaking of the graphene layer, and exposure of the metallic nickel surface, during the plasma treatment. Therefore, we attribute this reduction of the semiconducting behavior to a modification of the graphene/nickel coupling produced by these plasma/annealing/plasma treatments.

We additionally studied the role of the Ar-ion impacts (occurring during the Ar/H₂ plasma treatment) in these changes of the electronic properties. We found that after a pure Ar plasma treatment, the samples do not present the semiconducting behavior observed in samples treated with Ar/H₂ plasma (see Supporting Information).

Importantly, these two-dimensional dI/dV vs. V histograms are built with traces measured at different locations in the sample (including both regions highly covered by hydrogen and pristine regions) that show very different electronic behavior, as shown in Figure 1g and h. Therefore, to quantify the appearance of some semiconducting behavior after the hydrogen plasma treatments, we studied the accumulation of data points around zero dI/dV in the two-dimensional histograms shown in Figure 2. A line profile along $dI/dV = 0$ (dashed lines in Figure 2) is taken to represent the number of counts as a function of the tip voltage (Figure 3). For a

Figure 3. One-dimensional histograms extracted from a profile along the dashed line (zero differential conductance) in the two-dimensional histograms of Figure 2. Left panel: HOPG; right panel: CVD graphene sample. The consecutive histograms at different steps of the hydrogenation/dehydrogenation treatments are plotted in the same panel but vertically displaced for clarity. From these histograms one can observe that the number of counts at zero differential conductance for the pristine and annealed samples is negligible in comparison with the number of counts after the Ar/H₂ plasma treatments. Note that the counts of the histograms for pristine and annealed samples have been multiplied by 5 to facilitate their comparison.

Figure 4. Average energy bandgap after several hydrogenation/dehydrogenation steps for both HOPG (top panel) and CVD graphene samples (bottom panel). This energy bandgap was determined from the FWHM of the counts distribution in Figure 3.

conducting sample one would expect a complete absence of counts at $dI/dV = 0$. On the other hand, for a semiconducting sample with a well-defined bandgap value, the line profile along $dI/dV = 0$ would show a constant number of counts between two voltage values that define the gap. If one now considers the scenario of a heterogeneous semiconducting sample in which there are spots more conducting than others, the line profile along $dI/dV = 0$ would show a broad distribution whose full width at half maximum (FWHM) indicates the most probable bandgap on the sample. For both graphite and graphene pristine or annealed samples, these one-dimensional histograms show a negligible number of data points with zero dI/dV , thus confirming the semimetallic properties. On the other hand, samples treated with plasma show a strong number of counts with zero dI/dV which follows a nearly Gaussian distribution as a function of tip-sample bias. The number of zero dI/dV counts after the second plasma treatment is smaller, especially for the case of CVD graphene.

One can additionally estimate the average energy bandgap opened after the plasma treatment from the FWHM of the Gaussian peak in the histograms obtained for the plasma-treated samples (Figure 4). Surprisingly, we found that even though the topographic changes induced during these treatments are not fully reversible, the opening/closing of the energy bandgap is reversible. Moreover, in the case of HOPG the values of the mean energy bandgap obtained after hydrogenation and after the hydrogenation/dehydrogenation/hydrogenation process are very similar, 0.49 ± 0.04 and 0.40 ± 0.04 eV, respectively, which is in agreement with the values obtained for partially hydrogenated graphene by other methods.^[35] In the case of CVD graphene, the hydrogenated samples show an average bandgap opening of 0.45 ± 0.05 eV but the hydrogenated/dehydrogenated/hydrogenated

samples show the opening of a bandgap with a lower value (0.30 ± 0.03 eV). This reduction in the energy bandgap could be due to the observed irreversible topographic changes that can modify the reactivity of the surface.^[36]

3. Conclusion

Using STM and STS we have studied the effect of hydrogenation on the topography and electronic properties of graphene and graphite surfaces. An Ar/H₂ plasma was employed to chemically modify the surface of the samples. We introduced a method to statistically analyze thousands of STS spectra, which made it possible to determine that chemisorption of hydrogen induces the opening of an average energy bandgap of 0.4 eV around the Fermi level. Interestingly, although the topographic changes induced by the hydrogenation are not fully reversible, a moderate annealing of the crystals is enough to close this bandgap and the samples can be hydrogenated again to yield a similar semiconducting behavior. The method presented herein to average STS data provides a reliable way to study the effect of surface modification in samples where other techniques (such as angle-resolved photoemission spectroscopy, Raman spectroscopy, electronic transport measurements) cannot be applied because of, for example, the presence of a conducting substrate underneath.

4. Experimental Section

Graphene and Graphite Hydrogenation: All the hydrogenation steps were carried out using an Ar/H₂ plasma (composition 85:15) in a RIE system with a high-frequency generator operating at 13.56 MHz, capacitively coupled to the bottom electrode. The gas flow was kept constant at 200 sccm and the pressure in the chamber was 0.05 mbar. We chose the lowest plasma ignition power, $P = 3$ W (power density ≈ 4 mW cm⁻²), and tuned the circuit impedance to reduce the built-in dc self-bias between the bottom electrode and the plasma down to zero. As proved in Reference [18], under the chosen conditions the sputtering of carbon from the graphene surface for the samples in electrical contact with the chamber electrode (the case here) was completely suppressed. Each exposure was performed for 40 min, which led to moderate hydrogen coverage and was directly followed by STM/STS measurements. Thermal annealing steps were performed on a hotplate at 280 °C in a nitrogen environment for 10 min each.

Scanning Tunneling Microscopy (STM): STM measurements were carried out by utilizing a PicoLE STM instrument from Agilent Technologies. The STM tips were obtained by mechanically cutting a high-purity Pt_{0.8}Ir_{0.2} wire 0.25 mm in diameter (Goodfellow). The STM images were acquired in constant-current operating mode in room conditions. Typical scanning parameters for obtaining STM images of HOPG and CVD graphene surfaces were in the range from 0.5 to 2 nA and tip bias voltage -0.2 to -0.5 V.

Scanning Tunneling Spectroscopy (STS): Fifty current–voltage (I – V) traces were measured at a certain spot on the sample (interrupting the feedback control loop during the measurements). The variation of the tunneling current was measured as the tip bias voltage was swept (0.01 s per trace). By measuring both the

forwards and backwards voltage sweep the thermal drift during the acquisition of a single I – V trace could be neglected and thus every I – V trace was measured at a fixed tip location. Then we changed the lateral position of the tip by 50–100 nm and another set of 50 traces was acquired. Note that the spectra were collected without distinction between the bright regions or the regions where the atomic resolution was retained. The procedure was repeated until 2000 traces were collected. The differential conductance versus voltage (dI/dV vs. V) curve was obtained by numerical differentiation of the I – V traces. Then the whole set of 2000 dI/dV vs. V curves were represented together in a 2D histogram which shows the most probable shape of the traces on the sample. Importantly, these two-dimensional dI/dV vs. V histograms are built with traces measured at different locations in the sample (including both regions highly covered by hydrogen and pristine regions) that show very different electronic behavior, as shown in Figure 1g and h. To build these 2D histograms both the bias voltage and the dI/dV axes were discretized into the number N of bins forming an $N \times N$ matrix (200×200 in our case). Each data point whose dI/dV and V values are within the interval of one bin adds one count to it. The number of counts in each bin is then represented with a color scale.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.C.-G. acknowledges fellowship support from the Comunidad de Madrid (Spain) and the Universidad Autonoma de Madrid (Spain) for the mobility grant to work in the Physics of Nanodevices Group (University of Groningen, Netherlands). M.W. and N.T. acknowledge financial support from the Ubbo Emmius program of the Groningen Graduate School of Science, the Zernike Institute for Advanced Materials, and the Netherlands Organization for Scientific Research (NWO-CW) through a VENI grant. A. is grateful for financial support from the Foundation for Fundamental Research on Matter (FOM G-08).

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [2] Y.-M. Lin, K. A. Jenkins, A. Valdes-Garcia, J. P. Small, D. B. Farmer, P. Avouris, *Nano Lett.* **2008**, 9, 422.
- [3] F. Xia, T. Mueller, Y. Lin, A. Valdes-Garcia, P. Avouris, *Nat. Nanotechnol.* **2009**, 4, 839.
- [4] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, A. K. Geim, *Science* **2007**, 315, 1379.
- [5] B. Ozyilmaz, P. Jarillo-Herrero, D. Efetov, D. A. Abanin, L. S. Levitov, P. Kim, *Phys. Rev. Lett.* **2007**, 99, 166804.
- [6] Y. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, *Nature* **2005**, 438, 201.

- [7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **2005**, 438, 197.
- [8] X. Du, I. Skachko, F. Duerr, A. Luican, E. Andrei, *Nature* **2009**, 462, 192.
- [9] A. Young, P. Kim, *Nat. Phys.* **2009**, 5, 222.
- [10] H. Heersche, P. Jarillo-Herrero, J. Oostinga, L. Vandersypen, A. Morpurgo, *Nature* **2007**, 446, 56.
- [11] D. Elias, R. Nair, T. Mohiuddin, S. Morozov, P. Blake, M. Halsall, A. Ferrari, D. Boukhvalov, M. Katsnelson, A. Geim, *Science* **2009**, 323, 610.
- [12] Z. Luo, J. Shang, S. Lim, D. Li, Q. Xiong, Z. Shen, J. Lin, T. Yu, *Appl. Phys. Lett.* **2010**, 97, 233111.
- [13] J. S. Burgess, B. R. Matis, J. T. Robinson, F. A. Bulat, F. K. Perkins, B. H. Houston, J. W. Baldwin, *Carbon* **2011**, 49, 4420.
- [14] R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, *Nat. Mater.* **2010**, 9, 315.
- [15] R. Balog, B. Jørgensen, J. Wells, E. Lægsgaard, P. Hofmann, F. Besenbacher, L. Hornekær, *J. Am. Chem. Soc.* **2009**, 131, 8744.
- [16] J. Zhou, Q. Wang, Q. Sun, X. Chen, Y. Kawazoe, P. Jena, *Nano Lett.* **2009**, 9, 3867.
- [17] H. Gao, L. Wang, J. Zhao, F. Ding, J. Lu, *J. Phys. Chem. C* **2011**, 115, 3236.
- [18] M. Wojtaszek, N. Tombros, A. Caretta, P. van Loosdrecht, B. van Wees, *J. Appl. Phys.* **2011**, 110, 063715.
- [19] www.graphene-supermarket.com
- [20] J. Paredes, A. Martínez-Alonso, J. Tascon, *Carbon* **2001**, 39, 476.
- [21] M. Fonin, M. Sicot, O. Zander, S. Bouvron, P. Leicht, U. Rüdiger, M. Weser, Y. Dedkov, K. Horn, *ACS Nano* **2012**, 6, 151.
- [22] C. Berger, Z. Song, T. Li, X. Li, A. Ogbazghi, R. Feng, Z. Dai, A. Marchenkov, E. Conrad, W. De Heer, *J. Phys. Chem. B* **2004**, 108, 19912.
- [23] S. Kwon, C. Ciobanu, V. Petrova, V. Shenoy, J. Bareno, V. Gambin, I. Petrov, S. Kodambaka, *Nano Lett.* **2009**, 9, 3985.
- [24] P. Sutter, J. Flege, E. Sutter, *Nat. Mater.* **2008**, 7, 406.
- [25] J. Coraux, *New J. Phys.* **2009**, 11, 023006.
- [26] M. Sasaki, Y. Yamada, Y. Ogiwara, S. Yagyu, S. Yamamoto, *Phys. Rev. B* **2000**, 61, 15653.
- [27] A. Vázquez de Parga, F. Calleja, B. Borca, M. Passeggi, Jr., J. Hinarejos, F. Guinea, R. Miranda, *Phys. Rev. Lett.* **2008**, 100, 56807.
- [28] Y. Murata, V. Petrova, B. B. Kappes, A. Ebnonnasir, I. Petrov, Y. H. Xie, C. V. Ciobanu, S. Kodambaka, *ACS Nano* **2010**, 4, 6509.
- [29] P. Ruffieux, O. Gröning, M. Biemann, P. Mauron, L. Schlapbach, P. Gröning, *Phys. Rev. B* **2002**, 66, 245416.
- [30] A. R. Muniz, D. Maroudas, *J. Appl. Phys.* **2010**, 108, 113532.
- [31] T. Zecho, A. Güttler, X. Sha, B. Jackson, J. Küppers, *J. Chem. Phys.* **2002**, 117, 8486.
- [32] Z. Luo, T. Yu, K. Kim, Z. Ni, Y. You, S. Lim, Z. Shen, S. Wang, J. Lin, *ACS Nano* **2009**, 3, 1781.
- [33] E. Lörtscher, H. Weber, H. Riel, *Phys. Rev. Lett.* **2007**, 98, 176807.
- [34] A. Grüneis, D. V. Vyalikh, *Phys. Rev. B* **2008**, 77, 193401.
- [35] F. Yavari, C. Kritzing, C. Gaire, L. Song, H. Gulapalli, T. Borca-Tasciuc, P. M. Ajayan, N. Koratkar, *Small* **2010**, 6, 2535.
- [36] D. W. Boukhvalov, M. I. Katsnelson, *J. Phys. Chem. C* **2009**, 113, 14176.

Received: September 13, 2011

Accepted: October 27, 2011

Published online: March 19, 2012