AIP | Applied Physics Letters

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Citation: Applied Physics Letters **106**, 053111 (2015); doi: 10.1063/1.4907613
View online: http://dx.doi.org/10.1063/1.4907613
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/106/5?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **106**, 053111 (2015)

Electronic modulations in a single wall carbon nanotube induced by the Au(111) surface reconstruction

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(Received 4 November 2014; accepted 25 January 2015; published online 4 February 2015)

The structural and electronic structure of single wall carbon nanotubes adsorbed on Au(111) has been investigated by low-temperature scanning tunneling microscopy and spectroscopy. The nanotubes were dry deposited *in situ* in ultrahigh vacuum onto a perfectly clean substrate. In some cases, the native herringbone reconstruction of the Au(111) surface interacted directly with adsorbed nanotubes and produced long-range periodic oscillations in their local density of states, corresponding to charge transfer modulations along the tube axis. This effect, however, was observed not systematically for all tubes and only for semiconducting tubes. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4907613]

Carbon nanotubes (CNTs) have raised wide attention following their discovery for potential applications in nanoelectronic device architectures thanks to their proven exceptional mechanical, electronic, or optical properties, whereby practically device reproducibility and precise control on their characteristics still remain a significant challenge.[1–4] In particular, the problem of contacting a nanotube to a metal is crucial, as the conduction properties of devices may be restricted to the interface conditions with the electrodes.[2,5–13] Despite recent progresses, the issue of building nanometer scale nanotube-metal contacts without introducing high levels of contact resistance remains a major challenge.[14,15] In this regard, scanning tunneling microscopy (STM) and spectroscopy (STS) experiments on CNTs adsorbed on a surface have provided highly valuable details on their structure and their related electronic properties.[16–25] In preliminary studies, however, little attention was given to the influence of the adsorption to a metal substrate, partly due to the inherent presence of a large number of co-adsorbed impurities from drop-casting deposition. Recently, important effects arising from the particular adsorption configuration and the local environment of single wall CNTs (SWCNTs) were observed by proper control of the CNT-substrate interface,[23–28] like localization of vibronic states,[29] many body effects,[30,31] or local metallization of semiconducting tubes.[32,33]

In this letter, we show by STM/STS that for a SWCNT adsorbed on the well-defined Au(111) surface, the herringbone reconstruction of the latter can induce periodic modulations in the nanotube electronic and topographic structure due to charge transfer modulations along the nanotube length. These results illustrate the importance of the adsorption configuration and the local environment in the electronic properties of SWCNTs on metals. In particular, although the fact that most of STM investigations of CNTs since the very first reports[18,19] were performed on a Au(111) surface, no effect arising from the native surface reconstruction has been reported. We assume that this could be due to the presence of an impurity layer that inherently forms during traditional sample preparation in ambient conditions, while our work refers to an impurity-free system where the interface nanotube-surface is perfectly defined.

The measurements were performed in an ultrahigh vacuum (UHV) low-temperature STM (Omicron LT-STM) at 4.7 K. The Au(111) substrate was prepared following standard UHV procedures using repeated cycles of Ar^+ sputtering and annealing providing an atomically clean surface. HiPco-produced SWCNTs (Carbon Nanotechnologies, Inc.) were deposited *in situ* onto the surface at room temperature via the vacuum compatible dry contact transfer (DCT) technique:[34,35] a CNT powder coated braid was brought directly in contact with the surface, resulting in the extraction of individual nanotubes around the mechanical impact areas. In some cases, the samples were post-annealed up to ~600 K for 1 h. STS measurements were acquired through lock-in detection of the ac tunneling current driven by a 797 Hz, 10 mV (rms) signal added to the junction bias under open-loop conditions (bias voltage here is defined as the sample potential referenced to the tip). $dI/dV(r,V)$ maps were performed by acquiring a series of STS spectra along the top of a nanotube. STM images were partly processed with WSxM software.[36] Nanotube types were identified from STM/STS data following procedures previously described.[17,19]

We performed systematic investigations on the interaction of a SWCNT with the well-defined Au(111) metal surface in UHV. The DCT deposition technique results in isolated individual nanotubes that are mostly aligned along the substrate crystallographic high symmetry direction[35] and preferentially lying along step edges on Au(111).[33] The cleanliness of the surface is considerably enhanced as compared to the traditionally used drop-casting deposition method.[24,25,35,37] On Au(111), the chevron pattern of the

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0003-6951/2015/106(5)/053111/4/$30.00

surface reconstruction is still clearly observed around the nanotubes (see Figures 1(a) and 1(b)) and atomically resolved STM images are routinely obtained.[37] Furthermore, the DCT technique obviates the necessity of sonicating the SWCNT dispersion in order to debundle the tubes, a process that potentially leads to defect formation on the nanotube surface[38] or chemical reaction with the solvent.[39,40] The system nanotube/metal surface is in this way unambiguously defined. The STM was used to characterize isolated SWCNTs on the clean substrate. 15 nanotubes were thoroughly investigated, among which 1/3 exhibited an oscillating behavior as described below. The ratio semiconducting to metallic tubes was found close to 2:1 as reported usually on this surface.[19]

According to tight-binding calculations,[2,41,42] the local density of states (LDOS) of a SWCNT presents singularities arising from the tube's one-dimensional character (van Hove singularities). Additionally, a nanotube can be of metallic or semiconducting type depending on its geometry. STM studies on SWCNT allow for complete characterization of the tube:[16–19] chiral angle and diameter can be measured on atomically resolved images, and STS gives direct access to the LDOS. It was thus shown that the configuration of adsorbed nanotubes is in good agreement with what can be expected for free-standing tubes.[16,17,19] However, due to the interaction with the substrate, fine effects take place, like a broadening of the van Hove singularities resulting from the hybridization with the surface wave functions.[19,43,44] A careful look at the region around the Fermi level reveals that the STS spectrum of a nanotube adsorbed on Au(111) is not symmetrically positioned around the zero bias voltage (Figure 1(e)). The middle of the band gap is measured above the Fermi level by a few tenths of eV in agreement with the previous measurements[16,17,19,23,45] and calculations.[43,46,47] A charge transfer between the nanotube and the surface is responsible for this asymmetry in the gap and was estimated to amount $\sim$0.1 electron for an armchair tube.[48] Variations are found on different nanotubes depending on their geometries as well as their adsorption configurations on the surface.[23]

The surface reconstruction of Au(111) consists in a linear contraction of the top atomic layer, where a transition from *fcc*- to *hcp*-like sites through bridge positions creates a double line corrugation and a characteristic zigzag pattern.[49] The reconstruction pattern usually influences the adsorption of molecular adsorbates such as C$_{60}$[50] or other aromatic molecules,[51–54] which eventually leads to different self-assembled structures in the *fcc* and *hcp* regions. The Shockley surface state of the reconstructed Au(111) presents additionally electronic modulations: delocalized surface-state electrons experience a weakly attractive potential in the *hcp* regions of the reconstruction compared to the *fcc* regions. Consequently, *hcp* regions possess relatively larger LDOS than *fcc* regions do.[55–57]

Due to their long size (up to several hundreds of nm), SWCNTs adsorbed on a Au(111) surface necessarily extend over several periods of the reconstruction pattern (6.3 nm, Ref. 49). Nevertheless, they can be locally sensitive to the periodic surface modulations.[25] We found that the reconstruction pattern can be responsible for periodic changes in the electronic configuration of the nanotube along its axis. This is illustrated in Figure 1 for a nanotube adsorbed along a step edge (lying on the lower terrace) making an angle of 15° with the substrate [1–10] direction. This nanotube was identified as a (6,5) semiconducting type, with a diameter of 0.75 nm and a band gap of 1.1 eV.[58] A line profile along the top of the tube (Figure 1(c)) shows long-range oscillations of the same period as the reconstruction pattern ($6.3/\cos(15^\circ) \sim 6.5$ nm). The apparent height of the tube is larger by about 0.3 Å over *fcc* regions than over *hcp* ones. For comparison, on the bare Au(111) surface, *hcp* regions are imaged higher than the *fcc* ones by about 0.05 Å, and the corrugation amplitude of the transition regions amounts $\sim$0.2 Å, as previously reported.[49] The corrugation oscillations on the nanotube, which are quasi-sinusoidal, are therefore roughly opposite to those of the underlying substrate, thus providing a hint on the electronic nature of this effect. We performed a spatially resolved STS map (SR-STS) by acquiring a series of STS spectra along the top of the nanotube, as shown in Figure 1(d). Oscillations with the same spatial period are

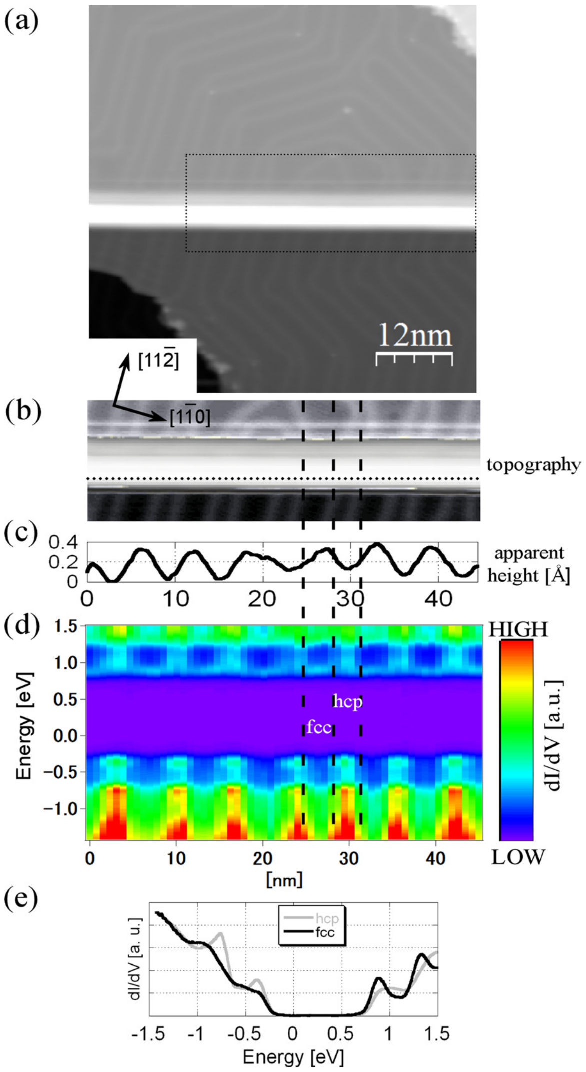

FIG. 1. (a) Large scale STM topographic image of a (6,5) nanotube along a step edge on Au(111) (tunneling current of 0.3 nA and sample bias of 0.9 V). (b) Zoom-in the region delimited by a dashed box in (a). (c) Apparent height at the top of the tube (dashed line in (b)) showing modulations with a period of $\sim$6.3 ± 0.2 nm. (d) SR-STS map along the nanotube axis (set point 0.9 V, 0.3 nA). (e) Comparison of STS spectra showing electron depletion and hole injection over *fcc* as compared to *hcp* regions.

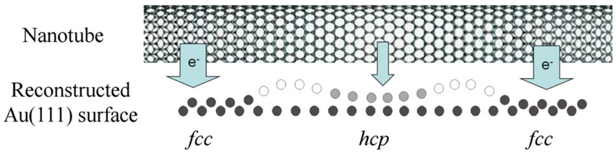

FIG. 2. Schematic illustration of the differences in interface dipole between *hcp* and *fcc* regions. For simplification, the nanotube is schematized as rigid and its corrugation is not represented.

found in the LDOS. The difference in the LDOS over *fcc* and *hcp* regions corresponds to a change in the line shape of the van Hove singularities (Figure 1(e)): over *fcc* regions, the peaks for negative energies (HOMO or filled states) decrease, while the peaks for positive energies (LUMO or empty states) increase. In other words, we observed charge transfer modulations consisting in a depletion of the valence band in favor of the conduction band over *fcc* regions as compared to the LDOS over *hcp* regions. As in both cases, the nanotube is p-doped (shift of the Fermi level towards the valence band), *fcc* regions correspond thus to an increased hole injection.

For small diameter tubes, lattice expansion should occurs upon charge injection following $\delta n \sim \delta R/R$ (R: radius of SWCNT, δn: amount of extra charge).[59,60] This electromechanical effect could contribute to the observed height modulations. However, as the modulations measured correspond to a rather large radius expansion ($\delta R/R \sim 4\%$), other electronic or topographic effects should also be responsible for a substantial part in these oscillations.

In brief, in *hcp* regions compared to *fcc* regions, the apparent CNT height is lower, while the Au(111) corrugated surface should be higher, which possibly results in a reduced CNT-substrate distance; also, the CNT occupied LDOS is higher, corresponding to a lower charge transfer, i.e., a lower hole injection from gold to CNT. As a consequence, interface dipole is lower in *hcp* regions (see Figure 2), which may be responsible for the observed periodic oscillations.

Many nanotubes measured, however, did not present any oscillation in their LDOS, and their apparent heights were either perfectly flat or eventually followed the reconstruction corrugation (see Figure 3), in apparent agreement with the previously published studies of CNTs on Au(111). Interestingly, we never measured LDOS modulations for metallic tubes. Indeed, different behaviors in electromechanical properties can be expected for metallic and semiconducting tubes according to calculations.[59,60] However, due to our limited sample size, we cannot conclude unequivocally about this issue.

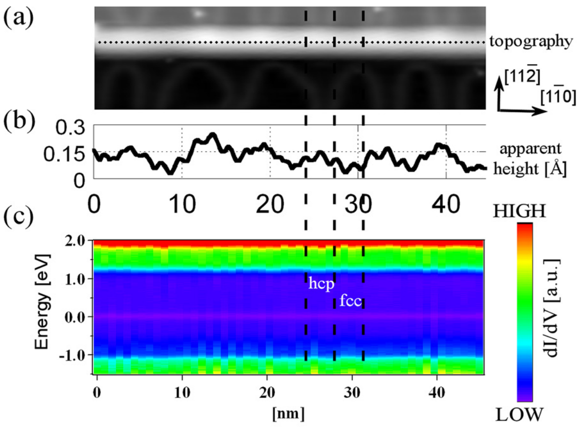

FIG. 3. (a) STM topographic image of a metallic (11,5) nanotube along a step edge on Au(111) (tunneling current of 0.3 nA and sample bias of 0.1 V). (b) Apparent height at the top of the tube (dashed line in (a)) following approximately the surface reconstruction corrugation. (c) Flat SR-STS map along the nanotube axis (set point 0.9 V, 0.3 nA).

In conclusion, we illustrated the important local modulations that can arise in the electronic structure of a single wall carbon nanotube adsorbed on the reconstructed Au(111) surface. We showed that the long-range surface reconstruction of Au(111) induced inhomogeneities in the adsorption registry and periodic oscillations in the electronic and topographic structure of a SWCNT due to charge transfer modulations along the nanotube length. Our results illustrate the great importance of the problem of local registry when considering the interface of a carbon nanotube with an electrode.[12,25,61]

The authors would like to thank Seiji Takemoto for interesting discussions. This work was supported by the Grant-in-Aid for Young Scientists (A), "Single-molecule chemistry on the single-walled carbon nanotubes," and partially by the Grant-in-Aid for Scientific Research on Priority Areas, "Electron transport through a linked molecule in nano-scale," from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and by Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering), MEXT, Japan.

[1] P. Avouris, Z. H. Chen, and V. Perebeinos, Nat. Nanotechnol. **2**(10), 605–615 (2007).
[2] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* (Springer-Verlag, Berlin, 2001).
[3] Z. F. Liu, L. Y. Jiao, Y. G. Yao, X. J. Xian, and J. Zhang, Adv. Mater. **22**(21), 2285–2310 (2010).
[4] Y. B. Chen, Y. Y. Zhang, Y. Hu, L. X. Kang, S. C. Zhang, H. H. Xie, D. Liu, Q. C. Zhao, Q. W. Li, and J. Zhang, Adv. Mater. **26**(34), 5898–5922 (2014).
[5] X. Cui, M. Freitag, R. Martel, L. Brus, and P. Avouris, Nano Lett. **3**, 783 (2003).
[6] Z. Chen, J. Appenzeller, J. Knoch, Y.-m. Lin, and P. Avouris, Nano Lett. **5**, 1497 (2005).
[7] J. J. Palacios, A. J. Pérez-Jiménez, E. Louis, E. SanFabián, and J. A. Vergés, Phys. Rev. Lett. **90**, 106801 (2003).
[8] J.-C. Charlier, X. Blase, and S. Roche, Rev. Mod. Phys. **79**, 677 (2007).
[9] T. Z. Meng, C. Y. Wang, and S. Y. Wang, J. Appl. Phys. **102**(1), 013709 (2007).
[10] N. Nemec, D. Tomanek, and G. Cuniberti, Phys. Rev. Lett. **96**, 076802 (2006).
[11] P. Bai, E. Li, K. T. Lam, O. Kurniawan, and W. S. Koh, Nanotechnology **19**(11), 115203 (2008).
[12] J. Svensson and E. E. B. Campbell, J. Appl. Phys. **110**(11), 111101 (2011).
[13] A. Zienert, J. Schuster, and T. Gessner, Nanotechnology **25**(42), 425203 (2014).
[14] G. S. Tulevski, A. D. Franklin, D. Frank, J. M. Lobez, Q. Cao, H. Park, A. Afzali, S. J. Han, J. B. Hannon, and W. Haensch, ACS Nano **8**(9), 8730–8745 (2014).
[15] Y. C. Che, H. T. Chen, H. Gui, J. Liu, B. L. Liu, and C. W. Zhou, Semicond. Sci. Technol. **29**(7), 073001 (2014).
[16] L. C. Venema, J. W. Jansen, M. R. Buitelaar, J. W. G. Wildoer, S. G. Lemay, L. P. Kouwenhoven, and C. Dekker, Phys. Rev. B **62**, 5238 (2000).
[17] T. W. Odom, J.-L. Huang, P. Kim, and C. M. Lieber, J. Phys. Chem. B **104**, 2794 (2000).
[18] T. W. Odom, J.-L. Huang, P. Kim, and C. M. Lieber, Nature **391**, 62 (1998).

[19] J. W. G. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature **391**, 59 (1998).
[20] J. Lee, S. Eggert, H. Kim, S.-J. Kahng, H. Shinohara, and Y. Kuk, Phys. Rev. Lett. **93**, 166403 (2004).
[21] L. Vitali, M. Burghard, M. A. Schneider, L. Liu, S. Y. Wu, C. S. Jayanthi, and K. Kern, Phys. Rev. Lett. **93**, 136103 (2004).
[22] M. Furuhashi and T. Komeda, Phys. Rev. Lett. **101**(18), 185503 (2008).
[23] S. Clair, Y. Kim, and M. Kawai, Phys. Rev. B **83**, 245422 (2011).
[24] H.-J. Shin, S. Clair, Y. Kim, and M. Kawai, Appl. Phys. Lett. **93**, 233104 (2008).
[25] H.-J. Shin, S. Clair, Y. Kim, and M. Kawai, Nat. Nanotechnol. **4**(9), 567 (2009).
[26] L. B. Ruppalt and J. W. Lyding, Nanotechnology **18**(21), 215202 (2007).
[27] P. M. Albrecht and J. W. Lyding, Nanotechnology **18**(12), 125302 (2007).
[28] S. Barraza-Lopez, P. M. Albrecht, and J. W. Lyding, Phys. Rev. B **80**(4), 045415 (2009).
[29] D. A. Kislitsyn, J. D. Hackley, and G. V. Nazin, J. Phys. Chem. Lett. **5**(18), 3138–3143 (2014).
[30] H. Lin, J. Lagoute, V. Repain, C. Chacon, Y. Girard, J. S. Lauret, F. Ducastelle, A. Loiseau, and S. Rousset, Nat. Mater. **9**(3), 235–238 (2010).
[31] F. Shao, F. X. Zha, C. B. Pan, J. Shao, X. L. Zhao, and X. C. Shen, Phys. Rev. B **89**(8), 085423 (2014).
[32] L. Vitali, M. Burghard, P. Wahl, M. A. Schneider, and K. Kern, Phys. Rev. Lett. **96**(8), 086804 (2006).
[33] S. Clair, Y. Kim, and M. Kawai, J. Appl. Phys. **110**, 073710 (2011).
[34] P. M. Albrecht and J. W. Lyding, Appl. Phys. Lett. **83**, 5029 (2003).
[35] S. Clair, C. Rabot, Y. Kim, and M. Kawai, J. Vac. Sci. Technol. B **25**(4), 1143–1146 (2007).
[36] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, Rev. Sci. Instrum. **78**, 013705 (2007).
[37] C. Rabot, S. Clair, Y. Kim, and M. Kawai, Jpn. J. Appl. Phys., Part 1 **46**, 5572 (2007).
[38] K. L. Lu, R. M. Lago, Y. K. Chen, M. L. H. Green, P. J. F. Harris, and S. C. Tsang, Carbon **34**(6), 814–816 (1996).
[39] J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, and R. C. Haddon, Science **282**(5386), 95–98 (1998).
[40] D. S. Kim, D. Nepal, and K. E. Geckeler, Small **1**, 1117 (2005).
[41] N. Hamada, S.-i. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).
[42] C. T. White and J. W. Mintmire, J. Phys. Chem. B **109**, 52 (2005).
[43] Y. Xue and S. Datta, Phys. Rev. Lett. **83**, 4844 (1999).
[44] C. D. Spataru, Phys. Rev. B **88**(12), 125412 (2013).
[45] A. Hassanien and M. Tokumoto, Carbon **42**, 2649 (2004).
[46] A. Rubio, Appl. Phys. A **68**, 275 (1999).
[47] N. Park, D. Kang, S. Hong, and S. Han, Appl. Phys. Lett. **87**, 013112 (2005).
[48] A. Rubio, D. Sánchez-Portal, E. Artacho, P. Ordejón, and J. M. Soler, Phys. Rev. Lett. **82**, 3520 (1999).
[49] J. V. Barth, H. Brune, R. J. Behm, and G. Ertl, Phys. Rev. B **42**, 9307–9318 (1990).
[50] F. Schiller, M. Ruiz-Osés, J. E. Ortega, P. Segovia, J. Martínez-Blanco, B. P. Doyle, V. Pérez-Dieste, J. Lobo, N. Néel, R. Berndt *et al.*, J. Chem. Phys. **125**, 144719 (2006).
[51] E. C. H. Sykes, B. A. Mantooth, P. Han, Z. J. Donhauser, and P. S. Weiss, J. Am. Chem. Soc. **127**(19), 7255–7260 (2005).
[52] M. Böhringer, K. Morgenstern, W.-D. Schneider, R. Berndt, F. Mauri, A. D. Vita, and R. Car, Phys. Rev. Lett. **83**, 324–327 (1999).
[53] F. Klappenberger, M. E. Canas-Ventura, S. Clair, S. Pons, U. Schlickum, Z. R. Qu, T. Strunskus, A. Comisso, C. Woll, H. Brune *et al.*, Chemphyschem **9**(17), 2522–2530 (2008).
[54] S. Clair, S. Pons, A. P. Seitsonen, H. Brune, K. Kern, and J. V. Barth, J. Phys. Chem. B **108**, 14585–14590 (2004).
[55] W. Chen, T. Madhavan, T. Jamneala, and M. F. Crommie, Phys. Rev. Lett. **80**, 1469 (1998).
[56] L. Bürgi, H. Brune, and K. Kern, Phys. Rev. Lett. **89**(17), 176801 (2002).
[57] F. Libisch, V. Geringer, D. Subramaniam, J. Burgdorfer, and M. Morgenstern, Phys. Rev. B **90**(3), 035442 (2014).
[58] Q. C. Zhao and J. Zhang, Small **10**(22), 4586–4605 (2014).
[59] M. Verissimo-Alves, B. Koiller, H. Chacham, and R. B. Capaz, Phys. Rev. B **67**(16), 161401(R) (2003).
[60] Y. N. Gartstein, A. A. Zakhidov, and R. H. Baughman, Phys. Rev. Lett. **89**, 045503 (2002).
[61] P. M. Albrecht, S. Barraza-Lopez, and J. W. Lyding, Small **3**(8), 1402–1406 (2007).