Phys. Status Solidi B **248**, No. 11, 2536–2539 (2011) / **DOI** 10.1002/pssb.201100070

physica status solidi b
www.pss-b.com
basic solid state physics

Raman study of nanotube–substrate interaction using single-wall carbon nanotubes grown on crystalline quartz

Jaqueline S. Soares[1], Eduardo B. Barros[2], Nitzan Shadmi[3], Ernesto Joselevich[3], and Ado Jorio*[,1]

[1] Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG 31270-901, Brazil
[2] Departamento de Física, Universidade Federal do Ceará, Fortaleza, CE 60455-760, Brazil
[3] Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Received 28 April 2011, revised 22 June 2011, accepted 26 August 2011
Published online 19 September 2011

Keywords carbon nanotube, quartz, Raman spectroscopy, tube–substrate interaction

* Corresponding author: e-mail adojorio@fisica.ufmg.br, Phone: +55-31-34096610, Fax: +55-31-34095600

In this work, we have studied the resonance Raman spectra of 17 single-wall carbon nanotube (SWNT) serpentines, using a 532 nm laser. Each serpentine consists of a series of straight, parallel, and regularly spaced segments, connected by alternating *U*-turns formed on top of crystalline miscut quartz. The interaction between the SWNT and the substrate affects the properties of nanotubes, generating different behaviors of the G-band. We observed variations in the G-band frequency along the SWNTs, which can be organized into three different groups, as a result of different types of interaction with the substrate, generated during the deposition of the SWNTs.

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Carbon nanotubes have been one of the most studied materials in the last 20 years, playing important role in the development of nanoscience. Their electronic and optical properties are promising for several technological applications [1]. The contact with a substrate can significantly change the nanotube and these interactions have been widely studied in the literature [2–22].

The development of nanotube epitaxy combined with the controlled application of external forces can generate complex carbon nanotube structures [16, 19–21]. The effect of nanotube–crystalline substrate interaction can be controlled and measured along the same physical nanotube; i.e., the tube–substrate interaction can be tuned by changing the tube–substrate orientation [22]. The effects on the electronic and vibrational properties of the single-wall carbon nanotubes (SWNTs) were observed using resonance Raman spectroscopy and electric force microscopy, clearly indicating periodic changes on the tube–substrate interaction. SWNT serpentines seem to generate a set of alternate doped-undoped tube segments, which creates complex superlattices through substrate interactions.

In this work we extend our study of the Raman spectra of SWNTs grown on quartz substrate with the serpentine morphology. Through the spectra collected along the tubes, we observed different behaviors of the G^+ band along SWNT serpentines and this behavior can be separated into groups, as discussed here.

2 Experimental details Carbon nanotube serpentines were grown by catalytic chemical vapor deposition (CVD) on miscut single-crystal quartz wafers, as previously reported [16]. The resulting vicinal α-SiO_2 $(1\,\bar{1}\,0\,1)$ substrate is insulating, and terminated with parallel atomic steps [16]. The Raman spectroscopy experiments were performed at room temperature in air at various points along the SWNT serpentines. Raman spectra of the sample were measured in the laser excitation wavelength (energy) of 532 nm (2.33 eV). The light was focused on the sample using a 100× objective. Raman spectra were measured on an ALPHA 300 spectrometer from WITEC equipped with charged-coupled device (CCD) detector.

3 Results and analysis We measured the Raman spectra of 17 serpentines. Their Raman spectroscopy behavior can be separated into three groups: (i) frequency has its maximum value at the center of straight segments along the steps and minimum at the center of the U-shaped segments [22], (ii) frequency changes very little, and

WILEY ONLINE LIBRARY
© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

(iii) frequency "jumps" at certain points in the SWNT serpentines. These three cases represent 30, 12, and 58%, respectively, of SWNT serpentines measured. Below we present each case.

Figure 1a shows the spectroscopic image of the G-band of SWNT serpentine on quartz substrate. We took spectra at different locations along the same carbon nanotube serpentine, as shown by the 150 locations indicated by the pointers in Fig. 1a. Figure 1b shows the frequency behavior for the G^+ band along the SWNT. The G^+ band frequency changes along the SWNT serpentine. Clearly, the ω_G^+ is observed to oscillate, showing maxima at the center of the straight tube segments (labeled S_i in Fig. 1a) and minima at the center of the *U*-turns (labeled U_{jk} in Fig. 1a), in accordance to observations reported in Ref. [22]. This variation in the higher frequency G^+ feature (~1588–1608 cm^{-1}) is clearly related to the tube–substrate interaction resulting from the tube–substrate morphology and formation dynamics [22]. Notice that a departure from this minima/maxima oscillatory behavior is observed at s ~75 μm in Fig. 1b. This anomalous ω_G^+ behavior is consistent with the departure from the serpentine-like morphology observed in the top-left of Fig. 1a, see structure (1a) and ω_G^+ (1b) from U_{13-14} to U_{10-11}. Departure from the oscillatory behavior is also observed for s ~30 μm in Fig. 1b. However, in this segment in U (U_{5-6}), Fig. 1a shows no interruption in the serpentine-like morphology. The Raman frequency indicates there must be a local change in the tube–substrate interaction near U_{5-6}.

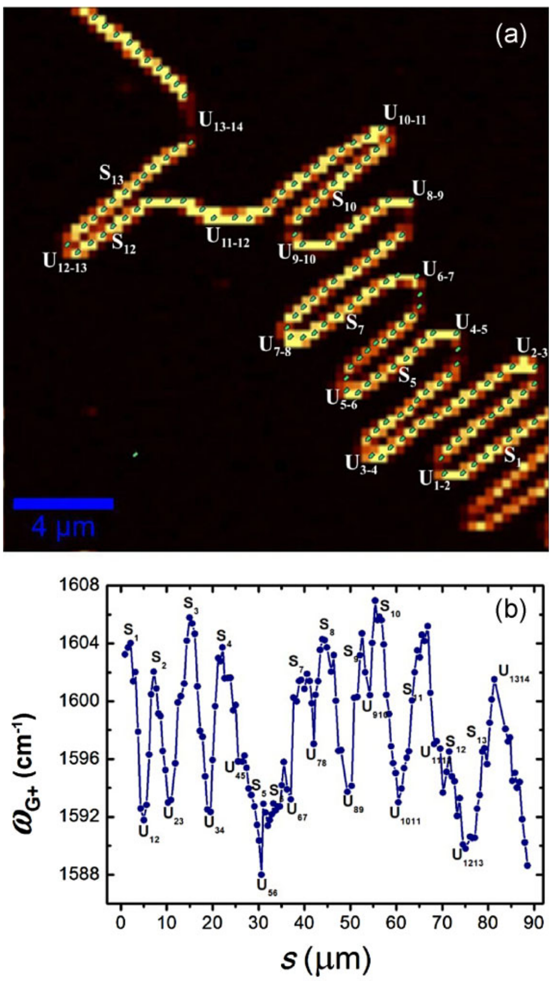

Figure 1 (online color at: www.pss-b.com) (a) Spectroscopic image of the G-band of SWNT serpentine on quartz substrate using the laser wavelength of 532 nm (E_{laser} = 2.33 eV). The growth direction of the single-wall carbon nanotube serpentine is from bottom-right to top-left. (b) The G^+ frequency of a SWNT observed in all points indicated by the pointers in (a) as a function of the distance s measured along the SWNT. S_i and U_{jk} locate the center of the straight segments and U-turns, respectively, showing that the frequency changes are correlated with the tube–substrate morphology.

Figure 2a shows the second case. We took spectra at different locations along a single nanotube serpentine, as shown by the locations indicated by the pointers in Fig. 2a. In Fig. 2b, the ω_G^+ frequencies are plotted as a function of the distance s (Fig. 2a), which is measured along the SWNT. In

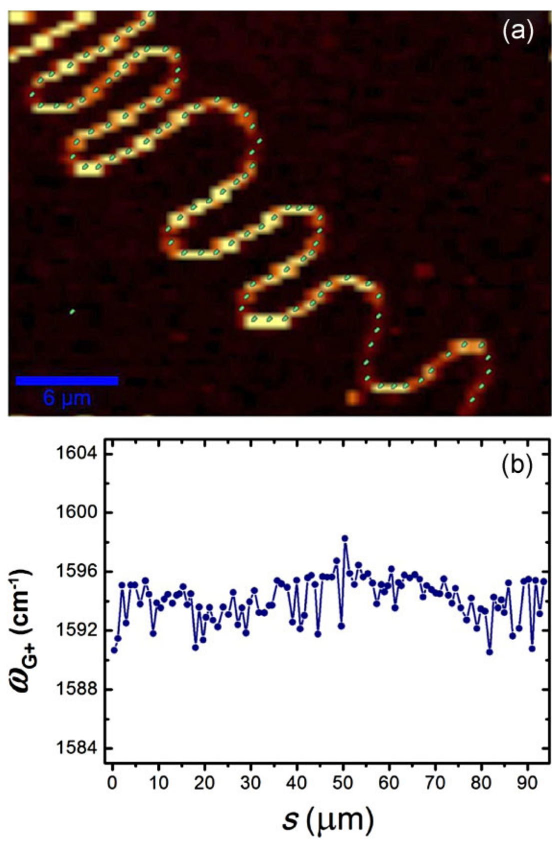

Figure 2 (online color at: www.pss-b.com) (a) Spectroscopic image of the G-band of a SWNT serpentine on quartz substrate using the laser wavelength of 532 nm (E_{laser} = 2.33 eV). The growth direction of the single-wall carbon nanotube serpentine is from top-left to bottom-right. (b) The G^+ frequency of this SWNT, observed in all points indicated by pointers in (a) plotted as a function of the distance s measured along the SWNT. Observe the small variation in the G^+ band frequency.

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

this case, the G^+ frequency changes are small, indicating a reduced (or absent) interaction with the substrate.

Finally, Fig. 3a shows the spectroscopic image of the G-band of a SWNT serpentine on quartz substrate representing the third case. Again, we took spectra at different locations along a single nanotube serpentine, as shown by the locations indicated by the pointers in Fig. 3a. In Fig. 3b, the ω_G^+ frequency for this SWNT is plotted as a function of the distance s (Fig. 3a), which is measured along the SWNT. The G^+ band frequency changes abruptly near the point indicated by the white arrow (Fig. 3a). In this point, some imperfection in the substrate fixes the tube, creating an abrupt change in frequency. Notice, this SWNT grows from the bottom-right to the top-left, in Fig. 3a, which represents moving from $s = 0$ to $s \rightarrow 50\,\mu m$ in Fig. 3b. It is known that uniaxial strain in SWNTs reduces ω_G^+ [23–25]. This is consistent with a picture where the fixed point in $s \sim 30\,\mu m$ would increase the strain on the tube after this point, induced by the growth procedure (“falling spaguethi” [16]).

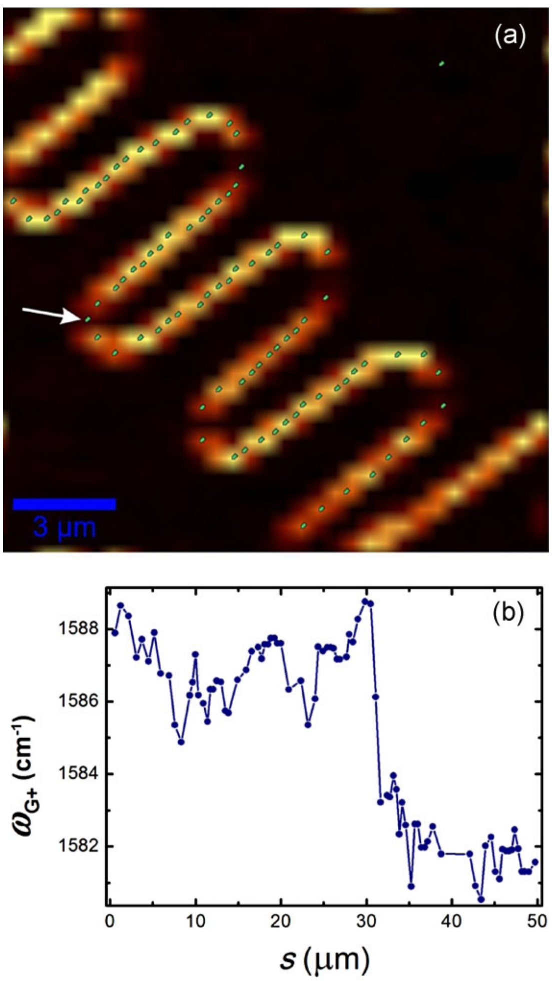

Figure 3 (online color at: www.pss-b.com) (a) Spectroscopic image of the G-band of a SWNT serpentine on quartz substrate using the laser wavelength of 532 nm ($E_{laser} = 2.33$ eV). The growth direction of this single-wall carbon nanotube serpentine is from bottom-right to top-left. (b) The G^+ frequency of this SWNT, observed in all points shown in (a), plotted as a function of the distance s measured along the SWNT.

4 Conclusions In summary, we have measured a SWNT-substrate system where the crystalline substrate can strongly affect the G-band frequency in three different ways, as a result of different types of interaction with the substrate, generated during the synthesis of SWNT serpentines.

For the first case (Fig. 1), the G^+ peak frequency is maximum at the center of the straight segments and lowest in segments through the steps of the substrate. The frequency variation can be explained by the strong tube adhesion to the substrate in the flat and the strain created during the synthesis of SWNT serpentine.

In the second case (Fig. 2), the SWNTs do not show a significant variation in the G^+ peak frequency. There are just fluctuations in the small interaction between the carbon nanotube and the substrate.

In the third case (Fig. 3), the G^+ peak frequency “jumps” at certain points in the SWNT serpentines. The tube can be stuck on imperfections in the substrate during the deposition of the carbon nanotube on the substrate, which creates great tension in the tube. Thus, the G^+ peak frequency has a downshift in the region which follows the fixed point. The observation of such effect led us to perform nanomanipulation experiments, where we wanted to test what happens to these “imperfection” points. What we see is that, when you strain the tube, the side you are stressing exhibits changes in the G^+ frequency, while the rest of the tube after the fixing point remains unchanged. Strain depends not only on the tube–substrate interaction but also on the dynamics of the serpentine formation process, which involves a competition between the tube–surface interaction and the gas-flow-related drag forces [16]. Due to the strong interaction between the SWNT and the substrate after the fixed pointed, the G^+ peak frequency has a downshift showing the strain effect.

Unfortunately we cannot relate the three different groups with any known parameter. We believe the different types of interaction are related to the growth dynamics of the serpentine formation process [26] and local aspects (such as local charging) that we do not control.

Finally, it is important to state that, on the three cases, our Raman spectroscopy results show the complete absence of the disorder induced D-band peak ($\sim$1300 cm^{-1}), which is normally observed in defective sp^2 carbon materials [4]. Furthermore, in all cases where the RBM peak is present, their frequencies are always unchanged along the whole SWNTs serpentines. For the G^- peak, they also exhibit changes, but because of its generally less intense profile, it is harder to define the G^- behavior.

Acknowledgements J. S. S. and A. J. acknowledge financial support from Rede Nacional SPM Brasil, Rede Nacional de Pesquisa em Nanotubos de Carbono, INCT em Nanocarbono, MCT-CNPq, and AFOSR/SOARD (award #FA9550-08-1-0236). E. B. B. acknowledges support from the IPDI. E. J. acknowledges support

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

from the Israel Science Foundation, the US-Israel Binational Science Foundation, the Kimmel Center for Nanoscale Science, and the Legrain, Djanogly, Alhadeff, and Perlman Family foundations.

References

[1] A. Jorio, M. S. Dresselhaus, and G. Dresselhaus, Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications. Top. Appl. Phys., Vol. 111 (Springer, New York, 2008).
[2] P. Avouris, Z. Chen, and V. Perebeinos, Nat. Nanotechnol. **2**, 605 (2007).
[3] M. Steiner, M. Freitag, J. C. Tsang, V. Perebeinos, A. A. Bol, A. V. Failla, and P. Avouris, Appl. Phys. A **96**, 271 (2009).
[4] M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, Phys. Rep. **409**, 47 (2005).
[5] A. Hartschuh, H. N. Pedrosa, J. Peterson, L. Huang, P. Anger, H. Qian, A. J. Meixner, M. Steiner, L. Novotny, and T. D. Krauss, Chem. Phys. Chem. **6**, 577 (2005).
[6] Y. Zhang, J. Zhang, H. Son, J. Kong, and Z. Liu, J. Am. Chem. Soc. **127**, 17156 (2005).
[7] T. Hertel, R. E. Walkup, and P. Avouris, Phys. Rev. B **58**, 13870 (1998).
[8] M. S. C. Mazzoni and H. Chacham, Appl. Phys. Lett. **76**, 1561 (2000).
[9] W. Orellana, R. H. Miwa, and A. Fazzio, Phys. Rev. Lett. **91**, 166802 (2003).
[10] C. Jiang, J. Zhao, H. A. Therese, M. Friedrich, and A. Mews, J. Phys. Chem. B **107**, 8742 (2003).
[11] Y.-H. Kim, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. **92**, 176102 (2004).
[12] A. Ismach, L. Segev, E. Wachtel, and E. Joselevich, Angew. Chem. Int. Ed. **43**, 6140 (2004).
[13] R. H. Miwa, W. Orellana, and A. Fazzio, Appl. Phys. Lett. **86**, 213111 (2005).
[14] S. Berber and A. Oshiyama, Phys. Rev. Lett. **96**, 105505 (2006).
[15] G. W. Peng, A. C. H. Huan, L. Liu, and Y. P. Fena, Phys. Rev. B **74**, 235416 (2006).
[16] N. Geblinger, A. Ismach, and E. Joselevich, Nat. Nanotechnol. **3**, 195 (2008).
[17] A. P. M. Barboza, A. P. Gomes, B. S. Archanjo, P. T. Araujo, A. Jorio, A. S. Ferlauto, M. S. C. Mazzoni, H. Chacham, and B. R. A. Neves, Phys. Rev. Lett. **100**, 256804 (2008).
[18] Y. You, T. Yu, J. Kasim, H. Song, X. Fan, Z. Ni, L. Cao, H. Jiang, D. Shen, J. Kuo, and Z. Shen, Appl. Phys. Lett. **93**, 103111 (2008).
[19] S. Jeon, C. Lee, J. Tang, J. Hone, and C. Nuckolis, Nano Res. **1**, 427 (2008).
[20] J. Huang and W. Choi, Nanotechnology **19**, 505601 (2008).
[21] J. Xiao, S. Dunham, P. Liu, Y. Zhang, C. Kocabas, L. Moh, Y. Huang, K.-C. Hwang, C. Lu, W. Huang, and J. A. Rogers, Nano Lett. **9**, 4311 (2009).
[22] J. S. Soares, A. P. M. Barboza, P. T. Araujo, N. M. B. Neto, D. Nakabayashi, N. Shadmi, T. S. Yarden, A. Ismach, N. Geblinger, E. Joselevich, C. Vilani, L. G. Cançado, L. Novotny, G. Dresselhaus, M. S. Dresselhaus, B. R. A. Neves, M. S. C. Mazzoni, and A. Jorio, Nano Lett. **10**, 5043 (2010).
[23] S. B. Cronin, A. K. Swan, M. S. Unlu, B. B. Goldberg, M. S. Dresselhaus, and M. Tinkham, Phys. Rev. Lett. **93**, 167401 (2004).
[24] X. Duan, H. Son, B. Gao, J. Zhang, T. Wu, Ge. G. Samsonidze, M. S. Dresselhaus, Z. Liu, and J. Kong, Nano Lett. **7**, 2116 (2007).
[25] B. Gao, L. Jiang, X. Ling, J. Zhang, and Z. Liu, J. Phys. Chem. C **112**, 20123 (2008).
[26] L. D. Machado, S. B. Legoas, J. S. Soares, N. Shadmi, A. Jorio, E. Joselevich, and D. S. Galvao, MRS Bull. (2011). accepted.

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim