JOURNAL OF CHEMICAL PHYSICS VOLUME 120, NUMBER 8 22 FEBRUARY 2004

Phase stability of nanocarbon in one dimension: Nanotubes versus diamond nanowires

A. S. Barnard[a] and I. K. Snook[b]
Department of Applied Physics, Royal Melbourne Institute of Technology University, GPO Box 2476V Melbourne, 3001 Australia

(Received 15 July 2003; accepted 24 November 2003)

Since their discovery in 1990, the study of sp^2 bonded carbon nanotubes has grown into a field of research in it's own right; however the development of the sp^3 analog, diamond nanowires, has been slow. A number of theoretical models have been proposed to compare the relative stability of diamond and graphite at the nanoscale; and more recently, to compare nanodiamonds and fullerenes. Presented here is a study of the phase stability of nanocarbon in one-dimension. The structural energies of carbon nanotubes and diamond nanowires have been calculated using density functional theory within the generalized gradient approximation, and used to determine the atomic heat of formation as a function of size. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1643354]

INTRODUCTION

In recent years carbon nanomaterials have been the subject of intensive experimental and theoretical efforts, probing their structural, energetic, mechanical, and electronic properties. The discovery of graphitelike bonded carbon nanotubes (CNT) by Iijima[1] in the early 1990s inspired a new branch in materials science, dedicated to the development of technology at the nanoscale. Numerous studies have been conducted, exploring the unique structural to electronic properties of nanotubes,[2] such as high mechanical strength, high thermal and chemical stabilities, excellent heat conduction.[3]

The mechanical properties of CNTs have been investigated theoretically[4–6] in numerous studies. The energetic, structural; and elastic properties (including Young's Modulus and Poison's ratio) of CNTs were calculated by Hernández *et al.* using nonorthogonal tight-binding; and later re-examined by Shenderova *et al.*[5] in comparison with diamond nanorods. Recent work by Troiani *et al.*[6] examined the properties of ductile nanotubes under axial strain using tight-binging calculations, finding that the nanotubes either developed a linear cumulene type chain or a junction before failing; in agreement with their observations using high resolution electron microscopy.

Although the sp^2 bonding of CNTs offer many structural advantages, the smallest nanotubular structure has been predicted to poses sp^3 bonding,[7] as sp^2 bonding appears to be unfavorable.[8] These structures were predicated by Stojkovic *et al.*[7] to be approximately 4 Å in diameter, and were later observed experimentally[9,10] with the results of Qin *et al.*[9] supporting the suggesting of sp^3 bonding more akin to diamond. Diamond based materials have also been suggested to be the optimal choice for nanomechanical designs, as they possess other unique structural to electronic properties such as high elastic modulus and strength-to-weight ratio.[11] This has prompted a number of theoretical studies investigating various aspect of diamond at the nanoscale.

Although a number of studies have reported on structure and properties of semiconductor nanowires including carbon,[12] the development of diamond nanowires has been slow. The growth of carbon nanowires has been achieved using a number of techniques;[13–16] and aligned diamond nanowhiskers have been successfully synthesized,[17] showing well-defined characteristics of diamond.[18] Diamond nanocylinders with a diameter of approximately 300 nm have been fabricated,[19] and most recently, nanorods of single crystalline diamond have been reported.[20] The details of the respective experimental techniques used for the successful synthesis of diamond nanowire to date are outlined in Refs. 16–20.

Recently it has been shown from *ab initio* calculations that nanocrystalline diamond is structurally stable in one dimension,[5,21] under certain conditions. The stability, characterized by the variation in these structural properties from that of bulk-diamond, was found to be dependent on both the surface morphology and the crystallographic direction of the principle axis of the nanowire.[21] In a study conducted by Shenderova *et al.*,[5] the stiffness and fracture force of hydrogenated diamond nanorods has been compared with those of single-walled and multiwalled carbon nanotubes, also concluding that the mechanical properties of the nanorods depend on both the diameter of the nanorod, and the orientation of the principle axis. Similarly, the electronic structure of fine (stable) dehydrogenated and hydrogenated diamond nanowires has been briefly examined by Barnard *et al.*,[22] with results indicating that the band gap of diamond nanowires is not only smaller than that of bulk diamond, but that it varies depending upon the surface morphology, diameter and (again) the orientation of the principle axis.

Still few diamond nanowires structures have been observed experimentally, which raises questions as to the phase stability of one-dimensional (1D) diamond structures. If dia-

---

[a] Electronic mail: amanda.barnard@physics.org
[b] Electronic mail: ian.snook@rmit.edu.au

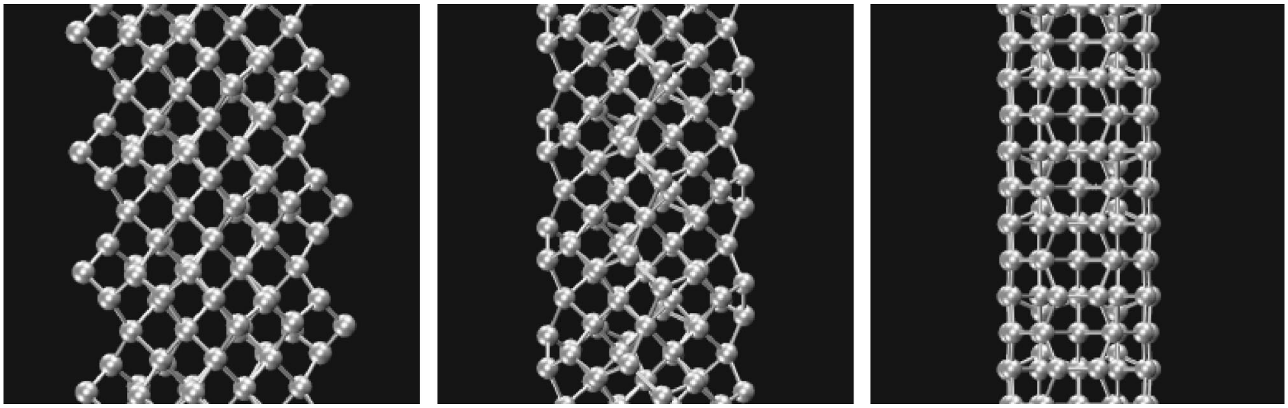

FIG. 1. Examples of the diamond nanowire morphologies considered in this study, including dodecahedral (left), cylindrical (center), and cubic (right).

mond is to play a significant role in the future of nanodevices, it is important to gain a full understanding of the phase stability of dehydrogenated diamond nanowires and carbon nanotubes, to determine if diamond nanowires are energetically favorable, compared to carbon nanotubes. Theoretical work compiled regarding carbon phase stability[23–29] has so far only concentrated on 0D structures such as graphite nanoparticles and nanodiamond. These models predict that for particles under 5–6 nm in diameter nanocrystalline diamond is more stable than graphite. As an extension of this, we have recently outlined a model for examining the relative stability of graphite, nanodiamond and fullerenes,[30] as well as the intermediary structures known as bucky-diamonds.[31] This model successfully predicted that at the ultrananoscale fullerenes, and not nanodiamond, are the most stable allotrope. This intersection occurred at a cubic nanodiamond diameter of approximately 1.9 nm, indicating a ''window'' of stability for nanodiamond.

This model has now been applied to carbon nanotubes and stable diamond nanowires, in an attempt to ascertain if diamond nanowires are thermodynamically viable.

STRUCTURE AND ENERGETICS

The structure of a nanotube may be describe entirely in terms of the length and chirality. The chirality and diameter are uniquely defined in terms of the magnitude of the components of the chiral vector $C_h = n\overline{a}_l + m\overline{a}_2 \equiv (n,m)$, where n,m are integers and $\overline{a}_1, \overline{a}_2$ are the unit vectors of a hexagonal, graphene sheet. The chiral vector C_h therefore connects two crystallographically equivalent sites on the sheet. The particular chiralities known as ''armchair'' and ''zig–zag'' are named for the cases where $m=n$ and $m=0$, respectively. The term ''chiral'' is used for all other values of m. Both zig–zag and armchair structures are considered here, for all $n=3$ to 12.

Three stable dehydrogenated nanowire morphologies have been included in this study, characterized by pure dodecahedral forms and combinations of cubo-dodecahedral forms, with increasing average lateral diameter. To assist in clarity, one cubo-dodecahedral group is denoted as ''cylindrical'' due to the circular cross section, and the other as ''cubic'' due to the square or rectangular cross section. The dodecahedral structures are bounded by (110) surfaces in all lateral directions, with a square cross section; and have a principle axis in the [100] direction. The cylindrical nanowires considered here are bounded by four C(100) surfaces and four C(110) surfaces in the lateral directions, with a circular cross section, and have a principle axis in the [100] direction. The cubic diamond nanowires are bounded by two C(100) surfaces and two C(110) surfaces in the lateral directions, with a rectangular cross-section, and have a principle axis in the [110] direction. The initial structures have been ''cleaved'' from a bulk diamond lattice, with both C(110)(1×1) single dangling bond and C(100)(1×1) double dangling bond surface structure. Three nanowires of each morphology have been considered (with increasing diameter), with periodic boundary conditions (PBC) applied in the x direction and sufficient vacuum space added in the y and z directions to create infinite 1D structures. Examples of these nanowires are shown in Fig. 1, viewed laterally from the [100] direction.

All nanowire and nanotube structures have been relaxed using density functional theory (DFT) within the generalized gradient approximation (GGA), with the exchange-correlation functional of Perdew and Wang (PW91).[32] This has been implemented via the Vienna *ab initio* Simulation Package (VASP),[33,34] using ultrasoft, gradient-corrected Vanderbilt-type pseudopotentials.[35,36] The valence orbitals are expanded in a plane-wave basis up to a kinetic energy cutoff of 290.00 eV. The relaxation technique used here is an efficient matrix-diagonalization routine based on a sequential band-by-band residual minimization method of single-electron energies,[37,38] with direct inversion in the iterative subspace. Both the ionic positions and super-cell volume have been relaxed. Thus both the symmetry and the lattice parameter are free to alter, resulting in expansions or contractions of the entire structures. We have successfully applied this technique to the relaxation of bulk diamond,[39] nanodiamond,[40] diamond nanowires,[21] and fullerene[30] structures in previous studies.

Phase stability model

The method use here to estimate the phase stability of the relaxed carbon nanotubes and diamond nanowires is based on the atomic heat of formation, as a function of size. The atomic heat of formation of dehydrogenated diamondlike $[\Delta H_f^o(\mathrm{D})/N_\mathrm{C}]$ and fullerenic $[\Delta H_f^o(\mathrm{F})/N_\mathrm{C}]$ structures is expressed in terms of the C–C bond energy E_CC and dangling bond energy E_DB, such that

$$\frac{\Delta H_f^o(\mathrm{D})}{N_\mathrm{C}} = 2E_\mathrm{CC}^\mathrm{D} + \frac{N_\mathrm{DB}}{N_\mathrm{C}}\left(E_\mathrm{DB}^\mathrm{D} - \tfrac{1}{2}E_\mathrm{CC}^\mathrm{D} + \Delta H_f^o(\mathrm{DB})\right) + \Delta H_f^o(\mathrm{C}), \tag{1}$$

$$\frac{\Delta H_f^o(\mathrm{F})}{N_\mathrm{C}} = \frac{3}{2}E_\mathrm{CC}^\mathrm{F} + \Delta H_f^o(\mathrm{C}) + \frac{E_s}{R^2}, \tag{2}$$

where, N_C is the number of carbon atoms, N_DB is the number of dangling bonds on the surface of the structure and $\Delta H_f^o(\mathrm{C})$ is the standard heat of formation of carbon at 298.15 K. A dehydrogenated surface has been used for the diamond nanowires [see Eq. (1)], as the main intention here is to compare diamond nanowires with carbon nanotubes, which do not have a hydrogenated surface. We note that the various bond energies E_CC and E_DB are calculated at 0 K (using DFT) while $\Delta H_f^o(\mathrm{C})$ is determined at 298.15 K, but it has been assumed in this model that the corrections required due to this are small, and have therefore been ignored in this treatment.

This model also assumes that the strain energy of a nanotube contains only two in-plane elastic constants, and that the chiral graphene sheet is homogeneous and elastically isotropic. Hence, ignoring higher order effects such as torsional bending, the deformation energy consists of stretching (first-order) and bending (second-order) terms. In nanotubes, the stretching term is the cohesive energy of the carbon atoms, and the bending term provides the strain energy associated with curvature of the cylindrical structure. Therefore the strain in an elastic cylinder can be approximated as bending and stretching of a suitable elastic sheet, where the strain (bending) energy of each atom ($E_\mathrm{strain}/N_\mathrm{C}$) per unit area ($A$) is given in terms of the sheet thickness (h), by

$$\frac{E_\mathrm{strain}}{N_\mathrm{C}} = \frac{A\kappa h^3}{N_\mathrm{C} 24 R^2}, \tag{3}$$

where κ is the bending modulus of the sheet, and R is the radius of curvature. For a nanotube, if we assume a cylindrical model, R is also equal to the mean radius, $A = 2\pi RL$, and $N_\mathrm{C} = 2\pi RL\rho$. This results in an expression for the strain energy per carbon atom, which is linearly dependent on the inverse square of the curvature of the structure,

$$\frac{E_\mathrm{strain}}{N_\mathrm{C}} = \left(\frac{\kappa h^3}{\rho 24}\right)\frac{1}{R^2} = E_s \frac{1}{R^2}. \tag{4}$$

This is a suitable definition for use here as E_s may be obtained by fitting the calculated energy to the inverse of the square of the nanotube curvature. Hence, the strain energy and cohesive energy may be obtained from the slope and intercept of a linear fit to the energy per ion versus $1/R^2$ respectively, as

$$\frac{E}{N_\mathrm{C}} = E_s \frac{1}{R^2} + \frac{E_\mathrm{cohesive}^\mathrm{F}}{N_\mathrm{C}}, \tag{5}$$

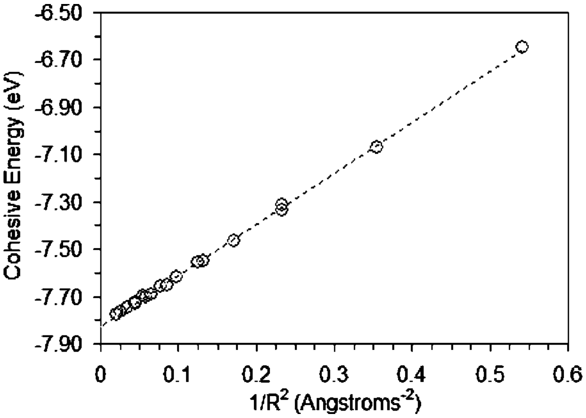

FIG. 2. The calculated energy per atom vs the inverse square of the radius of curvature, for the zig–zag and armchair carbon nanotubes ($n=3-12$) structures, with the linear fit.

where E is the total nanotube energy calculated explicitly with DFT (see Fig. 2), for all the zig–zag and armchair nanotubes from $n=4$ to 12.[42] There are many ways of defining the strain energy in nanotubes,[43–46] however the type of approach used here (which has also been successfully applied before[47]) has proven to be most useful in the presented model.[48] The stain energy obtained here is in agreement with those obtained using other models,[43–46] after suitable conversions are made for units and approximations.

Similarly, E_CC^D and E_DB^D for the diamond nanowires may also be obtained by extrapolating the energy per atom versus the number of dangling surface bonds per atom (see Fig. 3). The slope and intercept of the linear fit gave values for the cohesive energy of -7.55 eV (where E_CC^D is half the cohesive energy) and a dangling bond energy of 1.32 eV, respectively.

DISCUSSION OF RESULTS

The fitted values for E_CC^D, E_DB^D, E_CC^F [as $E_\mathrm{cohesive}^\mathrm{F} = (3/2)E_\mathrm{CC}^\mathrm{F}$] and E_s [with the experimental value for $\Delta H_f^o(\mathrm{C}) = 7.432$ eV (Ref. 41)] were then inserted in to Eqs. (1) and (2), and the atomic heat of formation calculated for the nanotubes and diamond nanowires. This was then plotted

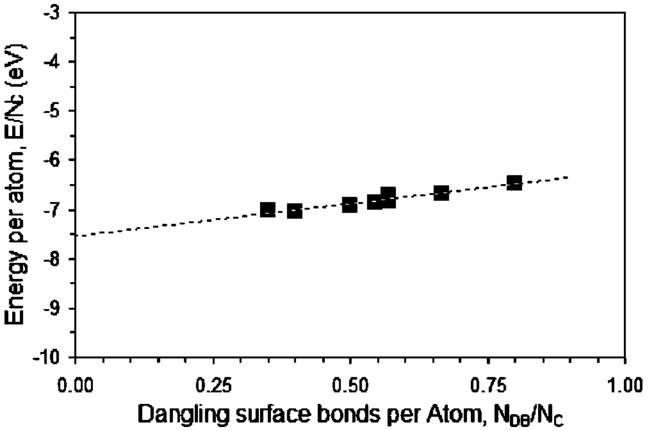

FIG. 3. The calculated energy per atom vs the dangling surface bonds per atom, for the stable diamond nanowire structures, with the linear fit.

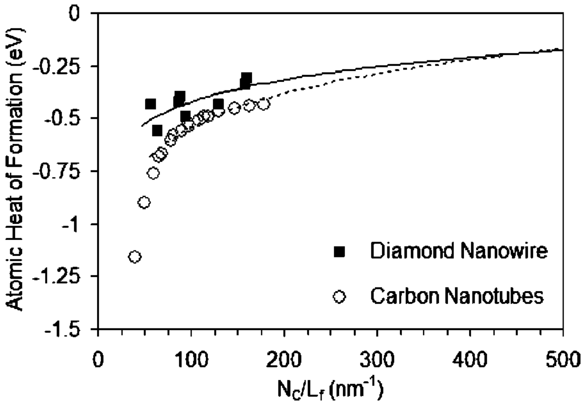

FIG. 4. The calculated atomic heat of formation vs the number of atoms per unit length, for the stable diamond nanowire structures and carbon nanotubes, with the extrapolations indicated by the lines of best fit. The diamond nanowires with a significantly lower heat of formation, almost matching that of carbon nanotubes, are representative of the dodecahedral morphology, whereas the diamond nanowires with the higher heat of formation (well above that of carbon nanotubes) are representative of the cubic and cylindrical morphologies.

as a function of the number of carbon atoms per unit length, rather than the number of carbon atoms,[30] as these are effectively infinite structures. In all cases the final, relaxed length was used. This is shown in Fig. 4, along with the lines of best fit. By extrapolating the fits the intersection of diamond nanowires and carbon nanotubes was found to be ~450 atoms/nm. This is approximately equivalent to a diamond nanowire of ~2.7 nm in diameter, or an $n=27$ armchair nanotube.[49]

However, Fig. 4 shows that the atomic heat of formation of nanowires varies considerably among the structures, with three points falling almost among the nanotube results. This variation is due to the different morphologies of the diamond nanowires, and it is the dodecahedral nanowires that have formation energies akin to nanotubes. These nanowires retained the diamond sp^3 bonding following relaxation, and have been found previously to represent the most structurally stable nanowire morphology.[21] This significant result indicates that diamond nanowires with C(110) surfaces, and a principle axis in the [100] direction are not only structurally stable, but almost as energetically favorable as comparable carbon nanotubes.

As part of our previous study of nanodiamond crystals and fullerenes,[30] the atomic heat of formation of graphite was estimated using experimental values for the bond energies (rather than calculated values). Using the fit obtained from this work, the intersection of diamond nanowires and nanotubes with graphite was also investigated. In order to preserve the correct dimensionality, the number of atoms in the graphite model was scaled (per unit length) in two chiral directions, equating to $\theta=0$ and $\theta=30°$ (where θ is the chiral angle). Both directions were examined, to determine whether scaling of this type would be meaningful. The intersection of the heat of formation as a function of atoms per unit length for diamond nanowire and carbon nanotubes with graphite was then obtained for each "chiral scaling." These results, along with the phase stability crossing-point between diamond nanowires (averaged over morphologies) and carbon nanotubes, are contained within Table I. Table I also contains (based in the number of carbon atoms per unit length of each crossing-point) an estimate of the corresponding diameters of diamond nanowires, and chiral index n of an armchair nanotube.

These results indicate a "window" of stability for diamond nanowires, between approximately 450 to 870–930 atoms per unit length. The upper limit of this range (where graphite becomes the most energetically preferred allotrope) is sensitive to the chiral scaling direction, indicating some uncertainty surrounding this phase stability crossing point. At the lower limit of this range, it is apparent that although carbon nanotubes are energetically preferred, the exact phase stability crossing-point is sensitive to the morphology of the diamond nanowire. However, irrespective of these uncertainties, the results show that thermodynamic stability of diamond nanowires may only be expected in a *very limited size range*, at best. This will obviously have an impact of the effective synthesis of these structures.

This size range is however in agreement with a number of other experimental and theoretical studies. Nanocrystalline diamond has recently been obtained directly from carbon nanotubes at high pressure,[50] and theoretical simulations [using the empirical many-body potential energy functional (PEF) and (canonical) molecular dynamics at 1 K] by Erkoç *et al.*[51,52] have shown the transformation of carbon multiwalled nanotubes into ta-C nanowires, in line with experimental observations.[53]

CONCLUSIONS

Presented here is a theoretical investigation of the relative phase stability of 1D carbon nanostructures, using a heat of formation model previously used successfully to compare the phase stability of diamond nanocrystals and fullerenes. The results of this study indicate that carbon nanotubes represent the most energetically preferred form for fine 1D carbon nanostructures, and that (the sp^3 analog) diamond nanowires occupy a "window" of stability. This window ranges from approximately 2.7 nm to 3.7–9 nm in (lateral)

TABLE I. Size ranges of phase stability for 1D carbon nanostructures, including approximate corresponding diameters of diamond nanowires and chiral index of carbon nanotubes.

Carbon nanostructure	N_C/L_f (nm^{-1})	DNW Diameter (nm)	CNT chiral index n
Carbon nanotubes (CNT)	$\lesssim 450$	$\lesssim 2.7$	<27
Diamond nanowires (DNW)	~450 to 870[a]–930[b]	~2.7 to ~3.7[a]–~3.9[b]	53[a]–57[b]
Graphite	>870[a]–930[b]	$\gtrsim$3.7[a]–~3.9[b]	>53[a]–57[b]

[a] Graphite scaled in the $\theta=0$ chiral direction.

[b] Graphite scaled in the $\theta=30°$ chiral direction.

diameter, beyond which graphite is energetically preferred. The limits of this range are sensitive both to the nanowire morphology, and the method used to scale the graphite structures (required to ensure dimensional consistency).

These results are considered to be useful in estimating the size range for which diamond nanowires may be expected during synthesis, and as a guide to the relative stability of some sp^2 and sp^3 carbon in 1D nanostructures. Further work is required to investigate the relative stability of other nanocarbon structures such as nanopeapods, bucky-wires[54] and amorphous carbon nanostructures in 1D.[53]

ACKNOWLEDGMENTS

We would like to thank the Victorian Partnership for Advanced Computing and the Australian Partnership for Advanced Computing supercomputer center for their support of this project, and Associate Professor Salvy Russo for useful suggestions.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998).
[3] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
[4] E. Hernández, G. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. **80**, 4502 (1998).
[5] O. A. Shenderova, D. W. Brenner, and R. S. Ruoff, Nano Lett. **3**, 805 (2003).
[6] H. E. Troiani, M. Miki-Yoshida, G. A. Camacho-Bragado, M. A. L. Marques, A. Rubio, J. A. Ascencio, and M. Jose-Yacaman, Nano Lett. **3**, 751 (2003).
[7] D. Stojkovic, P. Zhang, and V. H. Crespi, Phys. Rev. Lett. **87**, 125502 (2001).
[8] L.-M. Peng, Z. L. Zhang, Z. Q. Xue, Q. D. Wu, Z. N. Gu, and D. G. Pettifor, Phys. Rev. Lett. **85**, 3249 (2000).
[9] L.-C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, and S. Iijima, Nature (London) **408**, 50 (2000).
[10] N. Wang, Z. K. Tang, G. D. Li, and J. S. Chen, Nature (London) **408**, 50 (2000).
[11] O. A. Shenderova, V. V. Zhirnov, and D. W. Brenner, Crit. Rev. Solid State Mater. Sci. **27**, 227 (2002).
[12] R. Q. Zhang, S. T. Lee, C.-K. Law, W.-K. Li, and B. K. Teo, Chem. Phys. Lett. **364**, 251 (2002).
[13] S. Botti, R. Ciardi, M. L. Terranova, S. Piccirillo, V. Sessa, and M. Rossi, Chem. Phys. Lett. **355**, 395 (2002).
[14] R.-M. Liu, J.-M. Ting, J.-C. A. Huang, and C.-P. Liu, Thin Solid Films **420**, 145 (2002).
[15] A. Xia, Z. Huizhao, Y. Li, and X. Chengshan, Appl. Surf. Sci. **193**, 87 (2002).
[16] Y. H. Tang, N. Wang, Y. F. Zhang, C. S. Lee, I. Bello, and S. T. Lee, Appl. Phys. Lett. **75**, 2921 (1999).
[17] E.-S. Baik, Y.-J. Baik, and D. Jeon, J. Mater. Res. **15**, 923 (2000).
[18] E.-S. Baik, Y.-J. Baik, S. W. Lee, and D. Jeon, Thin Solid Films **377**, 295 (2000).
[19] H. Masuda, T. Yanagishita, K. Yasui, K. Nishio, I. Yagi, T. N. Rao, and A. Fujishima, Adv. Mater. (Weinheim, Ger.) **13**, 247 (2001).
[20] Y. Ando, Y. Nishibayaski, K. Kobashi, and A. Sawabe, *14th European Conference on Diamond, Diamondlike Materials, Carbon Nanotubes, Nitrides, and Silicon Carbide: Mechanical and Thermal Applications*, Salzburg, Austria, 2003.
[21] A. S. Barnard, S. P. Russo, and I. K. Snook, Nano Lett. **3**, 1323 (2003).
[22] A. S. Barnard, S. P. Russo, and I. K. Snook, Phys. Rev. B **68**, 235407 (2003).
[23] N. W. Winter and F. H. Ree, J. Comput.-Aided Mater. Des. **5**, 279 (1998).
[24] J. A. Nuth, Nature (London) **329**, 589 (1987).
[25] P. Badziag, W. S. Veowoerd, W. P. Ellis, and N. R. Greiner, Nature (London) **343**, 244 (1990).
[26] M. Y. Gamamik, Nanostruct. Mater. **7**, 651 (1996).
[27] N. M. Hwang, J. H. Hahn, and D. Y. Yoon, J. Cryst. Growth **160**, 87 (1996); **162**, 55 (1996).
[28] P. Keblinski, S. R. Phillpot, D. Wolf, and H. Gleiter, Nanostruct. Mater. **12**, 339 (1999).
[29] Q. Jiang, J. C. Li, and G. Wilde, J. Phys.: Condens. Matter **12**, 5623 (2000).
[30] A. S. Barnard, S. P. Russo, and I. K. Snook, J. Chem. Phys. **118**, 5094 (2003).
[31] A. S. Barnard, S. P. Russo, and I. K. Snook, Phys. Rev. B **68**, 073406 (2003).
[32] J. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[33] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[34] G. Kresse and J. Hafner, Phys. Rev. B **54**, 11169 (1996).
[35] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[36] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[37] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[38] D. M. Wood and A. Zunger, J. Phys. A **18**, 1343 (1985).
[39] A. S. Barnard, S. P. Russo, and I. K. Snook, Philos. Mag. B **82**, 17 (2002); **82**, 1767 (2002).
[40] A. S. Barnard, S. P. Russo, and I. K. Snook, Philos. Mag. Lett. **83**, 39 (2003).
[41] *Handbook of Chemistry and Physics*, 81st ed. (CRC, Boca Raton, 2000–2001).
[42] The $n=3$ nanotubes have been ignored, as their structure was found to alter significantly from the ideal CNT structure, in keeping with the results of Ref. 8.
[43] J. P. Lu, Phys. Rev. Lett. **79**, 1297 (1997).
[44] D. A. Walters, L. M. Ericson, M. J. Casavant, J. Liu, D. T. Colbert, K. A. Smith, and R. E. Smalley, Appl. Phys. Lett. **74**, 3803 (1999).
[45] Zhan-chun Tu, Phys. Rev. B **65**, 233407 (2002).
[46] N. Park, K. Lee, S. Han, J. Yu, and J. Ihm, Phys. Rev. B **65**, 121405 (2002).
[47] X. Hua, T. Çağin, J. Che, and W. A. Goddard III, Nanotechnology **11**, 85 (2000).
[48] A. S. Barnard and S. P. Russo, J. Phys. Chem. B **107**, 7577 (2003).
[49] These values are only approximate however due to uncertainties, the largest of which is the quality of the ‘‘best fit’’ to the calculated values; especially in the case of the diamond nanowires. Uncertainties have not been shown for the purposes of clarity.
[50] H. Yusa, Diamond Relat. Mater. **11**, 87 (2002).
[51] S. Erkoç, Int. J. Mod. Phys. C **11**, 1247 (2000).
[52] S. Erkoç and O. B. Malcioğlu, Int. J. Mod. Phys. C **13**, 367 (2000).
[53] K. H. Chen, C. T. Wu, J. S. Hwang, C. Y. Wen, L. C. Chen, C. T. Wang, and K. J. Ma, J. Phys. Chem. Solids **62**, 1561 (2001).
[54] A. S. Barnard, S. P. Russo, and I. K. Snook, J. Nanosci. Nanotech. **4**, 1 (2003).