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Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Bond switching regimes in nickel and nickel–carbon nanoclusters

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ARTICLE INFO

Article history:

Received 18 January 2010

In final form 9 February 2010

Available online 13 February 2010

ABSTRACT

Understanding the fundamental dynamics in carbon nanotube (CNT) catalysts is of primary importance to understand CNT nucleation. This Letter reports on calculated bond switching (BS) rates in pure and carbon containing nickel nanoclusters. The rates are analyzed in terms of their temperature dependent spatial distribution and the mobility of the cluster atoms. The BS mechanism is found to change from vibrational to diffusional at around 900 K, with a corresponding strong increase in activation energy. Furthermore, the BS activation energy is observed to decrease as the carbon content in the cluster increases, resulting in an effective liquification of the cluster.

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1. Introduction

The unique electronic, mechanical and optical properties of carbon nanotubes (CNTs) make these materials excellent candidates for application in numerous fields, including microelectronics, medical applications and materials science [1]. For example, CNTs may be used as interconnects in silicon IC manufacturing as their current carrying capacity is 10^9 A/cm² before damage or breakdown of the materials is observed [2]. Also, the very high thermal conductivity of CNTs allows their use in dissipating heat from chips [3]. Other possible applications include CNT-based composites, hydrogen storage, and their use as electrochemical devices, field emission devices, gas sensors and probes [4]. Recently, Aliev et al. demonstrated the possibility of CNT based artificial muscles [5].

Most applications heavily rely on either post-growth purification or selective growth (especially for electronic applications). Catalytic chemical vapor deposition (CCVD) of CNTs is regarded as a promising method for obtaining the required selectivity. In CCVD, a hydrocarbon gas is decomposed on the surface of a suitable nanoparticle catalyst. Examples of catalysts include iron-group metals (Ni, Fe, Co) and their alloys, coinage metals (Cu, Ag, Au), and late transition metals (Pd, Pt) [6–8].

Currently, two qualitative growth models are proposed in literature. In the vapor–liquid–solid model (VLS) [9], carbon is assumed to dissolve into the catalyst with subsequent precipitation of excess carbon on the metal surface [10]. This precipitation leads to CNT growth. Another mechanism, the surface-mediated carbon transport model, has been proposed to explain the low temperature nanotube growth by plasma enhanced CVD (PE-CVD) [11–13]. Indeed, the low temperature in PE-CVD conditions implies that

the catalyst is in a solid state, rather than in a liquid state as required in the VLS model.

Associated with the optimum condition of the catalyst for CNT growth, also the phase of the nanoscale catalyst has been investigated [14–16]. In general, the liquid phase is defined as the phase satisfying two conditions: a disordered state and diffusive atom motion. However, it is difficult to observe diffusion of atoms directly in nanoclusters. Hence, numerical simulations are useful to study the phase of such small nanoclusters.

In this Letter, we address the fundamental kinetics in carbon containing nickel nanoclusters in a temperature range relevant for single walled carbon nanotube (SWNT) growth. Bond switching (BS) rates are calculated and analyzed in terms of their spatial distribution in the cluster and the mobility of the cluster atoms. The present results are discussed and where possible comparison is made to previous findings. We conclude that (i) the bond switching mechanism governs the fundamental dynamics in the nanocatalyst, and (ii) the carbon concentration in the nanocatalyst determines the CNT nucleation rate.

2. Computational methods

The BS rates were calculated using classical molecular dynamics (MD) simulations. The interatomic potential used is a recently developed many-body potential [17], which we have previously successfully applied to simulated melting of nickel nanoclusters and the simulated synthesis of metallofullerenes [18,19]. The equations of motion are integrated using the Velocity Verlet scheme with a time step of 0.5 fs [20].

The BS rates are obtained as follows. First, five gas phase clusters are constructed: Ni₁₀₈, Ni₁₀₈C, Ni₁₀₈C₅, Ni₁₀₈C₁₀, and Ni₁₀₈C₅₃₀. Each of these clusters is thermalized for 200 ps at each temperature, in the range 400–1500 K, with an interval of 100 K.

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The clusters are then allowed to evolve for 50 ps under NVE conditions, during which the BS rates are obtained. The BS rate is defined as the sum of the number of bonds broken and bonds formed per unit of time [21], and is determined by comparing neighbor lists at each time step, as obtained after minimization using steepest descent. This ensures that for each neighbor list comparison, the corresponding structures are in a local energy minimum, and not in a transition state.

3. Results and discussion

The calculated bond switching rate for Ni–Ni in a Ni₁₀₈ cluster is shown in Fig. 1 as an Arrhenius plot in a temperature range of 400–1500 K. The BS rate is found to be in the order of 100 events/ps at low temperature (400 K), rising to about 1000 events/ps at the highest investigated temperature (1500 K). The fundamental dynamics of the system are thus very rapid, occurring on sub-pico-second timescales for all temperatures investigated. As a consequence, the system does not reside in one specific local energy minimum, occasionally jumping to another minimum (even at 400 K), but rather moves almost continuously between near-degenerate minima. This has important consequences for simulating the long time-scale evolution of CNT growth, as will be explained at the end of this Letter.

At around 900 K, a sharp increase in BS rate with rising temperature is observed. From the linear fits to the data before and after this crossing point, activation energies of 0.033 ± 0.008 eV and 0.296 ± 0.005 eV are found for the low temperature region and the high temperature region, respectively. The associated pre-exponential factors are calculated to be $3 \times 10^{14} \text{ s}^{-1}$ and $1 \times 10^{16} \text{ s}^{-1}$, respectively. Note that for a single rate-limited thermally activated process with constant activation energy, an Arrhenius plot gives a straight line. Hence, the occurrence of two straight lines in the plot is indicative for two different mechanisms occurring in the two temperature windows, and is attributed to a phase change. Indeed, plotting the bond energy as a function of temperature reveals a steep increase at around 900 K, indicative for a first

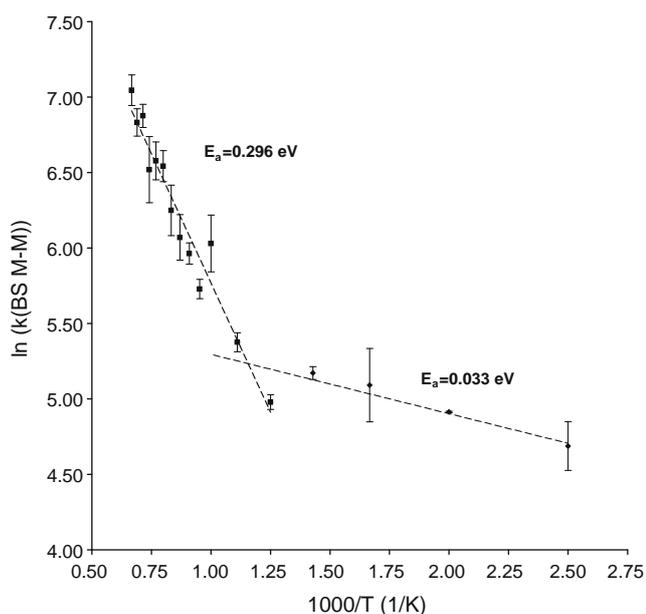


Fig. 1. Calculated bond switching rates for pure Ni₁₀₈ as a function of $1000/T$ in the temperature range 400–1500 K, indicating two regimes with different BS mechanisms.

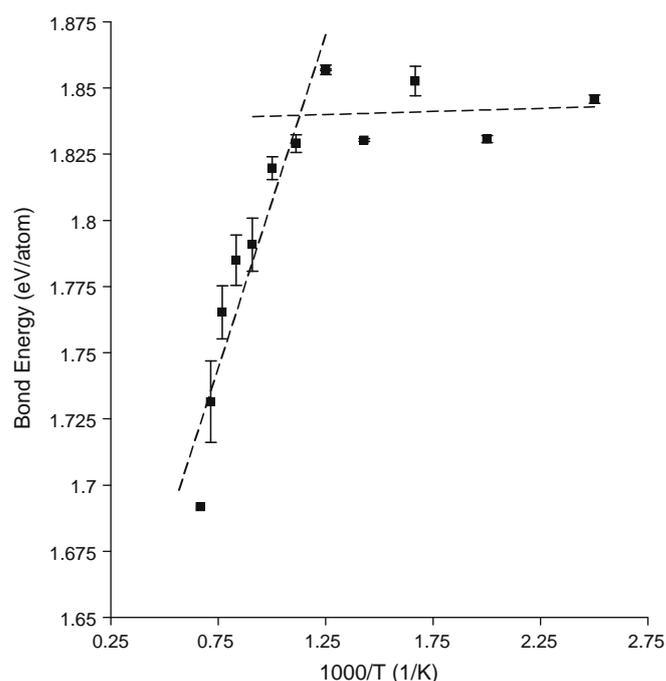


Fig. 2. Calculated bond energy as a function of $1000/T$. The abrupt decrease in bond energy with increasing temperature above 900 K is indicative for a phase change.

order phase change (see Fig. 2) [22], and coinciding with the change in BS mechanism. At low temperature (below 900 K), the bond energy remains nearly constant with increasing temperature. On the other hand, increasing the temperature to 900 K and beyond, leads to a sharp drop in bond energy, resulting in an increase in the atoms mobility. This is demonstrated in Fig. 3, showing the variation of the position of a randomly chosen atom relative to the center of mass of the cluster, for different temperatures. From the figure, it can be seen that at low temperature (600 K, light grey curve), the metal atom does not move except for its small vibra-

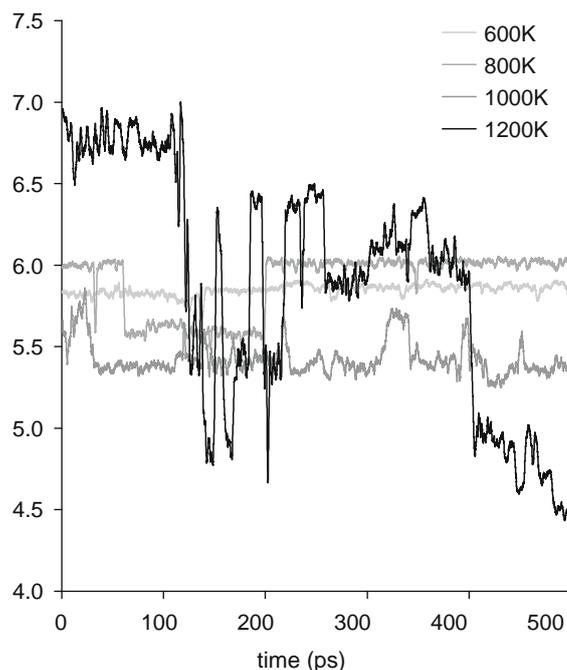


Fig. 3. Variation of position as a function of time for a randomly chosen Ni atom in the cluster at different temperatures.

tional movement. Increasing the temperature reveals the increasing mobility of the atoms, showing small diffusive steps or jumps at 800 K (medium grey curve), small multiple diffusive jumps at 1000 K (dark grey curve), and large multiple diffusive jumps at 1200 K (black curve). Hence, we may conclude that at low temperature, the cluster is in a purely solid state, and the atoms are merely vibrating around their equilibrium positions. As all occurring BS events consist of formation and breaking of bonds due to this vibrational motion, we call this mechanism 'vibrational bond switching'. In this regime, there is only one or a few BS events per atom involved. With increasing temperature, however, the atoms are no longer confined to their equilibrium positions (due to the increased mobility), and they can diffusively change their local environment. We therefore call this mechanism 'diffusional bond switching'. In this regime, there are multiple bonds broken and formed for each atom involved.

This occurrence of two temperature dependent mechanisms, however, is not caused by a variation in the spatial distribution of the BS events. Indeed, the spatial distribution can be determined by subdividing the cluster in shells, and calculating the fraction of BS events occurring in each shell relative to the total number of BS events at each temperature. The result is shown in Fig. 4. Independent of temperature, we find about 70% of the total number of events occurs in the bulk, and about 30% takes place near the surface. Here, we define 'bulk' when both atoms of the (broken or formed) bond have six neighbors or more. Note that while this definition is somewhat arbitrary, changing the number of neighbors to identify each atom as 'bulk' or 'surface' does not change the qualitative results; i.e., only the fractional number of bulk and surface events changes, independent of temperature. Thus, the fraction of surface and bulk events to the total number of events does not change with temperature, and can hence not explain the temperature dependent change in BS mechanism.

During CNT growth, several fundamental processes can be distinguished [13]: (1) adsorption of the hydrocarbon precursor molecule on the catalyst surface; (2) dissociation of the hydrocarbon molecule; (3) diffusion of the growth species on the surface or in the bulk of the catalyst particle; (4) incorporation of the carbon in the growing carbon network; and (5) nucleation of the CNT. It has been demonstrated that diffusion of carbon (i.e., step (3)) is

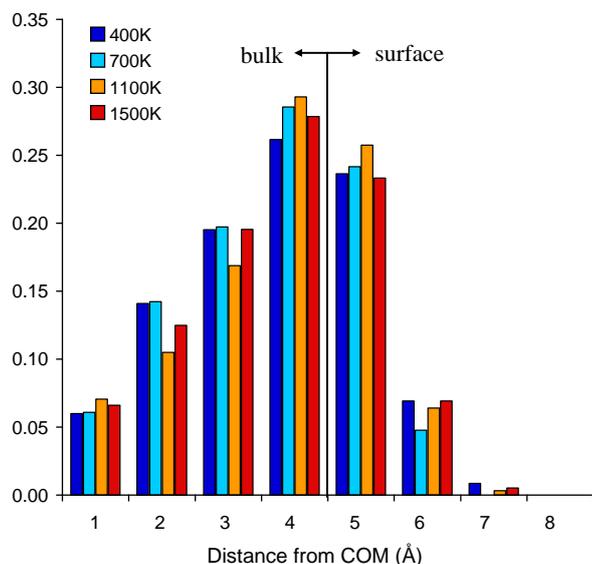


Fig. 4. Calculated contribution of atomic shells in the cluster to the total bond switching rate. Both core atoms and surface atoms contribute nearly equally to the total BS rate at all temperatures investigated.

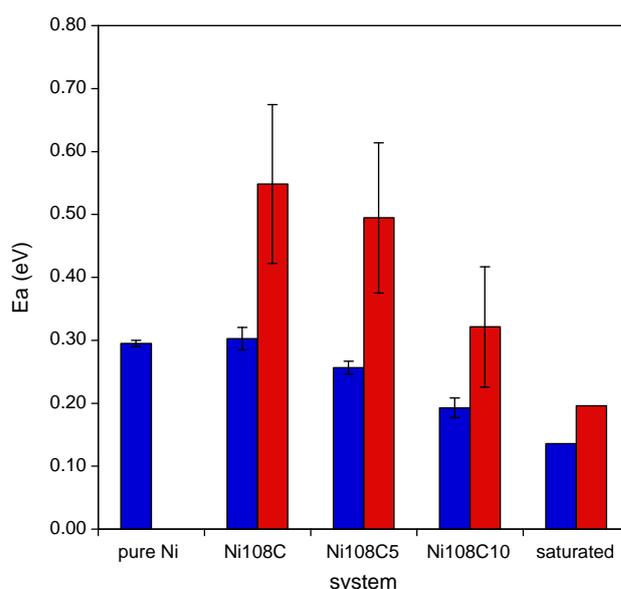


Fig. 5. Calculated Ni–Ni and Ni–C bond switching activation energies as a function of carbon concentration in the nickel nanocluster.

the rate limiting step in PECVD growth, while in thermal CVD the dissociation process (i.e., step (2)) is the rate limiting step [13]. These steps are often regarded as sequential, with each process maintaining a constant rate (i.e., not influenced by the carbon concentration).

Here, we have studied the effect of the carbon concentration on the bond switching rates, which are fundamental to the above described processes. In Fig. 5, the bond switching activation energy is plotted as a function of the number of carbon atoms dissolved in the nickel cluster. The activation energies were determined for a temperature range relevant for SWNT growth, i.e., 900–1500 K. It can be seen from the figure that with increasing carbon content in the cluster, the activation energy decreases, both for the Ni–Ni bond switching (blue¹ bars) as for the Ni–C bond switching (red bars). For Ni–Ni, the BS activation energy is found to decrease from about 0.30 eV in the case of a pure Ni cluster to 0.14 eV in the case of a saturated Ni₁₀₈C₅₂₉ cluster, while a decrease from 0.55 eV to 0.20 eV is observed for Ni–C. This change in activation energy is due to a change in BS rates. Indeed, as more carbon dissolves in the metal cluster, the BS rate does not remain constant, but rather increases, and thus the increasing carbon content 'liquifies' the metal cluster. As a direct consequence, the carbon content allows the metal particle to reshape, while maintaining its crystalline structure. This interpretation also corresponds to experimental results: Hofmann et al. [23] observed liquid-like behaviour of the Ni catalyst during CVD growth of SWNTs and carbon nanofibers (CNFs) at 580 °C, where the Ni exhibits fast self-diffusivity, while maintaining long-range crystalline order in contrast to real liquids. The authors also noted the importance of dynamic coexistence for particles of the size as studied here, corresponding to our previous calculations for Ni clusters of this size [18]. Yoshida et al. likewise observed the continuous fluctuation of the iron nanoparticle catalyst during SWNT growth at 600 °C [24]. The nanoparticle structure was demonstrated to be Fe-carbide (cementite).

The decrease in BS activation energy at increasing carbon content can be explained as follows. As the carbon concentration increases, the average number of carbon neighbors per nickel atom

¹ For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

increases, and the average number of metal neighbors per metal atom decreases. The potential energy surface governing the interactions between the atoms, on the other hand, shows a stronger interaction per bond for any atom as its number of neighbors decreases (i.e., the Ni–C interaction is stronger (per bond) in NiC than in NiC₂) [17]. Hence, as the carbon concentration in the cluster increases, the average Ni–C bond energy decreases. Consequently, the BS rate increases, and the effect is most pronounced at lower temperature. As a result, the slope of the Arrhenius plot, and hence the activation energy decreases. For Ni–Ni, two opposite factors are operative. As the carbon content in the cluster increases, the average Ni–Ni bond becomes stronger for the reason given above, which drives a decrease in the BS rate. On the other hand, the increase in Ni–C BS rate with increasing C content seems to drive an increase in the Ni–Ni BS rate, compensating for the former factor. The net result is a bond switching rate which remains nearly constant at the lower temperature and decreases at the higher temperature as the carbon content increases, leading again to a decreasing slope of the Arrhenius plot, and hence a decreasing activation energy.

The results presented here demonstrate the necessity to take the carbon concentration in the nanocatalyst into account when describing the CNT growth process. While it has been shown that in PECVD the diffusion step is rate-limiting [13], this rate is not likely to be constant. Indeed, each diffusional step requires the breaking and formation of C–Ni bonds, and possibly C–C bonds. Hence, as the activation energy for BS is found to be dependent on the carbon concentration, it can be expected that also the diffusion itself will be concentration dependent. Consequently, the CNT nucleation rate is dependent on the C solubility and C concentration in the nanocluster.

From a practical point of view, these results demonstrate the difficulties in simulating full CNT growth. Most MD growth simulations of SWNTs allow a C flux to the metal particle that is orders of magnitude too high [25–31], resulting in much too high growth rates. Especially the diffusion and relaxation effects taking place between consecutive impacts are generally not accounted for. These processes can be taken into account by using so-called accelerated MD simulations [32]. Unfortunately, however, these methods rely on the principle of infrequent events, i.e., it is assumed that the system resides in a local energy basin for a certain amount of time which is long compared to the jumps between minima (nanoseconds or longer). From the current results, it is clear that the nucleation step of SWNTs violates this assumption as the BS rate occurs on the sub-ps timescale. Hence, these methods cannot be applied directly to these systems.

4. Conclusions

Classical molecular dynamics (MD) simulations were performed to investigate the bond switching (BS) mechanisms in pure nickel and carbon containing nickel nanoclusters in a temperature range relevant for SWNT growth. It is found that the mechanism changes from vibrational BS to diffusional BS at around 900 K, due to the increased mobility of the cluster atoms. The activation energy for bond switching is shown to decrease with increasing carbon con-

centration, thereby effectively liquifying the metal cluster. It is therefore concluded that (i) the bond switching mechanism governs the fundamental dynamics in the nanocatalyst, and (ii) the carbon concentration in the nanocatalyst determines the CNT nucleation rate. These results demonstrate the important effect of the fundamental dynamics in the nanocatalyst on the initial nucleation step of SWNTs. Moreover, from a practical point of view, it is clear that these results render the long time scale simulation of SWNTs difficult.

Acknowledgments

E. Neyts acknowledges the FWO-Flanders (Fund for Scientific Research-Flanders) for financial support. Y. Shibuta acknowledges the Grant-in-Aid for Young Scientists (a) (No. 18686017, No. 21686021) from the MEXT, Japan. The authors also gratefully acknowledge financial support from the Prime Minister's Office through IAP VI. The authors would also like to thank Prof. Toshio Suzuki for inviting E. Neyts as a visiting researcher at the University of Tokyo.

References

- [1] M. Meyyappan, L. Delzeit, A. Cassell, D. Hash, *Plasma Sources Sci. Technol.* 12 (2003) 205.
- [2] G. Zou et al., *Carbon* 47 (2009) 933.
- [3] K. Kordás, G. Tóth, P. Moilanen, M. Kumpumäki, A. Uusimäki, *Appl. Phys. Lett.* 90 (2007) 123105.
- [4] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, *Science* 297 (2002) 787.
- [5] A.E. Aliev et al., *Science* 323 (2009) 1575.
- [6] Ç. Öncel, Y. Yürüm, *Fullerenes Nanotubes Carbon Nanostruct.* 14 (2006) 17.
- [7] D. Takagi, Y. Homma, H. Hibino, S. Suzuki, Y. Kobayashi, *Nano Lett.* 6 (2006) 2642.
- [8] O.V. Yazyev, A. Pasquarello, *Phys. Stat. Sol. B* 245 (2008) 2185.
- [9] R.S. Wagner, W.C. Ellis, *Appl. Phys. Lett.* 4 (1964) 89.
- [10] J. Gavillet, A. Loiseau, C. Journet, F. Willaime, F. Ducastelle, J.-C. Charlier, *Phys. Rev. Lett.* 87 (2001) 275504.
- [11] S. Helveg et al., *Nature* 427 (2004) 426.
- [12] F. Abild-Pedersen, J.K. Nørskov, J.R. Rostrup-Nielsen, J. Sehested, S. Helveg, *Phys. Rev. B* 73 (2006) 115419.
- [13] S. Hofmann, G. Csányi, A.C. Ferrari, M.C. Payne, J. Robertson, *Phys. Rev. Lett.* 95 (2005) 036101.
- [14] C.L. Cleveland, W.D. Luedtke, U. Landman, *Phys. Rev. B* 60 (1999) 5065.
- [15] F. Baletto, R. Ferrando, *Rev. Mod. Phys.* 77 (2005) 371.
- [16] Y. Shibuta, T. Suzuki, *J. Chem. Phys.* 129 (2008) 144102.
- [17] Y. Shibuta, S. Maruyama, *Comput. Mater. Sci.* 39 (2007) 842.
- [18] E.C. Neyts, A. Bogaerts, *J. Phys. Chem. C* 113 (2009) 2771.
- [19] E.C. Neyts, A. Bogaerts, *Carbon* 47 (2009) 1028.
- [20] W.C. Swope, H.C. Anderson, P.H. Berens, K.R. Wilson, *J. Chem. Phys.* 76 (1982) 637.
- [21] S. Maruyama, Y. Yamaguchi, *Chem. Phys. Lett.* 286 (1998) 343.
- [22] P.N. Ghosh, *J. Mol. Struct.* 26 (1975) 343.
- [23] S. Hofmann et al., *Nano Lett.* 7 (2007) 602.
- [24] H. Yoshida, S. Takeda, T. Uchiyama, H. Kohno, Y. Homma, *Nano Lett.* 8 (2008) 2082.
- [25] Y. Shibuta, S. Maruyama, *Physica B* 323 (2002) 187.
- [26] Y. Shibuta, S. Maruyama, *Chem. Phys. Lett.* 382 (2003) 381.
- [27] Y. Awano, S. Sato, D. Kondo, M. Ohfuti, A. Kawabata, M. Nihei, N. Yokoyama, *Phys. Stat. Sol. A* 203 (2006) 3611.
- [28] J. Zhao, A. Martinez-Limia, P.B. Balbuena, *Nanotechnology* 16 (2005) S571.
- [29] F. Ding, A. Rosén, K. Bolton, *Carbon* 43 (2005) 2215.
- [30] F. Ding, A. Rosén, K. Bolton, *J. Chem. Phys.* 121 (2004) 2775.
- [31] F. Ding, K. Bolton, A. Rosén, *Comput. Mater. Sci.* 35 (2006) 243.
- [32] A.F. Voter, F. Montalenti, T.C. Germann, *Annu. Rev. Mater. Res.* 32 (2002) 321.