



Modification and shaping of carbon nanotubes with an electron beam

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Abstract: The paper reviews the modification and shaping of electron beam irradiation on carbon nanotubes (CNTs), as well as how this could be potentially useful for electron beam modification of nanotubes. The influence of irradiation on the mechanical property, electrical property and field effect of CNTs is discussed. Several examples are given with particular emphasis on the cutting, shaping and welding of CNTs by the electron beam in an electron microscope. It is shown that the change of incident electron energy and ambient temperature will lead to the different irradiation results. It is expected that electron irradiation studies will continue to play an important role in the research on CNTs.

Keywords: carbon nanotube; electron irradiation; modification; shaping

Introduction

Carbon nanotubes (CNTs) have generated huge activity in most areas of science and engineering during the recent years due to their unprecedented physical and chemical properties. No previous material has displayed the combination of superlative mechanical, thermal and electronic properties attributed to them [1-8].

Since the beginning of the era of nanotubes, transmission electron microscopy (TEM) has been proved to be one of the most useful and versatile techniques for their characterization [9-12]. In addition to providing information about the structure of nanotubes, TEM also allows direct observation of the evolution of carbon structures undergoing electron beam irradiation [13, 14] and the growth-reversal of catalytic carbon nanotubes can be controlled under electron-beam irradiation [15-18]. What's more, nanotube irradiation with electron beam can be deliberately used to alter the chemical, mechanical, and electronic properties of the tubes and may even trigger dramatic structural changes [19-27]. Under certain experimental conditions, damage can be healed and electron irradiation can lead to new and exciting morphologies of nanotubes [28]. Electron irradiation is, thus, capable of cutting graphite layers of tubes and curving or bending the sheets by introducing topological defects. Therefore, existing CNTs are morphologically transformed, new CNTs are generated from graphitic precursors, or initially separate CNTs are welded together under the beam [29].

Electron beam irradiation of nanotubes could be useful to locally modify the nanotube structure in several applications. The nano-engineering of tubes by selectively thinning or bending them would be of advantage when individual nanotube devices have to be tuned for dedicated functions [30, 31]. Creating junctions of single-walled nanotubes (SWNTs) would be useful for making multi-terminal nanotube devices such as transistors on a chip. The coalescence of tubes within a bundle could be used to increase the diameter of the tubes. CNTs can be cut with a scanning electron microscope even at low electron voltage when a degraded vacuum is present [32]. The injection of carbon atoms into tubes by an electron beam is of interest when nanotubes are used as pipelines for the migration of atoms. In such a way, nanotubes could act as channels for mass transport on the nanoscale [28].

In this paper we will explore the progress that has already been made in electron beam modification and shaping of CNTs. The techniques used in the literature to cut, weld and shrink CNTs will be presented. We will review the effect of electron irradiation on the mechanical, electrical and field emission properties of CNTs. Finally the conditions of irradiation, including temperature and incident energy, are illustrated.

Modification of CNTs with electron beam

Mechanical property

There is both experimental and theoretical evidence that electron irradiation of nanotubes should give rise to covalent bonds between tubes in bundles, shells of multi-walled nanotubes, and layers in graphite [17, 33]. Recent experiments have demonstrated that electron irradiation of bundles of single-walled carbon nanotubes resulted in dramatic increase of the bundle bending modulus at moderate irradiation doses, followed by a decrease in mechanical properties at higher doses [20]. To understand such a behavior, Sammalkorpi [34] employs molecular dynamics simulations with empirical potentials and analytical approximations to calculate defect production rates and mechanical properties of the irradiated nanotubes. The observed peak in the bending modulus originates from a trade-off between irradiation-induced bundle stiffening via inter-tube covalent bonds and a drop in the Young's modulus of individual nanotubes due to vacancies. Therefore, irradiation is a good tool to enhance the mechanical properties of nanotube bundles when they are used as reinforcement agents.

Electrical property

In the past years, the electrical characterization of carbon nanotubes (CNTs) has been a subject of intense research [35]. These one-dimensional objects show most interesting electrical properties. For example, the conductivity of CNTs depends on their diameter and chirality. In particular, it has been found theoretically [36] and later experimentally [37] that two-thirds of all possible single-walled nanotubes are one dimensional semiconductors, whereas the remaining one-third are one-dimensional metals [38]. With the focused beam in a field emission TEM, the outermost layer can be selectively removed [30]. Since the surface layer is known to carry the majority of charge during electrical transport, the conductivity of MWNTs could be modified drastically by perforating the outermost layer [28].

Electron irradiation creates paramagnetic point defects in MWNTs, but their resistance to radiation is at least as good as bulk graphite. No radiolysis was observed in agreement with the semimetallic character of the nanotubes. It appears that the Fermi level position is very sensitive to the presence of defects in the rolled graphene plane. Electron irradiation is hence a powerful tool to modify the electronic structure of carbon nanotubes. The radiation-induced defects, which were nearly exclusively point defects, were found to significantly modify the electronic properties of the tubes near the Fermi level, as assessed by electron spin resonance [19].

Electronic transport measurements performed in situ reveal a striking dependence of conductance on nanotube geometry. As the diameter of the nanotube is reduced to near zero into the carbon chain regime via electron irradiation, we observe negative differential resistance [31]. The contact resistance of nanotubes decreases by orders of magnitude when exposed to electron beam and for all of the measurements the values ranged between 80Ω and 10 kΩ at room temperature. A minimum in the resistivity was found as a function of irradiation dose. This minimum is interpreted as a result of a twofold effect of the irradiation: the domination of covalent bond formation between tubes in a bundle due to broken bonds in the tube walls and the amorphization of the sample at high dose. Despite this improvement, the temperature dependence of the resistivity remains hopping-like [21]. MWNTs tend to reach a state of defect density saturation unlike single-walled nanotubes. It was also suggestive that knock-on collision may not be the primary cause of structural degradation, rather a local gradual reorganization, i.e. $sp^2+\delta$, $sp^3 \rightleftharpoons sp^2$ C. These studies allowed favorable electrical contacts through local 'soldering' [39].

Field effect

Single-walled carbon nanotubes (SWNTs) are known to be either metallic or semiconducting, based on their chirality [37, 40]. A number of investigations on gated semiconducting nanotubes have led to the development of field-effect transistors (FETs) and single-electron transistors [41]. In order to determine the degradation of the electrical characteristics of carbon nanotube field effect transistors (CNT-FETs) exposed to energy beams, as for example it happens during the fabrication of the device, electrical force microscopy (EFM) images and Monte Carlo simulation of electron trajectories were employed. The CNT-FET device characteristics show a temporary degradation, which depends on the beam energy and irradiated area, and is produced by the charging of the underlying silicon [42].

The effect of a low-energy e-beam on nanotube transport properties is significantly large, not only changing its transport properties by orders of magnitude, but also modifying the very nature of the devices from metallic to semiconducting. Among existing scenarios, the most likely candidate that could give rise to this effect seems to be modulation of band structure by local electric fields. Using local gates, it is possible for one to generate and tune the band gap of such devices, without generating structural modifications or defects [43].

Metallic devices with high conductance and negligible response to gate voltage, when exposed to electron irradiation, begin to show signs of semiconducting behavior with drastically reduced conductance. Conductance at low temperature is dominated by Coulomb blockade, and the metallic nanotubes, which initially showed "gapless" Coulomb oscillations, show an abrupt discontinuity in these oscillations with a gap opening near the region of zero gate voltage after the e-beam exposure [43].

Pristine devices, which exhibited negligible gate voltage response at room temperature and metallic single-electron transistor characteristics at low temperatures, when exposed to an electron beam, exhibited ambipolar field effect transistor (room temperature) and single-electron transistor (low temperature) characteristics. This metal-semiconductor transition is attributed to inhomogeneous electric fields arising from charging during electron irradiation. This, combined with the benefits of ballistic transport through nanotubes, is a promising way of fabricating nanoscale metallic field effect transistors and other futuristic electronic devices [43].

Shaping CNTs with electron beam

Cutting of CNTs

Although nanotubes are relatively easy to synthesize, at present it is difficult to control at the synthesis level the geometrical configurations, including length, number of walls, chirality, etc. A versatile method for cutting and shaping nanotubes would be particularly useful [32].

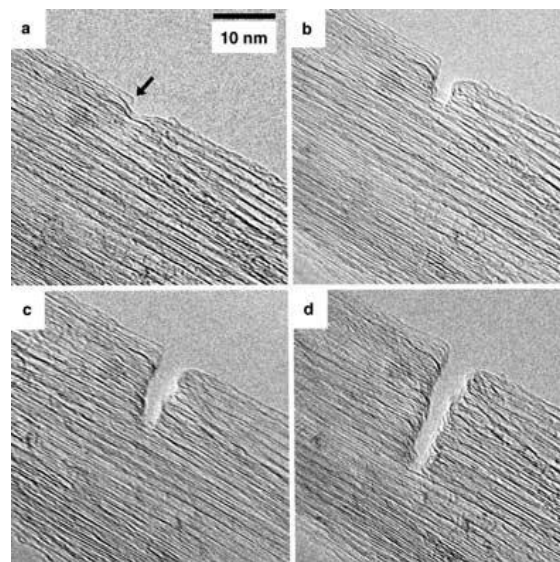


Fig. 1. The series shows the cutting of a gap into a bundle of SWNTs by moving a focused electron beam across the bundle [44].

Yuzinsky reported on a method to locally remove material from carbon nanotubes using the low-energy focused electron beam of a scanning electron microscope. Using this method, clean precise cuts can be made into nanotubes, either part-way through creating hinge like geometries or fully through creating size-selected nanotube segments. This cutting mechanism involves foreign molecular species and differs from electron-beam-induced knock-on damage in transmission electron microscopy [32]. It was found that the most important factor affecting the cutting speed was the presence of water vapor within the chamber. Water, at the same pressure, would increase the cutting speed even more, up to ten times as fast [32]. Fig. 2 shows a nanotube on a TEM grid before and after cutting.

Water vapour is likely to cause etching of the outer layers of carbon structures under electron irradiation, even with beam energies that were otherwise expected to be harmless to MWNTs. In the TEM system, the etching rate could be reduced to an

almost negligible level by cooling a cold finger with liquid nitrogen. This and the morphology of the damage imply that water vapour, which is present as a background gas in many vacuum chambers, can damage the nanotube structure through electron beam-induced chemical reactions [45].

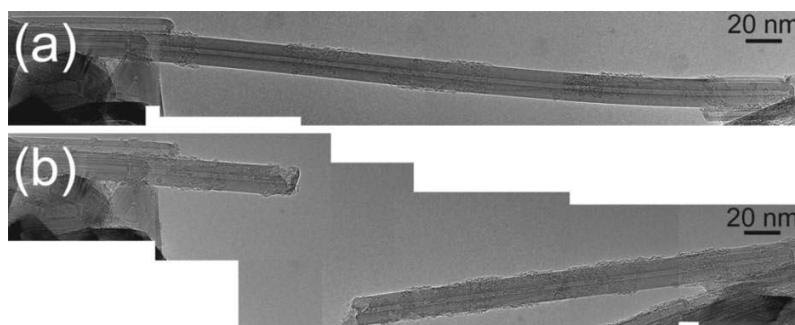


Fig. 2. Composite TEM micrographs of (a) a nanotube in its pristine state suspended on a TEM grid, (b) the same nanotube after cutting [32].

Radiolysis of water molecules is the driving force behind this etching mechanism. Highly reactive $\text{OH}\cdot$, $\text{H}\cdot$, and $\text{HO}_2\cdot$ radicals can react with carbon atoms to form CO , CO_2 , various hydrocarbons and hydrogen gas, leading to mass loss of the original carbonaceous specimen (and similar reactions can be expected when oxygen molecules are ionized in the vicinity of the sample) [32]. We propose that this etching mechanism is responsible for damaging the nanotubes. This mechanism is fundamentally different from previously reported electron-beam-irradiation damage of nanotubes as seen in a TEM, where incident electrons eject carbon atoms from the nanotube and must have an incident energy of at least 86 keV [46].

Interestingly, bundles of nanotubes would consistently be cut faster than individual nanotubes, despite the greater amount of material that must be removed. This suggests that bundles will adsorb more water at a given pressure than individual nanotubes [47]. Since the presence of water greatly accelerates cutting, we can therefore expect nanotube bundles to be easier to cut [32].

Welding of CNTs

A phenomenon that is observed quite frequently in scanning and transmission electron microscopy is the deposition of hydrocarbon contamination on the irradiated areas of the specimen. Hydrocarbon molecules originating from contamination of the specimen prior to microscopy or from the vacuum chamber of the electron microscope are highly mobile on the specimen surface. Once they diffuse into the specimen area under the electron beam, cracking occurs so that immobile amorphous carbon is left. Further irradiation of the deposit can lead to graphitization. In such a way, carbon can be deposited on the specimen surface in a controlled way [48]. This technique has been used to manipulate carbon nanotubes on the nanoscale, for example, for contacting nanotubes [49] or to establish a connection (soldering) between two nanotubes [38].

The junction between crossing tubes is of interest in view of possible applications of nanotubes as devices or conducting nanowires in electronics. Two crossing nanotubes normally would not join, even at high temperature, because the structure of a junction, containing heptagons in the regions of negative curvature, is less stable

than two perfect individual tubes. Again, the presence of vacancies and dangling bonds at the point of contact can induce the formation of a junction. This has been achieved in an in situ experiment in the TEM and confirmed by molecular dynamics simulations [50]. Banhart [38] joins CNTs mechanically by aggregation of hydrocarbons and successive transformation into amorphous carbon in the beam of an electron microscope, as is shown in Fig. 3. Under certain conditions of deposition, the aggregates tend to ramify and form tree-like carbon objects on the nanoscale [29, 51, 52].

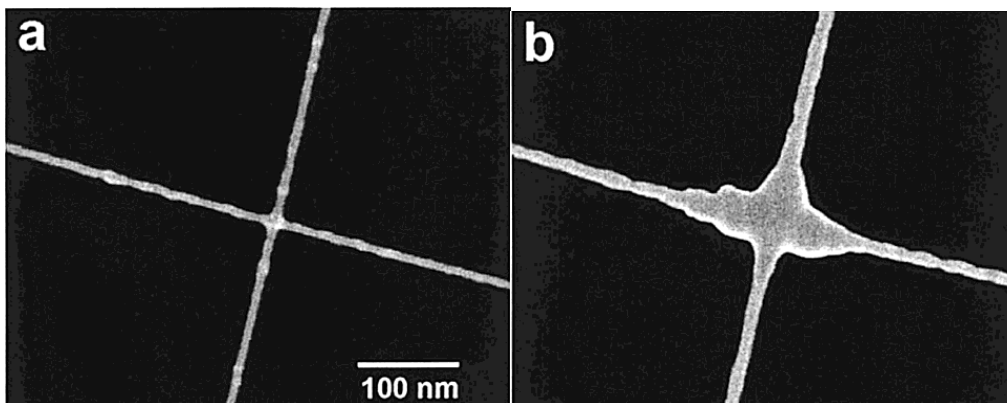


Fig. 3. SEM images of a nanotube junction before (a) and after (b) soldering by deposition of amorphous carbon [38].

Another way of joining nanotubes is to establish a junction between neighbouring carbon nanotubes within bundles. Owing to the weak van der Waals interaction that holds them together in the bundle, the tubes can easily slide on each other, resulting in a shear modulus comparable to that of graphite. This low shear modulus is also a major obstacle in the fabrication of macroscopic fibres composed of carbon nanotubes. Here, the stable links between neighbouring carbon nanotubes within bundles are introduced, using moderate electron-beam irradiation inside a transmission electron microscope. There is a 30-fold increase of the bending modulus, due to the formation of stable crosslinks that effectively eliminate sliding between the nanotubes. Crosslinks were modelled using first-principles calculations, showing that interstitial carbon atoms formed during irradiation in addition to carboxyl groups, can independently lead to bridge formation between neighbouring nanotubes [20].

Irradiation of a bundle with electrons can also lead to the coalescence of two parallel tubes so that a tube with double diameter is generated [22]. Vacancies induce coalescence via a zipper-like mechanism, imposing a continuous reorganization of atoms on individual tube lattices along adjacent tubes. Other topological defects induce the polymerization of tubes. Coalescence seems to be restricted to tubes with the same chirality, explaining the low frequency of occurrence of this event [22].

The end-to-end nanotube junction would be produced by electron irradiation. Because the presence of amorphous carbon, graphene fragment coatings and defects on the nanotube surface greatly influence the structure transformations in various nanotube structures under the electron beam. While nanotube with amorphous carbon, graphene fragment coverage and defects undergo rapid transformation leading to structure disintegration, those without such coverage or

defects are more resistant to beam damage. The data indicates that electron beams could be used to join nanotubes end-to-end without damaging the side-walls [53].

Effects of irradiation conditions

Incident electron energy

It was evidenced that the previously observed behaviors are attributable to anisotropic ejection and not to beam heating or isotropic ejection. Thus, beam heating is not expected to be the primary mode of damage in SWNTs. Instead, damage is expected to occur primarily by ballistic ejection, where an essentially elastic interaction between an incident electron and a carbon nucleus causes the corresponding atom to be displaced from the nanotube lattice [46, 54].

This has been confirmed by experiments where it was seen that no structural changes could be induced in carbon nanostructures at beam energies below the displacement threshold [17, 46]. The displacement threshold energy is an important parameter which gives us the electron energy necessary to displace an atom permanently from its position in a knock-on scattering event with the nucleus [55, 56]. Calculations utilizing known ejection threshold energies predict that an isolated nanotube will damage preferentially on surfaces that lie normal to the electron beam. The threshold electron energies are 86 keV for SWNTs [46] and slightly higher (approximately 100 keV) for MWNTs (depending on the direction of electron incidence) [17]. As the electron energy is increased from 86 to 139 keV (with the upper bound assuming an isotropic graphene sheet), atoms first on the top and bottom surfaces and then on the side walls become susceptible to ballistic ejection. Above 139 keV, all atoms can be ejected. These conclusions have been corroborated by transmission electron microscopy observations of nanotubes using 80–400 keV electrons [46].

However, as the threshold energy is lower in amorphous carbon, grahitization can be achieved by displacements in the amorphous phase at an electron energy of 80 keV. Irradiation-induced graphitization has therefore to be carried out at electron energies between the displacement thresholds for amorphous carbon and graphite [38]. Due to cascade effects, the displacement rates increase with increasing electron energy within the typical electron energy range of TEM [28]. At an electron energy of 100 keV, good TEM images can be obtained, whereas towards higher electron energies, the imaging becomes increasingly difficult [57]. Because an accelerating voltage of 100 kV for the routine imaging of nanotube material offers a reasonable balance between ballistic and inelastic damage rates. An optimal imaging condition for isolated SWNTs might be obtained at a tension below even 80 kV, affording the dual advantages of low damage rate and increased contrast due to a large atomic scattering factor (which scales with electron wavelength) [46].

According to the molecular-dynamics simulations, the ratio of ejected atoms increases with the increase in the electron energy. The higher the electron energy is, the earlier the irradiation damage proceeds. With the progress of the damage, the SWNT loses its resistance against the electron irradiation. This accelerates the irradiation damages and results in the larger ratios of ejection at high electron energies [58]. At low irradiation energies (below 300 keV), the atoms are preferentially ejected from the upper and lower parts of the tube, while at high energies (above 300 keV), the atoms are preferentially ejected from the side walls.

Typical values from a fraction of barn (at side wall for 150 keV electron) up to around 20 barn (for 1 MeV electrons) are obtained for the total cross section of knock-on processes for nanotubes [59]. These calculations of the total knock-on cross section for various nanotubes can be used as a guideline for transmission electron microscopy experimentalists using high energy focused beams to shape nanotubes, and also more generally if electron irradiation is to be used to change nanotube properties such as their optical behavior or conductivity [59, 60].

In addition, low-acceleration-voltage electron irradiation effects on single-walled carbon nanotubes were found by resonant Raman spectroscopy. The irradiation at acceleration voltages of 0.5 to 25 kV was found to extinguish the characteristic optical property of the nanotubes and reduce their tolerance against annealing in air, indicating that the nanotubes are inevitably damaged by ordinary scanning electron microscope observation. The acceleration voltage of around 1 kV caused the most extensive damage [61]. The acceleration voltage is far below the threshold of the well-known knock-on damage (86 kV) [46], indicating that the mechanism of this damage is completely different from that of knock-on damage [61]. The SWNTs damaged by the electron irradiation could be selectively removed by annealing in air. This technique would make it possible to fabricate various kinds of nanotube networks [62].

The intensity of electron beam changes as the aim of irradiation changes. The transformations of SWNTs and MWNTs as described in context were all achieved under an intense electron beam. More careful irradiation with a weaker beam can be used to join SWNTs at high specimen temperatures. The irradiation of SWNT bundles with a moderate beam can lead to the spontaneous coalescence of two adjacent tubes when the tubes are of the same type [28, 55].

Irradiation temperature

In most crystalline structures, knock-on displacements of atoms lead to either spontaneous recombination of the vacancy-interstitial pair or to persistent structural damage (visible as dislocation loops, voids, or amorphization). This also holds for the graphite lattice when irradiated at room temperature. The accumulation of interstitials (leading to new lattice planes between the basal layers) or of vacancies (leading to holes in the planes and, finally, to a rupture of the hexagonal network) destroys the lattice and does not result in new morphologies. The situation is different, however, when the temperature is high enough so that interstitials and/or vacancies are getting mobile [63]. Then, the lattice can reconstruct during the irradiation, and defect agglomerates are avoided [28]. Experimental [17, 64, 65] and theoretical [66] studies indicate that at temperatures above 200–300 °C the mobility of point defects is high enough for a fast reconstruction of the graphite lattice during irradiation. In addition, the simulations [67] indicate that at temperatures higher than 300 °C the annihilation of defects is efficient enough for almost perfect in situ self-healing of nanotubes. It is also found that, surprisingly, for a certain range of relatively low temperatures (about 130-230 °C) the temperature increase can have a negative effect on the self-healing [67].

In early irradiation experiments, the nanotubes were always at room temperature (the minimal heating by the electron beam can be neglected). Electron irradiation of SWNTs leads to a shrinkage and collapse of the tubes. This was already seen to happen very fast at room temperature [46, 57]. Later, irradiation experiments at

specimen temperatures above 300 °C revealed a variety of new morphologies. Electron irradiation-induced basal plane disordering in single- and multi-shell carbon nanotubes and onions is found to be inhibited at irradiation temperatures above 300 °C. At room temperature electron irradiation we observed a successive accumulation of radiation-induced defects up to a certain maximum density, seen as a partial to complete disorder of the graphitic lattice in tubes or onions. However, if prior to irradiation the specimen is heated to temperatures above 300 °C (the effect becomes much clearer at $T > 500$ °C) and held at that temperature during irradiation, visible defect-induced disordering is no longer seen, even at electron energies as high as 1.25 MeV and increased beam intensities up to 200 A/cm² [30, 68].

The simulation result [58] for the SWNT also shows higher resistance at higher tube temperature. At 300 K, the SWNT almost loses its original configuration, and the SWNT verges to be broken away. At 700 K, a lot of large membered rings and breaking of the bond are seen on the tube wall. At 1000 K, the SWNT maintains the shape of the cylinder. However, the tube wall is no longer composed of hexagonal honeycomb lattice [58]. Fig.4 a–c illustrate the schematic views of the (10,10) type of SWNT at various temperatures after 50 ns electron irradiation at 200 keV. The rate of the irradiation is 40 electrons/ ps. The target SWNT has 3 nm length. As the fluidity of the carbon atoms is relatively high at high temperature, the frequency of the recombination of dangling bonds increases after the carbon atoms are removed by the electron bombardment. The high temperature promotes the surface reconstruction of the tube wall through dangling bond saturation in the SWNT, and the structural transition to an amorphous like structure can be seen [58].

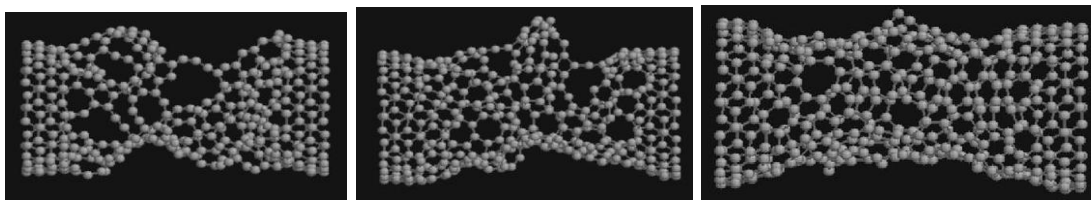


Fig. 4. Schematic views of the (10,10) type of SWNT after 50 ns electron irradiation at 200 keV (a) 300,(b) 700, and (c) 1000 K [58].

Temperature effects are of particular importance in the microscopy of carbon nanotubes. At room temperature, an accumulation of defects is seen up to a saturation density which depends on the electron energy and beam intensity. The type of radiation defect appears to be an agglomerate of interstitials, leading to the formation of new planes between existing basal planes. Interstitial atoms that are able to migrate in the open spaces between the basal planes with a migration energy of 0.8eV become mobile above 300 °C as has been stated above. These interstitials are most probably, as in single-walled tubes, bound to the basal planes and lead to fast recombination with vacancies at elevated temperatures. Consequently, electron microscopy studies of nanotubes requires specimen temperatures above 300 °C, better around 500 °C, when structural alterations of the tubes by the electron beam will be avoided [17].

Summary

Carbon nanostructures have shown new and unexpected ordering phenomena under irradiation with electron beam. These irradiation techniques could open new

opportunities for nanoengineering a large variety of nanostructural materials. Although a huge amount of work has been devoted to the study of radiation alterations in CNTs, there are still many open questions to be answered. The technological potential of electron irradiation of nanotubes is far from being realized. This is primarily because, until now, theory was not able to quantitatively predict the expected defect structures as a function of the irradiation parameters, and experiments were not performed with sufficient spatial control.

Acknowledgements

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References

- [1] Treacy, M. M. J.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, 381, 678.
- [2] Martel, R. T.; Schmidt, H.; Shea, R.; Hertel, T.; Avouris, P. *Appl. Phys. Lett.* **1998**, 73, 2447.
- [3] Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, 297, 787.
- [4] Coleman, J. N.; Khan, U.; Blau, W. J.; Gunko, Y. K. *Carbon* **2006**, 44, 1624.
- [5] Salvetat, J. P.; Briggs, G. A. D.; Bonard, J. M.; Bacsá, R. R.; Kulik, A. J.; Stockli, T.; Burnham, N. A.; Forro, L. *Phys. Rev. Lett.* **1999**, 82, 944.
- [6] Bikiaris, D.; Vassiliou, A.; Chrissafis, K.; Paraskevopoulos, K. M.; Jannakoudakis, A.; Docoslis, A. *Polym. Degrad. Stab.* **2008**, 93, 952.
- [7] Dintcheva, N. T.; La Mantia, F. P.; Malatesta, V. *Polym. Degrad. Stab.* **2009**, 94, 162.
- [8] Chang, C. P.; Yuan, C. L. *J. Mater. Sci.* **2009**, 44, 5485.
- [9] Zhou, O.; Fleming, R. M.; Murphy, D. W.; Chen, C. H.; Haddon, R. C.; Ramirez, A. P.; Glarum, S. H. *PC World (San Francisco, CA)* **1994**, 12, 1744.
- [10] Mukhopadhyay, K.; Koshio, A.; Sugai, T.; Tanaka, N.; Shinohara, H.; Konya, Z.; Nagy, J. B. *Chem. Phys. Lett.* **1999**, 303, 117.
- [11] Zhang, L.; Feng, C.; Chen, Z.; Liu, L.; Jiang, K. L.; Li, Q. Q.; Fan, S. S. *Nano Lett.* **2008**, 8, 2564.
- [12] Silva, G. G.; Musumeci, A. W.; Gomes, A. P.; Liu, J. W.; Waclawik, E. R.; George, G. A.; Frost, R. L.; Pimenta, M. A. *J. Mater. Sci.* **2009**, 44, 3498.
- [13] Kiang, C. H.; Goddard, W. A.; Beyers, R.; Bethune, D. S. *J. Phys. Chem.* **1996**, 100, 3749.
- [14] Burden, A. P.; Hutchison, J. L. *Carbon* **1997**, 35, 567.
- [15] Stolojan, V.; Tison, Y.; Chen, G. Y.; Silva, R. *Nano Lett.* **2006**, 6, 1837.
- [16] Hashimoto, A.; Suenaga, K.; Gloter, A.; Urita, K.; Iijima, S. *Nature* **2004**, 430, 870.
- [17] Banhart, F. *Rep. Prog. Phys.* **1999**, 62, 1181.
- [18] Ajayan, P. M.; Colliex, C.; Bernier, P. *Microsc. Microanal. Microstruct.* **1993**, 4, 501.
- [19] Beuneu, F.; Huillier, C.; Salvetat, J. P.; Bonard, J. M.; Forro, L. *Phys. Rev. B* **1999**, 59, 5945.
- [20] Kis, A.; Csanyi, G.; Salvetat, J. P.; Lee, T. N.; Couteau, E.; Kulik, A. J.; Benoit, W.; Brugger, J.; Forro, L. *Nat. Mater.* **2004**, 3, 153.
- [21] Miko, C.; Milas, M.; Seo, J. W.; Couteau, E.; Barisic, N.; Gaal, R.; Forro, L. *Appl. Phys. Lett.* **2003**, 83, 4622.

- [22] Terrones, M.; Terrones, H.; Banhart, F.; Charlier, J. C.; Ajayan, P. M. *Science* **2000**, 288, 1226.
- [23] Crespi, V. H.; Chopra, N. G.; Cohen, M. L.; Zettl, A.; Louie, S. G. *Phys. Rev. B: Condens. Matter.* **1996**, 54, 5927.
- [24] Kim, H.; Kaufman, M. J.; Sigmund, W. M. *J. Mater. Res.* **2004**, 19, 1835.
- [25] Zobelli, A.; Gloter, A. C.; Ewels, P.; Colliex, C. *Phys. Rev. B* **2008**, 77.
- [26] Nielsen, K. L. C.; Hill, D. J. T.; Watson, K. A. J.; Connell, W.; Ikeda, S.; Kudo, H.; Whittaker, A. K. *Polym. Degrad. Stab.* **2008**, 93, 169.
- [27] Sengupta, R.; Sabharwal, S.; Bhowmick, A. K.; Chaki, T. K. *Polym. Degrad. Stab.* **2006**, 91, 1311.
- [28] Banhart, F. *J. Mater. Sci.* **2006**, 41, 4505.
- [29] Banhart, F. *Phil. Trans. Math. Phys. Eng. Sci.* **2004**, 362, 2205.
- [30] Li, J. X.; Banhart, F. *Nano Lett.* **2004**, 4, 1143.
- [31] Yuzvinsky, T. D.; Mickelson, W.; Aloni, S.; Begtrup, G. E.; Kis, A.; Zettl, A. *Nano Lett.* **2006**, 6, 2718.
- [32] Yuzvinsky, T. D.; Fennimore, A. M.; Mickelson, W.; Esquivias, C.; Zettl, A. *Appl. Phys. Lett.* **2005**, 86.
- [33] Telling, R. H.; Ewels, C. P.; Barbary, A. A.; Heggie, M. I. *Nat. Mater.* **2003**, 2, 333.
- [34] Sammalkorpi, M.; Krasheninnikov, A. V.; Kuronen, A.; Nordlund, K.; Kaski, K. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2005**, 228, 142.
- [35] Rius, G.; Verdager, A.; Chaves, F. A.; Martin, I.; Godignon, P.; Lora-Tamayo, E.; Jimenez, D.; Perez-Murano, F. *33rd International Conference on Micro- and Nano-Engineering* (Elsevier Science Bv, Copenhagen, DENMARK, **2007**) p. 1413.
- [36] Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, 60, 2204.
- [37] Wildoer, J. W. G.; Venema, L. C.; Rinzler, A. G.; Smalley, R. E.; Dekker, C. *Nature* **1998**, 391, 59.
- [38] Banhart, F. *Nano Lett* **2001**, 1, 329.
- [39] Gupta, S.; Patel, R. J.; Smith, N.; Giedd, R. E.; Hui, D. *Diamond Relat. Mater.* **2007**, 16, 236.
- [40] Odom, T. W.; Huang, J. L.; Kim, P.; Lieber, C. M. *Nature* **1998**, 391, 62.
- [41] Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, 393, 49.
- [42] Rius, G.; Martin, I.; Godignon, P.; Bachtold, A.; Bausells, J.; Lora-Tamayo, E.; Perez-Murano, F. *Microelectron. Eng.* **2007**, 84, 1596.
- [43] Vijayaraghavan, A.; Kanzaki, K.; Suzuki, S.; Kobayashi, Y.; Inokawa, H.; Ono, Y.; Kar, S.; Ajayan, P. M. *Nano Lett.* **2005**, 5, 1575.
- [44] Banhart, F.; Li, J. X.; Terrones, M. *Small* **2005**, 1, 953.
- [45] Molhave, K.; Gudnason, S. B.; Pedersen, A. T.; Clausen, C. H.; Horsewell, A.; Boggild, P. *Ultramicroscopy.* **2007**, 108, 52.
- [46] Smith, B. W.; Luzzi, D. E. *J. Appl. Phys.* **2001**, 90, 3509.
- [47] Marti, J.; Gordillo, M. C. *J. Chem. Phys.* **2003**, 119, 12540.
- [48] Hart, R. K.; Kassner, T. F.; Maurin, J. K. *Philos. Mag.* **1970**, 21, 453.
- [49] Yu, M.; Dyer, M. J.; Skidmore, G. D.; Rohrs, H. W.; Lu, X.; Ausman, K. D.; Ehr, J. R. V.; Ruoff, R. S.; *Nanotechnology* **1999**, 10, 244.
- [50] Terrones, M.; Banhart, F.; Grobert, N.; Charlier, J. C.; Terrones, H.; Ajayan, P. M. *Phys. Rev. Lett.* **2002**, 89, 075505.
- [51] Banhart, F. *Philos. Mag. Lett.* **1994**, 69, 45.
- [52] Wang, H. Z.; Zhu, H. G.; Li, D.; Wang, X. *Carbon* **2002**, 40, 2117.

- [53] Satishkumar, B. C.; Paulson, S.; Johnson, A. T.; Luzzi, D. E. *J. Nanosci. Nanotechnol.* **2006**,6,1350.
- [54] Williams, D. B.; Carter, C. B. *Transmission Electron Microscopy-A Textbook for Materials Science* (Cambridge University Press New York, **1999**).
- [55] Lulli, G.; Parisini, A.; Mattei, G. *Ultramicroscopy* **1995**,60,187.
- [56] Zaiser, M.; Lyutovich, Y.; Banhart, F. *Phys. Rev. B* **2000**,62,3058.
- [57] Ajayan, P. M.; Ravikumar, V.; Charlier, J. C. *Phys. Rev. Lett.* **1998**,81,1437.
- [58] Yasuda, M.; Kimoto, Y.; Tada, K.; Mori, H.; Akita, S.; Nakayama, Y.; Hirai, Y. *Phys. Rev. B* **2007**, 75.
- [59] Zobelli, A.; Gloter, A.; Ewels, C. P.; Seifert, G.; Colliex, C. *Phys. Rev. B* **2007**, 75, 9.
- [60] Crespi, V. H.; Chopra, N. G.; Cohen, M. L.; Zettl, A.; Radmilovic, V. *Appl. Phys. Lett.* **1998**, 73, 2435.
- [61] Suzuki, S.; Kanzaki, K.; Homma, Y.; Fukuba, S. Y. *Jpn. J. Appl. Phys. Part 2-Lett.* **2004**, 43,1118.
- [62] Suzuki, S.; Takagi, D.; Homma, Y.; Kobayashi, Y. *Jpn. J. Appl. Phys. Part 2-Lett.* **2005**, 44,133.
- [63] Koike, J.; Pedraza, D. F. *J. Mater. Res.* **1994**,9,1899.
- [64] Urita, K.; Suenaga, K.; Sugai, T.; Shinohara, H.; Iijima, S. *Phys. Rev. Lett.* **2005**, 94, 4.
- [65] Burden, A. P.; Hutchison, J. L. *J. Cryst. Growth* **1996**,158,185.
- [66] Krasheninnikov, A. V.; Lehtinen, P. O.; Foster, A. S.; Nieminen, R. M. *Chem. Phys. Lett.* **2006**, 418, 132.
- [67] Kotakoski, J.; Krasheninnikov, A. V.; Nordlund, K. *J. Computat. Theor. Nanosci.* **2007**, 4, 1153.
- [68] Banhart, F.; Fuller, T.; Redlich, P.; Ajayan, P.M. *Chem. Phys. Lett.* **1997**, 269, 349.