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Irradiation effects in carbon nanotubes

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Abstract

As recent experimental and theoretical studies demonstrate, irradiation of carbon nanotubes with energetic particles can successfully be used for nano-engineering, e.g. for creating molecular junctions between the nanotubes, making nanotube-based quantum dots and composite materials with enhanced mechanical properties. We briefly review the recent progress in our understanding of ion-irradiation-induced phenomena in carbon nanotubes with a specific stress on theoretical results. We point out the issues which still lack complete comprehension and further outline the most promising ways of using beams of energetic particles for nanotube-related nano-engineering.

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1. Introduction

Carbon nanotubes (CNTs) [1] are hollow cylindrical molecules consisting of single or many sheets of graphite wrapped into cylinders with diameters of from less than 1 nm up to hundreds of nm. CNTs have extraordinary mechanical and electrical properties. For example, their density-normalized Young's modulus and strength are estimated bo be, respectively, about 19 and 56 times that of steel [2]. Depending on the way of how the graphite sheets are rolled up, CNTs can be either metals or narrow-band semiconductors, which, along with their inherent nm-size, makes them ideal candidates for the use in nanoelectonics. There are many other exciting potential applications [1,2] of CNTs.

These possible applications have stimulated much research work which has resulted in a nearly exponential growth of nanotube-related patents and scientific publications [2] during the last decade. Among them, a considerable number of papers address interactions of CNTs with beams of energetic particles – electrons [3–12] and ions [13–31].

The interest in effects of irradiation on CNTs is triggered by recent observations of fascinating irradiation-induced phenomena like coalescence [3,4] and welding [5] of CNTs, tunnelling barrier formation in CNTs by energetic Ar ions [14], creation of links between nanotubes [20], etc. Experiments also show that ion bombardment and CNTs as masks against irradiation (to protect the areas below the tubes from sputtering) may be

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employed for fabricating ultra-narrow metal nanowires [32] as an alternative to the conventional electron-beam lithography. Given that electron and ion irradiation is routinely used nowadays for modifying properties of semiconductors, beams of energetic particles are also expected to be widely employed for nanotube-based materials processing.

Besides these practical aspects, it should be pointed out that the damage creation mechanisms in CNTs are quite interesting in their own right, since they substantially differ from those in bulk carbon systems (graphite and diamond), not to mention metals or dielectrics. Indeed, CNTs are nano-objects with a large fraction of surface atoms. Unlike metals, CNT-based materials are highly anisotropic with a low atomic density, but as mentioned above outstanding mechanical properties. CNTs are ballistic conductors with high heat and charge conductivity, which indicates that irradiation-induced electronic excitations and charge accumulation effects are not so important as in the typical insulator.

In this review we briefly summarize the experimental/theoretical data on irradiation effects in carbon nanotubes. Since ion irradiation of CNTs has received much less attention than electron irradiation (for the latter see, e.g., a review article [6]), we dwell mostly upon ion bombardment with a specific stress on theoretical results. We discuss the most promising applications of electron and ion irradiation of CNT-based materials and outline the matters which still lack complete understanding while being important for further progress in this field.

2. Peculiarities of defect production in irradiated carbon nanotubes

When an energetic particle such as an electron or ion hits the target, different mechanisms of damage creation can work. Depending on the target material and the particle characteristics, the main mechanism can be the kinetic energy transfer, electronic excitations, ionization, etc. For CNTs, the most important mechanism is the knock-on atom displacements due to kinetic energy transfer, both for electrons and ions. [1] Electronic excitations and ionization effects seem to be less important [6] due to a high thermal and electrical conductivity of graphene shells (recall also that the graphite melting temperature is 4200 °C).

In order to understand damage production in CNTs, it is necessary to consider the atomic structure of CNTs in more detail. The atom networks of typical CNTs are shown in Fig. 1. CNTs may have only one shell (single-walled nanotubes, SWNTs) or many shells (multiwalled nanotubes, MWNTs). The former can bundle up to form a triangular lattice due to attractive van der Waals interactions (see Fig. 1(b)). However, all these structures retain graphitic arrangements of carbon atoms.

In SWNTs, the collision of an energetic particle with a carbon atom will result in displacement of the atom, i.e. formation of a vacancy (single- or multi-vacancy) and a number of primary knock-on atoms which, if their energy is high, leave the tube or displace other atoms in the SWNT. If their energy is low, they can adsorb onto the tube walls. These adsorbed atoms (adatoms) play the role of interstitials [24,25]. Notice that due to the quasi-one-dimensional morphology, all displaced atoms can be sputtered from the SWNT, so that no interstitial can exist in the system.

The incident particle and carbon atoms sputtered from the SWNT can further create some damage in a nearby SWNT or absorb onto its surface. Due to voids in the SWNT sample, the interstitial-vacancy separation can be large (preventing instant recombination) even at modest energies of incident particles. Open spaces in the CNT sample suggest that the interstitial atom in a SWNT bundle can also be treated as an *adatom* adsorbed onto the nanotube surface.

Along with the simple defects, a number of more complex defects can be formed, e.g. the pentagon/heptagon Stone–Wales (SW) defects [33] associated with a rotation of a bond in the CNT atom network, other topological defects in the

[1] As for ion irradiation, we consider relatively heavy ions and low ion energies when the nuclear stopping power prevails over the electronic slowing down.

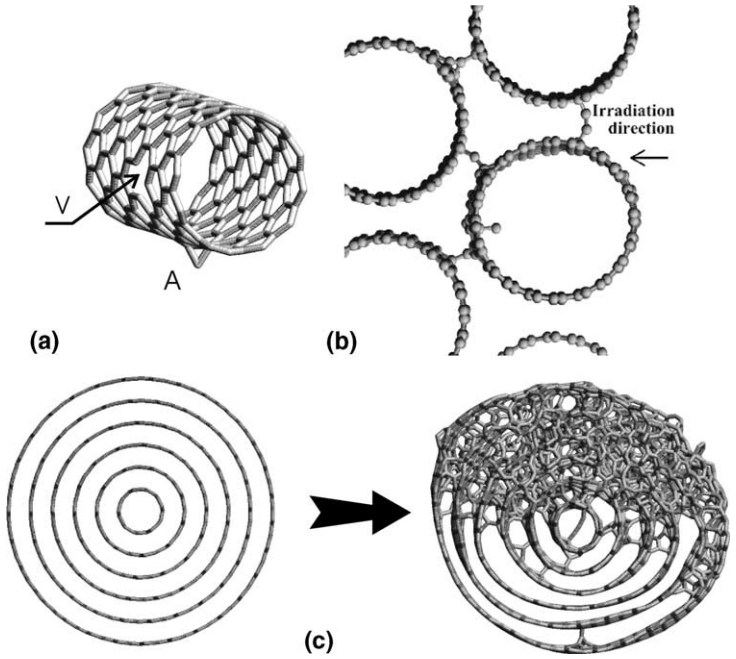

Fig. 1. Molecular models of irradiated carbon nanotubes. A short fragment of a single-walled nanotube with a vacancy (V) and a double-coordinated carbon atom (A) adsorbed onto the outer surface of the tube (a). A bundle of nanotubes (view along the tube axes) after the impact of a 500-eV Ar ion (b). A multi-walled nanotube before and after 300-eV Ar ion irradiation with a dose of 2×10^{16} cm^{-2} (c).

graphitic network (non-hexagonal rings), amorphous complexes, etc. Besides this, defect-mediated covalent bonds between adjacent SWNTs in the bundle can appear. Likewise, similar links between shells can appear in MWNTs. The behavior of these complex irradiation-induced defects is governed in part by annealing and diffusion of original defects-vacancies and interstitials.

The damage formation in CNTs is quite different from that observed in most other solids. Because of the open structure of the CNT, even recoils which have received energy only slightly above the threshold energy can be displaced quite far, which is in contrast to many other types of materials.

There are also differences in defect annealing. In semiconductors like Si a vast majority of all Frenkel pairs produced are known to recombine below room temperature [34]. In dense metals, nearly all the interstitials and vacancies produced during the ballistic phase of the cascade recombine with each other after only a few picoseconds, regardless of the sample temperature [35]. Defects in CNTs can also anneal, but it happens at elevated temperatures [6], and the annealing mechanisms are somewhat different from those in metals (see Section 5).

Defects in CNTs can be created only if the incident particle is energetic enough to displace carbon atoms. For graphitic structures the threshold energy T_d (the minimum energy transferred to the atom required to produce the Frenkel pair which does not spontaneously recombine) is estimated to be about 20 eV (different values from 15 up to 30 eV have been reported, see [6] and references therein). Knowing this value, the minimum kinetic energy of the incident particle required for damage production can be estimated.

3. Electron irradiation of carbon nanotubes

Electron irradiation effects in CNTs have been studied at length [6–10] both experimentally and

theoretically. The transmission electron microscope (TEM) has usually been used for these studies since it can not only create the damage in CNTs by energetic (up to 1.25 MeV) electrons but also monitor the irradiation-induced changes. The minimum incident electron energy required to remove a carbon atom by a knock-on collision was found to be 86 keV [7], which correlates with the values of T_d given in the literature for graphitic structures.

Early experiments [8] provided evidence that SWNTs exposed to focused electron irradiation were severely locally deformed and develop neck-like features along their bodies due to the removal of carbon atoms by knock-on displacements. Uniform irradiation of SWNTs [9] also resulted in surface reconstruction and drastic dimensional changes, as a corollary of which the apparent diameter of the CNTs shrinked from $\approx$1:4 to 0.4 nm.

The reason for these transformations were vacancies in the walls of the SWNTs created by energetic electrons. The vacancies proved to be unstable (see Section 5) under high beam dose when a large number of atoms are removed very rapidly and at high temperatures, which gave rise to surface reconstructions and diameter reductions. Notice that vacancies are created in CNTs spatially non-uniformly: carbon atoms are most rapidly removed from surfaces lying normal to the electron beam [7].

These vacancy transformations were the driving force for the irradiation-mediated coalescence [3] of SWNTs. Vacancies were found to induce coalescence via a zipper-like mechanism, imposing a continuous reorganization of atoms in individual tube lattices along adjacent tubes. Creation of vacancies by the focused electron beam followed by dangling bond saturation was demonstrated to result in welding of crossed SWNTs to form molecular junctions [5] as well as for fusing fullerenes inside carbon nanotubes [11] and boron-nitrogen nanotubes [12] to form a SWNT inside. Because boron-nitrogen nanotubes are insulating, the latter use of the electron beam opens new ways for making complex systems with predetermined electrical properties.

Electron irradiation of MWNTs resulted in forming vacancies on their walls and eventual amorphization upon high-dose irradiation [6,10]. In general, MWNTs seem to be more stable than SWNTs [6] because Frenkel pairs created inside the MWNT can easily recombine. The irradiation-induced damage manifested itself in the deterioration of mechanical properties of MWNTs exposed to prolonged 2-MeV electron irradiation [10].

4. Ion irradiation of carbon nanotubes

Interactions of ion beams with carbon nanotubes have been studied both experimentally [13–22] and theoretically [22–31]. Below we give a short overview of the most important works on ion irradiation of CNTs.

4.1. Experiments on ion irradiation of carbon nanotubes

Irradiation of MWNTs with diameters of about 10 nm by 3 keV Ar ions followed by X-ray photoelectron spectroscopy and TEM probing [13] demonstrated that the bombardment resulted in the appearance of carbon dangling bonds, which can be understood in terms of single- and multi-atom vacancies. A gradual amorphization of the carbon network was reported, and for maximum irradiation doses used (more than 10^{19} ions/cm^2) MWNTs with originally hollow cores transformed to nano-rods composed of amorphous carbon, but the irradiation did not change the sp^2 hybridization of carbon to sp^3 hybridization. The amorphization of MWNTs by 3 keV Ar ions with a much lower irradiation dose of 4×10^{16} ions/cm^2 was also reported [15].

Spatially localized Ar ion irradiation (with doses up to $\sim10^{16}$ ions/cm^2) of individual MWNTs deposited on SiO_2 substrates was used [14] to create a defective region which worked as a potential tunnel barrier for electrons in the MWNT. A fast increase in the tube resistance with the irradiation dose was reported. It was demonstrated that a double-barrier structure fabricated by such method can work as a quantum dot. However, the types of defect and their spatial distribution were not identified, although knowing

this is important for understanding the Coulomb oscillations observed in the system and how the current flows through the damaged MWNT shells.

Self-irradiation with 100 eV C^+ ions was used for making CNT-amorphous diamond nanocomposites [16] in which conducting mats of SWNTs were protected against wear by 50-nm amorphous diamond films. Proton irradiation [17] was demonstrated to result in C–H bond formation and chemical functionalization of SWNTs. Experiments also indicate that magnetized-plasma ion irradiation can be used for encapsulating fullerenes [18] and intercalating cesium inside SWNTs [19] via nanotube open ends and irradiation-induced defects in the tube walls.

The impact of low-dose ($\sim 10^{12}$ ions/cm^2) ion irradiation on bundles of SWNTs was experimentally studied as well [20]. The bundles were irradiated with an 500-eV Ar^+ ion beam followed by transport measurements. The results suggest that irradiation gives rise to current re-distribution between the damaged and undamaged tubes in the same rope, which can be interpreted as evidence for the formation of irradiation-mediated links between individual SWNTs in the bundle.

Although the impact of irradiation-induced defects on the electronic properties of the sample was dramatic, the types of the defects were not characterized in that work. The standard program SRIM was used to estimate the defect spatial distribution, but the applicability of the SRIM code for estimating the radiation damage at such low energies in highly anisotropic covalent systems like SWNT bundles is questionable, since the code treats the irradiated sample as an amorphous structure with a homogeneous mass density, and only binary collisions between the ion and the sample atoms are taken into consideration.

4.2. Molecular dynamics simulations

At the same time, a lot of insight into defect production in individual and bundled-up CNTs upon low-energy ion irradiation can be obtained from empirical-potential molecular dynamics (MD) simulations, which, unlike the SRIM code, take into account the nature of chemical bonds and particular atom arrangements in CNTs. The reactive bond order Brenner potential [36,37] and its extension [38] make it possible to describe realistically not only covalent interactions between carbon atoms in one and the same CNT, but also van der Waals-type interactions between the CNTs.

Irradiation of individual SWNTs with 50–3000 eV Ar ions was modelled in [24,25]. 10-nm-long fragments of SWNTs were considered. Although SWNTs can be several microns long in experiments, using 10-nm-long nanotubes was enough to realistically simulate energy dissipation after ion impacts. The SWNTs were assumed to be suspended by their ends (such CNTs can experimentally be manufactured [39]). It was found that single vacancies and vacancy-related defects [9] (which single vacancies can turn into) were the most prolific defects in nanotubes which appeared after ion impacts. Double-coordinated carbon adatoms (Fig. 1(a)) on both external and internal sides of the nanotube walls [40] were also common. Besides this, other complex defects like SW defects and amorphous regions were observed.

In order to quantitatively characterize the damage in the SWNT at different energies of incident Ar ions, in Fig. 2 we plot the number of C atoms with a coordination other than three [2] as a function of ion energy (open circles) and the number of sputtered C atoms (triangles). The former quantity may be considered as a characteristic of the overall damage in the nanotube produced by the ion. We also present in Fig. 2 the number of two-coordinated atoms (open squares). This quantity divided by three roughly gives the number of atoms in vacancies and vacancy-related defects in the system [25].

It can be seen from Fig. 2 that, if the energy of the incident ion is higher than the defect creation threshold energy (about 50 eV [24]), the number of defects increases with the energy up to roughly 600 eV, then it remains practically constant. The reason for such behavior is that at low energies the damage production grows with ion energy, since there is simply more energy available for it. At

[2] Recall that all carbon atoms in an intact CNT are three-coordinated.

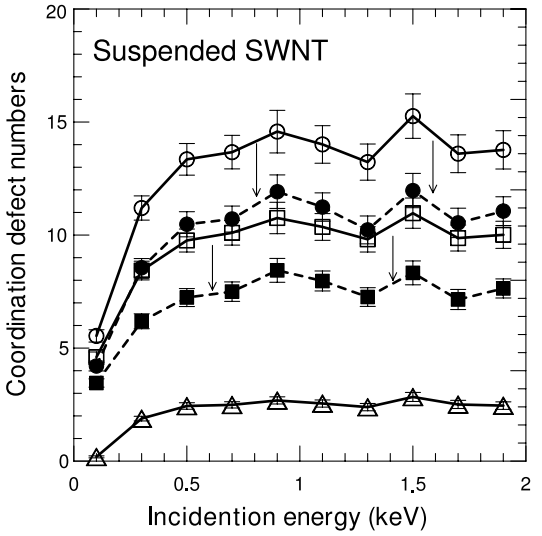

Fig. 2. Average coordination defect numbers for suspended nanotubes as a function of incident Ar ion energy. Open/full circles stand for the number of C atoms with a coordination other than three before/after annealing (the overall damage), open/full squares for the number of two-coordinated atoms before/after annealing. Triangles correspond to the number of sputtered C atoms. The arrows visualize the relationship between the curves before and after annealing (from [25]).

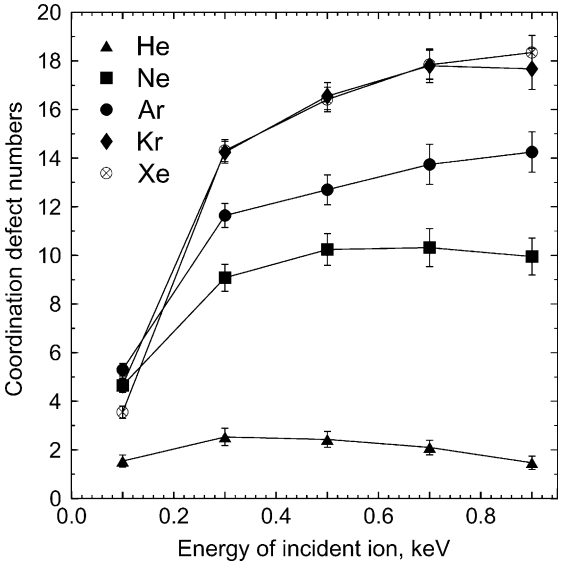

Fig. 3. Average coordination defect numbers (the total damage) in single-walled nanotubes as functions of incident ion energy (from [30]).

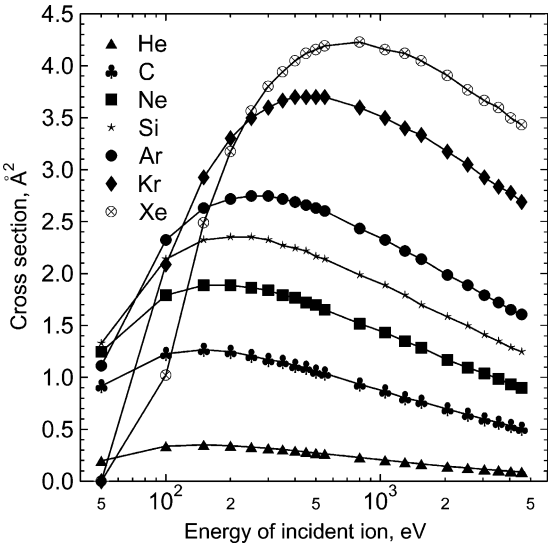

Fig. 4. Cross-section for the defect production in nanotubes as a function of incident ion energy for various ions (from [30]).

higher ion energies, although defect production in the SWNT drops as the nuclear collision cross-section for defect production decreases (see below), there are more energetic C primary recoils which damage the SWNT. The decrease in damage due to the diminution in the cross-section and the damage enhancement due to the recoils approximately counterbalance each other at energies higher than 1 keV.

Qualitatively similar results were obtained for other types of ions [30] with energies up to 1 keV (see Fig. 3). It is interesting to notice that in this interval of energies the damage created by Xe and Kr ions is roughly the same (despite the difference in ion masses). This behavior can be understood in terms of the cross-section for the defect production in a SWNT. We estimated the cross-sections for different ions by calculating the maximum impact parameter for which the ion transfers at least 25 eV (in our model, this is the threshold energy for displacing an atom in the CNT) to a C atom in a binary collision. The cross-sections S ($S = \pi p^2$ where p is the impact parameter) for various ions are presented in Fig. 4. It is evident that the averaged cross-sections for Kr and Xe ions are roughly the same. This is why the damage created

by these ions is approximately equal in the energy range considered.

When a CNT deposited on a substrate (supported CNT) is irradiated, in addition to the damage created by the ion and primary recoils, the CNT can be damaged by atoms sputtered from the substrate. The role of substrates was addressed in [25]. Two different types of substrates were considered: a heavy-atom metallic substrate (platinum) and a light-atom semiconductor substrate with covalent bonds between atoms (graphite). It was found that at low temperatures the defect production depends on the type of the substrate and the damage is higher for metallic substrates composed of heavy atoms due to sputtered substrate atoms and backscattered carbon recoils (see Fig. 5). Similar to the case of suspended CNTs, the most abundant defects were single- and multi-atom vacancies, and the number of defects increased with the energy of incident ions up to roughly 600 eV then it remained practically the same. Annealing of the CNT samples decreased the amount of defects by 20–50%, and the residual damage after annealing was practically independent of the substrate type.

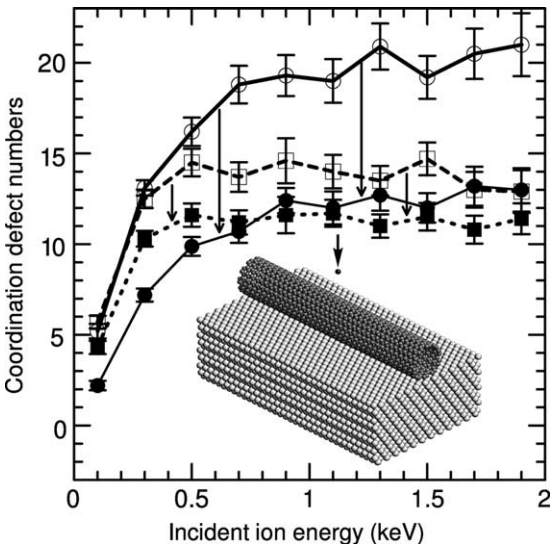

Fig. 5. Average coordination defect numbers for a nanotube lying on various substrates as functions of incident Ar ion energies. Open/full circles stand for the number of C atoms with a coordination other than three before/after annealing for a nanotube lying on Pt substrate, open/full squares for a nanotube lying on graphite substrate. Arrows visualize the relationship between the curves before and after annealing. The inset shows the original atom configuration of the nanotube-Pt substrate system for ion impact simulations.

4.3. Linking nanotubes to substrates and each other

Ion irradiation of supported CNTs should result in the pinning of CNTs to both metallic and graphite substrates [25]. This should happen through the formation of chemical bonds between the nanotube and substrate atoms near irradiation-induced defects (by saturating dangling bonds), thus increasing the CNT-substrate adhesion.

Simulations [27] also demonstrated that Ar irradiation can result in the bonds not only between the CNTs and substrates, but also between adjacent CNTs in bundles (see Fig. 1(b)), with the number of bonds being linearly proportional to the ion energy. Recent ab initio calculations [41] indicate that similar links can appear in irradiated graphite. Likewise, cross-linking and chemical functionalization of CNTs can potentially be achieved with the use of CH_3^+ species [22,23] with energies up to 80 eV or low-energy (3 eV) carbon ions [22]. In agreement with theoretical predictions, experiments on irradiation of MWNTs with CF_3^+ ions provide strong evidence for CNT chemical functionalization [22]. However, due to small ion energies (and thus small ion ranges), this method could hardly work for bulk CNT samples.

Along with making links between CNTs, ion irradiation can be employed for welding CNTs together, which is important for making a mechanically stable network of joined CNTs. As discussed above, a focused electron beam can be used [5] for this purpose. Simulations [28] indicate that ion irradiation combined with high-temperature annealing should also result in welding of crossed nanotubes, both suspended and deposited on substrates. For the latter, the optimum Ar ion energies were predicted to be about 0.5 keV, whereas the optimum irradiation doses should be about 10^{15} cm^{-2}. Higher doses will result in a

heavy damage of the carbon network and even CNT break-up [28].

4.4. Carbon nanotubes as masks against ion irradiation

Another quite interesting application of irradiation of CNT on metallic substrates has been reported. Experiments demonstrated that ion bombardment and CNTs may be employed for fabricating metal nanowires using MWNTs as masks [32]. By irradiating with 300 eV Ar^+ ions, a Au/Ti wire about 10 nanometers in width has been formed underneath a MWNT lying on a thin Au/Ti layer deposited earlier on a SiO_2 substrate [32]. The key idea is illustrated in Fig. 6.

After forming the nanowire due to metal layer sputtering everywhere except for the area beneath the nanotube, the MWNT could be removed by an atomic force microscope (AFM) or dissolved. Because CNTs are micrometer-long and nanometer-wide objects and since they can be positioned very accurately using the AFM by pushing them mechanically [42], the described technique may potentially be employed for developing a large and complicated network of metal nanowires.

A computational study [26] was done to estimate the theoretical limit for the minimum width of a metal nanowire, which could be produced using this method. MD simulations of Ar ion irradiation of MWNTs showed that the bombardment results in the sputtering of carbon atoms from the MWNT, formation of vacancies on the MWNT walls and interstitial atoms between the shells. High irradiation doses lead to the complete amorphization of the MWNT, but the amount of sp^3 bonds is very small, which is in agreement with experimental results [13]. By estimating the sputtering yield from a MWNT (notice that the yield is lower for carbon than for typical metals) and taking into account the thickness of the metal layer, a universal equation was derived which for a given nanowire material allows one to estimate the theoretical limit on the minimum width of the wire as a function of the original thickness of the metal layer. It was shown that this technique potentially provides a better resolution than the present-day electron beam lithography, although a low AFM operation speed prevents mass production of

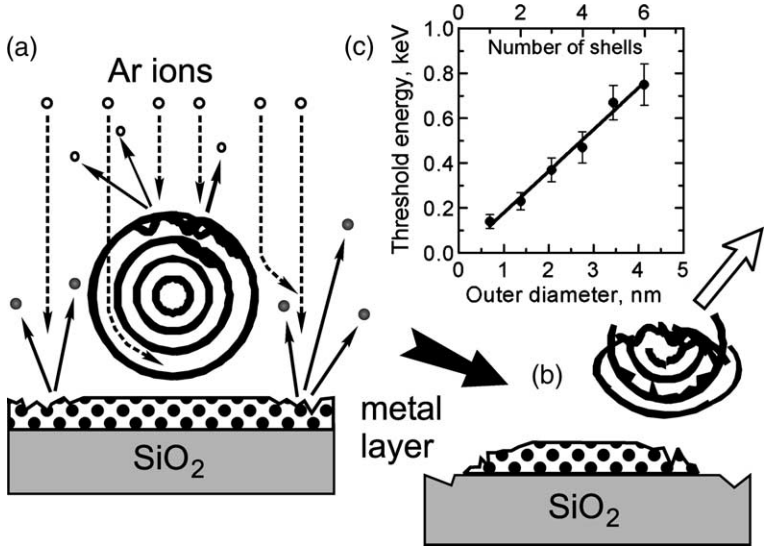

Fig. 6. Schematic illustration of the setup for using multi-walled nanotubes as masks against ion bombardment. Before irradiation a nanotube has been deposited on a thin metal layer on a SiO_2 substrate (a). Ion irradiation results in sputtering of metal atoms and nanotube amorphisation. After irradiation the nanotube can be removed by AFM (b). Threshold energy of incident ions (the maximum energy at which no energetic recoil hit the area below the nanotube) as a function of tube outer diameter (number of shells) (c).

metal wires using nanotubes as masks against ion bombardment.

This setup may also be used for spatially selective ion implantation into the parts of the sample which have not been covered with nanotubes. Thus, the threshold energy of incident ions (the maximum energy at which no energetic recoil hit the area below the nanotube) is an important characteristic. The threshold energy as a function of the MWNT outer diameter (number of shells) was evaluated [26] for various MWNTs. The threshold energy was found to linearly grow with the number of shells (see Fig. 6(c)). An analytical approximation was derived which makes it possible to estimate the minimum diameter of a MWNT needed to prevent the substrate below the MWNT from sputtering and ion implantation for a given energy of the incident ion.

5. Annealing of irradiation-induced defects

Experiments on electron irradiation of both SWNTs and MWNTs indicate that irradiation-induced damage in nanotubes can easily be annealed already at temperatures higher than 300 °C [6].

Two mechanisms seem to govern the defect annealing [25]. The first mechanism is vacancy healing through dangling bond saturation and by forming non-hexagonal rings and SW defects. An illustration of this mechanism is given in Fig. 7 where the front walls of one and the same SWNT just after ion impact (a) and after annealing (b) are shown. It is seen that during annealing the double vacancy in the middle of the carbon network has been transformed to an agglomeration of non-hexagonal rings. The annealing also gave rise to the transformation of the single vacancy and the nearby carbon adatom in the upper right-hand corner of the network to a SW defect. It is also noticeable that the annealing led to the local diameter reduction. The annealing should eventually result in disappearance of the SW defect, especially if an extra carbon adatom (which works as the catalyst for the transformation thus substantially reducing the defect annihilation barrier) is nearby [43].

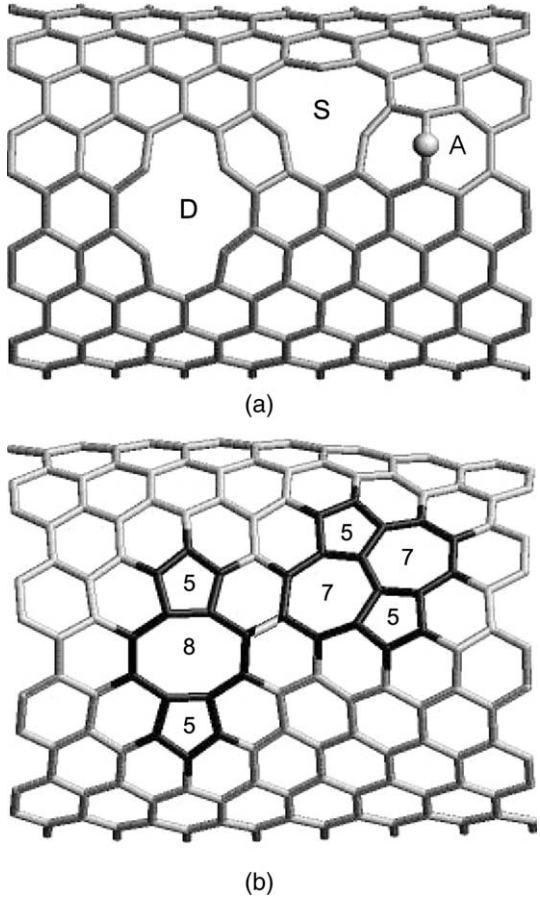

Fig. 7. Front walls of one and the same SWNT just after ion impact (a) and after annealing (b). During annealing the double vacancy (D) in the middle of the carbon network transformed to an agglomeration of non-hexagonal rings. The single vacancy (S) and the nearby carbon adatom (A) in the upper right-hand corner of the network transformed to a Stone–Wales 5–7 defect.

Similar vacancy mending occurs upon electron irradiation [9]. Notice that ion irradiation creates more severe local damage than electron irradiation, since in the former case a vacancy clusters may easily be formed by an energetic ion impact, whereas in the latter case the predominant defects are single vacancies. Nevertheless, this mechanism works for ion irradiation as well.

The second mechanism of annealing is the migration of carbon interstitials, followed by Frenkel pair recombination. The interstitial can

migrate over the surface of SWNTs (isolated or bundled-up). Early calculations [44,45] indicated that the migration energy E_m is very low, but more rigorous recent results [46,47] give higher values (0.5–1 eV; the actual value depends on the tube diameter and chirality), which is in a good agreement with experimental values of $E_m \sim 0.8$ eV [6]. Migration of interstitials in the open spaces between the adjacent shells in MWNTs seems to be similar to that in graphite ($E_m \sim 0.1$ eV for single carbon interstitials in graphite). Further studies are required to determine E_m in MWNTs more accurately.

A combination of these two mechanisms gives rise to a very efficient in situ defect annealing under irradiation at high (>300 °C) temperatures [6]. Thus, CNTs have surprisingly high ability to heal the irradiation-induced damage, which should facilitate the nanoengineering of CNT-based materials. Annealing of defects is also the driving force for irradiation-mediated CNT welding and coalescence.

6. Conclusions and outlook

This short review has summarized the recent advances in our understanding of interactions of CNTs with beams of energetic particles. Because of the high anisotropy of the atomic network and due to their outstanding mechanical and electronic properties, CNTs show a wealth of fascinating irradiation-induced phenomena which can readily be used for carbon nano-engineering.

Reasoning from the aforesaid experimental and theoretical data, beams of energetic particles (especially spatially-localized electron and ion beams) can be used in the future for making arrays of CNT-based quantum dots by creating defects in predetermined positions. Combined with high-temperature annealing, irradiation offers a way to join CNTs together, which is important for carbon-based electronics. Ion irradiation may further be employed for CNT doping by introducing impurities, which should also allow one to control electronic properties of CNTs. Irradiation-induced defects (mainly vacancies) could increase chemical reactivity of CNTs, thus opening another route for tailoring CNT characteristics.

Other plausible application of irradiating CNTs have been discussed in the literature, e.g. making CNT-polymer reinforcement materials with an irradiation-enhanced adhesion between polymers and CNTs [22,48,49]. It is well known that both electron and ion irradiation can create links between polymers chains. However, since the damage formation mechanism in the polymer matrix (predominantly electronic effects) is different from that in a CNT, it is not quite clear yet whether similar links between broken polymer chains and CNTs could be formed and what the mechanical characteristics of the sample could be. The electron rather than ion beam should be used for macroscopic sample irradiation due to much larger ranges of the electron damage.

The idea of using CNTs for channelling particle beams has been discussed [50,51]. It has theoretically been shown that both straight and bent CNTs can effectively be used for high-energy (>1 GeV) proton channelling [50]. However, the perfect alignment of CNT with respect to the beam direction seem to be a formidable obstacle, since otherwise the sample will quickly be destroyed as experiments [21] indicate.

Finally, with respect to using CNT as masks against irradiation, they may also be used for spatially-selective ion implantation, especially for low-energy (a couple of keV) applications. After irradiating a sample having a CNT network on the surface, ions will be implanted everywhere except for the regions below the nanotubes provided that the nanotubes are thick enough to stop the ions.

To implement in practice all the ideas discussed above, many issues which still lack understanding should be addressed. In particular, the behavior and mobility of irradiation-induced defects is still uncertain, although this matter is quite important for our comprehension of not only damage annealing but also CNT growth mechanisms. As for the putative ability of CNTs to channel energetic particles, more research is necessary, especially on the possibility to channel heavy ions with energies below 1 MeV, which is important for semiconductor technology.

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References

[1] M.S. Dresselhaus, G. Dresselhaus, P. Avouris (Eds.), Carbon Nanotubes, Synthesis, Structure, Properties and Applications, Springer, Berlin, 2001.
[2] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Science 297 (2002) 787.
[3] M. Terrones, H. Terrones, F. Banhart, J.-C. Charlier, P.M. Ajayan, Science 288 (2000) 1226.
[4] M. Terrones et al., Appl. Phys. A (Mater.-Sci.-Process.) 65 (2002) 355.
[5] M. Terrones, F. Banhart, N. Grobert, J.-C. Charlier, H. Terrones, P. Ajayan, Phys. Rev. Lett. 89 (2002) 075505.
[6] F. Banhart, Rep. Prog. Phys. 62 (1999) 1181.
[7] B.W. Smith, D.E. Luzzi, J. Appl. Phys. 90 (2001) 3509.
[8] C.-H. Kiang, W.A. Goddard, R. Beyers, D.S. Bethune, J. Phys. Chem. 100 (1996) 3749.
[9] P.M. Ajayan, V. Ravikumar, J.-C. Charlier, Phys. Rev. Lett. 81 (1998) 1437.
[10] J.P. Salvetat, J.M. Bonard, N.H. Thomson, A.J. Kulik, L. Forró, W. Benoit, L. Zuppiroli, Appl. Phys. A (Mater. Sci. Process.) 69 (1999) 255.
[11] D.E. Luzzi, B.W. Smith, Carbon 38 (2000) 1751.
[12] W. Mickelson, S. Aloni, W.Q. Han, J. Cumings, A. Zettl, Science 300 (2003) 467.
[13] Y. Zhu, T. Yi, B. Zheng, L. Cao, Appl. Surf. Sci. 137 (1999) 83.
[14] M. Suzuki, K. Ishibashi, K. Toratani, D. Tsuya, Y. Aoyagi, Appl. Phys. Lett. 81 (2002) 2273.
[15] P. Vincent, A. Brioude, C. Journet, S. Rabaste, S.T. Purcell, J.L. Brusq, J.C. Plenet, J. Non-Cryst. Solids 311 (2002) 130.
[16] H. Schittenhelm, D.B. Geohegan, G.E. Jellison, A.A. Puretzky, M.J. Lance, P.F. Britt, Appl. Phys. Lett. 81 (2002) 2097.
[17] B. Khare, M. Meyyappan, M.H. Moore, P. Wilhite, H. Imanaka, B. Chen, Nano Lett. 3 (2003) 643.
[18] G.H. Jeong, R. Hatakeyama, T. Hirata, K. Tohji, K. Motomiya, N. Sato, Y. Kawazoe, Appl. Phys. Lett. 79 (2001) 4213.
[19] G.H. Jeong, R. Hatakeyama, T. Hirata, K. Tohji, K. Motomiya, T. Yaguchi, Y. Kawazoe, Chem. Commun. 1 (2003) 152.
[20] H. Stahl, J. Appenzeller, R. Martel, P. Avouris, B. Lengeler, Phys. Rev. Lett. 85 (2000) 5186.
[21] V.A. Basiuk, K. Kobayashi, T.K.Y. Negishi, E.V. Basiuk, J.M. Saniger-Blesa, Nano Lett. 2 (2002) 789.
[22] B. Ni, R. Andrews, D. Jacques, D. Qian, M.B.J. Wijesundara, Y. Choi, L. Hanley, S.B. Sinnott, Appl. Phys. A: Mater. Sci. Process. 105 (2001) 12719.
[23] B. Ni, S.B. Sinnott, Phys. Rev. B 61 (2000) 16343.
[24] A.V. Krasheninnikov, K. Nordlund, M. Sirviö, E. Salonen, J. Keinonen, Phys. Rev. B 63 (2001) 245405.
[25] A.V. Krasheninnikov, K. Nordlund, J. Keinonen, Phys. Rev. B 65 (2002) 165423.
[26] A.V. Krasheninnikov, K. Nordlund, J. Keinonen, Appl. Phys. Lett. 81 (2002) 1101.
[27] E. Salonen, A.V. Krasheninnikov, K. Nordlund, Nucl. Instr. and Meth. B 193 (2002) 603.
[28] A.V. Krasheninnikov, K. Nordlund, J. Keinonen, F. Banhart, Phys. Rev. B 66 (2002) 245403.
[29] A.V. Krasheninnikov, K. Nordlund, J. Vac. Sci. Technol. B 20 (2002) 728.
[30] J. Pomoell, A.V. Krasheninnikov, K. Nordlund, J. Keinonen, Nucl. Instr. and Meth. B 206 (2003) 18.
[31] F.Z. Cui, Z.J. Chen, J. Ma, G.R. Xia, Y. Zhai, Phys. Lett. A 295 (2002) 55.
[32] W.S. Yun, J. Kim, K.H. Park, J.S. Ha, Y.J. Ko, K. Park, S.K. Kim, Y.J. Doh, H.J. Lee, J.P. Salvetat, L. Forro, J. Vac. Sci. Technol. A 18 (2000) 1329.
[33] A.J. Stone, D.J. Wales, Chem. Phys .Lett. 128 (1986) 501.
[34] P. Partyka, Y. Zhong, K. Nordlund, R.S. Averback, I.K. Robinson, P. Ehrhart, Phys. Rev. B 64 (2002) 235207.
[35] T. Diaz de la Rubia, R.S. Averback, R. Benedek, W.E. King, Phys. Rev. Lett. 59 (1987) 1930;
See also erratum: Phys. Rev. Lett. 60 (1988) 76.
[36] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
[37] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, S.B. Sinnott, J. Phys.: Condens. Matter 14 (2002) 783.
[38] S.J. Stuart, A.B. Tutein, J.A. Harrison, J. Chem. Phys. 112 (2000) 6472.
[39] J. Nygård, D. Cobden, Appl. Phys. Lett. 79 (2001) 4216.
[40] K. Nordlund, J. Keinonen, T. Mattila, Phys. Rev. Lett. 77 (1996) 699.
[41] R. Telling, C. Ewels, A. El-Barbary, M. Heggie, Nature Mater. 2 (2003) 333.
[42] C. Thelander, L. Samuelson, Nanotechnology 13 (2002) 108.
[43] C.P. Ewels, M.I. Heggie, P.R. Briddon, Chem. Phys. Lett. 351 (2002) 178.
[44] Y.H. Lee, S.G. Kim, D. Tománek, Phys. Rev. Lett. 78 (1997) 2393.
[45] M. Heggie, B.R. Eggen, C.P. Ewels, P. Leary, S. Ali, G. Jungnickel, R. Jones, P.R. Briddon, Electrochem. Soc. Proc. 98 (1998) 60.

[46] P.O. Lehtinen, A.S. Foster, A. Ayuela, A. Krasheninnikov, K. Nordlund, R.M. Nieminen, Phys. Rev. Lett. 91 (2003) 017202.
[47] A.V. Krasheninnikov, K. Nordlund, P.O. Lehtinen, A.S. Foster, A. Ayuela, R.M. Nieminen, Phys. Rev. B 69 (2004).
[48] C.A. Cooper, S.R. Cohen, A.H. Barber, H.D. Wagner, Appl. Phys. Lett. 81 (2002) 3873.
[49] S. Frankland, A. Caglar, D.W. Brenner, M. Griebel, J. Phys. Chem. B 67 (2002) 3046.
[50] S. Bellucci, V.M. Biryukov, Y.A. Chesnokov, V. Guidic, W. Scandale, Nucl. Instr. and Meth. B 202 (2003) 236.
[51] Y.-N. Wang, Z.L. Mišković, Phys. Rev. A 66 (2002) 042904.