

Atomistic simulations of irradiation effects in carbon nanotubes

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 (Dated: July 1, 2006)

In this paper we first review recent work on the basic science of the mechanisms of irradiation-induced defect production and migration in carbon nanotubes. We then discuss a few ways in which understanding of the irradiation effects can be used to modify the properties of single nanotubes as well as macroscopic materials based on them. The results illustrate that there indeed exist several ways in which defects can have potentially useful effects on nanotube-based materials.

PACS numbers:

I. INTRODUCTION

Systematic studies of radiation effects in materials started largely due to the need to understand the destructive effects of ion beams on fission reactor materials [1, 2], and this line of study has had a profound impact on how we consider radiation effects in solids. Studies of the destructive effects of radiation have been carried out in virtually all classes of materials: metals due to their use as structural materials in nuclear reactors, ceramics due to their use in nuclear waste storage, and even semiconductors due to their uses as radiation detectors.

On the other hand, irradiation is nowadays also widely used in a beneficial way, to modify materials to achieve desired functionality in them. The best known, and commercially clearly most important, example is the use of ion implantation to introduce a controlled amount of dopants into a desired depth in semiconductors [3]. However, even in this application the destructive nature of the ion beams plays a central role: the irradiation amorphizes the semiconductor crystal, and good understanding of the damage removal process is central to achieving the desired beneficial effects [4]. There is, however, a range of applications where the defects in the solid themselves provide beneficial effects directly. For instance, heavy ion irradiation of GaAs-based quantum wells has been shown to be able to improve on the operation speed of the devices by up to two orders of magnitude due to trapping of carriers at defect clusters [5–7].

Our motivation for studying radiation effects in carbon nanotubes comes from searching for beneficial effects. There are currently no plans for major application of carbon nanotubes in hard radiation environments such as fusion or fission reactors (although applications in space might involve some radiation tolerance issues). At first thought might seem paradoxical to even consider deliberately using irradiation on carbon nanotubes: since the material is hard to manufacture at good quality levels, why would one want to use an inherently destructive method like radiation on it? This simplistic argument is valid in the sense that high enough doses of any destructive irradiation will eventually turn carbon nanotubes into amorphous carbon, a material which obvi-

ously can be obtained in much easier ways. However, it is made invalid by two important considerations. First, the graphene (two-dimensional honeycomb-pattern-ordered carbon) network making up nanotubes is a very strongly bound one, and hence moderate dose irradiation certainly need not destroy an entire nanotube, just local regions of it. Secondly, as in the case of the GaAs quantum wells, it is at least in principle possible the defects themselves can have beneficial effects on a material.

In this paper we will review our recent work on the basic science of defect production in nanotubes by irradiation, as well as potentially useful application of these defects. As the results will clearly illustrate, there indeed exist several ways in which defects can have potentially useful effects on nanotube-based materials. The work discussed is mostly based on already published work, but also some entirely new results on defect migration will be presented.

II. OVERVIEW OF SIMULATION METHODS

In this section we overview the methods we have used to simulate irradiation effects in nanotubes, with the aim of giving the reader an impression of what the suitable connection between theory level and physical phenomenon is. We focus on methods suitable to study atom-level structures and dynamics, and hence do not discuss methods used to study electronic transport or optical excitations.

Density-functional theory (DFT) methods [8] are, despite some known shortcomings (for examples see [9, 10], the primary tool for simulation of the electronic structure of bulk materials. In these methods the true electron structure is approximated with one-electron wave functions of “non-interacting” electrons, and a special exchange correlation functional is used to describe electronic interactions. Iterative methods are used to find the ground state electron configuration for any known atomic one. They have been widely used to study defects in irradiated materials, and can nowadays sometimes also be used to do molecular dynamics over a few picoseconds [11]. DFT methods are, however, generally limited to simulations of a few hundred atoms, or in plane-wave implementations to regions of space of the order of $(10 \text{ \AA})^3$. However, carbon nanotubes are of course very small systems, and hence it is entirely possible to fit in an entire

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segment of a small single-wall nanotube within a DFT simulation cell. Using periodic boundaries in the tube length directions, and sufficient amount of free space in the two other directions, one can realistically simulate a segment of a very long nanotube. DFT methods have thus been used extensively to simulate defect energetics and mobility in nanotubes [12, 13].

An interesting alternative to DFT for carrying out quantum mechanical simulations is the tight-binding (TB) method [14, 15]. In this method only the outermost electrons and their hopping integrals with the nearest neighborhood are treated quantum mechanically, while a classical pair potential is used to describe short interatomic distances. The TB models involve parameters which need to be adjusted either to DFT or experimental data, so they can not be considered a “first-principles” model. However, they do retain a quantum mechanical treatment of the interatomic interactions while being orders of magnitude faster than DFT, making them a good alternative to study carbon nanotubes. We have tested the DFT-based TB method from Frauenheim’s group [16] extensively against DFT calculations, and found that it does generally give a good description of defects in nanotubes [13, 17, 18]. Moreover, due to its speed, it can be used to study larger nanotubes than what is practical with DFT.

Although both DFT and TB methods can nowadays be used to examine atom dynamics to a limited extent, the method of choice for accessing large systems and long time scales remains molecular dynamics employing analytical potentials. These potentials involve a set of analytical equations (which in practice may be handled as numerical data), the parameters of which are fitted to empirical and/or DFT data. It is always questionable whether they describe properly effects not directly dependent on the original fitted data, i.e. are “transferable”. Analytical potentials developed with physically motivated functional forms and fitted into different kinds of materials properties have often been found able to describe a wide range of materials properties outside the original fitting database at least qualitatively sensibly (for examples see e.g. [? ? ?]). MD simulations of radiation effects are thus usually most valuable in providing insight into qualitative mechanisms, which can not be studied directly by experiments. But in certain cases they have also proved to also be able to reproduce e.g. sputtering yields [19], ion beam mixing [20] and ion implant depth profiles [21] quantitatively correctly within the experimental uncertainty. We have employed them extensively to study carbon nanotubes, as will be discussed in the following sections.

Molecular dynamics simulations involve numerical solution of the Newton equations of motions to determine the time evolution of a system of particles interacting with each other, and possibly also some external force field [22, 23]. The force field can come from DFT, TB or analytical potentials. The simplest variety of MD, direct solution of the equations of motion, is ideally suited to study ion-induced radiation effects since this correctly accounts for the non-equilibrium ballistic motion of high-energy ions as well as the subsequent thermalization of

the ion [2]. Efficient and realistic simulation of radiation effects often requires the basic MD methods [22] to be amended with a few solutions specific to radiation effects. These include almost always inclusion of electronic stopping as a frictional force [24], realistic high-energy repulsive interactions [25] and an adaptive time step [24]. To dissipate the heat emanating from the cascade away from the simulation cell temperature scaling (velocity damping) at the boundaries is often carried out, although sometimes this step is left out and the temperature is simply allowed to spread out in the simulation cell. If the cell is large enough that the associated temperature rise is not significant, this can be considered acceptable. Multiple-time step schemes [26] may be useful for speeding up the initial stages of the simulation when atoms have highly disparate velocities. However, if long simulation of the system after the cascade has thermalized is required, the overall gain in simulation time is not likely to be large.

Direct comparison of MD data with experiments is often complicated by the limited time scale (typically of the order of nanoseconds) of MD simulations. Hence most diffusion processes and long-term relaxation of molecular structures are not included in the MD, which at worst may completely hinder comparison of MD results with experiments. Kinetic Monte Carlo (KMC) methods can sometimes solve this problem [27–29]. The basic algorithm of this method is known in different sub-fields of physics and chemistry variously as the Bortz-Kalos-Lebowitch [28], Gillespie [30], kinetic Monte Carlo, dynamic Monte Carlo [29], or residence-time algorithm. Common to all these is that they take as input the rates of relevant processes in a system, which typically are the defect migration rates and incoming ion flux, and simulate the time evolution of the objects. The algorithm selects the processes proportional to their rate, so no effort is wasted in time steps with no events occurring. In atomic kinetic Monte Carlo (AKMC) simulations all atom coordinates are included but only one or a few defects (typically vacancies) are moving. In object kinetic Monte Carlo (OKMC) only the mobile defects are followed, and the lattice atoms are not explicitly described at all. Since only the objects of interest are simulated, this allows for simulation of large time and length scales. However, even this method is limited by the number of objects that can be handled and the number of jumps they take. Typically thousands or even millions of jumps of a fast-moving individual defect are needed before a recombination or clustering reaction occurs. A variety of OKMC is event kinetic Monte Carlo (EKMC) where the jumps are not explicitly treated, but instead the next reaction is selected stochastically.

Finally we mention a well established method not yet widely used to simulate nanotubes. Theoretical treatment of paper has long utilized fiber network simulation methods, where the basic object is a long elastic fiber [?]. Since nanotubes are one-dimensional objects, it is natural that a fiber model may be useful for simulating their properties. The main drawback is that fiber models usually treat the fibers as rigid, which is a good approximation for multi-wall, but not single-wall nanotubes.

FIG. 1: Some important defect structures in a carbon nanotubes. a) unreconstructed vacancy, b) reconstructed 5-1db vacancy, c) divacancy, and d) adatom on the outside of the tube.

Nevertheless, these models can be used to examine theoretically the properties of macroscopic nanotube-based materials [31].

III. DEFECT PRODUCTION AND PROPERTIES IN NANOTUBES

For keV ion irradiation of carbon nanotubes the most important mechanism of damage creation is the knock-on atom displacements due to kinetic energy transfer, i.e. nuclear stopping. Protons may be exceptions to this rule, but it is not clear yet whether electronic effects can produce damage in the tubes.

To understand damage production in carbon nanotubes it is necessary to consider the atomic structure of the tubes in more detail. The atom networks of typical nanotubes are shown in Fig. 1. Nanotubes may have only one shell (single-walled nanotubes, SWNTs) or many shells (multi-walled nanotubes, MWNTs). The former usually bundle up to form a triangular lattice due to attractive van der Waals interactions, see Fig. 2 (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 multiple one). The structure of the vacancies is slightly non-obvious. Although the initial structure is most likely that obtained by simply plugging out an atom from the graphene network, this structure is not the ~~ground state~~ of the vacancy. Instead it tends to reform into a structure where two of the dangling bonds form a bond with each other, while the third atom is displaced out of the nanotube network, a so called 5-1db defect [32], see Fig. 1. Also the larger vacancies tend to reconstruct in similar manners to reduce the number of dangling bonds.

The primary knock-on atoms produced in the initial irradiation event can, 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, forming a structure with one atom above or below the middle of a carbon-carbon bond in the graphene network [33, 34], see Fig. 1. It is virtually impossible to insert a carbon atom in the middle of a hexagon, due to the basic chemical bonding energetics of carbon. Hence no interstitial in the conventional crystallographic sense can exist in a SWNT. However, the adsorbed atoms (adatoms) behave very much like the interstitials in conventional materials [13, 34, 35]. In MWNT's it is possible to have carbon atoms between the nanotube shells, which are likely to behave pretty much like conventional interstitials in graphite [36].

Along with the simple defects, a number of more complex defects can be formed, e.g., the pentagon/heptagon

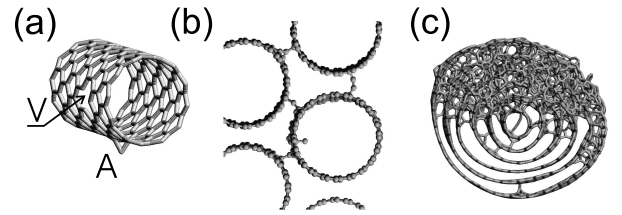


FIG. 2: Molecular models of irradiated carbon nanotubes. A short fragment of a single-walled nanotube with a vacancy (V) and a double-coordinated carbon atom adsorbed onto the outer surface of the tube (a). A bundle of nanotubes (view along the tube axes) after the impact of a 500-eV Ar ion (b). A multi-walled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

Stone-Wales (SW) defects [?] associated with a rotation of a bond in the nanotube atom network, other topological defects in the graphitic network (non-hexagonal rings), amorphous complexes, *etc.* Besides this, defect-mediated covalent bonds between adjacent SWNTs in a bundle can appear. Similarly, in MWNT's covalent bonds can appear between the individual tubes forming the multi-walled one. Although it is obvious that interstitials can have this effect, the surprising thing is that apparently also vacancies can have the same effect [37–39].

Simulations of irradiation of individual SWNTs with 50-3000 eV Ar ions were carried out in [34, 35]. The SWNTs were assumed to be suspended by their ends (such nanotubes can be manufactured experimentally [?]). It was found that single vacancies and vacancy-related defects [40] (which single vacancies can turn into) were the most prolific defects in nanotubes which appeared after ion impacts. Double-coordinated carbon adatoms [Fig. 2(a)] on both the external and internal sides of the nanotube walls [33] were also common. Besides this, other complex defects like SW defects and amorphous regions were observed.

In order to illustrate the damage in the SWNT at different energies of incident Ar ions, in Fig. 3 we plot the number of C atoms with a coordination other than three [66] as a function of ion energy (solid circles). This quantity may be considered as a characteristic of the overall damage in the nanotube produced by the ion.

It can be seen from Fig. 3 that, if the energy of the incident ion is higher than the defect creation threshold energy (about 50 eV [34]), the number of defects increases with the energy up to roughly 600 eV, after which 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 higher ion energies, although defect production in the SWNT drops as the nuclear collision cross section for defect production decreases [41], 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

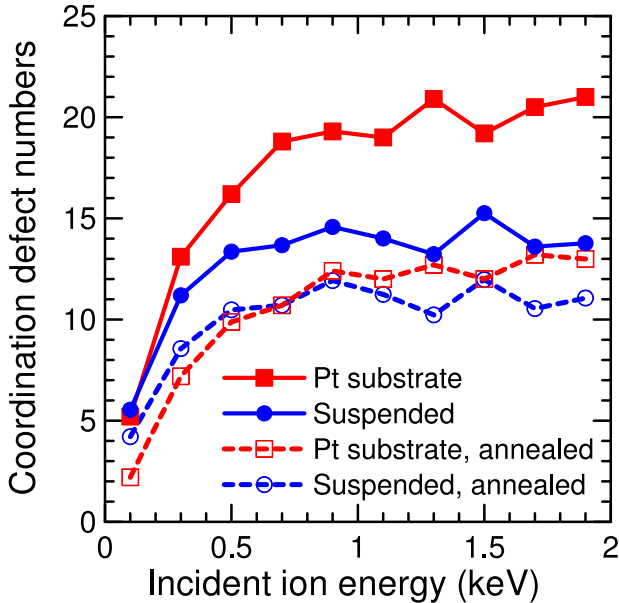


FIG. 3: Average coordination defect numbers for irradiated nanotubes as functions of incident Ar ion energy. Full circles/squares stand for the number of C atoms with a coordination other than three for for suspended/supported nanotubes. Open circles/squares are the corresponding coordination defect numbers after 100 ps annealing at 1500 K.

obtained for other types of ions [41] with energies up to 1 keV.

When a nanotube deposited on a substrate is irradiated, in addition to the damage created by the ion and primary recoils, the tube can be damaged by atoms sputtered from the substrate, see Fig. 3. Similar to the case of suspended tubes, 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, after which it remained practically the same. In both cases, annealing of defects (see below) decreased their amount by 20-50%, and the residual damage after annealing was practically independent of the substrate type.

IV. DEFECT MIGRATION IN NANOTUBES

A. Migration mechanisms

For complete understanding of radiation damage in a material, one needs to be able to handle not only the damage production during irradiation events, but also the long-term damage evolution. This is the case in conventional materials like metals and semiconductors, where it is well established that both basic defect types, the interstitial and vacancy, are rapidly mobile already at room temperature [42–45]. Early experiments in graphite [36, 46, 47] and very recent ones in nanotubes [48] indicate that this is the case in nanotubes as well. As summarized in the previous section, during the last 6 years we and others have gathered a relatively comprehensive

picture of the primary state damage production in carbon nanotubes. During the last three years we have been deriving defect migration parameters which form the basis for modeling the long-term damage evolution. In the following we will describe our main results on damage annealing and the KMC model for defects in nanotubes we are developing.

Before we discuss the defect migration, we emphasize that carbon nanotubes have an inherent mechanism of defect annealing which requires no defect migration, namely vacancy healing through dangling bond saturation and by forming non-hexagonal rings. This mechanism is common for both ion [?] and electron [?] irradiation. Although a similar effect can of course also occur in other materials with covalent bonds, it has a unique importance in nanotubes because the finite width of the tube allows the entire tube to change shape to saturate the bonds. Because of the small width and high energy associated with dangling bonds in carbon, the bond saturation can easily overcome the increase in strain energy.

The vacancies in carbon nanotubes can migrate by switching dynamically the dangling bonds. As described above, the ground state of the vacancy is the reconstructed 5-1db structure. While it has been known for some time that this structure can migrate efficiently via an intermediate state where all dangling bonds are saturated [40], the exact migration mechanism was only recently clarified [13]. The migration occurs as a two-stage process. Recall that in the 5-1db structure the 3-fold symmetry is broken by the formation of one covalent bond and one atom being out of the plane. This structure can rotate around the position of the original missing atom, see left part of Fig. 4 [13, 38]. The other crucial stage is that the atom with the dangling bond can form a bond with one of the reconstructed atoms on the opposite side, forming for a moment an unstable four-fold bonded state. One of the pre-existing bonds in this state can then break, leading effectively to a change in the position of the 5-1db structure, see right part of Fig. 4. A combination of the 5-1db movement and rotation mechanisms allows for an overall movement of the vacancy. Note that according to the DFT calculations presented in Ref. [13], the intermediate 4-fold bonded state where all dangling bonds appear to be saturated is actually unstable. The migration energies are dependent on the nanotube chirality, but in all practical cases larger than or about equal to 1 eV.

The interstitial can migrate over the surface of SWNTs (isolated or bundled-up). Early calculations [49, 50] indicated that the migration energy E_m is very low, but more rigorous recent results [12, 13] give higher values (0.5 – 1.2 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 [47]. Migration of interstitials in the open spaces between the adjacent shells in MWNTs is likely to be similar to that in graphite ($E_m \sim 0.1$ eV for single carbon interstitials in graphite [49, 50]).

At any temperature where the interstitial is mobile, defect annealing can occur by recombination of interstitials and vacancies. As in for instance Si [?], the re-

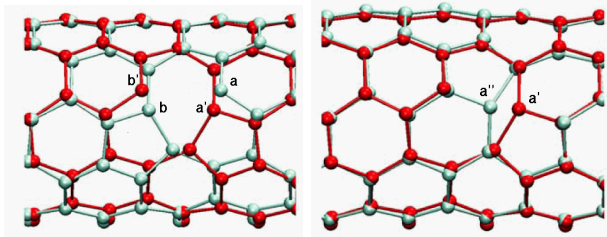


FIG. 4: Illustration of the migration of the vacancy. Left: rotation of the reconstruction of the vacancy. The lighter atoms are the initial positions and the darker ones the final. The primed characters denote final positions of the atoms. The original dangling bond atom a forms a new bond while one of the bonds of atom b breaks. Right: switch in the position of a 5-1db structure. The darker atoms are the initial positions and the lighter ones the final. The atom a' moves to state a'' ; at the midpoint it can be considered to have four bonds.

combination efficiency depends on from which direction the interstitial approaches the vacancy, and it is possible to form metastable states of close-by interstitials and vacancies (or at least their clusters) [?]. Nevertheless, at elevated temperatures ~~certainly~~ interstitial-vacancy recombination is expected to occur efficiently.

Combined the two mechanisms of damage annealing (dangling bond saturation and defect recombination) lead to very efficient annealing under irradiation at high ($> 300^\circ\text{C}$) temperatures [47]. Thus, nanotubes have a high ability to heal irradiation-induced damage, which should facilitate the nanoengineering of nanotube-based materials. Annealing of defects is also the driving force for irradiation-mediated nanotube welding and coalescence.

B. Kinetic Monte Carlo simulations on defect migration

To be able to quantitatively predict the damage annealing when more than two defect reactions are present, one needs to use either rate equations or kinetic Monte Carlo. Since nanotubes are limited in size in two dimensions, KMC methods are especially well suited for ~~carbon nanotubes~~.

We have developed a new Monte Carlo simulation method for modeling defect migration on walls of a single-wall carbon nanotube with arbitrary chirality and curvature. ~~The kinetics of point defects, such as vacancies and carbon adatoms, may govern the growth, reactivity, local electronic structure [51] and irradiation-induced transformations [13, 52?] of carbon nanotubes.~~ As far as we know, our code is the first attempt to use Monte Carlo methods to model migration of defects on arbitrary carbon nanotubes.

The activation energies and paths for the defect migration needed in the KMC algorithm have been obtained ~~with~~ DFT and TB calculations [13, 18]. As a first approximation, we have included the migration, coalescence and annihilation of point defects on the carbon nanotube

walls.

As a test to our method, we have simulated electron irradiation of a (10,10) single-walled carbon nanotube with experimentally reasonable conditions (diameter of the electron beam $d \approx 15.0$ nm, on average 1 displacement/atom/s, no sputtering) at different temperatures. The resulting defect concentrations are presented in Figures 5 and 6 after 10 s and 60 s of ongoing irradiation, respectively.

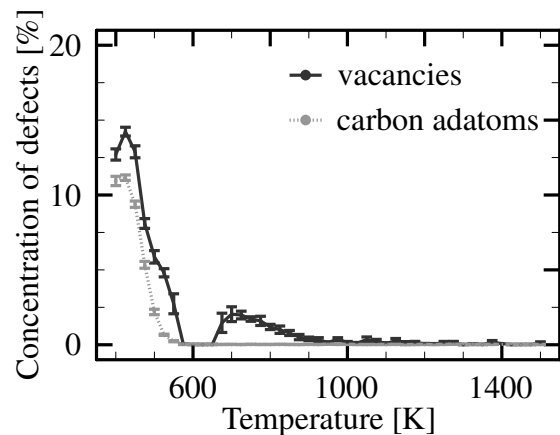


FIG. 5: Defect concentration in a (10,10) carbon nanotube after 10 s of electron irradiation as a function of the temperature.

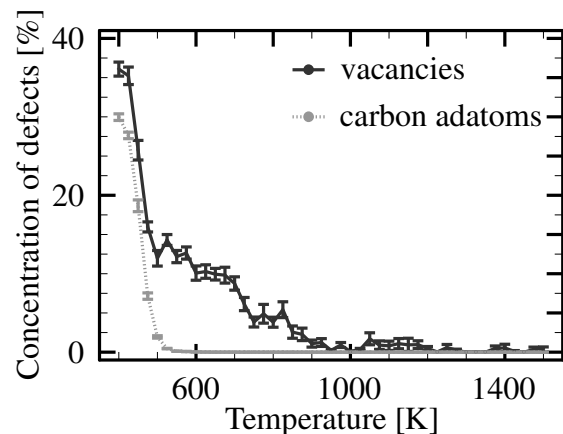


FIG. 6: Defect concentration in a (10,10) carbon nanotube after 60 s of electron irradiation as a function of the temperature.

The irradiation temperature was found to have a significant effect on the defect concentration on the irradiated carbon nanotube. At low temperatures (near 300 K), mobilities of both vacancies and carbon adatoms are low enough for the defect creation rate to introduce new defects faster than the old ones can escape from the irradiated area. This leads to defect agglomeration and thus to

formation of amorphous-like structures. As the temperature increases (about 300-900 K), adatoms are mobile enough to either annihilate with the vacancies or to escape from the irradiated area. Vacancies, however, still typically coalesce to multivacancies. At even higher temperatures, both the vacancies and adatoms are mobile enough to escape from the irradiated area before coalescing, thus leaving the lattice undamaged.

In addition to estimating the optimum irradiation temperature for the experiments, our method can for example be used to study the nanotube growth process and the experimentally observed shrinkage of nanotubes [52?].

V. POSSIBLE APPLICATIONS OF IRRADIATING NANOTUBES

As indicated in the introduction, we have considered ~~also~~ many possible applications of irradiation of carbon nanotubes. Here we give a short summary of some of the application areas considered.

A. Mechanical properties

The basic cohesion of carbon nanotube materials is governed by two effects. The strong sp^2 bonds between carbon atoms bind together a single nanotube (either single-wall or one layer of a multi-wall one) and give it outstanding strength properties. These single nanotubes are bound to each other by van der Waals (also known as dispersion) interactions which are roughly 3 orders of magnitude weaker per atom pair than the covalent bonds. This interaction is basically the same as the well-known graphite interlayer interaction [53]. Because it is so weak, the first macroscopic materials made based on carbon nanotubes have had strengths which are orders of magnitude lower than those of a single tube, since the nanotubes can easily slide by each other [54].

To manufacture nanotube-containing materials which would have strengths comparable to those of a single nanotube, it is a rather obvious idea to attempt to somehow introduce covalent bonds between the nanotube shells or a nanotube and its surroundings. For instance in nanotube-epoxy composites this has been achieved by purely chemical means [?]. We have examined whether irradiation can be used to introduce covalent bonds between the tubes and what the effect of these bonds on the strength would be.

As mentioned above, both interstitials and vacancies can introduce covalent bonds between layers of a multiwall nanotube or between nanotube layers. These defects can have both beneficial and detrimental effects on nanotubes. In an isolated single-wall nanotube, vacancy-like defects decrease both the Young's modulus, tensile strength and critical strain [55] significantly. The Young's modulus is affected relatively weakly, while the latter quantities are affected by as much as a factor of two. However, the crucial question is what happens in

multi-wall tubes or between different tubes. Considering the simplest possible case of covalent bonds between the shells in a double-walled nanotube, we showed that the interlayer shear strength can increase by orders of magnitude even by a very low concentration of defects [39]. Such a large positive effect by far offsets the minor decreases in e.g. the Young's modulus.

Going to larger length scales, we ~~also have~~ considered the effects of irradiation on macroscopic nanotube materials. So called carbon nanotube paper or buckypaper [? ?] is a material analogous to conventional paper in that it consists of long intertwined fibers. Whereas conventional paper consists of cellulose fibers bound together by glue material, nanotube paper consists of single-walled or multiwalled carbon nanotubes first forming bundles. These bundles are then intertwined and bound together by van der Waals bonding (see Fig. 7).

The mechanical properties (such as the stiffness and tensile strength) of existing carbon nanotube paper samples are not particularly good, since the tubes are bound together only by weak van der Waals bonding. We have considered whether the irradiation-induced covalent bonds could be used to strengthen nanotube paper. Using a fiber network model we were able to reproduce the correct order of magnitude of the experimental stiffnesses of unirradiated nanotube paper. Then including the strength of irradiation-induced bonds between the tubes in the model, we have predicted that irradiation can potentially be used to strengthen nanotube materials by at least an order of magnitude [31].



FIG. 7: Left: image of single-wall carbon nanotube paper on aluminum foil, compared in size to a one euro coin. Right: Scanning electron microscopy image of the same nanotube paper.

B. Using carbon nanotubes as masks against ion irradiation

Although carbon nanotubes are very interesting as one-dimensional electrical conductors by themselves, they can also be used to manufacture nanowires of other materials. The key idea is simple: use a carbon nanotube as a mask against sputter erosion of a thin film. If the nanotube is thick enough compared to the thin film, and the irradiating conditions such that the thin films sputters efficiently compared to the nanotube, the thin film will be eroded everywhere except below the nanotube. After irradiation selective chemical etching can be used to remove the remains of the nanotube, leaving only the nanotube metal wire beneath.

This idea was realized experimentally by Sun *et al*, who irradiated an Au/Ti thin film with a multi-walled carbon nanotube on top with 300 eV Ar ions [?]. The experiment resulted in a metal nanowire about 10 nm in width. Based on extensive molecular dynamics simulations we derived and parametrized an equation which allows one for a given material to estimate the lower limit of the possible widths of the metal nanowire [56]. For instance, for a 10-nm thick gold film we predicted a minimum width of about 3 nm. This is less than the minimum widths obtainable by conventional electron lithography [?].

Such a lower limit exists basically because for an extremely narrow nanotube, the carbon in the nanotube would sputter away before the metal film does. On the other hand, by selecting irradiation conditions where the carbon sputtering yield is less than that of the metal, it can be possible to obtain nanowires thinner than the film thickness.

In the original experimental implementation, and also in our study, the idea for using this approach for practical use relied on moving a single nanotube to a desired location. This clearly could be useful for the very common laboratory experiments on single nanosize diodes and transistors, but hardly for large-scale production. But we note that in recent years great progress has been made in growing large numbers of nanotubes from one electrode to another on chips [?]. If this approach is perfected to industrial reliability levels, tubes grown in such a way might also be useful as masks to make metal nanowires on a large scale.

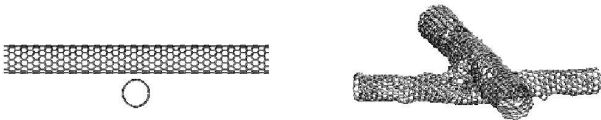


FIG. 8: Left: two nanotubes placed in a cross configuration Right: The same tubes after XXX eV Ar ion irradiation to a dose of YY ions/cm².

C. Welding carbon nanotubes

From the above discussion it is clear that both electron and ion irradiation can cause major atomic rearrangement in nanotubes. Hence it is not surprising that at high enough doses, irradiation can even affect a complete joining of initially separate nanotubes. This was first shown with in situ electron irradiation in a microscope [57–61]. It was explained with TB simulations of the formation of vacancies due to the electron irradiation, which then affected the joining of the tubes [57, 58, 61].

We considered the ion irradiation welding of nanotubes by simulating two crossed carbon nanotubes and examining whether ion irradiation can be used to join the tubes. These simulations had the obvious problem that the defects produced in the simulations could not migrate significantly on the MD time scale, whence the amount of damage would clearly be overestimated in the simulations. To partly solve this problem, we heated up the

tubes to a high temperature of 2000 K (CHECK) between each ion irradiation event. This heating leads to efficient recombination of dangling bonds, but still does not allow for long-range defect migration and recombination produced by that [35]. Hence one can expect that the damage in the nanotubes is overestimated by our simulations.

Our simulations showed that nanotubes can indeed be joint by ion irradiation [62], see Fig. 8. The tube quality after the welding is clearly poor. However, the welding has since our simulations also been carried out experimentally [63–65]. In the experiments of Raghuveer *et al* [64], the smallest nanotubes in the system vanish due to sputtering, whereas the largest ones join together with no major obvious difference in the tube quality before and after the irradiation. Thus their results essentially confirm both our prediction that tubes can be joint, and the argument that the damage in the tubes will be overestimated by the MD simulations.

VI. CONCLUDING REMARKS

In this paper we have discussed the basic effects of ion irradiation on carbon nanotubes, as well as how this could be potentially useful for ion beam modification of nanotubes.

We showed that the basic features of point defect structure, production and migration in nanotubes start to be fairly well understood based on DFT, TB and classical potential simulation, and that the results are in part confirmed by experiments. The first systematic data on defects larger than the divacancy and diinterstitial is now starting to emerge, although here more additional work still needs to be done. Likewise, the knowledge of defect behavior between the walls of multiwalled tubes and between different tubes is still incomplete and somewhat uncertain.

We also discussed both simulation and experimental work showing how irradiation may be potentially useful to modify the mechanical properties of nanotubes and even joining them completely. This work clearly demonstrates that achieving such effects with ion beams is feasible; however, what it does not show is whether ions are the only or most affordable way of achieving the effect. For instance it is also well known that purely chemical means can be used to introduce covalent bonds between nanotubes and their surrounding and thus improving mechanical properties [?]. It remains to be seen whether the ion beam methods offer any distinct and unique advantages over the presumably much cheaper chemical means.

Acknowledgments

We thank Mr. K. Oskenkörva for providing continued inspiration for this work. Dr. K. Arstila is acknowledged for taking the SEM image of carbon nanotube paper. The work was made possible by the Academy of Finland

under several research projects and the Centres of Excellence programme, as well as generous grants of computer

time from CSC, the Finnish IT Center for Science.

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