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Irradiation-assisted substitution of carbon atoms with nitrogen and boron in single-walled carbon nanotubes

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Abstract

Doping of carbon nanotubes with boron and nitrogen should provide more control over the nanotube electronic structure. In addition to the chemical substitution and arc-discharge methods used nowadays, we suggest using ion irradiation as an alternative way to introduce B/N impurities into nanotubes. Making use of molecular dynamics with analytical potentials we simulate irradiation of single-walled nanotubes with B and N ions and show that up to 40% of the impinging ions can occupy directly the sp^2 positions in the nanotube atomic network. We further estimate the optimum ion energies for the direct substitution. As annealing should further increase the number of sp^2 impurities due to dopant atom migration and interaction with vacancies, irradiation-mediated doping of nanotubes is a promising way to control the nanotube electronic structure.

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1. Introduction

The remarkable electronic properties of carbon nanotubes [1] (CNTs) combined with their excellent mechanical and thermal characteristics have stimulated a huge body of research work on CNT growth methods and nanotube applications. The use of CNTs in nanoelectronics has been widely discussed, as in addition to their inherent nm-sizes, they can be either semiconductors or metals with ballistic transport properties. The electronic properties of a CNT are completely governed by the tube chirality, i.e. the way the nanotube is rolled up from the graphene sheet. Unfortunately, as grown CNTs present a mixture of tubes with different atomic structures, and despite a substantial effort [2], at the moment there is no way to reliably separate CNTs depending on their metallicity.

To have more control over the electronic properties, it has been suggested to dope CNTs with B

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and/or N atoms [3–7]. This is a natural choice of the dopant, as B/N has roughly the same atomic radius as C, while it possesses one electron less/more respectively. The N doping has received particular attention, as N-impurities can also give rise to CNT functionalization [4] and transformations of the atomic network to bamboo-like structures [5,6].

A number of methods based on arc-discharge techniques [5,8] and substitutional reactions [7] have been developed for the doping. Unfortunately, instead of occupying the substitutional sp^2 position in the graphitic network, a substantial part of the dopant is chemisorbed [9] on the CNT surface or binds to irregular carbon structures in sp^3 sites [5]. Besides this, substitutional reactions are hardly possible for nanotubes with diameters less than 8 nm [7]. Problems with incorporating B atoms into the carbon lattice of nanotubes have also been reported [8]. All of these further limits the applicability of these techniques.

In this work we offer an alternative way to introduce B/N impurities into CNTs. We suggest using ion irradiation as a tool to dope CNTs with B and N. Ion beams have routinely been used in semiconductor technology for introducing impurities. However, as CNTs are nano-objects with a unique atomic structure, it is not clear a priori if it is possible to introduce substitutional impurities. Also it is not clear what the probability for direct substitution or the optimum energies could be. Making use of molecular dynamics with analytical potentials we simulate irradiation of single-walled nanotubes (SWNTs) with B and N and show that up to 40% of the impinging ions can directly occupy the sp^2 positions in the nanotube atomic network. Our simulations also indicate that a further increase in the number of sp^2 dopant atoms is possible after annealing due to the vacancy-mediated mechanism [7].

2. Method

To simulate impacts of the B/N impurity atoms into SWNTs, we employed classical molecular dynamics with analytical potentials. The simulation method is described at length in our previous publications [10,11] and therefore we present here only the details essential for this study.

The interactions between atoms of different types (C–B/N) were described by a Tersoff-like potential by Matsunaga et al. [12]. Note that the potential was developed for cubic boron carbonitride systems and its parametrization did not include any graphitic systems with sp^2-hybridization of atoms. However, as we show below, the energetics and geometry of particular atomic sp^2 configurations agree well with the DFT results reported in the literature. To check how the results are sensitive to the potential parameters, we also ran test simulations with the Brenner II potential (with parameters for carbon) assuming that B and N atoms are chemically equivalent to C, but have the correct atomic mass.

To realistically model energetic collisions, we smoothly joined the potentials with the ZBL repulsive potentials [13] at short interatomic separations [14]. We did not account for the electronic stopping as the ion energies were low and the nuclear slowing down governed the collisional phase.

3. Results and discussion

To test our B–C–N potential model, we first calculated the vacancy formation energy for a (10, 10) SWNT. The energy proved to be 6.8 eV, which is in line with the results (6.1 eV) reported in the literature [15]. We also computed the N atom adsorption energy for a (10, 10) SWNT. We found that the adatom on the outer surface of the tube occupies the bridge position (see Fig. 1(b)) with the distance between the N atom and its closest neighbour being $d_{\mathrm{N–C}} = 1.67$ Å and adsorption energy $E_a = 2.51$ eV. These results also agree well with the ab initio data [16]: 1.53 Å and 2.67 eV, respectively. Thus, one may hope that the potential reproduces at least qualitatively the main features of the N–C bonding in doped SWNTs.

Having tested our model, we moved on to simulations of SWNT bombardment with B and N ions. As the energetics of B/N substitutional defects in sp^2 sites sets the lower limit on the ion energy, we first calculated the energies of B/N atoms in the sp^2 substitution configurations (see Fig.

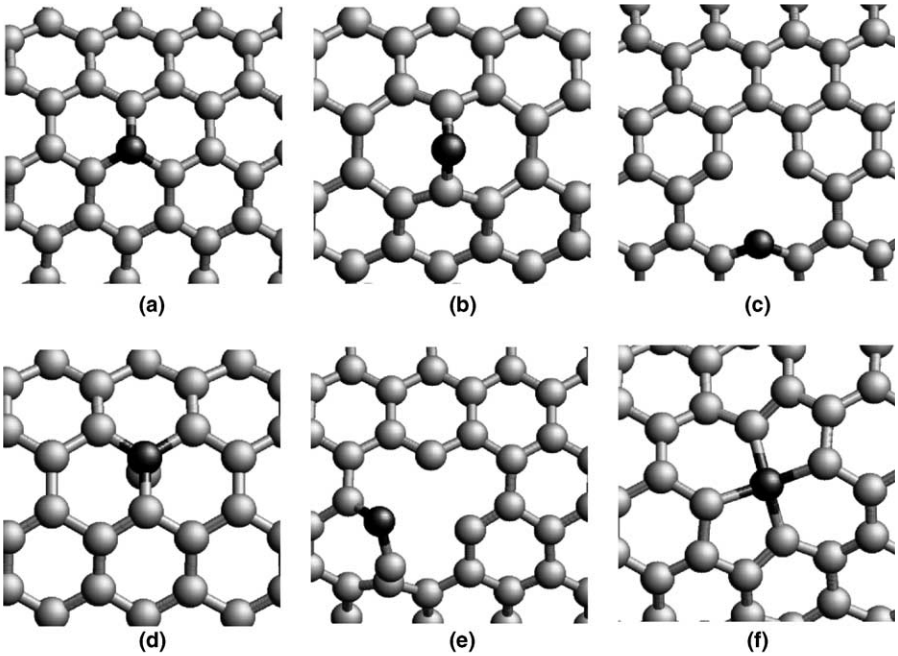

Fig. 1. Most abundant atomic configurations after B/N ion impacts. (a) Perfect sp^2 impurity configuration, (b) *bridge*, (c) *rocket*, (d) sp^2 + C, (e) *rocket* + C and (f) 5–6. The dark spheres represent the dopant atom, the light ones carbon atoms. The defect configurations shown in the second row exist only for B atoms.

1(a)). In our model, it costs 1.62 eV and 2.94 eV to substitute a C atom with B/N, respectively.

We simulated impacts of the ions with different energies onto a 100 Å long (10, 10) SWNT. The impact points in the central part of the SWNT were randomly chosen. The ion beam direction was assumed to be perpendicular to the SWNT axis. To get representative statistics, for each ion energy we ran 200 independent simulations and averaged the results. Periodic boundary conditions were used, and the Berendsen temperature control technique [17] was used at the tube boundaries. The simulation temperature was chosen to be 0 K. The system was quenched during 30 ps, which is the typical time of epithermal energy dissipation in carbon systems [18].

As the experiments will be carried out at finite temperatures, we also studied the annealing of defects. After the completion of the collisional phase we increased the temperature up to 1500 K and simulated the system behavior during 0.1 ns. This computational technique made it possible to account, at least partially, for defect annealing at low temperatures but on macroscopic time scale and thus get rid of spurious metastable configurations [10].

After each run we calculated the coordination number for every dopant atom. To differentiate direct substitution and annealing-mediated substitution, we analyzed defect configurations before and after the annealing.

We found that six defect types are predominant in the simulations with B and three of these with N. These defect configuration are shown in Fig. 1. These defect types make up 70–80% of all final configurations for bonded B before and 70–90% after the annealing. For bonded N these probabilities are 45–85% and 50–80%, respectively.

In addition to the perfect sp^2 position of the dopant and the bridge configuration described above, the most prolific atomic configurations proved to be as follow: In the *rocket* defect type the impact of the dopant atom has kicked a C away from the SWNT network and replaced another C (two carbon atoms are missing cf. sp^2 defect). This name was chosen because a rocket can be thought to be fitted into the empty space beside the dopant. The last three types of defects were found only for B. In the sp^2 + C defect type B has replaced a carbon atom which remains bonded to the dopant. The *rocket* + C defect type is the same as the *rocket* defect but with one additional two-folded C atom between B and the neighbouring C atom. Although this defect has a finite probability to appear, it is likely to be metastable as it was found only before the annealing. The defect typically transformed into a 5–6 defect, Fig. 1(f). We chose this notation in analogy with a similar defect consisting only of pure carbon [10]. Note that the latter defect might be an artefact of the force model used, but it had a relatively low probability to appear.

The number of atoms with different coordination per one impinging ion (coordination number probabilities) are shown in Figs. 2 and 3 for B and N as functions of ion energy. It is evident that the probabilities for three-coordinated dopant atoms have maxima near 50 eV. For boron, the probability can be up to 40%, and almost 50% for nitrogen.

The probability maximum at ~50 eV can be understood in terms of the kinetic energy transfer. In our force model, a C atom must have a kinetic energy of about 25 eV to leave its position in the atomic network. Within the binary collision approximation, this correspond to energies of ions of about 30 eV (for a head-on collision). However, the impact parameter is randomly distributed, so on the average the ion should have a higher energy. Besides this, an additional energy is required due to multi-atom interactions governed by the cut-off range – the ion kinetic energy is transferred to not only the recoil but also its environment. When the ion energy further increases the ions just go through the carbon network. Note that the number of defects in the nanotube network also decreases at higher energies due to lower momentum transfer [11].

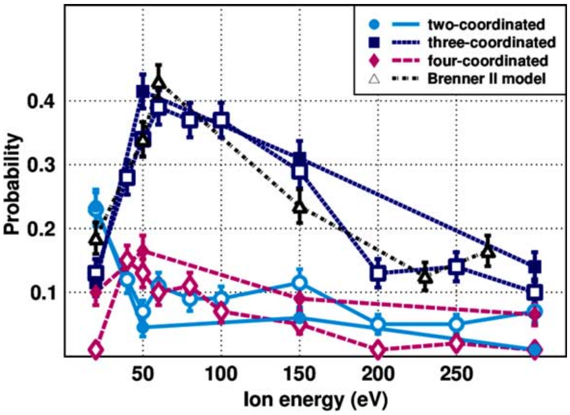

Fig. 2. Probabilities for coordination numbers for B as functions of the initial ion energy. The open/closed symbols stand for the results before/after the annealing. Triangles represent the probability for three-coordinated B calculated with the Brenner II potential model. Errorbars present the estimated standard deviation of the values.

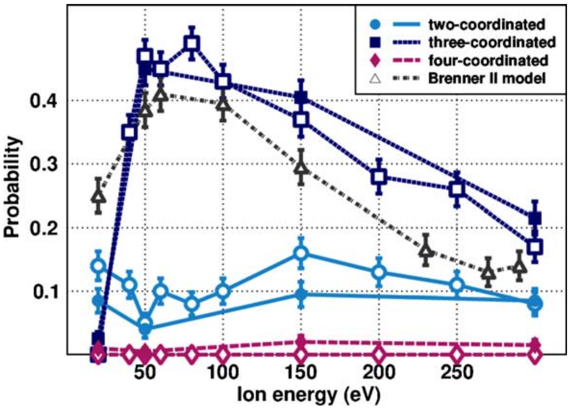

Fig. 3. Probabilities for coordination numbers for N as functions of the initial ion energy. The open/closed symbols stand for the results before/after the annealing. Triangles represent the probability for three-coordinated N calculated with the Brenner II potential model. Errorbars present the estimated standard deviation of the values.

Because dopant atoms can have the same coordination in different atomic configurations, we carried out a more detailed analysis of the final structures and the dopant bonding. The relative probabilities to appear are listed in Table 1 for different defect types. The maximum probabilities for dopant atom to end up in the sp^2 configuration is ~30% for B and ~40% for N. Thus, nearly all three-coordinated impurity atoms are in the sp^2 configuration.

Simulations with the Brenner II potential (assuming that B and N atoms are chemically

Table 1
Defect types and their relative abundance (the probability to appear) before (the first row) and after annealing (the second row)

Type	M_C	Boron			Nitrogen		
		50 eV	150 eV	300 eV	50 eV	150 eV	300 eV
sp^2	1	0.30 0.28	0.23 0.27	0.09 0.12	0.40 0.40	0.16 0.39	0.17 0.11
Bridge	0	0.04 0.05	0.01 0.00	0.01 0.00	0.03 0.00	0.05 0.00	0.01 0.02
Rocket	2	0.00 0.00	0.03 0.00	0.00 0.00	0.00 0.00	0.03 0.03	0.01 0.03
$sp^2 + C$	0	0.15 0.15	0.02 0.05	0.00 0.00	–	–	–
Rocket + C	1	0.00 0.00	0.01 0.00	0.05 0.00	–	–	–
5–6	2	0.01 0.00	0.00 0.00	0.00 0.04	–	–	–

M_C is the number of missing C atoms. The estimated average standard deviation is about 0.05 in values presented in the table.

equivalent to C, but have the correct atomic mass) gave basically the same results (see Figs. 2 and 3). The optimum ion energy proved to be the same, as well as the maximum probability for the substitution. This indicates that the results only weakly depend on chemical interactions, but are rather governed by the collisional phase. The qualitative and even quantitative agreement between the results obtained by the two models validates our findings for the direct substitution probabilities.

We did not systematically study how the optimum energy depends on the SWNT diameter, but our simulations unambiguously show that the substitution is possible for nanotubes with arbitrary diameters. Thus, if indeed the substitution reaction mechanism does not work for nanotubes with diameters less than 8 nm [7], the irradiation-mediated method should improve on that.

One can expect that annealing should further increase the number of sp^2 impurities due to dopant atom migration and interaction with vacancies. However, as migration occurs on the macroscopic time scale, and our annealing simulations likely underestimate the migration effects, we were unable to accurately account for the migration contribution. Studies on the evaluation of the impurity migration mechanisms are underway. This mechanism should be quite important for macroscopic samples as higher ion energies (far from the optimum ones) would be necessary to implant the dopant atoms in the bulk of the sample.

4. Conclusions

Making use of molecular dynamics with analytical potentials we simulated irradiation of single-walled nanotubes with low-energy B and N ions. We found the most abundant defect types which appear under irradiation. We show that up to 40% of the impinging ions can occupy directly the sp^2 positions in the nanotube atomic network. We further estimate the optimum ion energies for the direct substitution, which are around 50 eV. As annealing should further increase the number of sp^2 impurities due to dopant atom migration and interaction with vacancies, our results indicate that the irradiation-mediated doping of nanotubes is a promising way to control the nanotube electronic structure.

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