Confinement effects in irradiation of nanocrystalline diamond

Felipe Valencia a,b, José D. Mella a,b, Rafael I. González a,b, Miguel Kiwi a,b,* Eduardo M. Bringa c,d

a Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago 7800024, Chile
b Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, Avda. Ecuador 3493, Santiago 9170124, Chile
c CONICET, Argentina
d Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Mendoza 5500, Argentina

ARTICLE INFO
Article history:
Received 10 March 2015
Accepted 18 May 2015
Available online 23 May 2015

ABSTRACT
Swift heavy ion irradiation does not generate amorphous tracks in diamond, contrary to what happens in graphite or in diamond-like carbon. Since nanocrystalline diamond is of interest for several technological applications we investigate the reason for this difference, by means of large scale atomistic simulations of ion tracks in nanocrystalline diamond, using a thermal spike model, with up to 2.5 million atoms, and grain sizes in the range 5–10 nm. We conclude that tracking can be achieved under these conditions, when it is absent in single crystal diamond: for 5 nm samples the tracking threshold is below 15 keV/nm. Point defects are observed below this threshold. As the energy loss increases the track region becomes amorphous, and graphitic-like, with predominant sp² hybridization. This higher sensitivity to irradiation can be related to a very large decrease in thermal conductivity of nanocrystalline diamond, due to grain boundary confinement of the heat spike which enhances localized heating of the lattice.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction
The understanding of the response of materials to all sorts of irradiation has been a subject of interest for a long time. The energy transferred to electrons and nuclei is a key element to predict the way solids respond to irradiation. In particular, carbon-related materials offer a large variety of possible technological applications [1,2], from electrochemical storage [3] to field emission devices [4], biosensors [5] and gene delivery [6].

There is a need to develop techniques to modify the properties of diamond-related materials [7,8]. One possible way to do it, in a controlled fashion, is the use of ion irradiation [9,10]. In particular, fast ions used in Swift heavy ion (SHI) bombardment of a solid transfer energy to electronic excitations which in turn couple to the lattice, and lead to permanent modifications of the material along the ion path [11], in addition to surface effects like cratering [12] and sputtering [13].

Depending on the amount of energy deposited, determined by the electronic stopping power S, ion tracks can consist of isolated defects or a roughly cylindrical region of transformed material. For instance, SHI creates amorphous tracks in quartz [14], and significant defects in graphite [15,16], and diamond-like carbon (dlc) [17]. However, SHI bombardment of diamond only leads to some isolated defects,
probably due to nuclear stopping [18]. The largest stopping power that has been measured was in diamond irradiation experiments, with 1 GeV uranium bombardment [19], and amounts to around 48 keV/nm. We notice that surface craters in diamond have been created by highly charged ion bombardment, which also leads to extremely localized electronic excitations [20].

Molecular dynamics (MD) simulations, using a cylindrical thermal spike model, showed that it might be possible to amorphize diamond, but only for extremely high energy depositions (larger than 50 keV/nm) if one assumes an efficiency of 0.2 for the effective stopping power [21]. This efficiency provides the fraction of the experimental stopping power which is transferred to the lattice, and contributes to track formation. Recent simulations using a two-temperature model [22] showed that stopping powers between 3 and 9 keV/nm lead only to some lattice strain, with point defects starting to form at 13 keV/nm. Experiments and simulations for DLC showed that the amorphous sp3 structure transformed into an amorphous sp2 structure with lower density. Therefore, a significant expansion of the material leading to surface hillocks, with a height that increases with electronic stopping power [23]. The inelastic thermal spike model provides a good description of track sizes in DLC [17], assuming an electron–phonon mean free path of 0.9 nm.

Nanostructured materials display interesting behavior under irradiation [10]. In particular, nanocrystalline (NC) materials have been shown to exhibit increased radiation resistance both in the nuclear regime [24,25], and in the electronic regime [26]. However, the case of nano-diamond seems to behave in the opposite way, with enhanced radiation damage due to the NC nature of the samples. While NC metal samples display a thermal conductivity which is only slightly smaller than their coarse-grained counterparts, NC diamond has a thermal conductivity which could become 10–100 times smaller in the NC as compared with the single crystal case. This has been shown both by experiments [27–29], and simulations [30]. The change in thermal conductivity can be interpreted as a result of Kapitza resistance from the grain boundaries (GBs), or simply as a decrease of the phonon mean free path due to confinement in the nanograins, with GBs acting as scattering walls.

2. Method

Our simulations of the above described phenomena were performed using the modified reactive bond order (REBO) potential [31] within the LAMMPS code [32]. Nanodiamond targets were created for 5 nm (50a0 × 50a0 × 15a0), 7 nm (70a0 × 70a0 × 21a0), and 10 nm (100a0 × 100a0 × 30 a0) grain size, where a0 = 3.57 Å is the diamond lattice parameter. MD simulations of NC diamond samples have been carried out for grain sizes smaller than 5 nm to study their mechanical properties, using Voronoi tessellation as done by Bringa et al. [33]. Nanodiamond aggregates with 4–5 nm grain size can be achieved by detonation [34]. Given that nanocrystals are typically far from equilibrium we carry out an extensive relaxation of the samples. Initially, grain boundary atoms which are too close to each other are removed, resulting in a density with more than 99.8% of the single crystal density. Next annealing at 1800 K is carried out during 10 ps, together with a zero pressure barostat, before taking the samples back to 10 K. This low temperature simplifies defect analysis, and the results were similar to some selected 300 K simulations. The SHI track is introduced using a thermal spike model [35], with the same parameters which were successful in reproducing DLC results [23]. There are several models which include electron–phonon coupling in metals [36], and insulators [37], but this basic model offers good agreement with experiments for a number of materials, having been used for silica [38] and forsterite [39], and with a slightly modified model [40] it was also used for MgO.

The initial track is a cylindrical region along the z axis, with a 2 nm radius. All atoms inside the region are given a temperature consistent with the desired effective stopping power, with a heating time of 100 fs. An adaptive time step is used during the simulation to ensure energy conservation after the spike heating, with a maximum step of 1 fs. The simulation box is surrounded, in the xy plane, by a thin Langevin thermostat kept at the initial temperature. Spike evolution is followed during 50 ps, which is enough to guarantee cooling of the central spike with the help of the thermal bath in the outer boundary. Simulations shown here are for a spike located within a [001] oriented grain. Locating the spike near GB junctions increases disorder.

The track temperature is directly related to the effective stopping power. We use temperatures of 5 000 K, 10 000 K, 12 500 K, 15 000 K, 17 500 K, and 22 500 K, which correspond to effective stopping power $S_e$ of ~1.7, 3.4, 4.2, 5.0, 5.9, and 7.6 keV/nm, respectively. In order to relate this to the experimental $S_e$ we can assume an efficiency of 0.2, which provides excellent agreement between simulations and DLC experiments, to obtain $S_e$ values in the range 8.5–38 keV/nm, which can be achieved with single ion bombardment in current experimental facilities.

3. Results

The evolution of a given SHI track in nanodiamonds is represented in Fig. 1, for $S_e = 29.5$ keV/nm. The track is always confined within the original grain. In single crystal diamond a shock wave is formed and propagates outwards [21], but here the GBs dissipate an important fraction of the outgoing energy and defuse this shock wave. After 20 ps the latent track presents a well defined defect profile, which will not evolve further until the end of the simulation. There could always be some re-structuring of point defects for very long times, but to study that would require other simulation techniques.

Fig. 2 shows the final frame of our simulations, for an initial $d = 7$ nm grain size, and for different track temperatures. Lowest temperatures lead only to point defects and some strain in the diamond lattice, as already observed in single crystal diamond [21,22]. However, in the 25–30 keV/nm range an amorphous track is formed. This can be contrasted to the experimental single crystal diamond case, which does not show tracking even close to 50 keV/nm. We note that a complex track structure emerges, with an amorphous core
surrounded by point defects. This structure with an inner track and a track halo has been observed in several experiments, for instance in amorphous silica tracks [37]. The exact location of the amorphization threshold might shift using other potentials like EDIP [41], but the general features are not expected to change.

The influence of grain size in the possible structural modifications of the sample are shown in Fig. 3, for an initial track of stopping power $S_e = 17$ keV/nm. In the 10 nm sample there are only a few point defects, while the 5 nm sample exhibits an amorphous track. The 7 nm sample displays an intermediate situation, with a small amorphous inner track and a halo of point defects.

In order to illustrate the role played by GBs on thermal conduction and confinement we show in Fig. 4a the radial temperature profiles at different times, for $d = 7$ nm and $S_e = 38$ keV/nm. Notice that the spike lasts for about 20 ps, in contrast to diamond simulations [21] where it lasts for just a few picoseconds. In addition, it is relevant to emphasize that the outer box boundary is not affected by the central heat pulse, indicating that the size of our samples is large enough to follow the spike. In the center of the track the differences are of the order of 1000 K. In Fig. 4b we observe that for radii larger than 4 nm the temperature profiles overlap, which constitutes an indication that heat propagation is faster in the large (10 nm) samples. This fact implies that grain size plays a key role in the phonon transport across the material.

SHI can create amorphous tracks with a lower density than the surrounding system (Fig. 5a), as it has been seen for tracks in amorphous silica [22,37]. Density profiles in our irradiated samples give track sizes in the 1–4 nm range, similar to the size range for tracks in DLC for equivalent stopping powers [23]. In the track core densities are consistent with graphitization and measurements for sp²-bonded carbon [42,43], and other experimental papers reporting lower density for sp² carbon. Indeed, average atomic coordination of 3
and 4 can be associated with sp² and sp³ bonding, respectively, and the hybridization profiles in Fig. 5b show an sp² rich core. This sp² fraction increase is similar to what has been reported for tracks in DLC [23], and for cascade damage in tetrahedral amorphous carbon [44]. The presence of an amorphous track would affect the electrical conductivity of the sample, as in the case of amorphous pockets created by collision cascades in diamond [7].

Fig. 2 – Track formation for different initial track temperatures, for 7 nm grain size, and $t = 20$ ps. Atom colors represent the potential energy per atom, with grain boundaries displaying larger energy in comparison with atoms inside the grains. (A colour version of this figure can be viewed online.)

Fig. 3 – Effect of the thermal spike for different grain sizes, at the end of the simulation, for stopping power of $S_e = 17$ keV/nm. (A colour version of this figure can be viewed online.)
4. Summary and conclusions

Grain boundaries are typically assumed to reduce radiation effects [25,30], even in the electronic regime [26]. However, here we have shown an example where GBs enhance radiation effects in nanocrystalline C. Moreover, similar effects might be expected in other insulators with nanocrystalline structure. In fact, single crystal diamond does not amorphize under SHI radiation until a stopping power $S_0 \approx 50$ keV/nm is reached, which is a difficult limit to attain using single SHI. However, we find that nanocrystalline diamond, with a size of $\sim 5$ nm, has an amorphization threshold of about 15 keV/nm, due to confinement effects of the track inside a nanograin. Similar to what has been observed in dlc [23], the material goes from $sp^3$ to $sp^2$ bonding, with a significant density decrease due to this coordination change. The phase change might display some level of reversibility, according to recent experiments on nanodiamond to nano-onions, to nanodiamond transformations [45], allowing the tuning of the degree of transformation of the materials by means of localized heating.

Up to this date we are not aware of any experiments on radiation damage on NC diamond. Transmission electron microscopy (TEM) studies would clearly reveal structural changes [46]. Given the change in hybridization, Raman spectroscopy [47,48] would provide an indirect measurement of track formation, provided that the ion fluence is large enough to result in a large track volume fraction. GB effects, in addition to nanograin effects, conspire to reduce the equilibrium heat conduction by more than one order of magnitude, compared to samples with micron-sized grains [30]. We notice that amorphous C conductivity decreases by 3 to 4 orders of magnitude with respect to diamond, and irradiated samples containing ion tracks would be much less conducting. Therefore, thermal conductivity measurements could also provide evidence of track formation.

Here we probed bulk effects, but surfaces might lead to additional features. For instance, carbon onions with high conductivity and surface area might be generated, as has been shown for nanodiamond clusters [49]. Conversion of $sp^3$ to $sp^2$ bonding might also lead to surface hillocks, as in dlc irradiation, providing nanostructured templates [23]. Future simulations will treat surface effects, including the possible role of H and other elements on the tracking threshold. Also, future studies could involve the use of reactive potentials, like ReaxFF [50,51] to include the possible effect of nitrogen vacancies during irradiation, given that they help tailoring nanocrystalline diamond for photonics and labeling applications [52,53].

Acknowledgments

EMB thanks useful comments by D. Schwen, P. Erhart, and K. Nordlund, and support from PICT-0092 and a SeCTyP-UNCylo
was supported by CONICYT Doctoral Fellowship grant #21140948.

REFERENCES


