

Simulation and visualization of ion-implantation in diamond

Joan Adler, Amihai Silverman, Niv Ierushalmi, Anastassia Sorkin and Rafi Kalish

Technion - IIT, Haifa, Israel, 32000

E-mail: phr76ja@tx.technion.ac.il

Abstract.

We have explored aspects of ion implantation in diamonds with molecular dynamics and tightbinding atomistic simulations. Relevant experiments and their potential applications as well as our computer models and computational approaches are described. Our simulations have been designed to answer questions proposed by experimental researchers concerning optimal laboratory schedules for the preparation of samples with potential applications to diamond membranes and NV centers for quantum computers. Simulation and visualization of results enable us to peek inside samples where experimental techniques cannot tread. In order to provide the requisite Brazilian component a new connection between these models and bootstrap percolation is made.

1. Introduction

The Computational Physics group at the Technion carries out atomistic simulations in carbon systems, with an emphasis on geometric structure and vibrations, especially near defects and interfaces. Our simulations are made in close contact with several Technion experimental groups. Visualization is a major component of our studies to observe the system development, and we are often concerned with the structure deep inside the sample, which may not be accessible to non-destructive experiment.

After a brief introduction to the physics and chemistry of carbon allotropes, we will describe previous experiments and introduce some theoretical models that are relevant for their interpretation. Discussions of modelling with classical or quantum approximations or analyzing only initial and final states versus modelling the dynamics of the implantation process will be made. Early studies of damage in diamond will be reviewed. We will then recapitulate two recent calculations of processes involved in understanding experiments on samples prepared for applications relating to diamond membranes and NV (Nitrogen-Vacancy) centers. These are both designed to provide guidance to the experimental researchers about scheduling and temperature selections to achieve optimal sample quality. We will show how the use of animation aids in comprehension. The situations described in this paper are connected with R. Kalish's experiments, but the computational group also collaborates with A. Hoffmann, M. Sheintuch and Y. Yaish on other carbon projects.



2. Background and previous studies

2.1. Carbon Allotropes

Carbon has several allotropes. One is diamond, a transparent insulator and another, graphite, an opaque conductor. The vastly different properties stem from their different atomic coordination and band structures. Transformation between the two is highly relevant for their applications - damaged industrial diamond loses its insulating properties and can become a conductor while damaged diamond windows, e.g. on spacecraft, can lose transparency. Understanding of the damage process leads to its avoidance or application, as appropriate.

2.2. Implantation experiments

Ion implantation is a tool to explore the structure of materials, a means to create samples with specific structures in certain regions and a tool to introduce dopants. A classic example of the former is the Rutherford experiment that deduced the size of the nucleus by shooting α particles at gold foil and determining their angle of deflection. A classic example of the latter is the series of experiments in R. Kalish's laboratory [1] where diamond was transformed into a conductor by ion implantation.

2.3. Percolation theory

The percolation transition occurs when a two-component sample, one of whose components were previously disconnected has a changeover to a connected one. For example, in a mixture of randomly positioned glass and metal balls, when the concentration of metal balls increase from zero to 100% at some specific concentration of metal there will be a conducting path that spans the sample. In 1980 Kalish/Shapiro *et al.* [2] observed that regions of damaged diamond under implantation connect and insulating diamond becomes conducting carbon. A mean field percolation model was made and they conjectured the damaged regions are locally graphitic.

2.4. Static versus dynamic, classical versus quantum

Extensive calculations of energetics for samples with defects and interstitials are often made with the very best potentials, Density Functional Theory (DFT) approximations or even better wavefunction forms. Energy barriers are also commonly calculated. However full paths for sample transformations are very important in order to determine which experimental conditions, such as temperature or scheduling of annealing are optimal and these require true (molecular) dynamics which sometimes cannot be carried out with better than good classical or tightbinding potentials due to time/memory constraints.

2.5. Damage paths

Let us now consider the simplest case of irradiation. Atoms shot (Figure 1) into a diamond sample with sufficient energy make a damage cascade, and we asked what is the final step (Figure 2) of this cascade? In Figure 1 a cartoon of this situation is presented with the final state denoted by ?????? As shown in Figure 2 it was found [3] to be a split interstitial defect. This is a defect where two interstitial atoms share one lattice site. It was long known to be the most stable defect from calculations of the static energy, but the path to its creation was unclear previously. The two atoms at the centre of the defect are threefold coordinated (Figures 3 and 4) and the other atoms relax around it. An animation is shown in the supplementary material.

The next question is what happens when many atoms are fired towards the same region? As conjectured by Kalish/Shapiro, we found [4] that a locally graphitic region is created after annealing, see Figures 6 and 7. The image in Figure 4 was drawn with AViz, the other images from an older OpenGL code. In Figures 5, 6 and 7 we show only the 3-fold and 4-fold atoms, respectively (of the same sample) to enhance clarity.

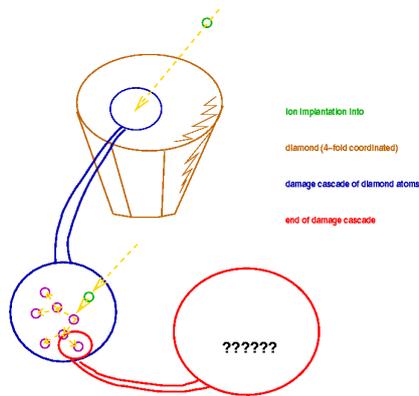


Figure 1. Before Saada, Adler and Kalish calculations.

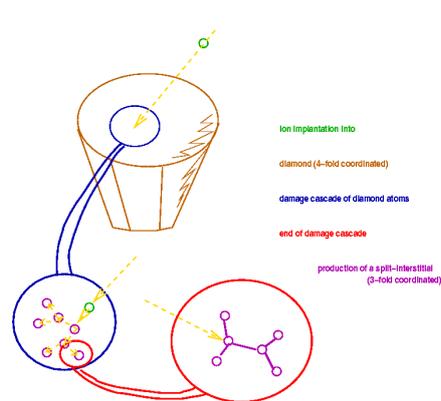


Figure 2. After our calculations.

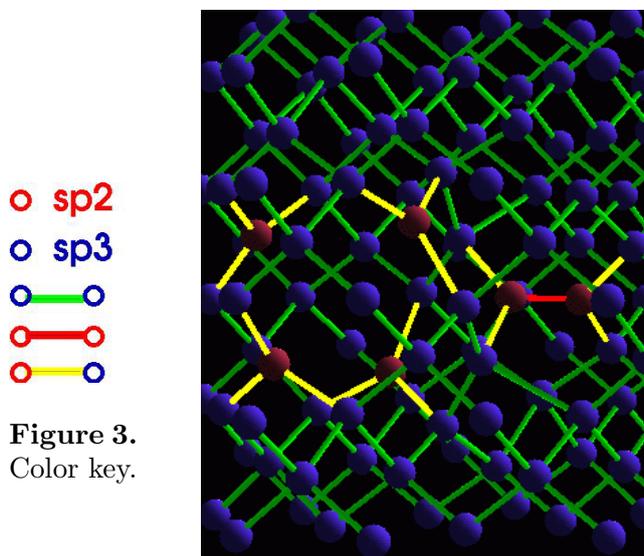


Figure 3.
Color key.

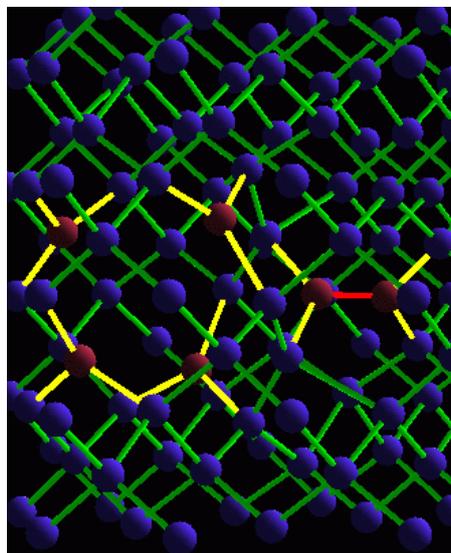


Figure 4. Formation of split interstitial.

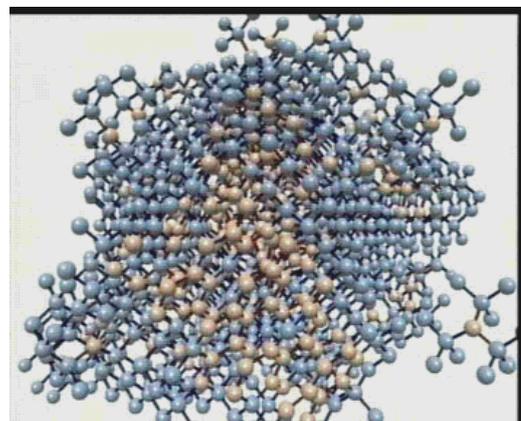


Figure 5. After irradiation with multiple atoms, and annealing, these atoms that have changed position. Red atoms 3-fold coordinated, blue atoms 4-fold.

We conclude this recapitulation with cartoons of before (Figure 8) and after (Figure 9) the Shapiro/Kalish calculations, envisioning multiple graphitic regions. Is this scenario realistic? Do the graphitic regions percolate? We expect that with sufficient irradiation, the regions should join and percolate. Explicit direct simulation of this has been on our “todo list” for nearly 30 years, but has been limited by computer resources so was always sidetracked by other projects. Hopefully it will be explored shortly now that we have improved parallel computing resources at the Technion.

2.6. Transformations

Irradiation causes local heating since there is an increase in kinetic energy. There are many ways to transform diamond to graphite and graphite to diamond, especially in the presence of hydrogen. For example - we can grow nanodiamonds (Figure 10) and nanographite (Figure 11). These images are from the thesis research of A. Sorokin and are described in [5]. The calculations were tightbinding MD with the OXON code. The transformations were often made by heating

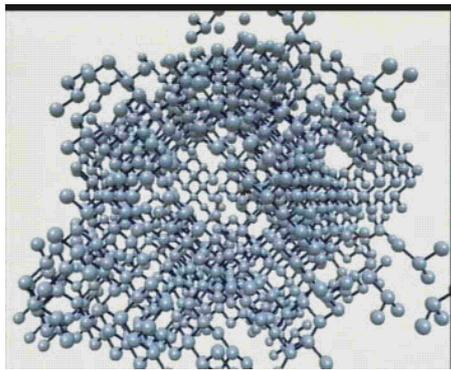


Figure 6. 4-fold coordinated atoms from Figure 5.

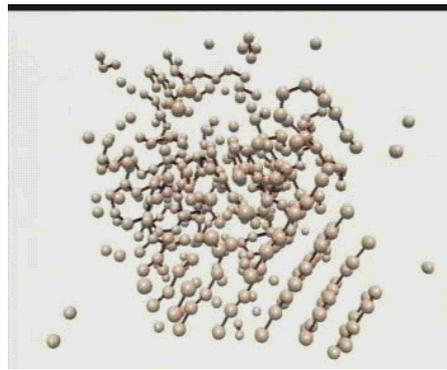


Figure 7. 3-fold coordinated atoms from Figure 5.

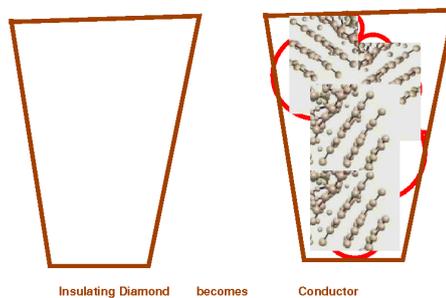
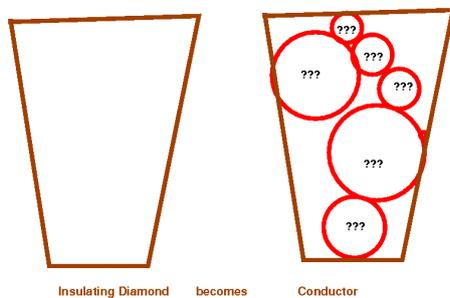


Figure 8. Before Shapiro/Kalish.

Figure 9. After Shapiro/Kalish.

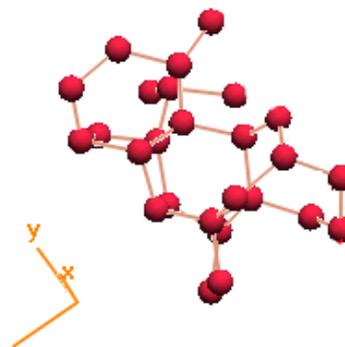
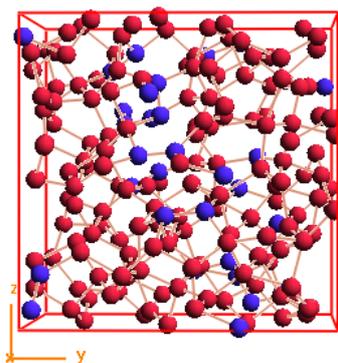


Figure 10. Initial sample before nanodiamond formation from [5] (left) and nanodiamond (right).

part of the samples while other parts were frozen, rather than by actual irradiation. The results depended on many factors and while we may claim that we were able to predict nanographite prior to its experimental identification, in fact we had seen this also much earlier in Saada et al[4]. Nanodiamonds such as ours were not identified earlier, possibly due either to insufficient equilibration, but more likely due to our improved methods for identifying the nanodiamond

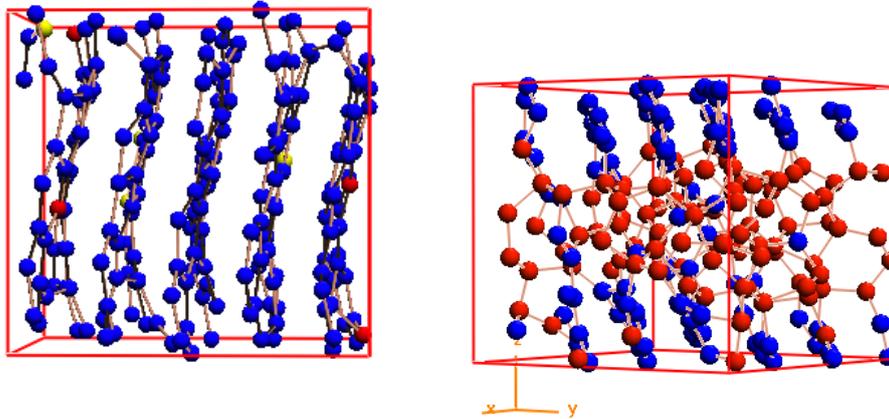


Figure 11. Nanographite formation from [5]. Intermediate cooling rate (right) and slow cooling rate (left). The pressure leads to flexed layers.

structures with our visualization tools. An animation of nanographite formation is shown in the supplementary material.

3. Diamond membrane creation

An overview of the preceding section suggests that three relevant parameters for conversion between diamond and graphite are:

- Implantation energy
- Implantation temperature
- Post implantation annealing

Let us now consider the application of these to the fabrication of diamond membranes, wherein photonic crystals and other sub micro-sized optical devices can be realized. Many spintronic devices are based on specific optically active atomic structures in diamond, such as the nitrogen-vacancy center, and rely on the membranes performance, [6]. One promising approach for realizing such membranes is by creating a heavily damaged layer (rich in broken bonds) in diamond by ion implantation. Following annealing, this layer converts to graphite, which can be chemically removed, leaving a free-standing diamond membrane. Unfortunately, the optical properties of the exposed diamond surface (the diamond-vacuum interface) of such membranes currently are insufficient for high-quality photonic devices and so their performance is as yet, unsatisfactory. Thus, it appears that application of the current ion-implantation/graphitization methods do not yield the optical qualities that would enable the utilization of such lift-off methods to obtain high-quality waveguides and other nanosized optical devices. Understanding the properties of this interfacial layer and finding ways to minimize its detrimental effects on the reflectivity of photons impinging from within the membrane are of major importance. Some laboratory studies along these lines have recently been performed, but further guidance from simulation is desirable.

3.1. Surface smoothness

Since we have already explored transformation of diamond to graphite, it seemed natural to apply our simulation approach to deducing which combination of the three factors of implantation energy and temperature and of annealing temperature would provide the smoothest membrane. We deduced in a recent study [7] where different implantation and annealing conditions were simulated, that cold implantation, followed by high-temperature annealing leads to the creation of the sharpest diamond-etchable graphite interface, which should exhibit optimal optical properties among diamond membranes created by the implantation/graphitization method.

In this study we used a Brenner potential and Langevin thermostat and had 5120 atoms in each sample. We inserted 20 carbon atoms sequentially inserted at a random place between layers 11 and 12 and shot at an angle of 7 degrees with a Kinetic Energy of 350eV see Figure 12. We found damage that extended for about 20 (out of 40) layers. 10 sets of random locations were each done according to 3 schedules with a range of temperatures for schedules 2 and 3, as shown in Figure 13 We show the variation over samples with identical conditions, (in this case we plot the fraction of sp^2 bonds for each layer number, annealed at 2000 with schedule 2) except for the random seed in Figure 14. We observe that damage profile details vary for each set of initial random locations, but the overall picture is similar.

A sample with schedule 2, annealed at 2000 degrees is shown in Figure 16, where we color bonds that connect 4-fold coordinated sp^3 atoms in blue and 3-fold coordinated sp^2 ones in yellow. We also analyzed the slope of the sp^2 fraction in each layer and the results are shown in Figure 15. The sharpest is for the case shown in Figure 16. Another visual technique was to omit the 3-fold coordinated atoms completely. All these were based on the sample states at the end of the simulation, prior to the actual etching. A movie of therotation of the middle sample from Figure 17 is shown in the supplementary material.

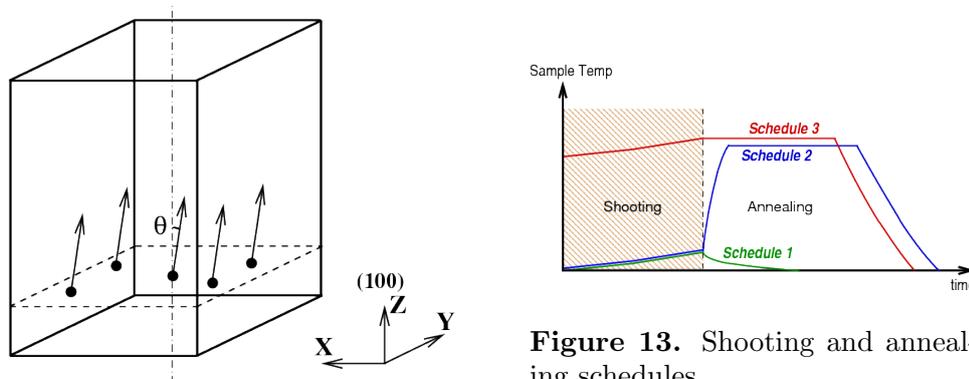


Figure 12. Model system.

Figure 13. Shooting and annealing schedules.

3.2. Bootstrap percolation model for the etching process

In the etching process, atoms are successively removed as sp^3 diamond bonds are successively converted to clusters of weak etchable sp^2 graphitic bonds. This is reminiscent of a type of correlated percolation, known as bootstrap percolation (BP). In BP all sites with insufficient neighbours are iteratively removed [8], with say $m = 3$ BP having dangling bonds and isolated sites removed; i.e. only sites with 3 neighbours remain. BP leads to smoothing (lower fractal dimension) of samples and although proposed in a magnetic context there has been dearth of condensed matter applications, with possible exceptions being a series of studies of orientational order in molecular hydrogen[9]. Simulating the etching of the graphite from the membrane is a potential application! This application is a little different from the standard lattice based BP

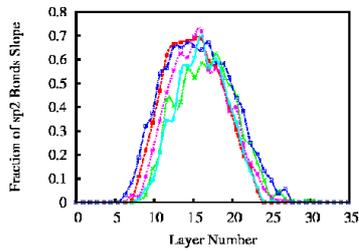


Figure 14. Sample variation.

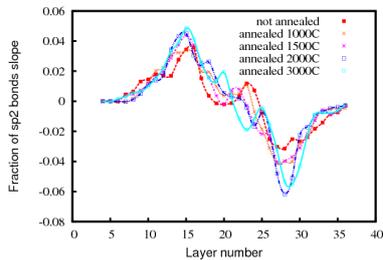


Figure 15. Slope of interface for different schedules.

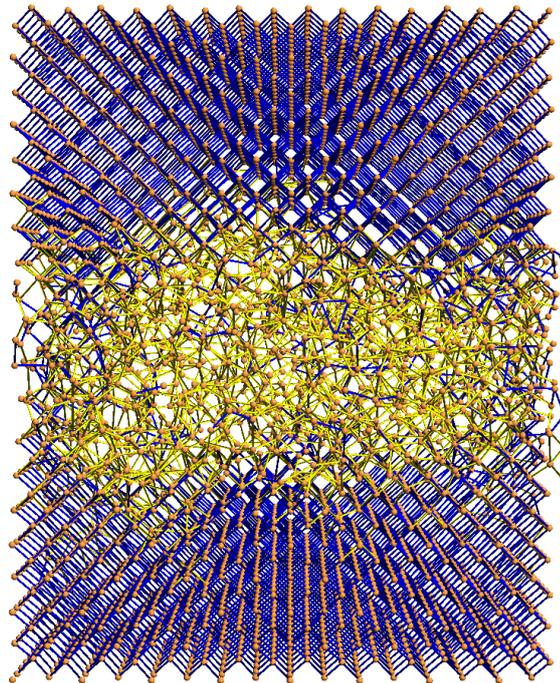


Figure 16. Sample after irradiation, showing 3-fold coordinated atoms in yellow.

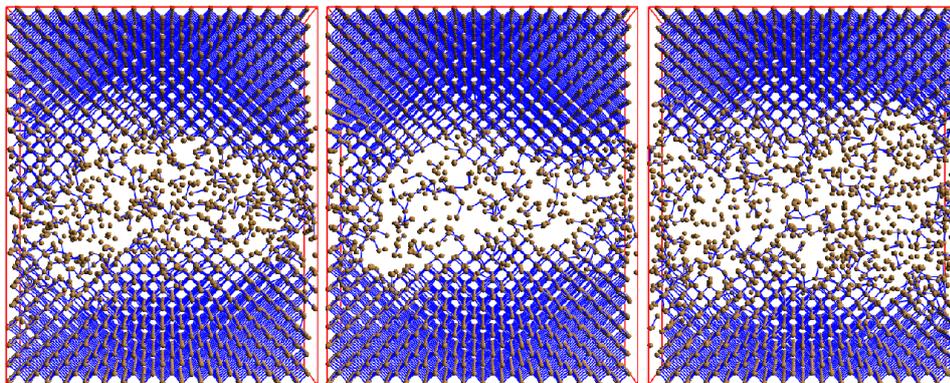


Figure 17. Three samples with schedules 1,2 and 3 (l. to r.) with bonds between 3-fold coordinated atoms removed.

toy models for two reasons. Firstly, the system is off-lattice and therefore a bond length has to be selected. Secondly, the bonding configuration of the site's neighbours has to be considered.

We compared the results of schedules 2 and 3 of [7] (called 1 and 2 on the website [10]). All atoms with less than 2 diamond neighbours within a distance of 1.55 angstrom were removed. The initial frame of one case is shown in Figure 18, the final cleaned upper surface in Figure 19 and the MATLAB construction to measure the fractal surface in Figure 20. A movie of the bootstrapping process is shown in the supplementary material. The MATLAB boxcounting routine gave results for the fractal dimension for schedule 2 of 2.2614 ± 0.0034 , and for schedule 3 of 2.2695 ± 0.0038 . This implies cold irradiation gives a smoother surface in agreement with [7]. More details are on the website [10].

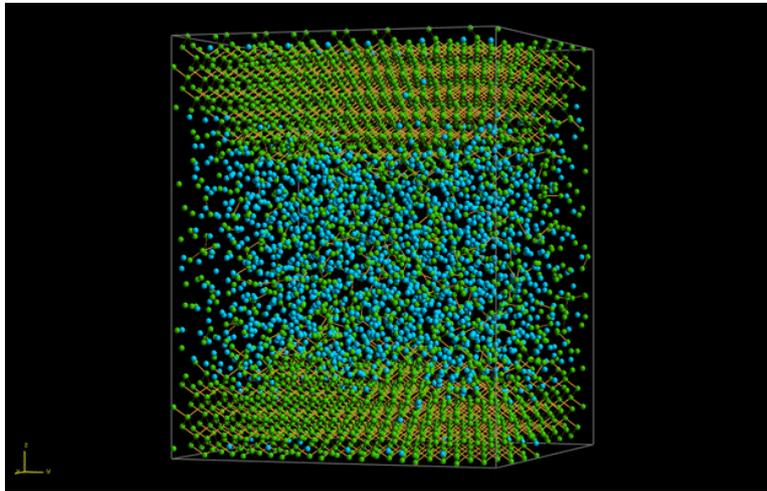


Figure 18. Sample after irradiation.

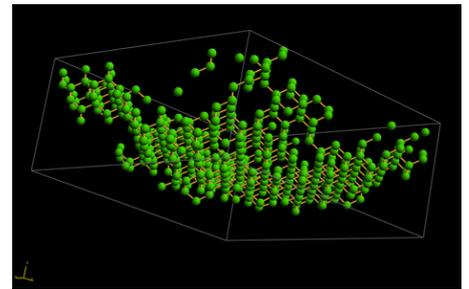


Figure 19. Final etched upper surface

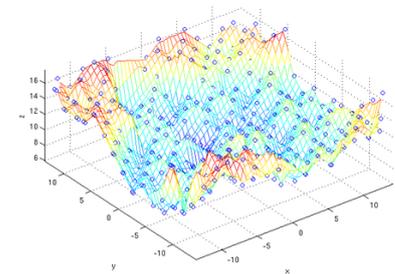


Figure 20. sample used for boxcounting to determine fractal dimension.

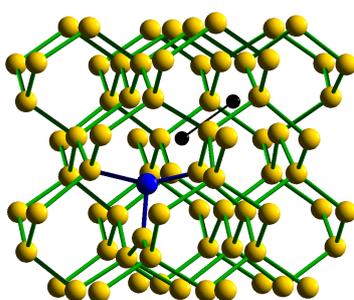


Figure 21. Nitrogen interstitial in blue (large ball) and two vacancies in black (small balls). Carbon atoms in yellow.

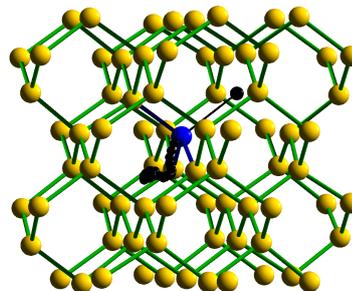


Figure 22. NV center after equilibration, successive locations of the Nitrogen atom are superimposed and can be viewed in a movie in the supplementary material.

4. NV center formation

Another process of interest for quantum computing applications is the creation of NV (Nitrogen-Vacancy) centers that are photoluminescent. In Rafi Kalish's laboratory research into optimal implantation techniques is underway. We have made a simulational study (both dynamics and energetics) with the dftb code to determine which schedules will optimize the realization of

NV (nitrogen-vacancy) centers in diamond. We found that when the nitrogen resides on an interstitial site, it fails to attract a vacancy, hence no NV center can be formed. However, if it occupies a split interstitial site and two vacancies reside in the second or third neighbor sites, an NV center will form following annealing at temperatures as low as 300°C and 650°C, respectively. This provides guidelines to experimentalists on how to increase the efficiency of NV formation in diamond. We were able to follow the dynamics of the creation process (as well as determine that other paths failed to create the center). In Figure 21 we show the initial sample and in Figure 22 the final state as well as the superimposed route. A movie is provided in the supplementary material, and on the website [11].

5. Conclusions

The special aspect of our approach is the close contact with the experimental laboratory. Experiments provide interesting problems to compute and simulations provide guidance to experimentalists. Our emphasis is on visualizing dynamic processes - simulation treads where microscopes cannot go.

Acknowledgments

Thanks to Alon Hoffman and the former students on carbon/diamond projects - David Saada and Yoel Koenka for collaboration over the years. Aernout van Enter is acknowledged for his updates on the progress of BP studies. The BP study of the membrane formation was carried out by Niv Ierushalmi as his project in the Computational Physics class; other projects from this class are described in [12].

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