Modeling Defects, Impurities, and Dopants in Nanodiamond

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Outline

• Defects in Bulk Diamond
• Defects in Nanodiamond

• Mapping Substitutional Nitrogen
  – Potential Energy Surface (PES)
  – Questions and Answers
    • Dependence on Surface Chemistry...
    • Dependence on Size...
    • Dependence on Impurity/Dopant Species

• Functional Defects in Nanodiamond
  – Predicting the Probability of Observation

• Concluding Remarks
Defects and impurities in diamond are common. 
- lattice irregularities or 
- extrinsic substitutional impurities (centered on a lattice site) or interstitial impurities (centered on a “bond” equidistant from lattice sites)

The defects can be detected using 
- Electron paramagnetic resonance (EPR), 
- Photoluminescence (PL) 
- Cathodoluminescence (CL), and 
- Absorption spectrum from the infrared (IR), ultraviolet (UV) and visible (VIS) parts of the spectrum.

They can also be understood using computer modeling
Dopants and Impurities

- Diamond may contain a wide variety of different types of atomic impurities.

- Many are introduced deliberately during the diamond growth, and the most commonly introduced elements are chosen to provide donor or acceptor states in the band gap
  - Nitrogen (to induce n-type conductivity)
  - Boron (to include p-type conductivity)

- Almost any element can be introduced into pre-grown diamond by ion implantation.

- Oxygen has not yet been spectroscopically confirmed as an impurity in diamond.
Why are Nanodiamonds Different?

• In bulk diamond, the lattice is isotropic, and defects experience equivalent forces along (equivalent) lattice directions

• Nanodiamonds exhibit a number of anisotropies that are not present in bulk-diamond
  – Geometric features with reduced coordination, such as the core-shell interface, surfaces, edges and corners.
  – Overall surface stress-induced contraction of the lattice constant (capillary effect).
  – Anisotropic strain resulting from facet dependent surface stresses (the strain along the <001> direction may not be the same as the <111> direction).

• The energy of a defect, dopant or impurity in nanodiamond depends upon the location within the particle, as well as the size, shape and structure of the particle as a whole.
Substitutional Nitrogen

- Diamond nanoparticles have the composition $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$, and the Nitrogen content is usually approximately 2% (confirmed experimentally).

- The question for computer modeling is not how much N is there, but how the N is distributed, and whether this distribution is likely to change if perturbed (cannot be addressed experimentally):
  - Are the N atoms are likely to be in the core or near the surfaces of diamond nanoparticles?
  - Are the N atoms will be positioned preferentially at specific locations, or will be randomly distributed?
  - Are the positions of the N atoms stable (with respect to diffusion)?

- To ensure the reliability of any nanodiamond-based nanotechnology the thermodynamic stability of impurities, dopants and functional defects must be known.
Mapping the Distribution of Impurities

- To map the possible locations for nitrogen substitution the Potential Energy Surface (PES) may be calculated.
- This may be done using a sample of “representative sites”, such as:
  - Substitution sites along 5 different crystallographic directions in a 2.2 nm (837 atom) cuboctahedral bucky-diamond
  - Substitution sites along 5 different crystallographic directions in a 2.3 nm (881 atom) cuboid nanodiamond
  - These provide a total of 9 crystallographic directions and unique extrema.

- In the following example, calculations are made with Density Functional Tight Binding
  - Using the DYLAX code and Slater Koster files supplied by the group of Thomas Frauenheim at the University of Bremen
  - Self consistent to the level of Mulliken charges.

Substitution “Paths” in Bucky-diamond

Path A1: Center to (100) surface

Path B: Center to (111) surface

Path C: Center to (100)+(111) edge

Path D: Center to (111)+(111) edge

Path E: Center to corner

Bucky-diamond PES

- Calculate the total energy at every substitution site along each path independently (>50 calculations)

Substitution “Paths” in Nanodiamond

Path A2: Center to (100) surface
Path F: Center to (110) surface
Path G: Center to (100)+(110) edge
Path H: Center to (110)+(110) edge
Path I: Center to corner

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Nanodiamond PES

• Calculate the total energy at every substitution site along each path independently (>50 calculations)

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Preferred Locations

• Truncated Octahedral Bucky-diamond
  – The bucky-diamond “core-shell” structure is apparent, and the inner surface of the “core” provides a local minima in the PES
  – Overall, the preferred location for N substitution is as part of a (100)2x1 dimer (either in the (100) surface or (100)/(111) edge)

• Cuboid Nanodiamond
  – Overall the preferred location for N substitution is on edges or corners

• In both cases, the extrema are energetically preferred over the core regions, i.e.: at equilibrium the N atoms are not dopants – they are more like adsorbates

• In both particles, the binding energy of the N atom in the bulk is still affected by the presence of the surfaces (or the bucky-diamond inner surface) – the impurity atom “sees” the surface up to 7 atomic layers away creating energy fluctuations...
Origin of the Energy Fluctuations

• The overall decrease in energy is due to the N atom lowering it’s potential energy by redistributing it’s residual charge at the extrema

• The donor electron from the nitrogen atom “sees” the nanoparticle extrema (or the inner surfaces of the bucky-diamond) when the extrema lies within the Bohr radius of the donor electron

• As the substitution sites are located closer and closer to the extrema, the donor electron “sees” alternative extrema and other geometric features in addition to the terminus of it’s own path

• These alternative extrema also offer opportunities for redistribution of excess charge, or they may contribute to the confinement of the charge

• The potential energy fluctuates (increases or decreases) depending on whether a redistribution of the residual charge of these C atoms at the extrema (with reduced coordination) is electronically accessible

Estimates of the Excitonic Radius

• The radial range of these energy fluctuations is indicative of the Bohr radius of the exciton in diamond nanoparticles
  – From these results we can estimate the Bohr radius of the electron to be approx. 0.6 nm

• This estimate of the Bohr radii based on the results presented here is larger than theoretical bulk-diamond results, based on the effective mass approximation (EMA)
  – For bulk diamond the Bohr radius of the electron in the longitudinal and transverse directions are 0.43 nm and 0.12 nm, respectively

• However, theoretical interpretations based on the EMA for electrons and holes in bulk electronic properties break down when applied to small nanoparticles – due to quantum confinement

• This estimate of 0.6 nm indicates a degree of quantum confinement that is consistent with experimental results reported for diamond nanoparticles of this size – see Raty et al., PRL (2003)
Question 1...

- Does the PES depend on the choice of surface chemistry?
- Would the PES be significantly different if the surfaces were passivated, instead of clean?
- ...Let’s try hydrogen passivated nanoparticles and find out...
Passivation – Hydrogenated Nanoparticles

Bucky-diamond

Nanodiamond

Clean vs. Hydrogenated – (100)2x1 Surfaces

Recall: These paths run from the center to a (100) surface dimer, where there is no buckification.

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Clean vs. Hydrogenated – Corners

Note: These are the most volatile sites, and the crystallographic direction is different in each particle.

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Question 2...

• Does the PES depend on the size of the nanoparticles?
• Would the PES be significantly different if the particle were smaller or larger?

• What would the PES look like if the particles were the same size as the “core region”?
  – Is there still an appreciable bulk-like “core region” if the nanoparticles are only 1.3 nm?

• ...Let’s try ~1.3 nm particles and find out...
Size – ~1.3 nm Nanoparticles

Path A1  Path B  Path C  Path D  Path E

Path A2  Path F  Path G  Path H  Path I
Is there still a bulk-like “core region”?

Note: Although scaled in the same way as the 2.2 nm particles, here $r_{1.3nm} \approx r_{2.2nm}$, but $R_{1.3nm} \neq R_{2.2nm}$.

Bucky-diamond

Nanodiamond

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2.2 nm vs. 1.3 nm – (100)2x1 Surfaces

Note: Following adjustment the results are shifted to account for \( R_{1.3\text{nm}} \neq R_{2.2\text{nm}} \), with the extrema aligned.

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~2.2 nm vs. ~1.3 nm – Corners

**Bucky-Diamond**

**Nanodiamond**

Note: Following adjustment the results are shifted to account for $R_{1.3\text{nm}} \neq R_{2.2\text{nm}}$, with the extrema aligned.

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Question 3...

• Does the PES depend on the choice of dopant or impurity species?

• Would the PES be significantly different if the dopant were changed?

• ...Let’s try Boron and find out...
Defect Energies in Bulk-Diamond

• We expect the overall defect energy to be different for B than N.

• For example, a plot of the binding energies of X-V complexes clearly illustrates the chemical trends for each atomic species (X).
  – But how do the differences change with respect to location?

The solid and open squares represent the binding energy for X-V$^0$ with respect to neutral and charged components, respectively. The solid and open circles represent the binding energy for X-V$^+$ and X-V$^-$. 

Dopant Species – Substitutional Boron

Nitrogen vs. Boron

Recall: These paths run from the center to a (100) surface dimer, where there is no buckification.

Answers

• Does the PES depend on the type of Surface Chemistry?
  – Yes. The comparison between clean and hydrogenated versions of the same particles indicated that, in the “shell region” the energy of the dopant/impurity is affected by surface passivation.

• Does the PES depend on the Size of the Nanoparticles?
  – Yes and No. Size dependence is evident as sites are within 3 – 5 monolayers from the extremum, along “volatile” paths (such as toward edges and corners).

• Does the PES depend on the Dopant/Impurity Species?
  – Yes. The comparison between Boron and Nitrogen indicate that the PES is dopant/impurity specific, and must be recalculated for each species.
Shape Dependence?

If there was no “shape dependence”
– the solid and open symbols should overlap.

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What does this tell us?

• It is energetically favorable for substitutional N impurities to be located at the extremes of the particles
  – With in the core, they are unstable with respect to diffusion
  – They prefer to act as an adsorbate, not as a dopant

• The specific locations (facets, edges or corners) depends on the size, shape (type of facets, edges or corners) and surface chemistry

• Dopants, impurities or defect-complexes will be able to “see” the extremes of the particle (facets, edges or corners) that fall within their Bohr radius
  – This is approx. 6 monolayers in the case of N
Functional defects

• N itself is not a particularly useful defect, as it is unlikely be a reliable n-type dopant in nanodiamond

• N does however, participate in defect complexes that are functional, such as the photoactive N-V color center

• In the same way that quantum dots or fluorescent beads are used to illuminate tumours, nanodiamonds can act as beacons for tumour-seeking drugs or antibodies

(right) Image showing the internalization of green fluorescent diamonds by a cancer cell
Basics of Photoactive Defect Complexes

Formed when a single N atom binds with a vacancy (missing carbon atom) at the nearest neighbouring lattice position.

- The energy levels structure of the N-V defect in diamond (for example) has ground state and excited state forming an electron spin triplet with $^3A$ and $^3E$ symmetries (Note that due to the spin-spin interaction in the diamond crystal, the ground state is split into ($m_s=0$) and ($m_s=\pm 1$) sublevels).

- The transition between the $m_s=0$ ground and excited states gives off red light when the defect is negatively charged, and green light when the defect is neutral.
Single N-V Fluorescence

- Fluorescence excitation of a single N-V defect in a 60-70 nm diamond nanocrystal at $T = 1.6 \text{ K}$ (top), grown using chemical vapour deposition (CVD).

- Fluorescent defects in nanodiamonds exhibit superior photo-stability over other bio-compatible dyes

- Hahn echo decay curve of a single N-V center in a diamond nanocrystal (bottom) shows reasonable photo-stability.
  - Photobleaching
  - Blinking

Superior Photostability

  - (A) Bright-field and epifluorescence (red pseudo-colour) images of the cell after fluorescent nanodiamond uptake.
  - (B) Three-dimensional reconstruction (left panel), showing the boundaries of the nucleus and the cytoplasm of the cell. Three-dimensional trajectory (shown in pseudo-colour, right panel) and displacements of a single fluorescent nanodiamond (labelled with a yellow box in a) inside the cell over a time span of 200 s.
Influence of Charge

- ZPL is at 575 nm in the neutral state, and at 637 nm for the negatively charged state.
  - In the images above the fluorescent nanodiamonds are prepared by 40 keV He+ ion beam irradiation and 800°C annealing. Corresponding fluorescence images (left) and spectra (right) are obtained for 70 nm green and 140 nm red nanodiamonds dispersed on cover glasses.

Influence of Size

- Independent studies have shown that the efficiency of N-V centers in nanodiamonds decreases rapidly with size
  - **LEFT:** Fluorescent intensity from green N-V defects in collections of nanodiamond samples with different characteristic sizes obtained by Wee et al, Diamond & Related Materials (2009)
  - **RIGHT:** Statistical results for thousands of diamond nanoparticles containing red N-V defects (left) by Rabeau et al, Nano Letters (2007)
Alternative: Fluorescent Si-V Defects

Recently, highly efficient luminescence from silicon-vacancy (Si-V) defects has been reported in nanodiamonds < 10 nm
- ZPL at 738 nm
- Photoefficiency comparable with micron-diamond

These defect centres are structurally analogous to N-V centers, with a silicon atom and a vacancy occupying neighbouring lattice sites.

The combined Raman–PL spectra at room temperature has a multi-line structure typical of nanodiamond, a Raman spectrum characteristic of bulk diamond is observed for the micro-sized specimen.

Mapping the PES for Si-V Defects

• How stable are Si-V defects in diamond nanoparticles:
  – As a function of size?
  – As a function of temperature?
  – And with different surface structure/chemistry?

• Where are Si-V’s likely to be located within diamond nanoparticles?
  – Core? Surface? Edge? Corner?

• Map the possible locations for Si-V substitution using the PES along the 5 different crystallographic directions in the 2.2 nm structure
  – Bucky-diamond, with clean and graphitized surfaces (as-grown)
  – Fully passivated nanodiamond, with a monolayer of hydrogen added to stabilize the surfaces (post-processed)
Structural Stability of Si and Si-V Defects

- Si and Si-V defects are very unstable within the core-shell bucky-diamonds (irrespective of position or substitution path) ...
- ... but can be made stable by passivating/functionaiizing the surfaces
  - Among all combinations tested, the Si-V defect was the most energetically stable, and >1.5 eV more stable than the N-V defects.

Relating Energy to Probability

• Based on the computational results, we can calculate whether a Si-V defect will be stable within the nanodiamond, and estimate the probability of observation.

• This is related to:
  – Probability of formation, at a nitrogen concentration $C$
  – Probability of escape
    • Position of the defect in the nanodiamond ($r$),
    • Energy of the defect at that position ($E_{\text{defect}}$),
    • Kinetic barrier to diffusion ($E_{\text{diff}}$), and the kinetic energy delivered by the probe ($E_K$).

\[
P_{\text{obs}}(R, E_K) = C \sum_{r=0}^{R} P(r) \exp \left\{ \frac{-E_{\text{defect}}(r)}{E_{K,\text{growth}}} \right\} \left[ 1 - \left( \frac{N_{\text{core}}}{N} \right) \exp \left\{ \frac{E_{\text{diff,core}} - E_{\text{defect,core}}}{E_K} \right\} \right] \]

\[+ \frac{N - N_{\text{core}}}{N} \exp \left\{ \frac{E_{\text{diff,shell}} - E_{\text{defect,shell}}}{E_K} \right\} \]

And the size needed for bio-applications?

Good news for the highly desirable 4 nm sized nanodiamonds.
0.15 % Probability of Observation, at room temperature.
(this is approximately 150x better than comparable results for the N-V defects)

Post-Formation Loss of Si-Vs

• The formation of both N–V and Si–V defects depends on a vacancy diffusing through the nanodiamond lattice and colliding with a (stationary) subsitutional impurity.

• The subsequent diffusion of the N–V and Si–V defects is vacancy assisted, so Si–V separation is possible if the Si–V (or N–V) binding energy is less than the Si–C exchange energy.
  – Recall, defects in nanodiamond are affected by the finite size, the location of the defect and the direction (path)

\[ E_b = E_f (V) + \left[ E_f (Si) - E_f (SiV) \right] \]

  – Related to Si–V binding energy, is Si–V attraction/repulsion as the V diffused spontaneously through the lattice within \( p \) lattice sites from the Si

\[ E_b (r, SiV) = E_d (V) \bigg|_{r+p} + E_d (Si) \bigg|_r - E_d (SiV) \bigg|_r \]
Concluding Remarks

• Defects, impurities and dopants in nanodiamond are aware of the finite size only when within the excitonic radius of the surface

• Near the surfaces they are either unstable (with respect to diffusion) or change their configuration such that the advantage of having them there (photoactivity, doping) is lost

• Anisotropy in this core-shell structure influences:
  – The preferred location and stability of extrinsic impurities such as nitrogen
  – The stability of functional photo-active defects used for bio-labeling

• Using computer simulations and simple theoretical models it is possible to understand these issues, and predict the ideal size and operating conditions for ensuring reliability in different applications