

# Can we Predict the Location of Nitrogen in Diamond Nanoparticles?

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While it has been known for some time that diamond nanoparticles contain unintentional impurities resulting from synthesis, the deliberate (controlled) doping of diamond nanoparticles is expected to be important for the development of nanodevices in the near future. The success and reliability of such devices will be largely dependent upon the positions of the dopants within the particles, and the nature of the bonding of the dopant atoms to the surrounding carbon atoms. Therefore, it is highly desirable to know whether dopants, such as nitrogen, will be preferentially located within the core or at the surface of diamond nanoparticles; or possibly at edges or corners. The issue is further complicated by the existence of bucky-diamond particles, which offer alternative substitution sites with naturally reduced coordination in the outer shells.

Experimentally, both as-grown and annealed samples of UDD have exhibited XPS spectra with peaks consistent with both N-sp<sup>3</sup> and N-sp<sup>2</sup> bonds, but a comparison of the N/O ratio in the samples indicated that nitrogen-oxygen groups desorbed during annealing [1]. These results suggest that N is positioned preferentially at the surface of UDD. However, other studies have found evidence of nitrogen being imbedded within the core of nanodiamonds [2,3], supported by two-phonon-excited luminescence spectra (showing peaks indicative of N<sub>2</sub> and N<sub>3</sub> defects)[4] and electron field emission studies [5], respectively. In general, these seemingly contradictory results make the theoretical study of the configuration of nitrogen in nanodiamond of great interest.

Presented here are results of density functional tight binding (DFTB) simulations examining the configuration and potential energy surface (PES) of substitutional N in isolated nanodiamond and bucky-diamond particles containing 881 and 837 carbon atoms, respectively. The nanoparticles measure ~2.2 nm in diameter, a size that occupies the boundary of stability for bucky-diamond and dehydrogenated nanodiamond [4]. The morphology of the nanoparticles have been selected so as to offer combinations of {100}, {110} and {111} surfaces, {100}/{110}, {100}/{111}, {110}/{110} and {111}/{111} edges, and {100}/{110}/{110} and {100}/{111}/{111} corners. The PES for N substitution along paths from the nanoparticle centre to each of these termini predict that N is unlikely to be positioned in the core these nanoparticles [5]. Further results on smaller ~1.3 nm particles, and hydrogenated versions of each structure indicated that the particular (energetically preferred) position will be sensitive to the specific size, shape and degree of surface passivation.

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