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Structural and Electronic Properties of Isolated Nanodiamonds: A Theoretical Perspective

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Structural and electronic properties of isolated nanodiamonds: a theoretical perspective

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Nanometer sized diamond has been found in meteorites, proto-planetary nebulae and interstellar dusts, as well as in residues of detonation and in diamond films. Remarkably, the size distribution of diamond nanoparticles appears to be peaked around 2-5 nm, and to be largely independent of preparation conditions. Using *ab-intio* calculations, we have shown that in this size range nanodiamond has a fullerene-like surface and, unlike silicon and germanium, exhibit very weak quantum confinement effects. We called these carbon nanoparticles *bucky-diamonds:* their atomic structure, predicted by simulations, is consistent with many experimental findings. In addition, we carried out calculations of the stability of nanodiamond which provided a unifying explanation of its size distribution in extra-terrestrial samples, and in ultra-crystalline diamond films. Here we present a summary of our theoretical results and we briefly outline work in progress on doping of nanodiamond with nitrogen.

1. Introduction

Nanoscale diamonds can have extra-terrestrial as well as terrestrial origins. Extra-terrestrial nanodiamonds have been discovered in 1987 by Lewis et al. [1] in primitive meteorites formed before the solar system. They have later been detected in protoplanetary nebulae [2] and in minute quantities in interplanetary dust originated from comets and asteroids [3]. Recently, nanodiamond vibrational signatures have been indirectly evidenced in some circumstellar disks [4]. A remarkable feature of extra-terrestrial nanodiamonds is their narrow size distribution: those found in meteorites have a median diameter of 2.6 nm, similar to that of nanodiamonds detected in nebulae.

On earth, nanodiamonds can be produced by detonation and by chemical vapor deposition techniques. Detonation synthesis [5] has been greatly optimized in the last 15 years and nanodiamonds produced in this way are now commercially available. These nanodiamonds are often called 'Ultra Dispersed Diamond' (UDD) because of their very narrow size distribution peaked, e.g. around ~ 4 nm. Recently nanodiamonds were produced using Chemical Vapor Deposition (CVD) techniques [6]. Under some specific conditions, it was shown that CVD deposited carbon films are assemblies of nanometer sized particles rather than microcrystallites. These films have been called `Ultra Nanocrystalline Diamond Films' (UCND).

The characterization of nanodiamond from both the sky and the earth has revealed interesting, common features, in particular the presence of graphitic-like sites, possibly at

the surface [7]. For example, UNCD films are believed to contain 2-5% of sp^2 bonded carbons, supposedly at grain boundaries and less than 1 % hydrogen. Aleksenskii et al. [7] performed a structural study of UDD using X-ray diffraction and small angle X-ray scattering and found that the majority of nanodiamond has a core size of about 4 nm, with a surface covered by a mixture of sp^2 and sp^3 bonded carbon atoms. Recently, we have proposed that nanoscale diamond obtained by detonation as well as found in meteorites indeed has a diamond core with a fullerene-like surface reconstruction and we have called these carbon particles bucky diamonds [8]. We will give a description of bucky diamonds in Session 3., after describing the properties of hydrogenated nanodiamonds smaller than ~ 2 nm in Session 2.

There is a growing interest in producing nanodiamonds in the laboratory, not only to understand their growth and formation in the solar and extra-solar systems, but also for their potential technological applications [9,10]. It has been proposed that nanodiamonds could be used to produce bright, low voltage (cold) cathodes and light- emitters, if nitrogen doped. The exceptional hardness, fracture strength, and inertness of UNCD films, together with their smooth surface make them unique materials for miniaturized mechanical systems and devices (MEMS), such as cantilevers and gears [9]. In addition, surface hydrophobicity makes UNCD films ideal for support of biological molecules, such a DNA [10], thus providing a material to integrate biological systems with electronic devices. Even at the molecular level, the recently synthesized 'diamondoids [11]', which are composed of a few linked adamantane cages, are considered possible building blocks of future diamond-based nanotechnological applications.

In spite of numerous studies of diamond at the nanoscale, the observed size distribution and stability of diamond nanoparticles has long remained an intriguing property. Recently we have carried out an investigation of the ultradispersity of diamond at the nanoscale using first principles calculations [12]. We have studied the relative stability of nanodiamonds as a function of size and of the surface hydrogen coverage. Our results show that as the size of diamond is reduced to about 3 nm, it is energetically more favorable for this material to have bare, reconstructed surfaces than hydrogenated surfaces. This inability to retain hydrogen at the surface may then prevent the growth of larger grains. These results are summarized in Session 4. of this paper. Finally, Session 5. contains our conclusions.

2. Hydrogentated diamond nanoparticles

Silicon and Germanium nanoparticles are known to show quantum confinement effects up to 5-7 nm and it is interesting to consider whether such effects could appear in nanodiamond as well. An early XANES study of CVD deposited diamond films [13] suggested that in diamond quantum confinement effects persist up to sizes much bigger than those of Si and Ge nanoparticles, that is up to about 27 nm.

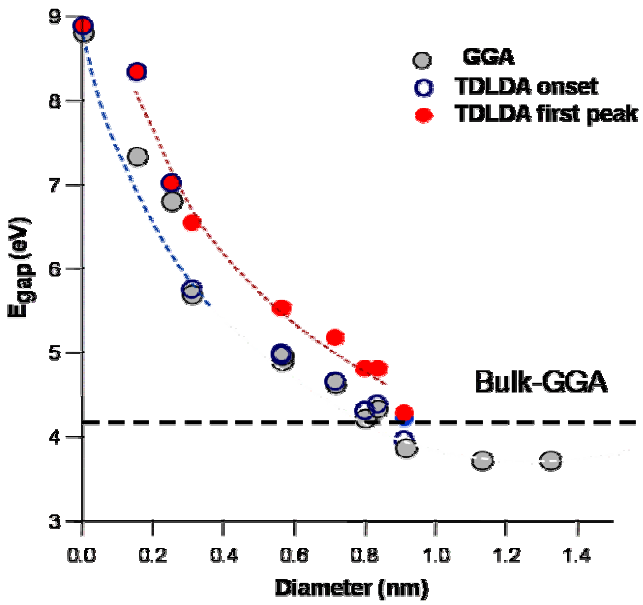

Figure 1: Calculated energy gap [E_{gap}] of hydrogentated diamond nanoparticles usinng Density Functional Theory in the Gradient Corrected Approximation (GGA) and Time dependent Density Functional Theory (TDLA), as a function of the nanoparticle diameter. See Ref. [8].

The fit to XANES spectra reported in Ref.[13] and used to substantiate this claim was later questioned by L.Ley et al. [14]. In addition, recent NEXAFS measurements [15] on nanodiamond films prepared by hot-filament CVD showed quantum confinement effects much smaller than those reported in Ref.[13].

In order to address the question of quantum confinement in diamond, we carried out a combined theoretical and experimental investigation of crystalline nanodiamonds and found that quantum confinement effects are smaller than in Si and Ge, i.e. they persist up to much smaller sizes [8]. The results of our first principles calculations are reported in Fig.1 where we show that for hydrogentated diamond nanoparticles of 1 nm or bigger, the optical gap is the same as in bulk diamond. These theoretical findings are consistent with emission and absorption measurement on soot samples, showing that at ~ 4nm quantum confinement effects are not present. We note that a key difference between the measurements reported in Ref. [8] and Ref.[13] is the sample crystallinity.

In our calculations we found that the surface structure and hydrogen composition can affect the electronic and optical properties of hydrogenated nanodiamonds. For example, reconstructions of the type of those reported in Fig.2 for a 66 C atom cluster can considerably lower the value of the gap below that of bulk diamond, as shown for sizes larger than 1 nm in Fig.1.

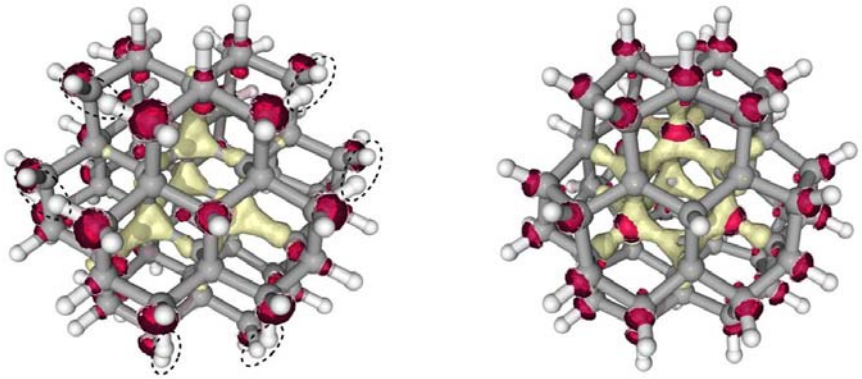

Figure 2: Ball and stick representation of the atomic structure of fully hydrogenated $C_{66}H_{40}$ (right hand side) and of $C_{66}H_{24}$ (Left hand side), with reconstructed surfaces. Grey and White spheres represent Carbon and Hydrogen atoms, respectively. Yellow and red contours represent the squared amplitude of the highest occupied molecular state of the clusters.

3. Bare Nanodiamonds

When all hydrogen is removed from the surface of nanodiamond, an interesting surface reconstruction is observed in our *ab-initio* molecular dynamics simulations at room temperature: a fullerene-like cap is formed on the diamond core, yielding a hybrid fullerene-diamond at the nanoscale, which we have called bucky-diamond. The reconstruction occurs spontaneously at room temperature. The atomic structure of two bucky-diamonds obtained using *ab-initio* simulations (C_{147} and C_{275}) and that of larger ones studied with semi-empirical tight-binding methods is reported in Fig.3.

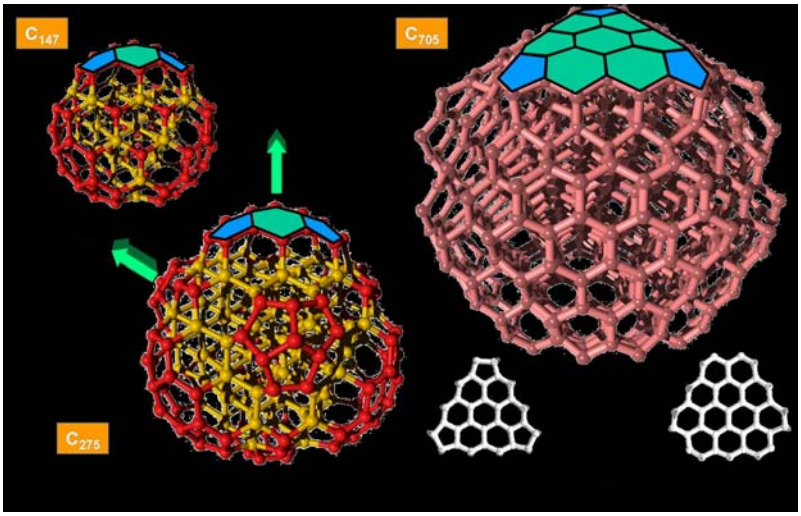

Figure 3: Ball and stick representation of bare nanodiamonds (bucky-diamonds). [See text and Ref.8]

X-ray emission and absorption measurements on soot samples have confirmed that indeed small nanodiamonds have a diamond core and a fullerene like reconstructions, thus also confirming models previous measurements and models developed in Ref. [7].

4. Ultradispersity at the nanoscale

Having established the atomic and electronic structure of both hydrogenated and bare nanodiamonds, we studied the relative stability of nanoparticles with the same carbon content but different hydrogen coverage, as a function of size, using a grand canonical formalism. The formation energy of a carbon particle is defined as:

$$E_{formation} = E_{total} - \mu_C N_C - \mu_H N_H - E_{vib}$$

Here N_x are the numbers of C or H atoms and μ_x is their respective chemical potential; E_{vib} and E_{total} are the vibrational and the total energy of a nanoparticle, respectively, obtained within Density Functional Theory. The formation energy thus expresses the difference in energy between a nanoparticle and a reservoir of carbon and hydrogen atoms whose energy is μ_x. In our calculations, we considered five core sizes containing 29, 66, 147, 211 and 275 C atoms and for all of them we found that the stability sequence of the particles with different surface structures is the same as a function of μ_H. In all the five cases, in going from the H_2 chemical potential to lower values, the stable structures are, in order of increasing stability, nanoparticles with fully hydrogenated surfaces, those with (111) reconstructed, hydrogenated surfaces and those with bare, reconstructed surfaces. Our results for the formation energy of two specific diamond clusters (with 66 and 275 C atoms, respectively) as a function of the hydrogen chemical potential are shown in Fig.4. This figure indicates that the difference in formation energy between particles with hydrogenated surfaces and those with bare surfaces is decreasing as the size of the nanoparticle is increased. This suggests that there exist a size in the nanometer range where a reversal of stability between hydrogenated and bare nanoparticles will occur and bucky diamonds (or parent structures) will become more stable than diamond nanoparticles with hydrogenated, reconstructed surfaces.

The computed difference in formation energy (Δ) between the stable hydrogenated structure and the bare diamond nanoparticle as a function of size is shown in Fig.5, where we assumed that Delta is dependent only on the number of surface carbon atoms. With this assumption

$$\Delta = E_{formation,\,bare}^{\;3/2} - E_{formation,\,stable}^{\;3/2}$$

is almost linear with the particle diameter. Our results show that for all values of the H chemical potential, Δ becomes *negative* when the diameter of the nanoparticle is comprised between 2 and 3 nanometers. In other words, Δ does not depend in any significant way on the hydrogen chemical potential, and thus to a large extent on different experimental synthesis conditions.

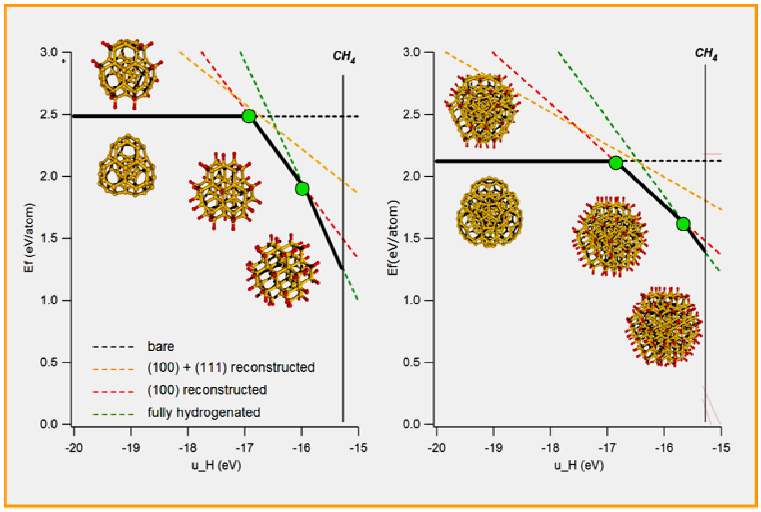

Figure 4: Formation energy of nanodiamonds with different hydrogen coverage and different core sizes (66 C atom and xx Carbon atoms on the left and right hand sides, respectively), as a function of the hydrogen chemical potential, which mimic different preparation conditions.

Our calculations show that between 2 and 3 nm, it is energetically more favorable for nanodiamond to have a bucky diamond-like structure and bare unreconstructed surfaces than having hydrogen at the surface. The presence of hydrogen is a necessary condition for the growth of diamond; therefore the release of surface hydrogen from growing nanodiamonds should result in the premature end of the growth of bulk samples between 2 and 3 nm. These findings help explain why nanodiamond size distributions are peaked around the same size, about 3 nm, irrespective of the preparation method used to generate the nanoparticles. Although our calculations cannot establish the exact size at which the crossover between hydrogenated and bare, reconstructed surfaces occur, they provide a robust, qualitative explanation of why the crossover occurs in the few nanometers range, and why it is the same irrespective of preparation conditions.

Based on the simple thermodynamic mechanism presented here, one might argue that it would be impossible to grow diamond on a micro- or macroscopic scale. To address this issue, it is necessary to compare the formation energies of nanodiamonds of various sizes with those of flat diamond surfaces. This comparison indicates that at the highest values of the H chemical potential (-15.5 eV) considered in our study, the infinite (100) surface is more stable than any nanodiamond, while at lower chemical potential, there exist a critical diameter above which the nanodiamond clusters are the most stable structure. For instance at a chemical potential value of -16.5 eV, if the particle grows to a diameter larger than 2.5 nm, then it becomes more stable than a bulk surface. These numerical results help explain how, by varying the hydrogen pressure (and thus the hydrogen chemical potential) in a CVD reactor, one can deposit either microcrystalline or ultrananocrystalline diamond films.

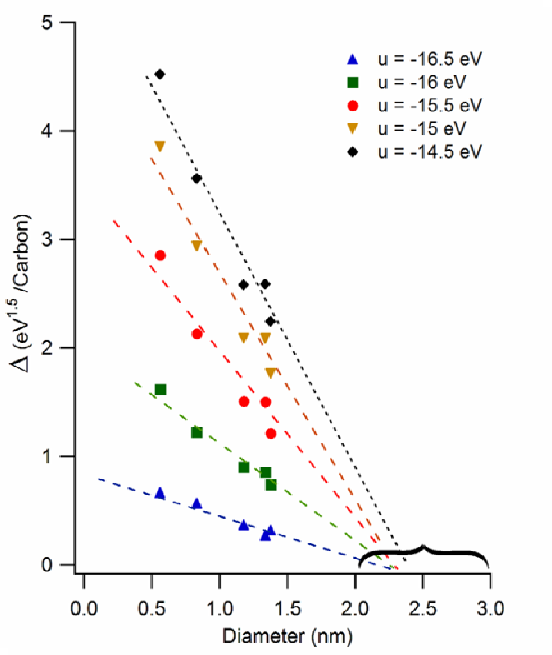

Figure 5: Difference in formation energy between nanodiamonds with fully reconstructed surfaces and the most stable structure found for a given value of the hydrogen chemical potential (u), as a function of the nanoparticle size.

5. Conclusions

In summary, using *ab-initio* methods with no adjustable parameters, we have proposed an explanation for the ultradispersity of diamond at the nanoscale which relies on simple thermodynamic arguments. We have shown that depending on the temperature and pressure of the hydrogen and carbon gases used in diamond growth processes, diamond will grow into nanoparticles with reconstructed, non hydrogenated surfaces of about 3 nm or into microcrystallites, if the typical conditions of diamond CVD growth are met. Our results, together with the proposed geometry of bucky diamond will help build structural models of UNCD and UDD films which can be used to study mechanical properties of these systems, as well as their interfaces with biological molecules.

Work is in progress to study doping of nanodiamond, which is a very promising areas for technological applications. In this area the research has been focused on nitrogen doping, where the general goal is to introduce carrier levels into the (nano)-diamond gap (this level is located 1.7eV below the conduction band minimum in bulk diamond) and thus increase the conductivity and lower the electron emission voltage threshold.

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