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Nanodiamonds : their Structure and Optical Properties

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Nanometer sized diamond is a constituent of diverse systems ranging from interstellar dusts and meteorites [1] to carbonaceous residues of detonations [2] and diamond-like films [3–5]. Many of the properties of bulk diamond have been well understood for decades, those of nanodiamond are mostly unexplored. We present a combined theoretical and experimental study showing that diamond has unique properties not only as a bulk material but also at the nanoscale, where size reduction and surface reconstruction effects are fundamentally different from those found , e.g. in Si and Ge .

We performed ab-initio calculations using Density Functional Theory (DFT), and carried out x-ray absorption and emission measurements on nanodiamonds synthesized in detonation waves from high explosives. In our DFT calculations, performed both within the generalized gradient approximation (GGA) and the time dependent local density approximation (TDLDA), we used a pseudopotential, plane wave approach. For particles with a diameter smaller than 1.4 nm we passivated the surface with hydrogen atoms, whereas for larger clusters we explicitly studied the geometry of surface reconstruction, in the absence of passivants. The x-ray absorption and soft x-ray fluorescence experiments were carried at the Stanford Synchrotron Radiation Laboratory (SSRL) and at the Advanced Light Source (ALS) in Berkeley on samples with a size distribution of 4±1 nm. The sample size and crystallinity were verified by x-ray diffraction and high resolution transmission microscopy.

The two theoretical methods show a rapid decrease of the energy gap from a value of 8.9 eV in methane to 4.3 eV in $C_{87}H_{76}$. This value is remarkably close to that of the optical gap in bulk diamond (4.23 eV) obtained using the same theory (GGA) and the same numerical approximations (e.g. energy cutoff) as those used for the nanodiamond calculations. As expected, the computed bulk gap is smaller than the experimental one (5.47 eV), due to well known errors of the local density approximation which usually underestimates band gaps in semiconductors and insulators. At 1 nm, the difference between the TDLDA and GGA energy gaps is about 0.1—0.2eV and the energy gap of the nanoparticle is very close to that of the bulk. This indicates that there is no appreciable quantum confinement effect on the optical gap of nanodiamond for sizes larger than 1 to 1.2 nm, contrary to what is found in Si and Ge with the same theoretical tools .

Depending on preparation conditions, nanodiamonds produced experimentally may not have an ideal diamond surface saturated by hydrogen atoms, but rather exhibit reconstructed surfaces. To investigate the effect of surface reconstruction on hydrogenated nanoparticles, we studied some representative cases. Starting from the unrelaxed, fully hydrogenated, geometries, we removed pairs of hydrogens whose interatomic distances were within 5 % of the H_2 bond length. All surfaces spontaneously reconstructed at low temperature but the reconstruction induced almost no change in the GGA gap values.

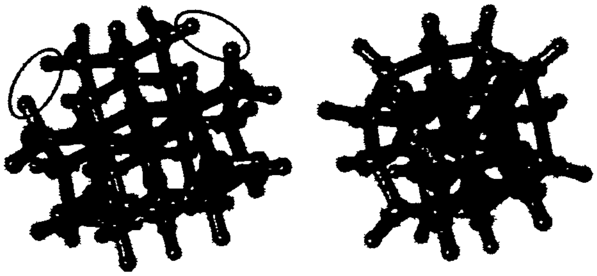

FIG. 1. Isosurfaces of the square modulus of the highest occupied (green) and lowest unoccupied (red) Kohn-Sham orbitals of $C_{29}H_{36}$ (left panel), and $C_{29}H_{24}$ (right panel). Although the $C_{29}H_{36}$ and $C_{29}H_{24}$ relaxed structures are rather different, the GGA gap value is found to be nearly the same in the two clusters [11]. However, the TDLDA spectra [12] of the two nanoparticles have a totally different shape and the surface reconstruction has lowered the energy gap by 0.5 eV in the time dependent formulation. The localization properties of the HOMO and LUMO are slightly modified in the presence of surface reconstruction. All the isosurfaces are drawn at 50% of their maximum value. Hydrogen atoms are in grey.

The results of our calculations, showing that quantum confinement has no appreciable effect on the optical gap of diamond clusters for radii larger than 1nm are consistent with the measured emission and absorption spectra. Fig. 2 shows the conduction band spectrum of diamond clusters, compared to those of bulk diamond and graphite, as obtained using x-ray absorption technique. The nanodiamond K-edge absorption and emission show the same basic spectral features in bulk diamond and in the nanoparticles. In particular, we did not observe any blue shift in the position of nanodiamond conduction and valence band edges, when compared to the bulk, contrary to a recent experimental investigation [4].

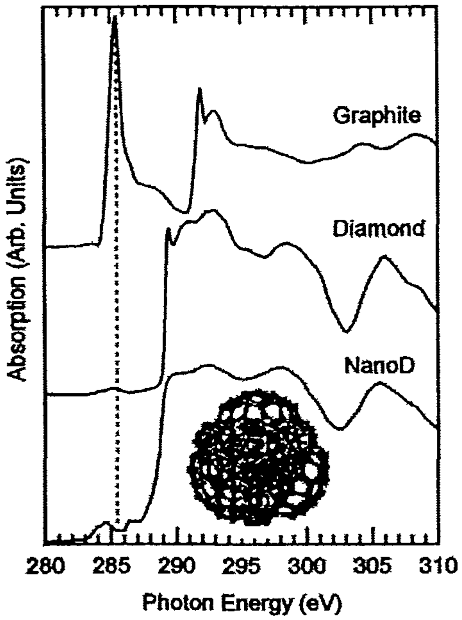

FIG. 2. Absorption spectra of nanodiamond compared to bulk diamond and graphite (HOPG). As insert : one "bucky diamond" reconstructed cluster containing 275 carbon atoms.

The spectra reported in Fig.2 also provide additional, interesting information. The core exciton feature clearly observed in the K-edge absorption of bulk diamond is broadened in the nanodiamond spectra. This may be due to a decrease in lifetime of the core-hole excitation due to confinement of the electron and core hole in the small diamond nanoparticles. We also note that the depth of the secondary gap at 303 eV is shallower in the nanodiamond spectra than in the bulk. This effect has been previously observed and attributed to decreasing diamond crystallite size [6].

Finally we note the presence of pre-edge features in the x-ray absorption spectrum of nanodiamond, which are absent in bulk diamond and graphite. Some features are common to bulk and nanodiamond but the pre-edge feature at 286.5 eV found in nanodiamonds is not observed in the bulk. This cannot be associated to a hydrogen terminated diamond surface since it persisted after the sample was annealed above the hydrogen desorption temperature. The small peak at 286.5 eV is similar to a feature observed in experimental emission spectra of small fullerenes [7] (C_{60}, C_{70}) and is suggestive of the presence of pentagons and hexagons on the nanoparticles surface. Indeed, we found that this peak can be attributed to a fullerene-like surface reconstruction occurring in non-hydrogenated nanoparticles.

We studied in detail the surface reconstruction of non hydrogenated clusters for sizes up to 3.0 nm using semi-empirical tight-binding Hamiltonians [8] , since the number of atoms is too large to be efficiently handled from first-principles. The insert in Fig.2 shows our results for the surface reconstruction of a bare 275 carbon atom cluster. Our tight binding simulations, using the potentials of Wang et al. [8] show similar surface reconstructions for 2 and 3 nm clusters (705 and 2425 atoms, respectively). The reconstruction, which is accompanied by an increased curvature of the surface, induces an effective tensile stress acting on the core of the nanocluster. This effect is at variance with the one found in Si and Ge dots where the geometry of the surface reconstruction is very different from the one found here and induces an effective compression on the nanoparticle core [9]. We note that the barrier between the ideal surface structure and the reconstructed surface is size dependent and increases as the size of the nanoparticle is increased, to become of the order of several tens of eV, as found in bulk diamond [10]. These nanoparticles with a diamond core and a fullerenic-like structure may be useful and representative models of nanodiamonds found in meteorites and may lead to a better understanding of their complex surface chemistry.

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[11] Our DFT calculations were carried out using a first-principles molecular dynamics code, JEEP 1.8.0 (F. Gygi, LLNL 1999-2001).
[12] The ABINIT code which a common project of the Universite Catholique de Louvain, Corning Incorporated, and other contributors (http://www.abinit.org).