

MECHANICAL AND ELECTRONIC PROPERTIES OF NANODIAMOND FILMS

M. G. Fyta ¹, P. C. Kelires ²

¹ Physics Department, University of Crete, Heraklion, P.O. Box 2208,
710 03, Heraklion, Crete, Greece

² Foundation for Research and Technology-Hellas (FORTH), P.O. Box 1527,
71110 Heraklion, Crete, Greece

ABSTRACT

Preliminary results of our recent studies on nanodiamond films are presented. Interest on this material is growing since it optimizes properties such as hardness, optical transparency and electrical conductivity of bulk diamond and has an enormous variety of applications in fields like optical windows, MEMS, electrochemical electrodes or tool coatings. Our results are obtained through tight-binding molecular dynamics (TBMD) computer simulations based on the hamiltonian of Mehl and Papaconstantopoulos. These calculations are supplemented by Monte-Carlo (MC) simulations within the Tersoff empirical potential approach. For each computer-generated structure with varying grain size, its structure, hardness and electronic density of states were calculated. The electronic structure seems to be affected by the grain size. An increase of the size leads also to an increase of the hardness of the material. When investigating the structure of the nanodiamond films we focused mainly on the nanocrystallites: while free-standing nanodiamonds are surrounded by a fullerene coating, this is not the case when they are embedded in the film

Keywords:

Nanodiamond films, amorphous carbon, bulk modulus, electronic density of states

INTRODUCTION

In recent years, novel carbon materials have been studied intensively because of their enormous potential utility. Nanodiamond films¹ are considered as such materials formed by different sized diamond nanocrystals and a small amount of amorphous or graphitic carbon. Many experiments have been carried out and different deposition techniques have been used to grow, characterize and explore the properties of nanodiamond films.

We study here the mechanical and electronic properties as well as the structure of nanodiamond films. Our analysis is based on tight-binding molecular dynamics simulations supplemented by Monte-Carlo simulations. Two different tight-binding hamiltonians were used (Wang and Ho² and Mehl and Papaconstantopoulos³), while the

empirical potential of Tersoff was used in the Monte-Carlo investigation. Both schemes have been tested and provide a fairly good description of the structure and energetics of a wide range of a-C phases^{4,5,6}].

METHODOLOGY

We use computational cells that include diamond nanocrystals and an amount of amorphous carbon to resemble nanodiamond films. The radii of the crystals in the cells differ as well as the density of the amorphous material. Since it is computationally much less demanding, our cells consisted of 0.8-1.4 nm nanocrystallites, which are considered as spherical, thus the amount of amorphous material in the cubic cells is greater than 5%. The orientation of the grains, for a preliminary study, is the same for all cells. We also used nanodiamonds of different orientations and larger sizes (results are shown elsewhere).

The calculations are based on cells of 216 and 512 atoms. The amorphous structure is constructed with the liquid-quench method (quick freezing from the liquid state) from 12000K to 0K with the Monte-Carlo/Tersoff method (using the semi-grand canonical (N,P,T) or (N,V,T) ensemble). The cells are then relaxed at 800K (for a total time of ~30ps using a time step of 1fs) and subsequently at 0K using the two tight-binding schemes (in the framework of a (N,V,T) canonical ensemble which forces to a subsequent relaxation of the volume for each structure). The temperature is controlled via a Nose-Hoover thermostat⁷.

HARDNESS

The bulk modulus of the nanodiamond films studied here is obtained by adjusting the energy-volume curves to the Birch-Murnacham equation. It is shown that increasing the grain size in these films leads to an increase of a few Gpa in the bulk modulus of the film. Thus controlling the average size of these nanodiamond grains is a way of controlling also the hardness of the nanodiamond film.

In order to calculate the hardness of the films, we took into account computational cells with grains of a specific radius per cell. For each cell we varied its density and determined its bulk modulus. This method was repeated, while the sizes of the nanodiamonds changed.

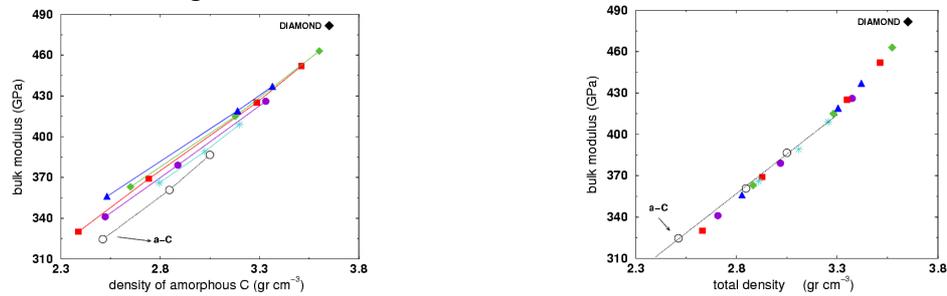


Fig. 1: Bulk modulus of nanodiamond films vs (a) density of the amorphous material and (b) total density of the film. The radii of the grains are: 6.4 Å (triangles), 6.2 Å (diamonds), 5.6 Å (squares), 5.3 Å (circles), 5.0 Å (stars). Opaque black circles denote structures of pure a-C.⁸

ELECTRONIC DENSITY OF STATES

The quantum mechanical effects are included in the electronic part of the hamiltonian in order to describe well the electronic structure of the system, especially the ground state. This allows as to calculate the electronic density of states for each simulated structure.

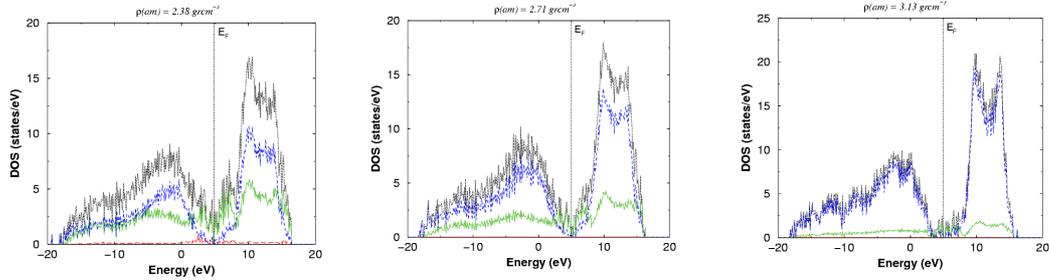


Fig. 2: 2-fold (long dashed lines), 3-fold (solid), 4-fold (dashed) and total (dotted) e-DOS for a nanodiamond with grains of 5.6 \AA radius and a high content of a-C ($\approx 70\%$). The graphs correspond to different a-C densities ($\rho_{am} = 2.4, 2.7$ and 3.1 gr cm^{-3} respectively).

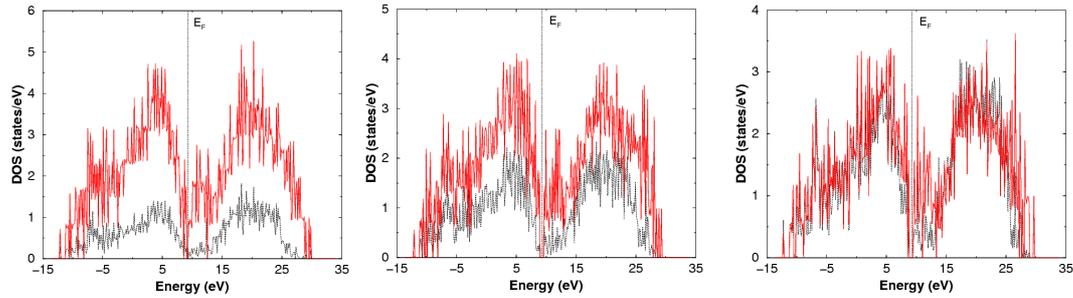


Fig. 3: Amorphous (solid) and nanocrystalline (dotted) contribution to the e-DOS of a film with one-sized nanocrystals (with radii 3.9 \AA , 4.4 \AA , 5.0 \AA and a-C contents of $\approx 78\%$, $\approx 67\%$, $\approx 54\%$ respectively). The amorphous density is low and approximately the same for these structures.

In figure 2 the e-DOS for samples of nanodiamond films with different densities is shown. There is an indication that a band-gap ``opens" as the density of the film increases. This feature, though, must still be explored. It is known, on the other hand, that the sp^2 bonded-grain boundaries in nanocrystalline diamond are responsible for the electrical activity of the nanodiamond films. This indicates that the contribution of the amorphous material of the film to the electronic structure must be explored. Thus preliminary results of the amorphous and nanocrystalline e-DOS for different grain sizes, but for the same amorphous density are presented in Fig. 3. Localized states at sp^2 and sp^3 bonds (across the grain boundaries and as dangling bonds respectively) are visible.

STRUCTURE

It has been shown⁹, that free-standing nanodiamonds develop a fullerene-like coating in their surface, while retaining a diamond core. In order to examine whether this trend remains if the nanodiamonds are embedded in a film, we relaxed diamond

grains of different sizes at low temperature using the Hamiltonians [1, 2]. In Fig. 4 nanodiamonds of ≈ 1.2 nm are shown.

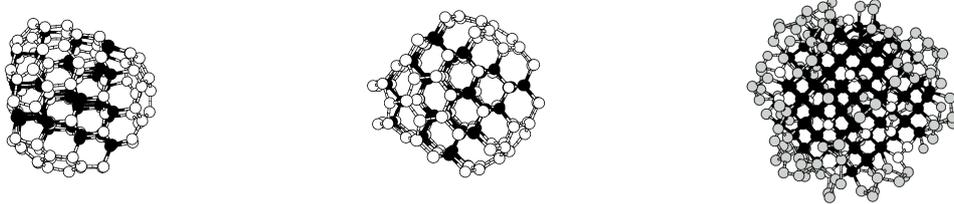


Fig. 4: Nanodiamonds relaxed at low temperature: free-standing [2], free-standing under low pressure (Monte-Carlo/Tersoff) and in a nanodiamond film of low density, respectively. In white and black are the 3-fold and 4-fold atoms, while in grey are the atoms of aC.

CONCLUSIONS

In conclusion, we have presented results of a theoretical study of nanodiamond films. It has been shown that films including large nanocrystals show greater hardness than others of the same density but with smaller nanocrystals. The bulk modulus of the material depends linearly on the total density, regardless of the grain size. The electronic structure (eDOS) shows the $\pi\pi^*$ spikes which govern the electrical activity of the material, as well as states localized at sp^2 bonds at the grain boundary and at sp^3 -type dangling bonds. As far as the structure is concerned, it has been shown that although free-standing nanodiamonds develop a fullerene-like reconstruction, this is not the case when they are surrounded by amorphous material. We are still investigating the consequences of this observation.

In spite, finally, of the fact that nanodiamond films studied here could be extended to include diamond grains which differ in size and orientation as well as smaller regions of a-C, we believe that the trends presented here refer to a general behavior of nanodiamond films.

REFERENCES

-
- ¹ D. M. Gruen, *Annu. Rev. Mater. Sci.*, **29**, 211 (1999)
 - ² M. S. Tang, C. Z. Wang, C. T. Chan and K. M. Ho, *Phys. Rev. B* **53**, 979 (1996)
 - ³ M. J. Mehl and D.A. Papaconstantopoulos, *Phys. Rev. B*, **54**, 4519 (1996)
 - ⁴ P. C. Kelires, *Phys. Rev. Lett.*, **73**, 2460 (1994); *Phys. Rev. B*, **62**, 15686 (2000)
 - ⁵ C. Z. Wang, K. M. Ho, *Phys. Rev. B* **50**, 12429 (1994)
 - ⁶ C. Mathioudakis et al, *Phys. Rev. B* **65**, 205203 (2002)
 - ⁷ S. Nose, *J. Chem. Phys.*, **81**, 51 (1984)
 - ⁸ Bulk modulus of a-C, C. Mathioudakis, P. C. Kelires and S. Logothetidis, unpublished work
 - ⁹ J. Y. Raty et al, *PRL*, **90**, 037401 (2003)