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Computational Study of Interstitial Hydrogen Atoms in Nano-Diamond Grains Embedded in an Amorphous Carbon Shell

Amihai Silverman[1], Alon Hoffman[2] and Joan Adler[3,*]

[1] *Taub Computer Center, Technion-IIT, Haifa 32000, Israel.*
[2] *Schulich Faculty of Chemistry, Technion-IIT, Haifa 32000, Israel.*
[3] *Department of Physics, Technion-IIT, Haifa 32000, Israel.*

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Abstract. The properties of hydrogen atoms in a nano-diamond grain surrounded by an amorphous carbon shell are studied with Tight Binding computer simulations. Our samples model nano-diamond grains, of a few nanometers in size, that nucleate within an amorphous carbon matrix, as observed in deposition from a hydrocarbon rich plasma. The calculations show that the average hydrogen interstitial formation energy in the amorphous region is lower than in the nano-diamond core, therefore hydrogen interstitial sites in the in the amorphous region are more stable than in the nano-diamond core. This formation energy difference is the driving force for the diffusion of hydrogen atoms from nano-diamond grains into amorphous carbon regions. An energy well was observed on the amorphous side of the nano-diamond amorphous carbon interface: hydrogen atoms are expected to be trapped here. This scenario agrees with experimental results which show that hydrogen retention of diamond films increases with decreasing grain size, and suggest that hydrogen is bonded and trapped in nano-diamond grain boundaries and on internal grain surfaces.

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1 Introduction

Hydrogen is an essential component of the gas mixture used for micro and nano crystalline diamond film nucleation and growth by Chemical Vapor Deposition (CVD) methods [1–3]. Extensive research has been carried out to determine the role of hydrogen in

*Corresponding author. *Email address:* phr76ja@technion.ac.il (J. Adler)

this process. When such deposition is made with energetic species, hydrogen-rich carbon films with nano-diamond grains a few nanometers in size, embedded into an amorphous carbon matrix [4], are created. The deposition parameters and properties of this class of films were extensively investigated and it was found that their formation is accompanied by a large hydrogen retention which was postulated to decorate the diamond grain boundaries [5]. It was recently reported by us and others that hydrogen retention in diamond films increases with decreasing diamond grain size [6]. In addition to the postulated location of hydrogen in the grain boundaries, other possible hydrogen locations are within the diamond grains as interstitial sites, forming defect-H clusters in the grains, on the diamond surfaces, or in non-diamond constituents between the grains (e.g., when nano-diamond crystallites are embedded in an a-C/graphite matrix). Hydrogen is extremely important to all structural changes in carbon materials, for example see [7].

In order to provide answers to key questions surrounding the location and properties of the hydrogen sites in diamond films, we carried out computer simulations with Tight Binding Molecular Dynamics (TBMD) methods. We calculated and compared the properties and energies of hydrogen atom interstitial sites in simulated samples of diamond, amorphous carbon and in mixed samples with an interface between a nano-diamond grain and an amorphous carbon shell. In a TBMD simulation, the band structure energy and the many body forces are calculated directly by diagonalizing the one electron Hamiltonian matrix [8–10]. Since the method is less computationally intensive than Local Density Approximation (LDA) [11,12] calculations, it allows us to study larger systems of atoms. Thus we can include important structural configurations such as nano-diamond in an amorphous matrix, and thereby study the interface region between diamond and amorphous structures. TBMD has been shown in the literature to give reliable results for amorphous carbon and amorphous hydrogenated carbon provided the selected TB parameters and simulation regime are appropriate [13].

Starting from translationally invariant pure diamond, our calculations were carried out in two stages. First, preliminary samples were prepared, using simpler molecular dynamics methods with empirical potentials [14, 15], because relatively long run times are sometimes needed at this stage. A melt-quench process [16, 17] was used to prepare either amorphous carbon, or a nano-diamond core surrounded by an amorphous carbon matrix. For the latter, some diamond sites were pinned during the melt-quench process to imitate a nano-diamond grain embedded into an amorphous carbon matrix after the nucleation process which was observed in the experiment [4]. Smaller samples, some with inverse structures of amorphous cores and crystalline surroundings, and others with melted stripes were previously generated in our group with this approach [18]. Mixed sample have also been prepared and investigated more recently by Kopidakis et al. in [19], who embedded nanocrystals in an amorphous matrix. We will return to a comparison with these below. Once the preliminary samples were obtained, a TBMD simulation using the Frauenheim's Tight Binding (FTB) model [8,10] was applied for both the C-H and C-C interactions to stabilize the sample, and obtain more accurate atomic configurations. In all cases, the initial sample was translationally invariant pure diamond.