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Dangling bond energetics in Carbon Nitride and Phosphorus Carbide Thin Films with Fullerene-like and amorphous structure

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Abstract

The energy cost for dangling bond formation in Fullerene-like Carbon Nitride (FL-CN_x) and Phosphorus carbide (FL-CP_x) as well as their amorphous counterparts: a-CN_x, a-CP_x, and a-C has been calculated within the framework of Density Functional Theory and compared with surface water adsorption measurements. The highest energy cost is found in the FL-CN_x (about 1.37 eV) followed by FL-CP_x compounds (0.62-1.04 eV).

1. INTRODUCTION

Predictive *Ab-initio* simulations are a powerful tool to address structural issues in materials as well as to predict novel compounds. We developed the Synthetic Growth Concept (SGC) based on the Density Functional Theory [1, 2] for simulations of film formation during vapor phase deposition. SCG treats structural evolution by sequential steps of atomic rearrangement where each step is assigned according to the previous relaxed states. For example, the properties of precursors for nanostructured compounds are described quantitatively together with their interaction when they form condensed phases.

Carbon-based nanostructured materials attract attention due to their electronic, mechanical, optical, and chemical characteristics, as recently pointed out in two edited books [3, 4]. We successfully applied SGC to develop a new class of carbon-based materials which can be unified by the term Fullerene-Like (FL) carbon-based solid compounds alloyed with N and P. Fullerene-like Carbon Nitride FL-CN_x is one of the most promising CN_x compounds with outstanding mechanical properties [5]. FL-CN_x is already industrially applied under the trade name of "rubber diamond" or "nitrogenated Diamond-Like C" as a fracture tough, highly elastic and wear resistant material. The FL-CN_x structure evolution and bonding configurations were successfully described by using SGC, thus contributing to the pioneering knowledge in its growth and characterization [2]. Making use of SGC, we more recently predicted FL phosphorus-carbide (FL-CP_x) [6, 7], and successfully guided its deposition by magnetron sputtering. The SGC predictions for remarkable mechanical properties of FL-CP_x - hardness, elasticity, etc. were also confirmed by experiments [8]. It is known that the surface of carbon-based films contains dangling bonds that react with hydrogen, oxygen and water molecules and form a chemically bonded surface layer [9-12]. Taking into account the prospects of FL compounds for, e.g., applications as protective overcoats in computer disk drive systems, etc., the water adsorption on FL carbon-based overcoats (which is directly related to the density of dangling bonds in these

materials) represents an important property. We have previously shown that FL compounds exhibit considerably lower water adsorption than amorphous phases with similar composition [13, 14]. Also, in our works [1-2 and 5-7], the formation mechanism and the structural role of various defects in solid fullerene-like carbon-based materials were studied in details.

The scope of this work is to compare the energy cost for formation of dangling bonds in CN_x, CP_x, and a-C. Our results show that the FL compounds exhibit higher energy cost for dangling bond formation (and correspondingly lower density of dangling bonds) compared to the amorphous counterparts. This provides technological advantages for the application of carbon-based FL compounds as protective and chemically resistant coatings.

2. COMPUTATIONAL DETAILS

Finite model systems simulating amorphous compounds of a-CN_x, a-CP_x, and a-C as well as systems in which N and P atoms are incorporated in curved and cross- or inter-linked graphene sheets to represent the FL compounds [2, 6] were considered. The amorphous systems were simulated as a mixture of sp^2/sp^3-coordinated networks.

The study involved both geometry optimizations and cohesive energy (E_{coh}) calculations performed by implementing the DFT in its Generalized Gradient Approximation (GGA) and within the framework of the SGC [1, 2, and 6]. In order to evaluate wide range of bonding configurations of defects in CN_x and CP_x systems, different possible substitutional sites for N and, respectively, P atoms were explored, the resulting model systems were further optimized and their energetics compared.

The cohesive energy E_{coh} of a model system is defined as the energy required for breaking the system into isolated atomic species, i.e.,

$$E_{coh} = E_{total} - \sum_i E_{i,total}^{isolated} ,$$

where *i* stands for different constituent atoms.

The energy cost of dangling bonds is calculated as differences in the cohesive energies $|\Delta E_{coh}|$ for a structure with, and respectively, without a dangling bond [1, 2], using the GAUSSIAN 03 program [15].

Concerning the DFT-GGA level of theory, the Perdew-Wang exchange-correlation functional (PW91) [16] and the B3LYP hybrid functional [17] were used. Both are known to provide an accurate description of the structural and electronic properties of FL thin films [1, 2, 6] and similar covalent systems [18-20]. The results reported in this work were obtained using the PW91 exchange correlation functional while the B3LYP simulations were carried out for test purposes, i.e., in order to make sure that the conclusions do not depend on the exchange correlation functional adopted. For C, N, and P, double-ζ basis sets augmented with polarization functions were used.

3. RESULTS AND DISCUSSION

3.1 Theoretical Modeling

Different model systems containing typical defects such as pentagons and cross-linked graphene sheets, known to correctly describe the precise atomic arrangement in FL-CN_x [1, 2], were theoretically simulated in the case of this compound. In addition to such structures, for the case of FL-CP_x also tetragon defects and inter-locked graphene sheets as well as cage-like formations were tested. Compounds with analogous composition, but representing amorphous structure, namely a-CN_x, and a-CP_x have been also simulated together with the pure a-C [13, 14]. These amorphous compounds were simulated by optimizing model systems consisting of randomly intersected N-containing, P-containing and pure sp^2/sp^3-coordinated segments, respectively. The simulations also employed randomly perturbed atomic positions followed by subsequent geometry optimization in the sense of SGC as applied in Refs.[1, 2, and 6].

Figure 1 displays FL-CN_x, FL-CP_x, a-CN_x, a-CP_x, and a-C model systems after geometry relaxations. For each compound, only the model systems containing the lowest cost dangling bonds are shown. Most characteristic structural feature in FL-CN_x is the curved graphene sheets containing mostly pentagon defects [1, 2]. As shown in [13], the energetically most favorable situation of a dangling bond in well-structured FL-CN_x is associated with the pyridine-like defects (Fig. 1 (a)) while in a-CN_x dangling bonds at peripheral sites (Fig. 1 (b)) are frequently occurring. In what concerns FL-CP_x, the emblematic cage-like structures containing a tetragonal defects leading to onion-like conformations can naturally contain a dangling bond (Fig. 1 (c)) due to the bond polarization introduced by the incorporated P atoms [6, 14]. In a-CP_x (Fig. 1 (d)), the dangling bond is less associated with typical structural defects than in FL-CP_x similarly to what applies for the pair of materials a-CN_x and FL-CN_x, but the situation is closely related to bond rotations/polarization induced by the incorporation of P-atoms. At the starting point of the simulations the a-C model systems consist of randomly interconnected pieces of graphene sheets and upon relaxation they evolve to (random) mix of mostly sp^2/sp^3-coordinated C networks in which dangling bonds form (Fig. 1(e)).

Table 1 shows the PW91 energy costs ΔE_{coh} for a dangling bond matching each of the relaxed structures displayed in Fig. 1. For FL-CN_x and FL-CP_x not only the lowest ΔE_{coh} (corresponding to Fig. 1a and 1c), but intervals of energy costs for dangling bond formation are reported. This is due to the fact that, in FL compounds, there is larger diversity of coexisting defects leading to a dangling bond (pyridine-like defects, pentagons, tetragons, cross-linkages, etc.). Thus, FL structures with higher cost for a dangling bond are taken into account in Table 1, but they are not displayed and explicitly considered in the present work since they were analyzed elsewhere [13, 14] and their occurrence agrees with the discussion conducted here.

In contrast to the situation in FL compounds, in their amorphous counterparts the dangling bonds after relaxation do not exhibit significant structural/geometrical diversity within each of these

systems. Thus, the energy costs for introducing of a dangling bond in a-CN_x, a-CP_x, and a-C (Fig. 1b, 1d, and 1e) are represented by single energy values in Table 1.

Table 1. *PW91 energy costs ΔE_{coh} for introducing a single dangling bond in each of the compounds of interest: FL-CP_x, a-CP_x, FL-CN_x, a-CN_x, and a-C. $\Delta E_{coh} = E_{coh}$ (model system with a dangling bond) - E_{coh} (analogous model system, but without dangling bonds).*

Compound	ΔE_{coh}, eV
FL-CN_x	1.34 – 1.39
a-CN_x	0.59
FL-CP_x	0.62 – 1.04
a-CP_x	0.55
a-C	0.47

As seen from Table 1, the energy cost for formation of a dangling bond is markedly higher in FL solid materials than in their amorphous counterparts. This is most pronounced in FL-CN_x for which the energy cost of a dangling bond is 0.7-0.8 eV higher than in a-CN_x suggesting much lower occurrence of dangling bonds in FL-CN_x. For the pair of FL and amorphous phosphorus-carbide materials, the difference between the two structures is less pronounced; only 0.1-0.5 eV higher than in a-CP_x. Yet, such a difference in energy costs is considerably larger than the thermal energy at growth environment temperatures for the considered carbon-based compounds which is ~ 0.06 eV giving credibility of the prediction for much lower occurrence of dangling bonds in FL-CP_x than in a-CP_x. Finally, a-C appears as the material with lowest energy cost for formation of a dangling bond suggestive for highest occurrence of dangling bonds. The theoretical results presented in Table 1 also show that:

i) Within the family of the solid FL materials, FL-CN_x exhibits 0.35 – 0.72 eV higher energy cost for dangling bonds than FL-CP_x. However, FL-CP_x still shows higher energy cost for dangling bonds than all the amorphous compounds considered here: the energy cost for a dangling bond in FL-CP_x is up till ~ 0.5 eV higher than in a-CN_x, which is the amorphous material studied in this work with highest cost of dangling bonds;

ii) The differences in the energy cost of dangling bonds in the amorphous compounds are not pronounced. The a-CN_x is associated with the lowest and a-C with the highest occurrence of dangling bonds;

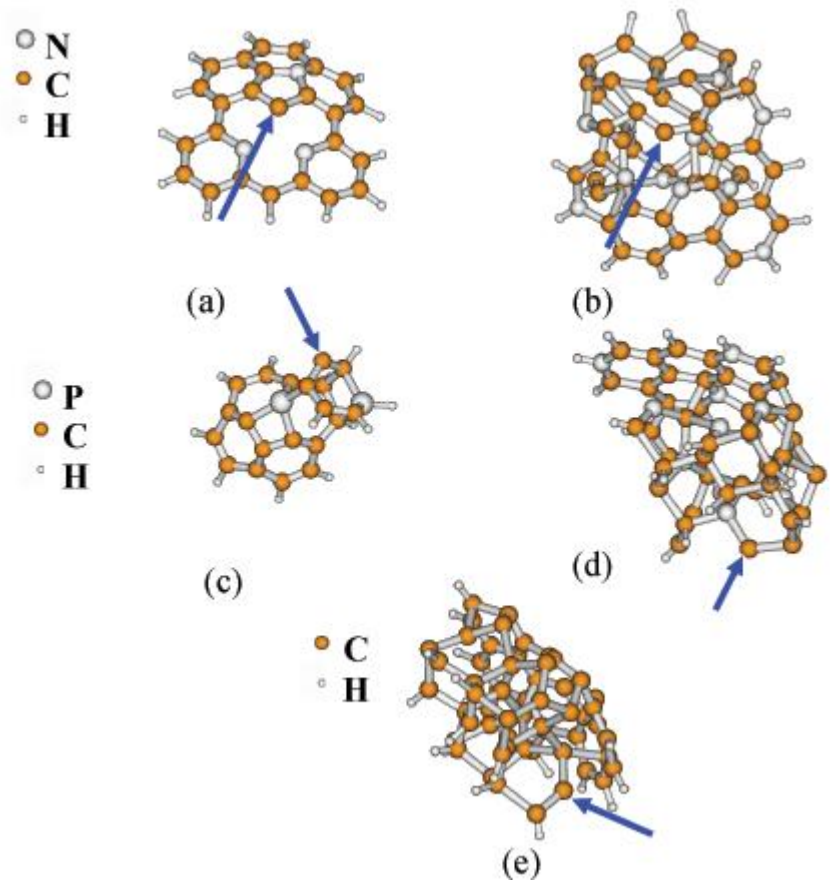

Figure 1: *Relaxed model systems containing a defect leading to a dangling bond (with lowest energy cost for each of the compounds): (a) a curved graphene plane containing a pyridine-like defect in FL-CN_x; (b) a dangling bond in amorphous a-CN_x; (c) a dangling bond occurring in a stable cage-like configuration which is emblematic for FL-CP_x; (d) a-CP_x with a dangling bond; (e) amorphous carbon (a-C) model system containing a dangling bond. The arrows indicate the location of the dangling bonds.*

The theoretical results reported above can be explained in terms of structural order/disorder of the compounds. Both FL-CN_x and FL-CP_x, although not (strictly) periodic systems, are to a large extent graphene conformations. In such highly ordered systems the defect/dangling bond formation have high energy cost. However, due to the P-atom bonding properties (its lower electronegativity than N, and its preference for tetrahedral coordination) at equal concentrations of P-atoms in FL-CP_x and N atoms in FL-CN_x, FL-CP_x contains more defects and exhibits higher graphene plane curvature than FL-CN_x. In FL-CP_x the graphene planes are even strongly inter-locked as suggested by both theoretical [2, 6] and experimental [5, 8] evidences. These structural features of FL-CP_x also correspond to more disorder, hence lowering the cost for introducing defects leading to dangling bonds. The same situation applies, although to a lesser extent since they are already intended as strongly disordered, to the amorphous compounds of CN_x and CP_x.

3.2 Experimental results

CN_x and CP_x films were deposited onto quartz substrates by magnetron sputtering, as described in Ref. [13, 14]. The target composition, substrate temperature, and the gas mixture in the plasma were chosen to obtain amorphous or FL compounds [8, 13, 14]. The apparatus designed and constructed for measurement of humidity adsorption has been described previously [13, 14]. It consists of a vacuum chamber housing a Piezoelectric Crystal Monitor. The chamber is evacuated to 10^{-8} Torr and then water is introduced trough a leak valve to pressures of up to 20 mTorr (equivalent to 50% RH at 50 ^{0}C). The mass of water adsorbed on the surface of the quartz crystal was calculated using the Sauerbrey equation $\Delta f = - C\Delta m$, where Δf and Δm are the change of frequency and the adsorbed mass of water, respectively [13].

Figure 2 compares experimental values of water adsorption with the theoretically calculated values obtained for the energy cost of dangling bond formation. The error bars, displayed for FL compounds only, indicate the variation of ΔE_{coh} due to the diversity of defects

in these systems (see Table 1). The decrease of water adsorption on different FL and amorphous films correlates very well with the predicted reduction of dangling bonds on the film surfaces.

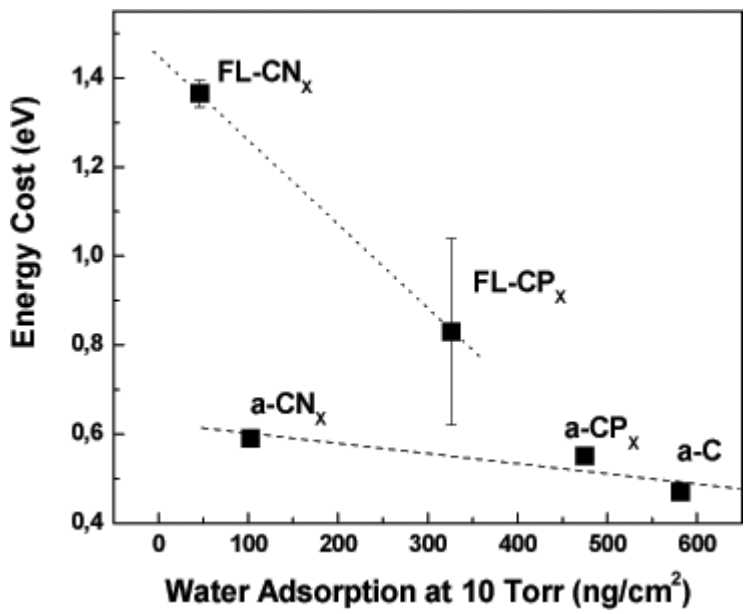

***Figure 2**: Correlation of energy cost (equals to ΔE_{coh} in theoretical calculations) versus experimental water adsorption on amorphous and fullerene-like carbon-based compounds. Both dashed lines are only for guiding the eyes. During the experiments the surfaces were held at 50 ^{0}C inside a vacuum-pumped chamber with 10 mTorr of water pressure (equivalent to 25% RH).*

Higher energy cost of dangling bonds and their lower occurrence for a given compound are perceived as a technological advantage since lower density of dangling bonds on the surface of the material is related to more pronounced chemical inertness and also to lower water uptake.

4. CONCLUSIONS

First-principles calculations reveal that the energy cost for formation of dangling bonds in FL-CN$_x$ and FL-CP$_x$ is considerably higher than for their amorphous counterparts: a-CN$_x$ and a-CP$_x$, being the lowest in pure a-C. FL-CN$_x$ exhibits the markedly highest energy cost for dangling bond formation. During synthetic growth of the FL thin films, this effectively leads to a lower occurrence of dangling bonds and, consequently, to an improved chemical inertness with a reduced water uptake. Experimental measurements of water uptake on the surface of all five

compounds considered in this work confirm these theoretical predictions. Technological advantages are predicted for novel carbon-based FL thin solid films when compared to the corresponding amorphous films.

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