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Density Functional Based Tight Binding (DFTB) Study on the Thermal Evolution of Amorphous Carbon

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Abstract

Density functional based tight binding (DFTB) model is employed to study the sp^3-to-sp^2 transformation of diamond-like carbon at elevated temperatures. The understanding could lead to the direct-growth of graphene on a wide variety of substrates.

Keywords

Diamond-Like Carbon, Graphene, DFTB, Fiber Structure, Cluster, Molecular Dynamics

1. Introduction

Graphene is an allotrope of carbon consisting of a single layer of carbon atoms connected by sp^2 hybridized bonds [1] [2]. It has been investigated due to its unique electrical, thermal and mechanical properties [3]-[5]. An important application of graphene is as a promising replacement for tin-doped indium oxide (ITO) as the next-generation large-area transparent conducting electrodes (TCE) [6] [7]. A particular advantage of using graphene (assuming defect-free) is its unique two-dimensional electron gas properties at room temperature, leading to exceptionally high mobility [7]. A common method to grow large area graphene is by chemical vapor deposition (CVD) [8]. However, such method requires deposition temperature of approximately 1000˚C [9]. Furthermore, the produced graphene film needs to be transferred to the substrate of interest. Research is on-going to circumvent these limitations and a recent approach has been to investigate graphene growth from amorphous carbon (a-C) [10]. Understanding the graphitization mechanism of a-C is therefore essential to produce quality graphene.

In 2013, Barreiro *et al.* reported the growth of graphene from catalyst-free a-C by current-induced annealing [11]. They observed the structural evolution both with *in-situ* transmission electron microscopy and with mole-

cular dynamics simulation [11]; and a-C clusters were simulated as part of the work. An intriguing observation was the formation of long fibers stem from the clusters at elevated temperature. These clusters with fibers acted as carbon source and were able to heal up defects on a graphene sheet [11]. DFTB method has successfully been used to model and predict properties of carbon allotropes [12]-[14]. DFTB is based on Density Functional Theory but uses empirical approximations to reduce computational time [15]. Formalism of DFTB can be found in [12] [15] [16]. In this work, we performed molecular simulation using DFTB method on a-C cluster to further understand the transformation dynamics of sp^3 to sp^2, as well as the origin and processes by which the carbonous fibers emerged.

2. Simulation Details

An amorphous carbon cluster with diameter 1 nm was constructed using the Materials Visualizer within the Materials Studio environment [17], as shown in **Figure 1**. The molecular dynamics simulation was performed using the DFTB+™ which includes the Van der Waals interaction. The dynamics were performed at temperatures of 300 K, 723 K (TFT annealing temperature), 1200 K, 1500 K and 2000 K. Duration of each dynamical simulation was 10 ps with 1 fs time-step to satisfy the Verlet assumption. Geometry optimization (structural relaxation) was performed prior to the dynamics simulation. Canonical Nose-Hoover isothermal constrained ensemble was used to supply heat to the system at constant volume and temperature. The molecular structures were optimized prior to any dynamical simulation.

3. Results and Discussion

The DFTB dynamics simulation on the a-C cluster revealed a progressive increase in the population of sp^2 sites as the temperature was raised in a stepwise manner. **Figure 2** shows the difference in the sp^3 population between 300 K and 2000 K. There were only two sp^3 sites remained in the cluster at the end of 2000 K annealing which is consistent with the work reported in Ref. [11]. In the absence of substrate effect the free-standing a-C cluster also expectedly evolved into a fullerene-like structure instead of graphitic layer [11]. Stone-Wales defect commonly found on graphene sheet [18] can also be seen in the outer surface of the annealed cluster. 5- and 7-member rings were observed on the outer surface of the cluster. Further study will focus on ways to minimize the defects during transformation and to promote formation of 6-member carbon rings.

This work provided detailed insight into the process by which a tetrahedral sp^3 transformed into a planar sp^2 at elevated temperature. The bond connecting the carbon atom on top of the tetrahedral and the center atom (indicated by an "X") weakened and eventually dissociates as the bond length increases, as illustrated in **Figure 3**.

Highly reactive carbonous "fiber structures" responsible for graphene formation and defect healing has been reported [11] but no detail was given as to how they developed. This work shed some light on the process. **Figure 4** shows two snapshots taken from the same dynamic trajectory at 1200 K. The cyan colored box highlights

1 nm
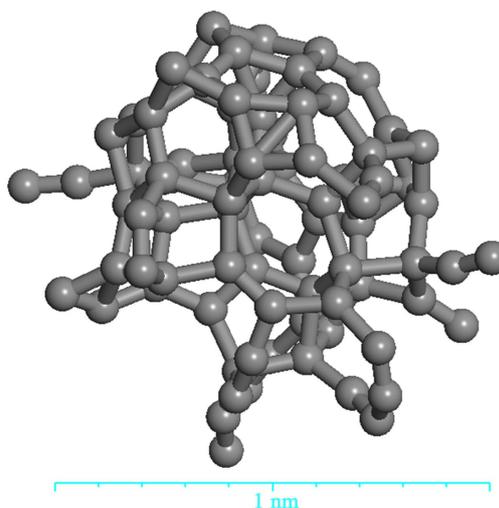
Figure 1. The constructed a-C cluster consists of a mixture of sp^3 and sp^2 sites.

(a)   (b)
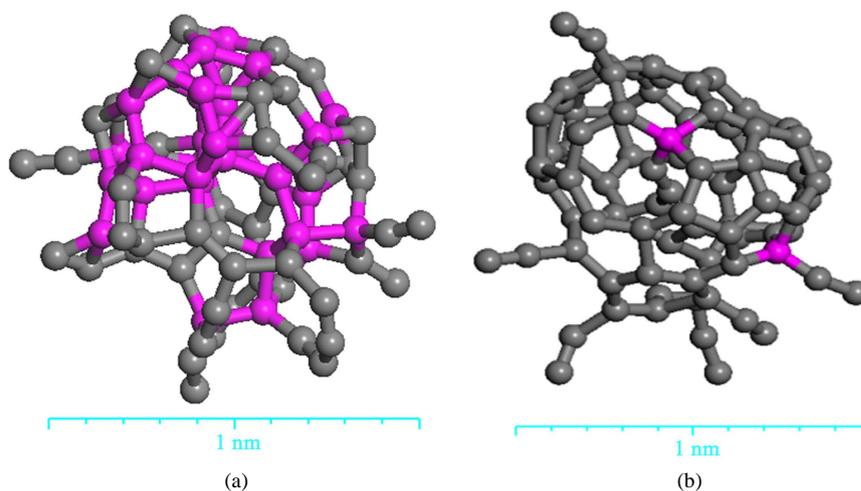
Figure 2. Population of sp^3 sites (magenta colored) on the a-C cluster at (a) 300 K and (b) 2000 K.
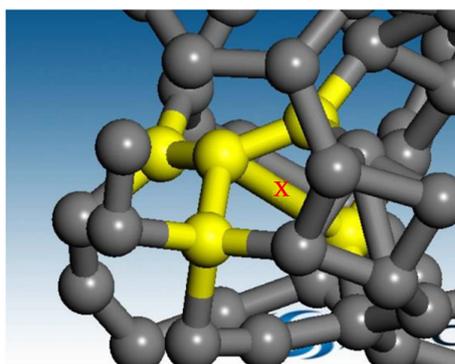
Figure 3. The sp^3-sp^2 transformation at elevated temperatures: weakening and dissociation of the C-C bond as indicated by an "X".

(a)   (b)
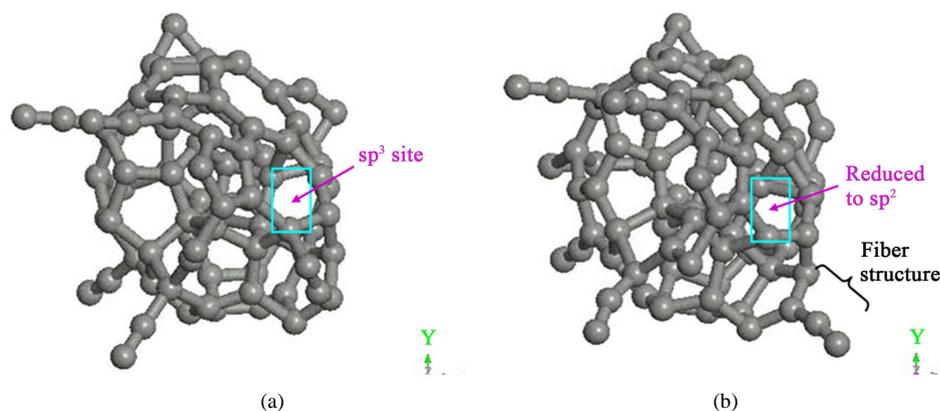
Figure 4. Two snapshots taken from the same trajectory at 1200 K. The enclosed cyan colored box shows (a) before and (b) after the sp^3 bond was transformed into sp^2, giving rise to a 7-member sp^2 hybridized carbon ring and a "fiber structure".

the dissociation of a sp^3 site occurred at time equals 6.77 ps, leading to a simultaneous emergence of a 7-member ring and a "fiber structure". Videos are available as ancillary files (**1**, **2**, **3**, and **4**) showing the molecular dynamics simulations performed at temperatures of 300 K, 723 K, 1200 K, and 2000 K, respectively. At room temperature (300 K), despite there were activities of bond formations and dissociations, the overall ratio of sp^3/sp^2 remained almost stable with virtually no formation of fiber structure. This is consistent with real-life

observation that amorphous carbon is stable at room temperature. As expected, there was notable increase in the amplitudes of vibrations with increasing temperature. The formation of carbonous fiber structures could be observed at 1200 K and this provides visual insights into the processes by which the fiber structures were being formed. At 2000 K, the carbon cluster transformed into a fullerene-like structure, consisting primarily of sp^2 sites.

4. Conclusion

A molecular simulation based on DFTB was performed on a-C cluster to investigate the sp^3-sp^2 transformation process in detail including the formation of highly reactive carbonous fiber structure. Understanding of such processes will enable the direct deposition of graphene from a-C on a wide variety of substrates, which is essential for the mass-production of cost-effective graphene-based transparent electrode.

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