MOLECULAR DYNAMICS SIMULATIONS OF AMORPHOUS CARBON STRUCTURES

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Abstract

The formation of different kinds of carbon structures have been studied by means of molecular dynamics simulations. Using this methods the amorphous structures were usually generated by quenching from different liquid configurations so far. It is not so common experimental method for the preparation of amorphous carbon. We have developed a tight-binding molecular dynamics approach for simulating the the growing procedure of the amorphous carbon structure. Our computer simulation method was similar to the atom-by-atom deposition on a substrate. The amorphous structures with fivefold, sixfold and sevenfold rings were obtained on diamond (111) surface.

I. INTRODUCTION

Different methods are used for preparations of a-C films. The ability of carbon atoms to have sp3, sp2 and sp bonding configuration leads to a large variation in structure and in electronic properties. In amorphous form of carbon one of the most important parameter is the sp2:sp3 ratio which basically determines the electronic density of states. Considering

the conductivity which is in a connection with atomic and electronic structure, these various methods produce a wide range for macroscopic parameters of a-C film.

Several electron and neutron diffraction measurements were employed on a-C sample in order to determine the atomic arrangement. The first well-know experiment was carried out on an evaporated sample using electron diffraction by a Japanese group [1]. On base of the measured data they proposed a microcrystalline model of amorphous carbon structure, consisting domains graphitic and diamond-like regions. A neutron diffraction was employed on anomalous a-C sample [2] in order to determine the atomic arrangement and to decide whether the structure has a temperature dependence or not [3]. The sample was prepared by arc-evaporation of graphite rod under a pressure of 10-6 atm.

II. STRUCTURAL MODELLING

There are two main possibilities for structural modelling. The first one is the Monte Carlo (MC) type method. Metropolis et al. were the pioneers of this kind of computer simulations [4]. Recently a new version of this method - the so-called Reverse Monte Carlo simulation - has been developed by McGreevy and Pusztai [5], which is convenient for investigation of amorphous materials. It is based on the results of diffraction measurements. The algorithm is quite simple and very similar to standard Metropolis Monte Carlo technique [4]. The method starts with an initial three dimensional configuration. A new configuration is generated by a random displacement of a randomly chosen particle. The new radial distribution function g(r) and/or structure factor S(Q) is calculated. In the following step g(r) and/or S(Q) are compared with the experimental result for the system that is being modelled using a standard chi test. If chi2 ¡ chi1 the new configuration is accepted, otherwise it is accepted with a probability that follows a normal distribution. If the new configuration is accepted it becomes the starting configuration, otherwise the old configuration is retained. This process is then repeated until chi converges in g(r) and/or S(Q) level i.e. we reach equilibrium. This method was applied for constructing large a-C and a-Si models [6,7].

Second, the Molecular Dynamics (MD) is an other useful tool for describing non-crystalline systems when the use of the traditional techniques is difficult. The Newton equations of motion can be solved for a small time interval if the interaction potential and the position of N particles are given for the last points of time. To integrate the MD equations of motion the Verlet algorithm [8] is usually used with time step equal to about a picosecond. The new position of a given particle is:

$$\vec{\mathbf{r}}(t + \Delta t) = \vec{\mathbf{r}}(t) + \vec{\mathbf{v}}(t)\Delta t + \frac{1}{2}\vec{\mathbf{a}}(t)\Delta t^2 + \mathcal{O}(\Delta t^3) \tag{1}$$

The motion of the particles is followed by repeating this procedure. By MD the dynamics of the systems can be followed, therefore it is useful to model fundamental phenomena like growth from vapor phase to a surface. In MC and MD cases the crucial point is the applied local potential. In our calculations MD simulation was performed with the tight-binding Hamiltonian of Xu, Wang, Chan and Ho [9] for carbon systems. All the parameters and functions of this method were fitted to the results of local density functional calculations for graphite, diamond and linear chains.

III. MODELS

We consider three types of structural modelling that have been applied to amorphous carbon. Beeman et al. constructed four models containing different numbers of carbon atoms and proportions of sp2 and sp3 sites [10]. These random network models contain 1120, 340, 356, and 519 carbon atoms. Odd membered rings can be found in each structure. Galli and her co-workers constructed an amorphous carbon structure with a computer simulation [11]. They carried out a first principle Molecular Dinamics simulation for 54 atoms using 2.0 g/cm3 of macroscopic density. The interatomic potential was constructed from the electronic ground state treated with density-functional techniques. The model was obtained by rapid cooling liquid carbon. Similar method was used by Stephan and his co-workers [12] in order to generate a-C models having different density in a range of 2.0-3.52 g/cm3. They applied a semiempirical density-functional approach. The models contained 128 carbon atoms.

IV. METHOD

In our case we simulated the growing procedure of the amorphous carbon structure, on diamond (111) surface. The formation of amorphous carbon structures on a substrate was simulated similarly to atom-by-atom deposition. Our motivation is the following: It is well-known that carbon usually is grown as amorphous film by vapor-growth technique and it is not so easy to prepare from liquid phase using rapid quenching.

Periodic boundary conditions were adopted to avoid surface effects. In our computer experiment there were three different sets of carbon atoms. The first one was the atomic current of carbon atoms forwarded to the target of a (111) diamond surface. The second set was the upper part of the substrate, which contained atoms at 0 K of initial temperature. The atoms of third set formed the bottom part of the substrate. These atoms were fixed at their ideal lattice sites.

a./ During the procedure a carbon atom started to move forward to the target surface. Its initial x, y coordinates in the current were randomly determined. As the cut off distance of our tight-binding potential was 2.6 A , to speed up the simulation, the initial z coordinates in the current were placed 3.6 A over the target. The initial velocities of the atoms in the current were randomly determined.

b./ If the particle arrived into the critical distance to the substrate, which was a little bit greater than the bond distance, procedure a./ was started again. In the meantime the old particle became the part of the bonded carbons, but it was kept moving. To simulate inelastic collision by the target surface the velocity of the current atom was decreased in each MD step by a given factor.

V. RESULTS AND DISCUSSIONS

In this paragraph, results of a-C film growth simulation is presented for two different volumes of the systems. The total simulation time of the atom-by-atom deposition was usually 5-10 psec. In this case the time step was equal to 0.5 femtosecond. Figure 1. shows the final structure of the first simulation in the unit cell. The current came from the Z direction randomly. The kinetic energy of incoming atoms were relative low, 1.29 eV. Figure 2. displays a model where the kinetic energy was 9.7 eV. This energy is very close to the value used during the a-C sample preparation. Both cases the substrate consist of 80 carbon atoms. The structure of the first model was a chain like amorphous structure while the second one contains more sp2 and sp3 atomic sites and rings. It means that the higher incoming energy produces less chains and more rings. Similar experimental results have been recently published [13.14].

Second we constructed larger models as can be seen in Fig. 3. The substrate contains 120 carbon atoms, and the average initial kinetic energy of incoming carbon atoms are also 9.7 eV. 196 carbon atoms forms the amorphous part of the model. In Figure 4. we present the calculated radial distribution function g(r), which is close to our experimental result measured by neutron diffraction. Figure 5. shows the angular distribution function.

VI. OUTLOOK

Our molecular dynamics simulation consist of atomic substrate which is at T=0 temperature. Applying Nose-Hoover thermostat (NH) [13,14] the temperature of the equilibrium system can be controlled and NH dynamics produces real fluctuations in the state variables. This NH is useful in understanding the role of substrate temperature for growth of amorphous carbon film.

In summary we have presented the formation of amorphous carbon structures under various simulation conditions. On the diamond surface deposition computer experiment the final structures were amorphous structures with fivefold, sixfold and sevenfold membered rings.

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FIGURE CAPTIONS

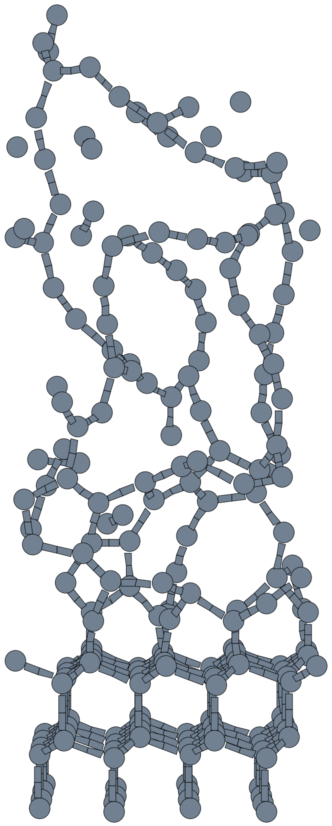

Figure 1. The final structure in the unit cell of the atom-by-atom deposition. The substrate of 0 K are at the bottom of the Figure. The kinetic energy of incoming atoms were relative low, 1.29 eV. This model is a chain like amorphous structure.

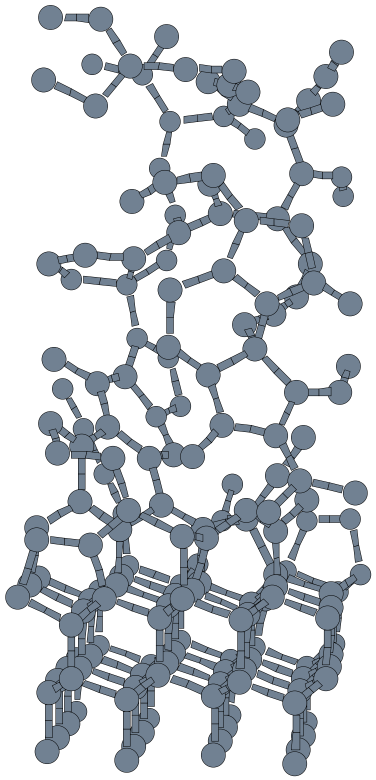

Figure 2. The second structure. The kinetic energy of incoming atoms were 9.7 eV.

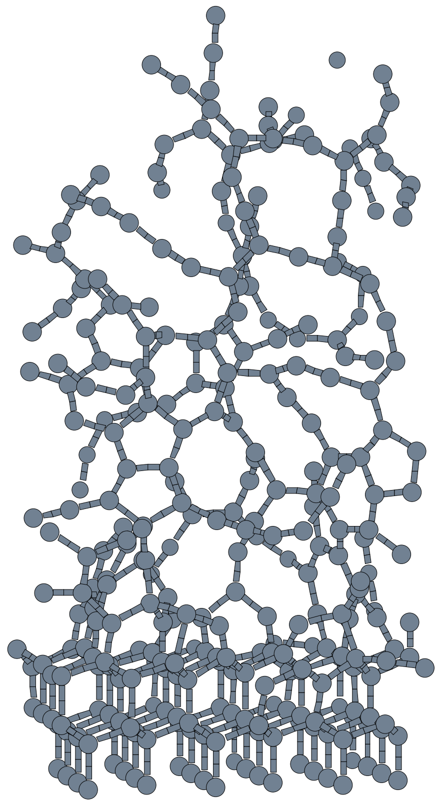

Figure 3. The final structure in the unit cell of the simulation for a large amorphous carbon model. The kinetic energy of incoming atoms were 9.7 eV. It contains 316 carbon atoms.

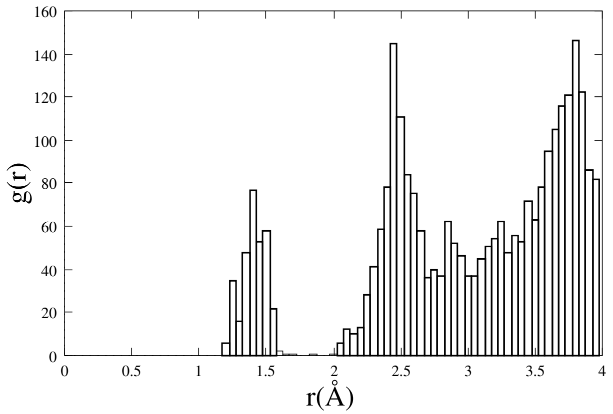

Figure 4. The radial distribution function for the large structure.

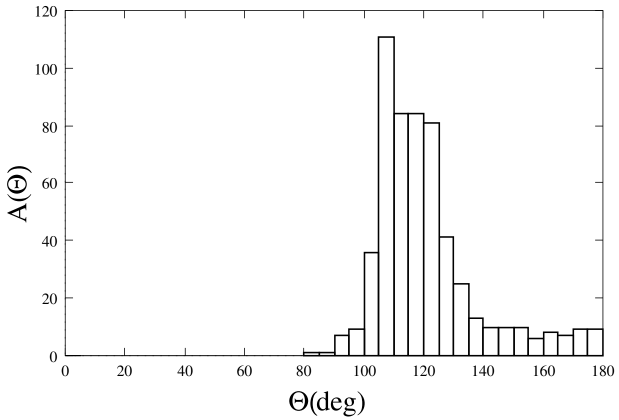

Figure 5. The angular distribution function of the large model of the atom-by-atom deposition.