Growth of amorphous semiconductors: tight-binding molecular dynamics study

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Abstract

In our computer simulation the preparation process was similar to the atom-by-atom deposition onto a substrate which is a standard procedure to prepare amorphous semicondutors. For the calculation of the interactions between carbon and silicon atoms, tight-binding potentials were used. The Newton equations of motion were solved by the Verlet algorithm. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Amorphous semiconductors (a-C, a-Si) attract continuing attention because of their technological applications and fundamental interest as well. The determination of the microstructure of these materials is important for their electronic properties. Earlier several electron and neutron diffraction measurements were employed on such samples to get information about atomic arrangement ([1–5] for a-C, [6–10] for a-Si). In the last decade the research on construction of realistic model structures for amorphous materials using computer simulations [11–17] has increased.

There are two main possibilities for computer simulation of amorphous structures. The first one is the traditional Monte Carlo (MC) method. Metropolis et al. were the pioneers of this kind of computer simulation [18]. This algorithm was used for preparing the well-known WWW a-Si models [11]. A new version of this method – so-called Reverse Monte Carlo simulation – has been developed and applied for constructing large a-Si models [12].

An alternative is to use the molecular dynamics (MD) for describing non-crystalline systems [13–16]. Galli and her co-workers constructed an a-C structure by computer simulation [13]. They carried out a first principle MD simulation for 54 atoms using 2.0 g/cm^3 macroscopic density. The inter-atomic potential was constructed from the electronic ground state treated with density-functional techniques. The model was obtained by rapid cooling of liquid carbon. Marks et al. [14] applied this method to construct a tetrahedral a-C network. A similar method was used by Stephan and his co-workers [15] to generate a-C models having densities in the range of 2.0–3.52 g/cm^3. They applied a semi-empirical density-functional approach. These larger models contained 128 carbon atoms. Recently a Japanese group generated a-Si models by rapid quenching using different quenching rates [16].

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2. Method

We simulated the growth procedure of the amorphous carbon and silicon structures on a diamond and silicon (1 1 1) surface, respectively. Our motivation was the following: amorphous semiconductors usually are grown by vapor-growth technique and it is not so easy to prepare from the liquid phase using rapid quenching. The formation of amorphous films on a substrate was simulated similarly to atom-by-atom deposition.

In MC and MD cases the crucial point is the applied local potential. The MD simulation was performed with the tight-binding Hamiltonian of Xu et al. [19] for carbon systems and Kwon et al. [20] for silicon atoms. All the parameters and functions of these methods were fitted to the results of local density functional calculations. The first Hamiltonian was successfully applied for preparation of fullerenes [21] and for structural model of a-C surface [22]. To avoid surface effects periodic boundary conditions in x and y directions were adopted. To integrate the MD equations of motion the Verlet algorithm was used with a time step equal to about a femtosecond.

There were three different sets of atoms in our computer experiment . The first one was the atomic current toward the target of a (1 1 1) surface. The second set was the upper part of the substrate, which contained atoms at 0 K initial temperature but they could move. The atoms of the third set formed the bottom part of the substrate. These atoms were fixed at their ideal lattice sites to stabilize the substrate.

During the growth procedure an atom started to move toward the target surface. Its initial x, y coordinates and the initial velocities were randomly distributed. As the cut-off distance of our tight-binding potential was 2.6 Å for carbon, to speed up the simulation, the initial z coordinates in the current were placed at 3.6 Å over the target. When the particle arrived within the critical distance at the substrate, which was greater than the bond distance, the particle became part of the bonded atoms. To simulate inelastic collision by the target surface the velocity of the current atoms were decreased in each MD step by a given factor
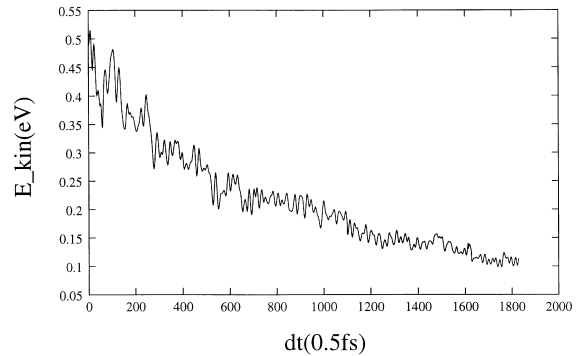

Fig. 1. The average kinetic energy of an atom belonging to the film in function of the time during the cooling procedure. The curve is near exponential.

which was <1. It was a simple model of energy dissipation on the substrate surface.

A test of this simple model was carried out on the following way: on a substrate of 96 moving carbon atoms keeping on room temperature permanently a film was grown during 9500 MD steps of 0.5 fs. The temperature (average kinetic energy) of incoming carbon atoms was 50 000 K. Finally the film contained 74 atoms. After stopping growing the structure was released to obtain detailed information about the cooling procedure. The average kinetic energy of an atom belonging to the film is shown in Fig. 1. The curve is near exponental in function of the time which means that our simple model of energy dissipation is relatively good interpretation of the phenomena.

3. Results

The results of a-C film growth simulation are presented for two different cases. The total simulation time of the atom-by-atom deposition was usually 5–10 ps and the time step was equal to 0.5 fs. A typical run is a month on a HP work station for a model.

Fig. 2 shows the final structure of the first simulation in the unit cell. The random current came from the z direction. The kinetic energy of incoming atoms was relatively low (6.5 eV). Fig. 3 displays a model where the kinetic energy was 13 eV. This energy is close to the value used during
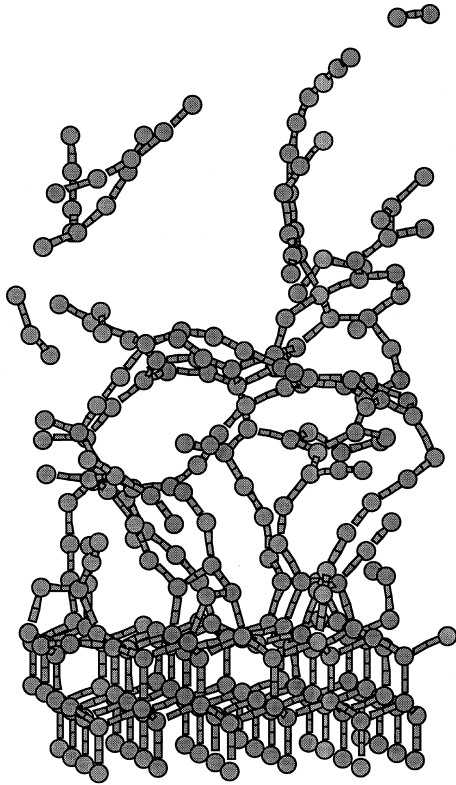
Fig. 2. The final structure in the unit cell of the atom-by-atom deposition. The substrate at 0 K is at the bottom of the figure. The kinetic energy of the incoming atoms was relative low (6.5 eV). This model yields a chain like amorphous structure. It contains 286 carbon atoms including 120 substrate atoms.
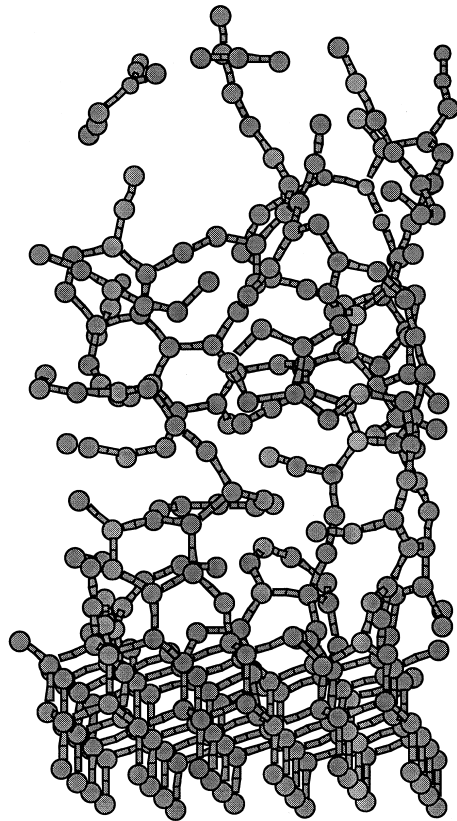

Fig. 3. The second structure. The average kinetic energy of incoming atoms were 13 eV. It contains 323 carbon atoms.

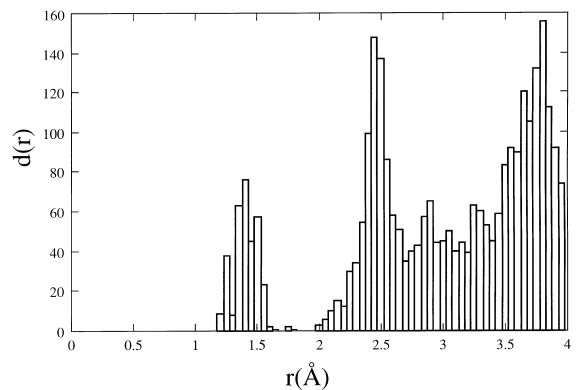Fig. 4. The radial distribution function for the model where the kinetic energy was 13 eV.

the a-C sample preparation. In both cases the substrate consist of 120 carbon atoms. The structure of the first model was a chain like amorphous structure while the second one contains more sp^2 and sp^3 atomic sites and rings. It means that the higher incoming energy produces fewer chains and more rings. Similar experimental results have been recently published [23,24]. The calculated radial distribution function $d(r)$ of the second model is shown in Fig. 4. RDF exhibits quantitative agreement with a number of experimental result measured by diffraction mentioned above within the interval of 1–4 Å.

We have few preliminary runs for a-Si growth as well. The first surprising result is that the network produced has a number of three membered rings i.e., triangles are present in the atomic ar-

rangement. Most of the theoretical models for a-Si do not contain such structure. Reverse MC simulation generating atomic configurations that are

consistent with the experimental structure factor has similar conclusions [12].

4. Conclusion

A tight-binding MD computer code has been developed to simulate the preparation procedure of amorphous semiconductor which are usually grown by vapor-growth technique. The results obtained shows that the higher incoming energy of carbon atoms produces less chains and more rings in the structure which is in good agreement with experiments.

Acknowledgements

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