

Hybrid simulation of plasma synthesis of linear-chain carbon on a semiconductor substrate

*E.A. Buntov**, *A.I. Matitsev*

Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russia

**e.a.buntov@urfu.ru*

Abstract. The paper presents the results of modeling the plasma synthesis of a carbon coating using ion stimulation. The hybrid quantum-classical method of molecular dynamics was used for the work. The effect of ion stimulation on the growth of a carbon film, as well as on the ratio of hybridization of carbon atoms in its composition, has been studied. Calculations have shown that ion stimulation with energies up to 20 eV increases the number of adsorbed carbon atoms. It was found that the content of sp^1 , sp^2 and sp^3 carbon is maximum at argon energies of 40, 70, 90 eV, respectively.

Keywords: linear-chain carbon, molecular dynamics, hybrid quantum-classical modeling.

1. Introduction

Carbon materials are one of the promising areas of research in the field of solid state physics and chemistry. The reason for the universality of carbon materials is the ability of carbon to hybridize various types of electron orbitals: sp^1 (carbyne), sp^2 (graphite), and sp^3 (diamond). Linear chain carbon (LCC) is a one-dimensional modification of carbon with sp^1 hybridization. Carbon chains can be alternating single and triple bonds (polyynes) $(-C\equiv C-)_n$ or only double bonds (cumulenes) $(=C=C=)_n$, while the chains will show either semiconductors (polyynes) or metallic (cumulene) properties [1].

Linear chain carbon (LCC) was synthesized several decades ago [2] and has already found several applications due to its unique mechanical and electrical characteristics [3]. According to studies, LCC materials have ultrahigh mechanical strength (greater than that of diamond) [4]. Carbyne has excellent biocompatibility; for example, LCC coatings are already used for medical implants [5]. The presence of unique optical properties, namely, their dependence on the chain length [6–8], gives great scope for the application of LCC coatings in nanooptics and nanophotonics [9]. In addition, many studies are devoted to the characteristics of carbon chains encapsulated in carbon nanotubes [10].

One of the known methods for obtaining thin LCC films is ion-plasma synthesis [11]. However, the synthesis of a pure carbyne crystal or sufficiently long carbon chains is still a complex technological problem. The reason for this problem is the extreme instability and reactivity of carbon chains, due to which the maximum predicted polyyne chain length is 48 atoms [12].

One of the options for studying the processes occurring during the synthesis is modeling by the method of molecular dynamics. For example, the synthesis and properties of amorphous carbon, graphene, and other carbon modifications have already been studied quite well using this method [13–16]. Thus, molecular dynamics can be considered a promising tool for studying the synthesis of LCC films. At the same time, classical molecular dynamics does not take into account many processes at the plasma-solid interface, which does not allow obtaining sufficiently accurate results. More accurate is the combined quantum-classical method of molecular dynamics (QM/MM - quantum mechanics/molecular mechanics), which combines the strengths of ab-initio QM calculations (accuracy) and MM approaches (speed).

The purpose of this work is to simulate the synthesis of a carbon film by the method of hybrid quantum-classical molecular dynamics. In the framework of the work, the effect of ion stimulation on the composition of a carbon film was theoretically studied.

2. Methods

Within the framework of the model (Fig.1), various carbon molecules were deposited on a Si(100) substrate with dimensions of $22 \times 22 \times 38 \text{ (\AA)}^3$ with a given probability of occurrence ($\text{C}_2\text{H}_2 - 37.3\%$, $\text{C}_2\text{H} - 31.1\%$, $\text{C}_4\text{H}_2 - 18.5\%$, $\text{C}_6\text{H}_2 - 6.2\%$, $\text{C}_2 - 3.1\%$, $\text{CH} - 1.9\%$, $\text{C} - 1.9\%$). These probabilities reflect the relative flux density of particles in plasma [17]. The particle energy was 1 eV, which, on average, corresponds to the energy of a low-temperature plasma. The substrate consisted of three layers (Fig.2): fixed (three atomic layers), kept at a temperature of 300 K (nine atomic layers), and free. To saturate broken silicon bonds, a monatomic layer of hydrogen was added to the underside of the substrate. For temperature control, the Berendsen algorithm was used. Besides, argon was added to the simulation area to simulate ion stimulation, the energy was changed from 10 to 160 eV with a step of 10 eV. The simulation step was chosen to be 0.05 fs to ensure the stability of the system, since hydrogen is used in the simulation, and also to take into account the high-frequency vibrations that occur in the emerging carbon chains. The time of each simulation was 20 ps.

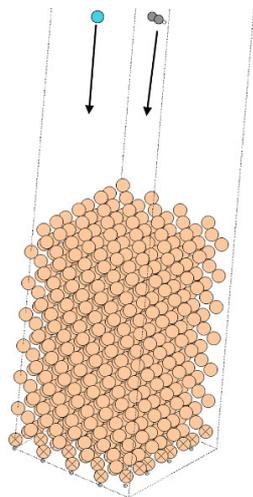


Fig.1. Structural-dynamic model of plasma fusion with ion stimulation.

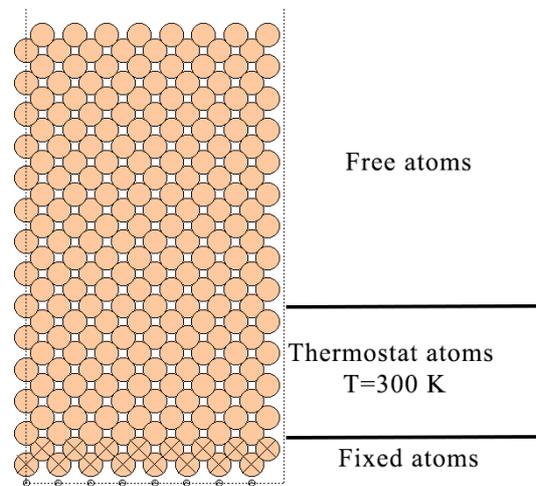


Fig.2. Substrate structure.

In the framework of the hybrid quantum-classical method, the system under study is divided into two subsystems [18]. The first subsystem, where the main processes take place, is described by quantum mechanics (QM), and the second subsystem is described by classical mechanics (MM) (Fig.3). This solution combines the advantages of the two methods, the accuracy of quantum calculations, as well as the speed of calculations and the size of the system, which can be achieved using a system of classical dynamics.

In our work, quantum mechanics calculations were performed using the GPAW package [19] using the PBE exchange-correlation functional. Initial system setup, heating, and imaging were performed using the ASE environment [20]. For calculations of classical mechanics, the LAMMPS package [21] was used, and ReaxFF was used as the potential, which is known to provide an accurate description of carbon nanostructures. This force field potential can reflect the hybridization of bonds in carbon chains, as well as the influence of other members without explicit parameterization.

To implement hybrid computing for the ASE environment, a proprietary module was developed. This module implements an additive electrostatic scheme for coupling subsystems, in which an electrostatic coupling term (E_I) is added to the energies of the subsystems:

$$E_{\text{QMMM}} = E_{\text{QM}} + E_{\text{MM}} + E_I, \quad (1)$$

In this method, in quantum calculations, the rest of the simulation area is described using the force field of a point charge, and the energy of electrostatic binding is equal to [22]:

$$E_I = - \sum_{i=1}^{N_{MM}} q_i \int \frac{n(r)}{|r - \tau_i|} dr + \sum_{i=1}^{N_{MM}} \sum_{\alpha=1}^{N_{QM}} \frac{q_i Z_\alpha}{|R_\alpha - \tau_i|} + E_{NES} \quad (2)$$

where $n(r)$ is the spatial (positive) electron density, Z_α is the atomic number, R_α are the coordinates of atoms in the QM region, ENES describes the remaining non-Coulomb interactions (in this work, the Lennard-Jones potential was used).

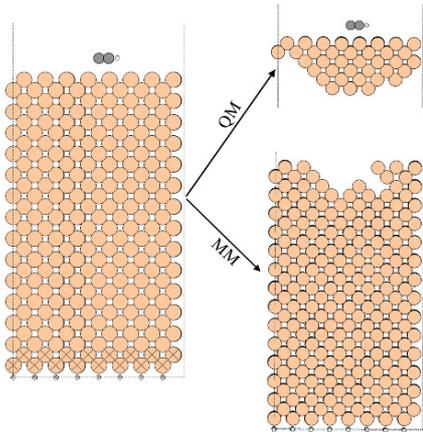


Fig.3. The concept of hybrid quantum-classical modeling.

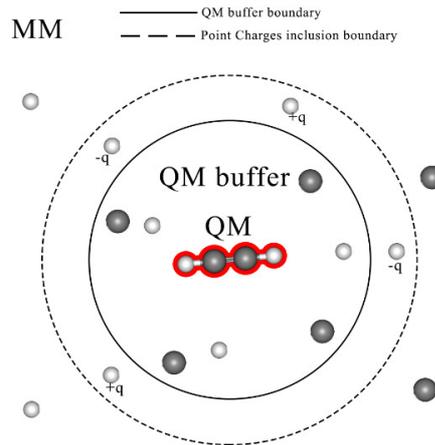


Fig.4. Concept of module for hybrid calculations.

Also in this module, to reduce the error at the boundary of subsystems, a buffer region was implemented, and to speed up calculations, it was decided to use a limited model of point charges. The circuit concept is shown in Fig.4.

3. Result and discussion

Fig.5 shows the dependence of the number of adsorbed carbon atoms on the energy of ion stimulation by argon atoms. As can be seen from the graph, when using ion stimulation with an energy of up to 20 eV, the number of carbon atoms adsorbed on the substrate surface increases. This phenomenon is associated with the destruction of the carbon-hydrogen bond and, thereby, the removal of hydrogen, which prevents further film growth. At the same time, with a further increase in energy above 20 eV, a decrease in the number of adsorbed atoms is observed. The latter phenomenon is associated with the destruction of the carbon-carbon bond, which reduces the number of adsorbed atoms.

To determine the effect of ion stimulation on the carbon hybridization ratio, the coordination number k was calculated. This number is defined as the number of nearest atoms and indicates the state of hybridization, i.e., the coordination number equal to 4, 3 and 2 corresponds to sp^3 , sp^2 and sp^1 hybridizations. The coordination number of an atom depends on the cutoff distance from the nearest neighboring atoms. The cutoff value in this work was set at 2 Å. Since carbon atoms can form bonds both with carbon atoms and with silicon and hydrogen atoms, the coordination number in this work includes C-C, C-H and C-Si bonds.

Fig.6 shows the dependence of the ratio of carbon atoms with different hybridization depending on the ion stimulation energy. As can be seen from the graph, the content of sp^1 , sp^2 , and sp^3 carbon in the film is maximum at argon energies of 40, 70, and 90 eV, respectively. The most interesting point is the region of 40 eV, where the percentage of sp^1 carbon increases by 26% due to a decrease

in the number of sp^2 carbon, which corresponds to the data from [23], where the sp^2 bond breaking energy was 40 eV. At the same time, in the region of 50 eV, a sharp decrease in the sp^1 carbon number to 13% is observed, which also corresponds to the data from the same work, where the sp^1 bond destruction energy was 45 eV. The high amount of sp^3 carbon in the region after 110 eV is mainly due to atoms that have penetrated deep into the substrate, that do not detach argon ions, while at the same time the number of atoms on the surface is significantly reduced.

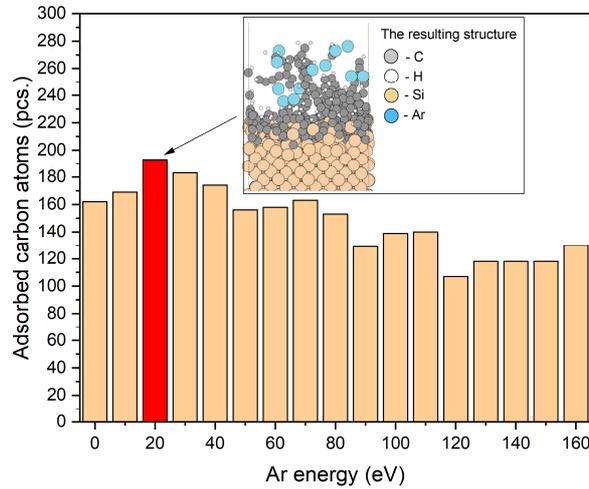


Fig.5. Effect of ion stimulation energy on the number of adsorbed carbon atoms.

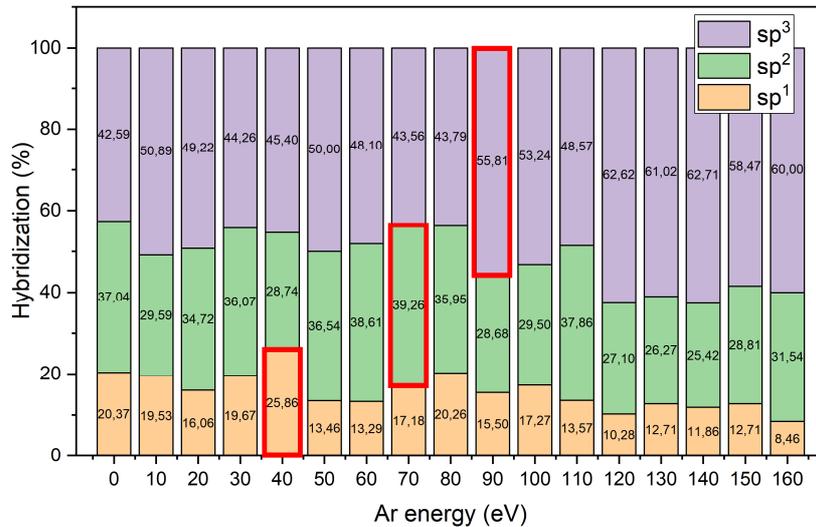


Fig.6. Percentage of carbon with different hybridization depending on Ar energy.

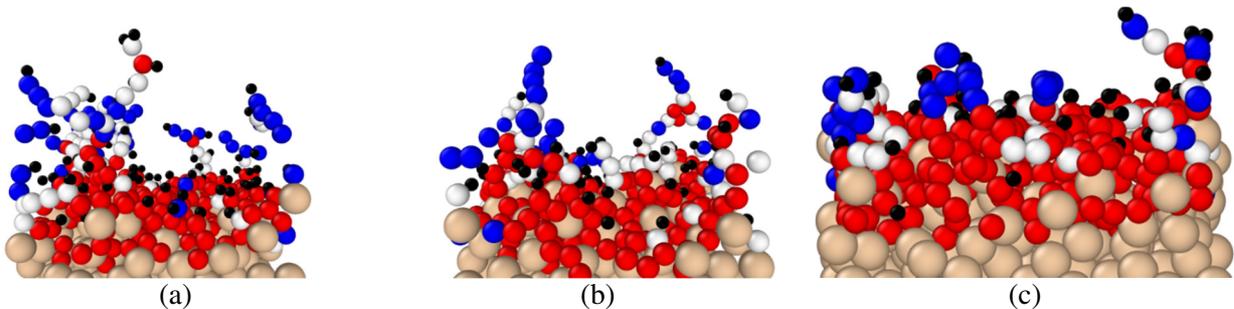


Fig.7. Film structures obtained by ion stimulation: (a) 40 eV; (b) 70 eV; 90 eV(s). Red atoms – sp^3 C; white – sp^2 C; blue – sp^1 C; brown – Si; black – H.

5. Conclusion

Within the framework of this work, a simulation of the plasma synthesis of a carbon coating using ion stimulation was carried out. The hybrid quantum-classical method of molecular dynamics with electrostatic coupling was used for modeling. The simulation results showed that, at the stimulation energy of up to 20 eV, the removal of the hydrogen bond leads to an increase in the number of adsorbed carbon atoms. It was revealed that the content of sp¹, sp², sp³ carbon is maximum at argon energies of 40, 70, 90 eV, respectively.

Acknowledgements

The research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University project within the Priority-2030 Program) is gratefully acknowledged.

6. References

- [1] Sladkov A.M., Kudryavtsev Y.P., *Russ. Chem. Rev.*, **830**, 229, 1963;
- [2] Guseva M.B., Babaev V.G., Kudryavtsev Yu.P., Alexandrov A.F., Khvostov V.V., *Diamond Relat. Mater.*, **4**, 1142, 1995; doi: 10.1016/0925-9635(95)00292-8
- [3] Babaev V.G., Guseva M.B., Novikov N.D., Khvostov V.V., Flood P., *Polyynes. Synthesis, Properties, and Applications*, (Boca Raton: CRC Press, 2005); doi: 10.1201/9781420027587
- [4] Liu M., Artyukhov V.I., Lee H., Xu F., Yakobson B.I., *ACS Nano*, **7**, 10075, 2013; doi: 10.1021/nn404177r
- [5] Guseva M.B., Babaev V.G., Novikov N.D., Alexandrov A.F., Khvostov V.V., Savchenko N.F., *Journal of Wide Bandgap Materials*, **9**, 273, 2002;
- [6] Samoc M., Dalton G.T., Gladysz J.A., Zheng Q., Velkov Y., Ågren H., Norman P., Humphrey M.G., *Inorg. Chem.*, **47**, 9946, 2008; doi: 10.1021/ic801145c
- [7] Eisler S., Slepko A.D., Elliot E., Luu T., McDonald R., Hegmann F.A., *J. Am. Chem. Soc.*, **127**, 2666, 2005; doi: 10.1021/ja044526l
- [8] Xiao J., Li J., Yang G., *Small*, **13**, 1, 2017; doi: 10.1002/smll.201603495
- [9] Ming C., Meng F.-X., Chen X., Zhuang J., Ning X.-J., *Carbon*, **68**, 487, 2017; doi: 10.1016/j.carbon.2013.11.025
- [10] Freitas A., Azevedo S., Kaschny J.R., *Physica E*, **84**, 444, 2016; doi: 10.1016/j.physe.2016.07.018
- [11] Babaev V.G., Guseva M.B., *Carbyne and Carbyneoid Structures*, **21**, 159, 1999; doi: 10.1007/978-94-011-4742-2_13
- [12] Chalifoux W., Tykwinski R., *Nat. Chem.*, **2**, 967, 2010; doi: 10.1038/nchem.828
- [13] Chena Y.-N., Ma T.-B., Zhu P.-Z., Yue D.-C., Hu Y.-Z., Chen Z., Wang H., *Surf. Coat. Technol.*, **258**, 901, 2014; doi: 10.1016/j.surfcoat.2014.07.061
- [14] Li X., Wang A., Lee K.R., *Comput. Mater. Sci.*, **151**, 246, 2018; doi: 10.1016/j.commatsci.2018.04.062
- [15] Neyts E., Bogaerts A., Gijbels R., Benedikt J., van de Sanden M.C.M., *Diamond Relat. Mater.*, **13**, 1873, 2004; doi: 10.1016/j.diamond.2004.05.011
- [16] Von Ranke N.L., Castro H.C., Rodrigues C.R., *Modelling*, **113**, 108145, 2022; doi: 10.1016/j.jmgm.2022.108145
- [17] Neyts E., Bogaerts A., Gijbels R., Benedikt J., van de Sanden M.C.M., *Diamond Relat. Mater.*, **13**, 1873, 2004; doi: 10.1016/j.diamond.2004.05.011
- [18] Groenhof G., *Methods Mol Biol.*, **924**, 43, 2013; doi: 10.1007/978-1-62703-017-5_3
- [19] Mortensen J.J., Hansen L.B., Jacobsen K.W., *Phys. Rev. B*, **71**, 035109, 2005; doi: 10.1103/PhysRevB.71.035109

- [20] Larsen A.H., Mortensen J.J., Blomqvist J., et al., *J. Phys.: Condens. Matter*, **29**, 273002, 2017; doi: 10.1088/1361-648X/aa680e
- [21] Thompson A.P., Aktulga H.M., Berger R., et al., *Comput. Phys. Commun.*, **271**, 108171, 2022; doi: 10.1016/j.cpc.2021.108171
- [22] Dohn A.O., Jónsson E.Ö., Levi G., et al., *J. Chem. Theory Comput.*, **13**, 6010, 2017; doi: 10.1021/acs.jctc.7b00621
- [23] Buntov E.A., Zatsepin A.F., *J. Phys. Chem. A*, **124**, 9128, 2020; doi: 10.1021/acs.jpca.0c05739