Graphitization of small diamond cluster — Molecular dynamics simulation

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Abstract

Molecular dynamics simulation was used to study graphitization process of a small diamond cluster at 1200, 1500, and 1800 K. The cluster was in the shape of a sphere of about 3 nm in diameter, and interaction between carbon atoms was described by the reactive bond order potential. Results obtained for 1500 K showed transformation of diamond nanoparticle into a carbon onion with diamond-like core and graphite layers in its outer shell. At 1800 K the process was faster and graphitization more effective. The whole final cluster was basically comprised of the onion structure, but it was irregular and separation between layers ranged from 0.2 to 0.3 nm.

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1. Introduction

The carbon onion, consisting of concentric graphitic shells, was discovered by Ugarte [1], who observed that carbon soot particles and tubular graphitic structures were transformed into carbon onions by intense electron-beam irradiation in a transmission electron microscope. Since that time, other methods that can be used to produce carbon onions have been developed; however, the high-temperature annealing of nanodiamond clusters (nD-c) [2] is the method that can provide carbon onions with uniform size in a large quantity. At the same time, graphitization process of nD-c has been extensively studied [3–9]. Using the high-temperature annealing of nD-c in vacuum [3] graphitization of the sample was observed in the temperature range from 1370 to 1870 K, and it was suggested that the transformation is initiated at the surface and propagates towards the centre. Similar conclusions about the graphitization process arose from studies carried out by Tomita et al. [4–6]. However, nD-c was transformed into carbon onion by annealing at 2000 K, and although the graphitic structure was dominant in carbon onions, a large number of sp³ bonds were observed and attributed to a residual diamond in the onion centre or imperfect shells with structural defects. The graphitization processes of nD-c were studied also in different gas atmospheres [7,8]. Xu et al. [7] found the onset temperature for graphitization of nD-c in argon at 940 K, whereas Qiao et al. [8] showed that the process began in the range 1370–1470 K and all particles transformed into carbon onions at 1670 K. It was also suggested that the graphitization process includes formation of graphite fragments, connection and twisting of graphite sheets between diamond {111} planes, and closure of graphite layers [8]. The influence of pressure on graphitization of nD-c was also studied [9], and it was concluded that merging and closing of graphite shells reduced the population of dangling bonds and decreased the surface energy.

Previous ab initio molecular dynamics (MD) simulations focused on graphitization mechanism of various diamond faces [10–12]. Their results provided additional insight into microscopic mechanisms of transition from nD-c to carbon onion, but application of ab initio methods to simulate graphitization of the whole nD-c, which consists of several thousands of carbon atoms, is very time consuming. However, for carbon atom a classical potential can be used, and for example application of Tersoff potential [13] to simulate graphitization of diamond [14]...
leads to the same results as ab initio MD simulations [10]. Therefore, in this work we used the Teresoff-type potential — the reactive empirical bond order (REBO) potential [15] that introduces many-body-effects and chemical bonding of carbon atoms, and we carried out MD simulation of nD-c at elevated temperatures and traced changes of the cluster structure with time.

2. Molecular dynamics simulations

A spherical nD-c of diameter of about 3 nm was obtained from a bulk system of carbon atoms arranged in the diamond structure. It contained 2425 atoms, and constituted an initial configuration in MD simulations. Interactions of carbon atoms were described by REBO potential, which was widely described in Ref. [15], and here we present only its main features. The binding energy of carbon atoms is expressed as follows

$$E_b = \sum_i \sum_{j<i} f_c(r_{ij}) \left[V_R(r_{ij}) - b_{ij} V_A(r_{ij})\right],$$

where $r_{ij}$ denotes a distance between the atoms $i$ and $j$. Introducing the switching function $f_c(r)$, whose value is one for the distances smaller than 0.17 nm and zero for distances larger than 0.2 nm, the sum in Eq. (1) is carried out over the nearest neighbours. $V_R(r)$ and $V_A(r)$ represent repulsive and attractive potentials, respectively. The bond–order function $b_{ij}$ depends on the local coordination and bond angles for the atoms $i$ and $j$. It gives realistic description of energies and lengths of carbon–carbon single, double and triple bonds. $b_{ij}$ also contains a term that correctly describes radical structures and incorporates non-local conjugation effects into a classical potential energy.

The interaction potential was used to calculate forces, and the Newtonian equations of motions were solved using the four-value predictor–corrector method [16] with the time-step 0.5 fs. To keep constant temperature of the system we used Berendsen algorithm [17]. MD simulations were carried out at 1200, 1500 and 1800 K, which correspond to annealing nD-c at those temperatures. Each simulation run consisted of $4.5 \times 10^6$ time-steps, i.e. the simulation length was 2.25 ns. The atom positions were recorded every 1000 time-steps that were used to trace time evolution of the systems. In addition, starting from the end configurations of the systems we carried out MD simulations at room temperature. In those cases the simulation lengths were 100 ps, and we calculated pair radial distribution functions and distribution of the angle between neighbouring carbon–carbon bonds.

3. Results and discussion

Initial MD simulation performed at 300 K showed that nD-c structure did not change in time. Most of the carbon atoms had tetravalent coordination, and their population is almost constant. One observed only a slight increase of the number of atoms with trivalent coordination. Next, we performed MD simulations at elevated temperatures. Populations of carbon atoms with tri- and tetravalent coordinations are shown in Fig. 1. It is visible that at 1200 K structure of nD-c rebuilt very slowly, and at long times a large fraction of the atoms had tetravalent coordination. When nD-c was annealed at 1500 K trivalent atoms accounted for about 55% of all atoms. Increasing temperature to 1800 K accelerated rebuilding of the diamond structure, and eventually about 87% of carbon atoms had trivalent coordination. For all temperatures studied, at long computational times, the ratio of atoms with tri- to tetravalent coordinations did not change; however, a small decrease of the interaction energy was observed indicating that slow rebuilding of the cluster structure continued.
At 1200 K trivalent atoms were localised on the cluster surface, i.e. a diamond core was surrounded by a shell composed of a fullerene-like carbon. At higher temperatures the number of trivalent atoms in the inner part of the cluster increased with time, and at 1500 K trivalent atoms were still mainly situated in the outer shell that is presented in Fig. 2a. When the cluster was annealed at 1800 K fast rebuilding of the cluster interior took place, compare Fig. 2b, and for longer elapsed times the tri- and tetravalent atoms were almost uniformly distributed across the cluster, however, population of trivalent atoms was dominant. This result is in accordance with observation of a number of sp³ bonds in carbon onions [4].

Examination of a slice that had been cut from the cluster provides additional insight into graphitization process of nD-c. Examples of the carbon atoms configuration within the slice of thickness 0.6 nm for nD-c annealed at 1800 K are presented in Fig. 3. Initially, some carbon–carbon bonds in the outer shell were broken, and later “embryos” of graphite layers also appeared in the interior of the cluster. The “embryo” layers are almost flat, but when they grow one observes bending of the layers, and an onion structure can be identified. The structure is irregular and “bridges” between neighbouring layers occur, which lead to interlayer spacing in the range from 0.2 to 0.3 nm that is smaller than that in the graphite structure.

The above results are confirmed by the distributions of interatomic distances and angles between neighbouring carbon–carbon bonds, which are presented in Fig. 4. For nD-c annealed at 1200 K the radial distribution function $g(r)$ has shape typical for diamond; however, the peaks have maximums at distances slightly larger then those for an ideal diamond arrangement of carbon atoms in graphite, and similar satellites specific for graphite planes appear at larger distances. The increase of the annealing temperature to 1500 K diminishes the diamond peaks, and at the same time the graphite peaks increase. When the cluster was annealed at 1800 K the radial distribution function became more uniform and distances characteristic for carbon atoms arranged in graphitic sheet, $0.142, 0.246, 0.284, 0.376, 0.426$ and $0.492$ nm, were observed. Apart from the peak at $r=0.154$ nm there is no other peak of diamond structure to support existence of very small fragments of diamond. There are no peaks corresponding to interlayer distances in graphite confirming irregular layer structure and interlayer spacing of carbon onion. A small peak at 0.2 nm, is probably an artefact connected with the switching function in the REBO potential. Similar peak at 0.21 nm was observed by Saada et al. [14] when the switching-off radius was 0.21 nm [13]. Dependence of the cluster structure on annealing temperature is also observed in the distribution of angle between neighbouring bonds. It is interesting to notice that although distances in the diamond core were larger than those in the ideal structure, the tetrahedral angle was maintained. On the other hand, broad distribution of the angle in the graphite structure and its maximum appearing at an angle smaller than 120° indicate presence of highly imperfect graphitic structures.

4. Conclusions

We applied MD simulation methods to study structure of nD-c at different annealing temperatures. It was found that at 1200 K nD-c transformed into bucky diamond [18], and raising the annealing temperature to 1500 K led to a cluster with graphitic shells and diamond core. When nD-c was annealed at 1800 K it was transformed into a carbon onion. Graphitization started at the
surfaces and very quickly involved the whole nanodiamond, including its core. These findings are in accordance with experimental results [3–6, 8]. With increasing annealing temperature the graphitization process became faster and more efficient. It must be noted that the structure of the carbon onions obtained from MD simulation was defective, and to obtain better results much longer simulation runs are required. Interlayer distances were smaller than those in graphite and to improve results the van der Waals interactions between graphitic layers should be included and this problem will be addressed in a further work.

References