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NANOSTRUCTURED SYSTEMS AND MATERIALS

Molecular Dynamics Simulation of Copper Removal from Graphene by Bombardment with Argon Clusters

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Abstract—The problem of developing a nondestructive method for purification of graphene to remove a deposited metal has been tackled. Bombardment of copper film-precoated graphene by argon clusters has been simulated in terms of molecular dynamics. With a flow of 30-eV clusters directed parallel to the graphene sheet plane, the full removal of copper from graphene is achieved. The mobility of Cu and C atoms, the distribution of a stress that is the most susceptible to cluster impact in the graphene plane, and the graphene sheet surface roughness during the simulated process have been determined.

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Efficient removal of hazardous heavy metals including copper from the environment is an important problem, since most of these metals are highly toxic. There are several available methods for removing heavy metals from water and air. These, for example, include chemical precipitation, membrane filtration, ion exchange, adsorption, and electrochemical processes. Among these methods, adsorption is one of the most promising and widely used methods because of its simplicity and low cost. Adsorption on graphene can be used to filter off many harmful invisible residues of organic and inorganic materials, including heavy metals. Magnetized carbon tubes have been tested for recovery of copper from water [1]. Syntheses of graphite-containing materials that have an extremely high absorption capacity were discussed in [2], as well as their use for the removal of environmental pollutants. Graphene is ineffective as an absorbent unless it is repeatedly used. This raises the problem of graphene cleaning for removal of the deposited materials, of which copper is of considerable practical interest. Ion beam cleaning is one of the simplest and most effective methods for purification of graphene. However, it is important to select an appropriate energy of incident ions so that not to damage the filter.

Ito and Nakamura [3] attempted a molecular dynamics (MD) simulation of plasma interaction on the surface of graphite using a modified Brenner potential [4]. It was shown that the graphite surface absorbs the majority of hydrogen atoms at an incident beam energy of 5 eV, whereas almost all hydrogen atoms are reflected from the surface at a beam energy of 15 eV. Vertical bombardment with Ar_{10} clusters having a kinetic energy of $E_k < 30$ eV, as simulated by the MD method [5], does not lead to the rupture of a graphene sheet in a series of 100 trials. Graphene was found to break at $E_k = 40$ eV.

The aim of this work was to study the removal of a copper film from graphene by irradiating the target with a low-energy argon cluster beam parallel to the graphene plane.

COMPUTER SIMULATION PROCEDURE

Interatomic interactions in graphene were described in terms of a modified Tersoff many-body potential [6]. The distance of covalent bonding was increased to 0.23 nm, and an additional weak attraction at $r > 0.23$ nm as defined by the Lennard–Jones potential with the parameters given in [7] was included. To eliminate the resulting torque at each graphene lattice site, the rotational component of the force generated by the atoms of adjacent sites was excluded. The analytic form of the local torsional potential was derived in [7].

Atomic interactions in the copper film were modeled with the use of the Sutten–Chen many-body potential [8]. The copper–carbon interaction was described by the Morse potential [9]. In the Ar_{13} cluster, the atoms were supposed to interact via the Lennard–Jones potential [10]. The interaction between Ar atoms and the target (Cu and C) atoms was defined by the purely repulsive Moliere potential [11]:

$$\Phi = Z_i Z_j \frac{e^2}{r}\left\{0.35\exp\left(-0.3\frac{r}{a}\right) + 0.55\exp\left(-1.2\frac{r}{a}\right) + 0.10\exp\left(-6.0\frac{r}{a}\right)\right\}, \quad (1)$$

where Z_i and Z_j are the atomic numbers of the ith and jth atoms, respectively; e is the elementary electric charge; r is the distance between the atoms; and a is the Firsov screening length [12]:

$$a = 0.885a_0\left(Z_i^{1/2} + Z_j^{1/2}\right)^{-2/3}. \quad (2)$$

Here, a_0 is the Bohr radius. We neglect weak attraction between the Ar and Cu atoms on one hand and the Ar and C atoms on the other hand, since the primary subject of this study is energy and momentum transfer, not chemical bonding [13].

The copper film formation on the graphene was simulated by separate MD calculation in two steps. At the first step, Cu atoms were placed over the centers of noncontiguous graphene cells so that the distance between the Cu and C atoms would be equal to the distance of 2.243 Å calculated by the density functional theory [14]. Onto this loose film consisting of 49 copper atoms, another 51 Cu atoms were deposited at random. Then, the system composed of 100 Cu atoms and 406 C atoms was equilibrated in the MD calculation over a duration of 1 million time steps ($\Delta t = 0.2$ fs).

Numerical solution of the equations of motion was carried out by the fourth-order Runge–Kutta method. The target obtained in this manner was subsequently bombarded with icosahedral Ar_{13}. clusters. Five starting points for placing the centers of the Ar_{13} clusters were uniformly spaced apart on a line parallel to the oy axis ("chair" direction; the angle between the normal to the graphene surface and the direction of flight of Ar atoms, $\theta = 90°$). This line was displaced to the left (along the ox axis) from the left edge of graphene by a distance of 1.5 nm and raised to such a height (in the direction of the oz axis) that the lower atom of an Ar_{13} cluster can slide on the graphene sheet carrying the copper film. The Ar_{13} clusters had the same initial orientation, since a change in their orientation has no significant effect on the final result. In the original starting point, all the atoms in the Ar_{13} cluster have got the same velocity along the direction of the ox axis. The clusters were successively directed towards the target. The lifetime (defined as the sum of the time of flight and the time of interaction with the target) of each cluster was limited to 8 ps. After this time, the Ar atoms of the degraded cluster were excluded from consideration and a new cluster began to move from another starting point. The cycle of bombardment with five clusters took 40 ps (hereinafter, the cycle number is denoted by n). A series of bombardments at an energy of 30 eV consisted of 25 cycles and had a duration of 1 ns. Even after 20 cycles, 8 copper atoms were still left on the graphene; however, no copper atoms remained any longer after 25 cycles. The heat generated in the system (in both the metal film and graphene) as a result of the bombardment was partially dissipated by flying-off Cu and Ar atoms and was also withdrawn by the model used in the Berendsen thermostat [15]. However, the effective functioning of the thermostat was observed only in the complete absence of cluster impacts. The use of the thermostat also allows for more correct comparison of the characteristics of the system before and after the cluster bombardment.

The effect of cluster bombardment is substantially independent of the electrical charge of the cluster, since the ion charge is neutralized on the surface via charge exchange when the ion strikes the target. The electron moves at a velocity of least three orders of magnitude above that of the nucleus motion. Therefore, the dynamics of the argon ion is similar to the dynamics of the neutral argon atom within the frame of the Oppenheimer approximation [16, 17].

The self-diffusion coefficient was determined through the mean square displacement of atoms as

$$D = D_{xy} + D_z = \lim_{t\to\infty}\frac{1}{2\Gamma}\left\langle\left[\Delta\mathbf{r}(t)\right]^2\right\rangle, \quad (3)$$

where $\Gamma = 3$ is the dimension of space, and D_{xy} and D_z are respectively the horizontal and vertical components of the self-diffusion coefficient. The brackets $\langle\ldots\rangle$ denote averaging over time.

To calculate the stresses arising in graphene, the graphene sheet was divided into elementary areas. Atomic stress $\sigma_J^i(l)$ on an elementary area l for each of the direction x, y, z with the current index J are determined by calculating the kinetic energy of atoms in this area and the projections of forces f_J^i, acting on the lth area from all the other atoms

$$\sigma_J^i(l) = \frac{1}{k}\left\langle\sum_i^k\frac{1}{\Omega}\left(mv_J^i v_J^i\right)\right\rangle + \frac{1}{S_l}\left\langle\sum_i^k\left(f_J^i\right)\right\rangle, \quad (4)$$

where k is the number of atoms on the lth area, Ω is the volume per atom, m is the mass of the atom, v_J^i is the Jth projection of the velocity of atom i, and S_l is the geometric area of the lth area. By this definition, a compressive stress may have either "+" or "–" sign in accordance with the direction of the force f_J^i. This feature differs the microscopic stress $\sigma_J^i(l)$ from the macroscopic stress $\overline{\sigma}_J < 0$.

The surface roughness (arithmetic average roughness) was determined as

$$R_a = \frac{1}{N}\sum_i^N|z_i - \overline{z}|, \quad (5)$$

where N is the number of nodes (atoms) on the graphene surface, z_i is the atomic level, and i, $\overline{z}$ the level of the graphene surface, with the z_i and $\overline{z}$ values being determined at the same time instant.

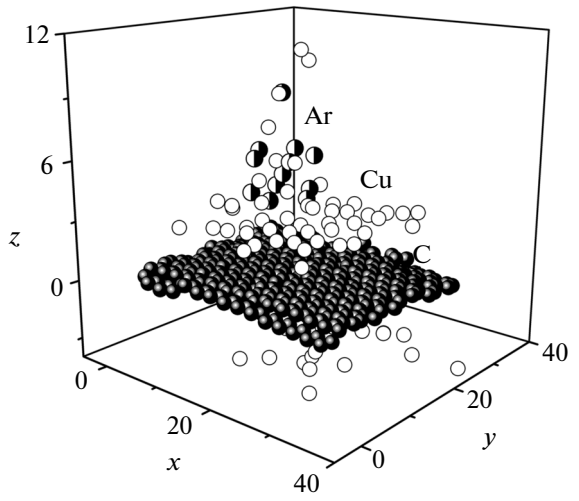

Fig. 1. Configuration of the "copper film on graphene sheet" system during cluster bombardment at a time instant of 0.32 ns. The coordinates are in angstroms.

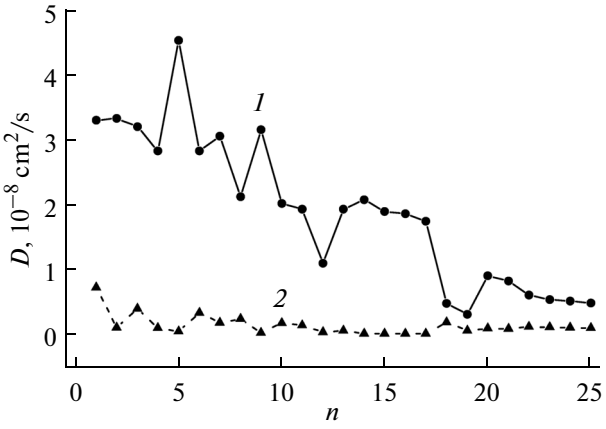

Fig. 2. Components of the self-diffusion coefficient (*1*) D_{xy} and (*2*) D_z of a copper film in a target bombardment series; n is the cycles of five strikes each.

The total energy of free single-sheet graphene at 300 K was found to be −7.02 eV in agreement with the value obtained by quantum- mechanical calculation (−6.98 eV) [18]. The heat capacity c_v of the copper film, as calculated through kinetic energy fluctuations, increases in the temperature range of $300 \le T \le 1300$ K from 19 to 28 J/(mol K) in satisfactory agreement with the growth rate of the experimental values of c_v for polycrystalline copper (24.45–32.16 J/(mol K)) [19]. The calculations were performed on basis of our computer programs developed for the purpose. A computer with a quad core processor having a clock frequency of 3.6 GHz was used. Calculation of 1-ns bombardment by 125 cluster impacts took 202 h of machine time.

RESULTS AND DISCUSSION

Preliminarily, we simulated the vertical ($\theta = 0°$) bombardment of a similar target with Ar_{13}, clusters, making 125 cluster impacts with energies of 5, 20, and 30 eV. The 5-eV bombardment resulted in consolidation of the copper film without knocked-off atoms. The removal of copper was observed at cluster energies of 20 and 30 eV (in this case, the purification was faster), but graphene edges were damaged. It was assumed that if a Cu atom departed from its nearest neighbor atom by a distance greater than $3r_{Cu-Cu}$ ($r_{Cu-Cu} = 2.5526$ Å is the distance between nearest neighbor atoms in a copper crystal), it did not return back to the system. In fact, by collision with Ar atoms most Cu atoms quickly flew off over distances of tens of r_{Cu-Cu}. The bombardment of the target with a horizontal beam of clusters at an energy of 10 eV was also attempted. After 125 collisions, the copper film was consolidated and displaced in the direction of flight of the clusters. The cluster energy was insufficient for removing copper from the graphene. In this study, we simulated the bombardment of the target with Ar_{13} clusters at an incidence angle of $\theta = 90°$ (horizontal direction) and an energy of 30 eV. At this incidence angle, the first impacts lift the front edge of the film, so that all the subsequent impacts usually hit the target. The film was cleared of copper by three fourths even after the first 50 impacts ($n = 10$).

The outcome of horizontal bombardment was thorough graphene sheet cleaning of the metal after 125 strikes by Ar_{13} clusters. The cleaning mechanism can be represented as the detachment of individual portions of the metal from the film surface. Flying at the "nap of the earth," an Ar_{13} cluster each time lost its bottom atom by a collision with the metal, slowed down by slipping on the film, and carried the upper Cu atoms away. The instant of time of target interaction with the Ar_{13}, cluster departing from the third starting point in the eighth cycle of impacts is reflected in Fig. 1. By this time instant, the graphene sheet has been partially cleaned of copper atoms. Cleaning begins on the side (near the *oy* axis) that is the first to receive cluster blows. By the impacts, the graphene-neighboring Cu atoms are consolidated in the direction of the cluster flight. From the back side (with respect to the direction of impacts) of the graphene sheet, the "tail" of copper atoms is formed. The cluster slides on the dense layer of the film and hits the upper Cu atoms. The Ar_{13} cluster itself is destroyed.

The change in the horizontal D_{xy} and vertical D_z components of the self-diffusion coefficient of copper atoms in the film depending on the number of cluster impact cycles n is shown in Fig. 2. It is seen that the values of D_{xy} are significantly higher than the values of D_z at the beginning of the bombardment. As n increases, D_{xy} and D_z decrease, with D_{xy} decreasing

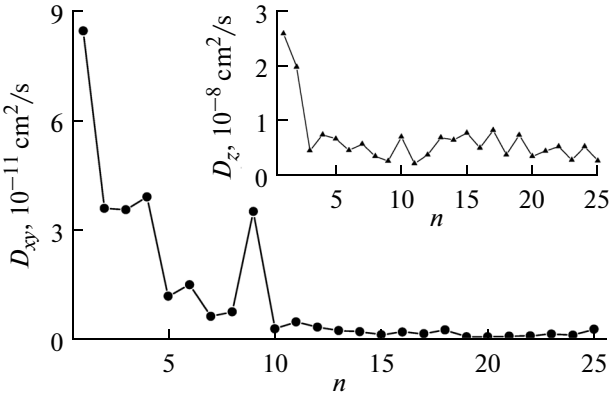

Fig. 3. Component D_{xy} of the self-diffusion coefficient of graphene in a target bombardment series. Inset: D_z for graphene in the same series.

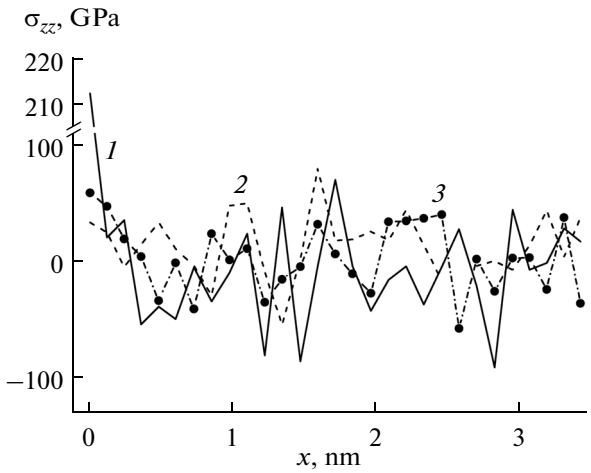

Fig. 4. Stress (σ_{zz}) distribution in the graphene sheet by the rows of carbon atoms along the "chair" direction during the bombardment of the target for the values of n of (*1*) 1 (full cycle of 5 impacts), (*2*) 12, and (*3*) 25.

more rapidly and both quantities strongly fluctuating. Spikes of these characteristics correspond to knocking Cu atoms out of the film. Ultimately, the graphene becomes free of Cu atoms and the values of D_{xy} and D_z approach one another.

The $D_{xy}(n)$ and $D_z(n)$ relationships for graphene are illustrated in Fig. 3. Unlike the case of copper film, the values of the vertical component of the self-diffusion coefficient in graphene are substantially higher than those of the horizontal component. This difference is also observed in the nonbombarded graphene, and it is due to the rigidity of horizontal bonds in it and the inclination of a flat crystal to turn in the third dimension. In the initial stage of bombardment, the values of D_{xy} and D_z for graphene is markedly higher than in the final stage when the Ar_{13} cluster in the absence of copper atoms simply slides on the surface of the graphene sheet. The drop in the D_z value for graphene is particularly rapid (within the first three impact cycles). During the next 22 impact cycles, the fluctuating D_z quantity is slowly decreasing. Such a behavior of the function $D_z(n)$ is due to the fact that relatively free Cu atoms in the initial noncompacted film strongly hit the graphene after colliding with Ar atoms. In the compacted film, the action of Cu atoms on the graphene is significantly weaker because of the redistribution of the impact energy to a group of copper atoms. In the horizontal direction, the mobility of C atoms depends on the metal coating relief, which substantially changes during the first ten impact cycles. It is in this range of values of n that strong fluctuations of D_{xy} take place.

Figure 4 shows the distribution of a stress σ_{zz} along the rows of graphene atoms in the "chair" direction. The long sides of the elementary areas in this case are oriented along the *oy* axis and the rows of atoms are successively passed by along the *ox* in the direction of motion of the cluster beam. The σ_{zz} fluctuation amplitudes are in most part slightly higher than those of other stresses (σ_{zx} and σ_{zy}) in the plane of the graphene sheet. Furthermore, there can be stronger spikes of local σ_{zz} stresses, for example, as is observed after the first cluster impact cycle ($n = 1$). Typically, an increase in n leads to a decrease in σ_{zz} oscillation amplitude (Fig. 4, curves *1*–*3*). In particular, the stress is significantly reduced in the area that accommodates the first row of the "chair" atoms. Thus, the bombardment of the target with Ar_{13} clusters does not enhance stresses in the graphene sheet plane.

Consider the effect of cluster bombardment on the surface condition of a graphene sheet. The change in roughness R_a during the passage of the whole series of impacts is shown in Fig. 5. The dashed line (line *3*) shows the level of the surface roughness of the graphene sheet in the presence of the copper film on it before the bombardment with argon clusters. The value of R_a stops increasing and stabilizes around an average value (0.00626 nm) after 20 ps. In equilibrium, the deviation from the mean value of R_a did not exceed 29% in the time interval of 0.18 ns. The first impact of the cluster on the surface increases R_a by at least 36%, and the value of R_a is increased by 78% after the fifth impact. Curves *1* and *2* illustrates the behavior of the function $R_a(n)$ after bombardment with the clusters emitted from the first and fifth starting points, respectively. In general, quite close $R_a(n)$ curves are obtained for these cases. It is seen that the function $R_a(n)$ increases with the number of cluster impact cycles. As n changes from 1 to 25, the value of the function $R_a(n)$ increases by factors of 2.9 and 1.9 in the first and the second case, respectively. After a series of 125 cluster

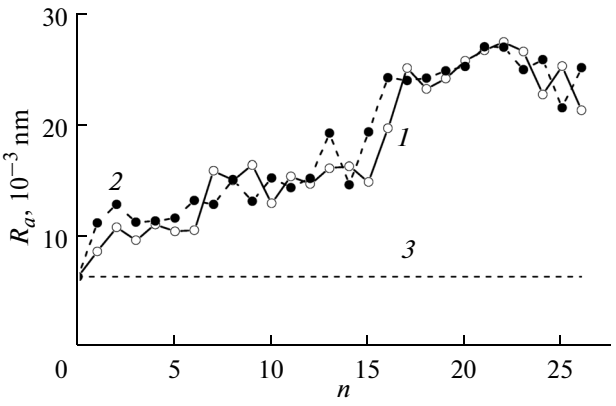

Fig. 5. The surface roughness of graphene in the bombardment of the system with Ar_{13} clusters emitted from the (*1*) first and (*2*) fifth starting points; (*3*) a graphene roughness level before the bombardment.

impacts, the surface roughness of the graphene sheet increased fourfold on average relative to the initial state of the graphene.

CONCLUSIONS

A method for graphene purification to remove a deposited metal has been proposed. In computer simulation, a graphene sheet can be completely cleaned of its copper coating film by bombardment of the target with Ar_{13} clusters having an energy of 30 eV. The cluster beam had a direction parallel to the plane of the graphene sheet and did not produce the destructive action on the graphene. The number of cluster impacts was insignificantly greater than the number of copper atoms adsorbed on the surface of the graphene sheet. During the bombardment, the copper atoms acquired horizontal mobility that was several times larger the mobility in the vertical direction. However, the horizontal mobility of Cu atoms decreased with the increasing number of impacts and approached the value of vertical mobility after knocking out all the atoms from the surface of the graphene sheet. In contrast, the vertical mobility of the atoms in graphene dominated the horizontal mobility during the entire process of its cleaning to remove the metal. Elevated stresses arising in graphene at the beginning of the bombardment on the graphene sheet edge facing the cluster beam are noticeably reduced after a few tens of cluster impacts. The effect of cluster bombardment was manifested in a fourfold increase in the roughness of graphene. Approximately the same enhancement of roughness was observed in the case of identical bombardment of a similar target with 10-eV Ar_{13} clusters. However, the desired effect of graphene cleaning of copper was not achieved in this case: the metal film lost only 12% of Cu atoms.

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