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Computer Simulation of Graphene Cleaning of Copper with Ar Clusters Irradiation

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Abstract – The process of graphene cleaning of copper film by bombarding of Ar_{13} clusters is investigated by the method of molecular dynamics. The kinetic energies of clusters are 5, 10, 20 end 30 eV and incident angles are θ = 90°, 75°, 60°, 45° and 0°. It is obtained that the cluster energy should be in the interval 20–30 eV for effective graphene cleaning. There is no cleaning effect at vertical incident (θ = 0°) of Ar_{13} clusters. Besides, graphene edges are significantly destroyed at such way of bombarding. The bombarding at 45° incident angle is the most effective at moderate amount of deposited copper. The bombarding at 90° gives an excellent result when a big amount of Cu is deposited on graphene. In this case the graphene edges are not damaged.

Keywords: Argon clusters, Copper, Diffusion coefficient, Graphene, Stress tensor.

1. Introduction

Graphene attracts a big amount of interest because of its unique physical properties and energy-band structure. It is possible now to receive a graphene of small size with the help of different technologies. However, work (Li et al., 2009) tells about the new technology of graphene film production of size up to 70 cm. Graphene is an impermeable material to gases and liquids in spite of atomic thickness. It conducts heat and electricity better than copper. Graphene atomic structure has the highest flexibility and mechanical strength. Unusual optical properties of graphene give its broad using in electronics and photonics.

As an absorbing material, graphene is an effective one only in the case of multiple using. Consequently, the question of graphene cleaning of deposited substances arises. The copper has the significant practical interest. The bombarding with the ion beam can be effective method of graphene cleaning. It is important here however, to find the correct bombarding energy to avoid the damage of graphene membrane.

The ion irradiation of material by beams with different energies and incident angles of a beam, inclination and rotation of sample is widely investigated (Lehtinen et al., 2011). Mechanisms of collision cascades and defects origin are explained theoretically (Ahlgren et al., 2011). However, the discovery of two-dimensional crystals such as graphene has formulated new tasks (Bell et al., 2009). Approaches using for analyzing of bulk materials can be inappropriate for studying of 2D-crystals irradiation because of special properties of atomically flat objects (Ahlgren et al., 2011). The using of nonoptimized ion beams, as a rule, results in destroying of sp^2-hybridization and influences the mobility of carriers defining transport properties of graphene. Method of molecular dynamics (MD) is the most perspective one for investigating of such objects. Surface pollution on graphene is removed with the help of ion beam (Siokou et al., 2011). It is obtained in (Stogniyi et al., 2001) that there is a smoothing of boundary of ultra thin film Co–Cu and Cu–Co structures up to atomic size level as a result of its irradiation by Ar ions with energy less than 50 eV and radiation dose $1.8 \cdot 10^{16}$ cm^{-2}.

MD simulation of plasma interaction on the graphite surface using modify Brenner potential is executed (Ito et al., 2008). It is shown that the graphite surface absorbs the most part of hydrogen atoms at the energy of incident beam 5 eV. At the same time, almost all hydrogen atoms are reflected from the surface at the beam energy 15 eV. Vertical bombarding by Ar_{10} clusters with kinetic energy of E_k < 30 eV executed in MD model (Inui, 2008) does not result to the break of graphene sheet during 100 treats. Graphene is broken at E_k = 40 eV.

The aim of the present work is to investigate stability of the thin film of copper on graphene under action of bombarding by Ar_{13} clusters with kinetic energies 5, 10, 20 and 30 eV and incident angle of a cluster beam 90°, 75°, 60°, 45° and 0°.

2. Computer Model

Tersoff potential is used for description of interatomic interactions in graphene (Tersoff, 1988). However, the distance of covalent bonding increases up to 0.23 nm. Addition weak attraction at $r >$ 0.23 nm giving by Lennord-Jons potential with parameters of work (Stuart et al., 2010) is included. In every node of graphene sheet a torsion component of power giving by atoms of contiguous nodes is excluded to remove the resulting torsion moment. Analytical form of local torsion interaction potential is given in (Stuart et al., 2010). Satten-Chen (SC) potential is used for simulation of copper–copper interactions. It is successfully used for modeling both bulk metals and metal clusters. For Cu the following parameters are used: m = 6, n = 9, ε = 12.382 meV, c = 39.432 (Rafii-Tabar, 2000). Morse potential is used for copper–carbon interactions with parameters: D_0 = 87 meV, α = 1.7 Å^{-1}, r_m = 2.2 Å (Oluwajobi et al., 2011). Interactions in Ar_{13} cluster are described by Lennard-Jons potential with parameters: σ_{Ar-Ar} = 0.3405 nm, ε_{Ar-Ar} = 0.0103 eV (Teng et al., 2007). Interactions between Ar atoms and a target (Cu or C) are described by repulsive Molere potential (Moore et al., 2004). Weak $Ar-Cu$ and $Ar-C$ attractions are not taken in to account because the main goal of present investigation is the transfer of energy and angular moment but not a chemical bonding (Delcorte, 2000).

Copper film on graphene is formed in a separate MD calculation during two steps. At the first step Cu atoms are placed under the centers of noncontiguous cells so the $Cu-C$ distance is equal to 2.243 Å (calculated through the density functional theory (Xu et al., 2010)). Additional 51 Cu atoms are randomly deposited onto this porosity copper film consisting of 49 atoms. Then the system containing 100 Cu atoms and 406 C ones is equilibrated in MD run duration of 1000000 time steps (Δt = 0.2 fs). Runge-Kutta method of the 4th order is used for numerical solving of motion equations.

The copper target is further used for bombarding with Ar_{13} clusters. In the case of vertical bombarding ($\theta = 0^o$) the virtual rectangular two-dimensional 5×5 grid covers the graphene sheet. The grid nodes are uniformly distributed over the sheet surface with indention from edges on a distance of σ_{Cu-C}. Virtual grid is lifted under graphene sheet at a distance of 1.5 nm. Every grid node gives the initial position for Ar_{13} cluster living 8 ps and interacting with a target (copper film). In the initial time moment all atoms of Ar_{13} cluster acquires speeds directed vertically down and corresponding to the kinetic energy 5, 10 or 20 eV.

In the case of bombarding at angles 90º, 75º, 60º and 45º five start points for Ar_{13} clusters centers are uniformly distributed along one line parallel *Oy* axes (armchair direction). This line is shifted to the left (along *Ox* axes) from the left graphene edge by a distance of 1.5 nm. Then the line is lifted (along *Oz* axes) so that φ angle between *Ox* axes and the line of impact direction was 15º, 30º and 45º and in the case of the "nap of the earth" flight – so that the lower atom of Ar_{13} cluster can slide over the graphene sheet. Interval equal to the graphene sheet length in *Ox* axes direction (zigzag direction) is divided into 25 equal parts with the length $L_i = L_x / 25$. At the beginning of every following cycle of cluster impacts the line of the start points of Ar_{13} clusters moved horizontally forward at a distance L_i. As a result the graphene sheet is covered by 125 equally distributed points to which cluster impacts are targeted. At start point all atoms of Ar_{13} cluster have the same speed. Clusters are directed to a target by turn. The life time (sum of transit time and that of interaction with target) of every cluster is 8 ps. By the end of this time Ar atoms of collapsed cluster are excluded from consideration and a new Ar_{13} cluster begins motion from other point. A cycle of 5 cluster bombardment lasts 40 ps (the cycle number is denoted as n). Every bombarding series including 25 cycles lasts 1 ns.

Self-diffusion coefficient D is set through the mean square displacement of atoms $\left\langle [\Delta \mathbf{r}(t)]^2 \right\rangle$

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

where D_{xy} and D_z are horizontal and vertical components of D, Γ is the dimension of space. Time averaging is denoted as $\langle ... \rangle$.

Stress in atom i location of metal film is defined as (Rafii-Tabar, 2000)

$$\sigma_{\alpha\beta}(i) = \frac{\varepsilon}{2a^2\Omega_i} \sum_{i\neq j}^{k} \left[-n \left(a / r_{ij}\right)^{n+2} + cm \left(1/\sqrt{\rho_i} + 1/\sqrt{\rho_j}\right) \left(a / r_{ij}\right)^{m+2} \right] r_{ij}^{\alpha} r_{ij}^{\beta}, \tag{2}$$

where Ω_i volume belonging to individual atom can be associated with volume of Voronoi polyhedron connected with i atom.

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

$$\sigma_J^i(l) = \frac{1}{k} \left\langle \sum_i^k \frac{1}{\Omega_i} \left(m v_J^i v_J^i\right) \right\rangle + \frac{1}{S_l} \left\langle \sum_i^k \left(f_J^i\right) \right\rangle, \tag{3}$$

where k is the number of atoms on l area, Ω_i is the volume per i atom, m is the mass of atom, v_J^i is J projection of i atom speed, S_l is the geometric area of l area. Compressive stresses by this definition may have either "+" or "-" sign in accordance with direction of f_J^i force. This feature differs the microscopic stress $\sigma_J^i(l)$ from macroscopic one $\bar{\sigma}_J < 0$.

The surface roughness (or average arithmetic profile deviation) is calculated as

$$R_a = \frac{1}{N} \sum_{i=1}^{N} |z_i - \bar{z}|, \tag{4}$$

where N is the number of nodes (atoms) on the graphene surface, z_i is the level of i atom, $\bar{z}$ is the level of graphene surface, z_i and $\bar{z}$ values are determined at the same time.

3. Results of Computer Experiment

3.1. The Bombarding of a Target with Vertically Incident Ar_{13} Clusters

There is an insignificant damage of graphene edges after vertical bombardment at energy 5 eV. There is no graphene surface cleaning in that case. Vertical bombardment with clusters energy 20 eV (Fig. 1a) gives the strong damage of the graphene edges. There is even flying out carbon atom. Copper atoms are not removed from the system. They become more compact and form a column.

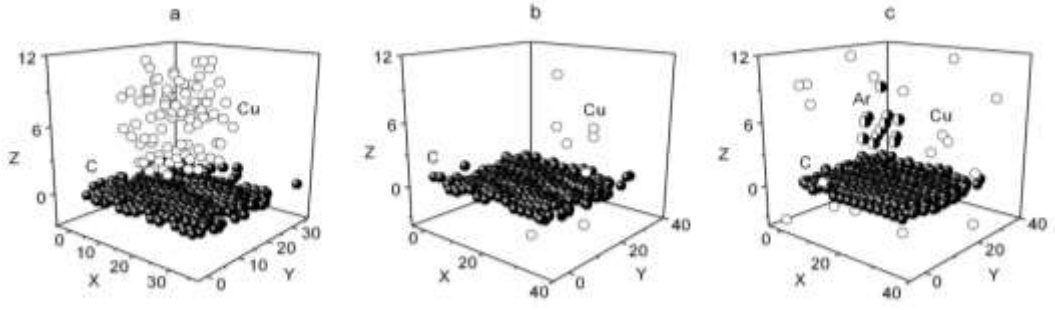

Fig. 1. Configurations of a system "copper film on graphene" bombarding by Ar_{13} cluster with energy 20 eV during final impacts cycle at the incident angles: (a) θ = 0°, (b) 45°, (c) 90°. Coordinates are in angstroms.

Stresses in xy plane of copper film at vertical bombarding have strong fluctuations which become weaker in the last 5th impact series (Fig. 2, energy of Ar_{13} clusters is 20 eV). Both σ_{zx} and σ_{zy} stresses have the same amplitude of fluctuations and σ_{zz} stress is characterized by essentially higher values and fluctuations (up to 5 times). At vertical bombardment the significant "splashes" of σ_{zz} stresses are observed at the graphene edges.

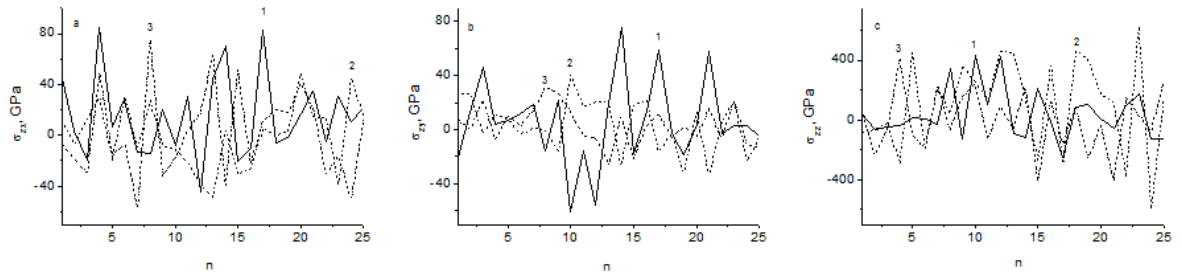

Fig. 2. Stresses acting in horizontal plane in the copper film on the graphene: a – σ_{zx}, b – σ_{zy}, c – σ_{zz} for series of vertical cluster bombarding with energy 20 eV: (1) 1st impact series, (2) 3rd impact series, (3) 5th impact series.

Cleaning effect at vertical impacts with energies of bombarding clusters 5, 10 and 20 eV has not archived. The graphene edges are damaged drastically.

3.2. The Bombarding of a Target With Inclined Cluster Beam

The graphene sheet is partly cleaned of copper atoms after bombarding with incident angle θ = 75º and that is almost cleaned of Cu atoms at angles θ = 45º (Fig. 1b) and θ = 60º. In every case after finishing of inclined bombarding the graphene sheet is removed in parallel or perpendicular (down) direction in relation to its plane. It allowed removing copper from graphene totally only after bombardment at 45º.

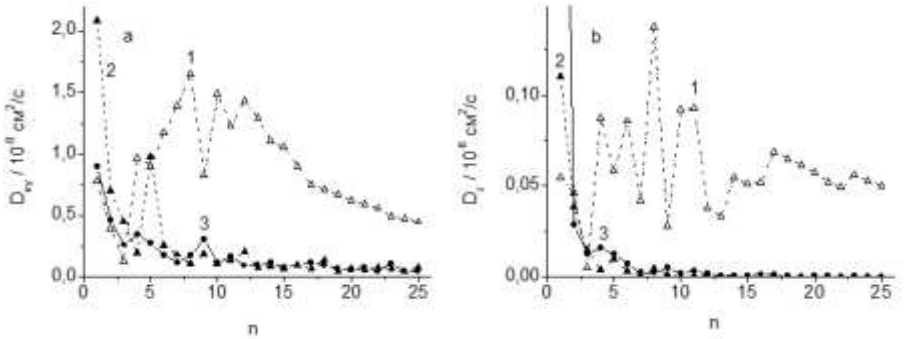

Fig. 3. (a) – horizontal D_{xy} and (b) – vertical D_z components of self-diffusion coefficient of Cu film at bombarding by Ar_{13} clusters with kinetic energy 20 eV and incident angles: (1) 45º, (2) 60º, (3) 75º; n is the cycles of 5 impacts each.

At any clusters incident angle the mobility of Cu atoms in horizontal plane exceeds considerably (in order) one in vertical direction. After the first cycles of cluster impacts there are high values of D_{xy} components, especially at the incident angle θ = 60º (Fig. 3). Vertical components D_z of copper film self-diffusion coefficient has almost the same behavior as D_{xy}.

Rather dense copper film on the graphene surface is present when the incident angle of clusters is 75°. Stresses varying at copper film colliding with clusters are shown in Fig. 4. Curves 1 present the case when cluster attacks from the first start point and curves 2 – from the firth one. Curves 1 and 2 corresponding to the same stress components have nearly identical amplitude of fluctuations. Ampli-

tude of σ_{zz} stress fluctuations produced by vertical forces is almost the order higher than that of σ_{zx} stress given by horizontal ones. After 8 cycles of cluster impacts the fluctuation amplitude of σ_{zz} quantity reduces. But it is far from values for σ_{zx} and σ_{zy} components. The reason for that is loosening of metal film in vertical direction.

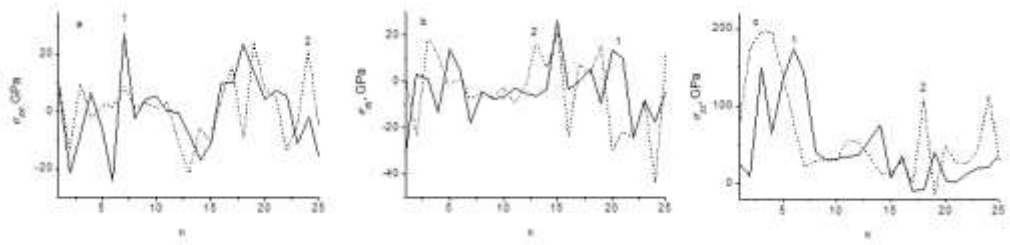

Fig. 4. Stresses of metal film: (a) σ_{zx}, (b) σ_{zy}, (c) σ_{zz} in xoy plane at Ar_{13} clusters bombardment at incident angle 75°. Clusters emitted from the (1) first and (2) fifth starting points.

On the contrary, stresses distribution in the graphene sheet doesn't almost depend on the direction of incident cluster beam. Clusters impacts are mainly weakened by the copper film. The graphene roughness increases significantly by the end of bombarding. It doesn't depend on the beam incident angle and energy of Ar_{13} clusters. Significant growth of roughness is limited by rigid bonds in graphene.

3.3. Cluster Bombarding of a Target By The Method of the "Nap Of The Earth" Flight

Sliding bombarding of a target with Ar_{13} clusters (method of the "nap of the earth" flight, incident angle of 0°) with energy 20 eV gives the total graphene cleaning of copper film (Fig. 1c). When the cluster energy is 10 eV a big amount of metal atoms is still on the graphene surface. The value of horizontal component D_{xy} of self-diffusion coefficient reduces sharply at the growth of metal film density under Ar_{13} cluster impacts with energy 10 eV. The significant increase of horizontal mobility of Cu atoms is observed at energy of 20 eV Ar_{13} clusters. The biggest values of self-diffusion coefficient components are observed with clusters energy 30 eV. The vertical mobility of Cu atoms is lower (in order) than horizontal one.

At energy 10 eV during the whole run the stress components of σ_{zx}, σ_{zy} and σ_{zz} for metal film in horizontal plane have comparably low values (Fig. 5). For the energy 20 eV at the initial bombarding ($n \leq 10$) all three stress components in horizontal plane have considerable fluctuations. The σ_{zz} component has the biggest fluctuation into the area of negative values. Amplitude of this fluctuation in 22.5 times higher than that of σ_{zy} quantity and in 7 times higher than that of σ_{zx} one. Such extensive fluctuations of stresses in Cu film at energy of bombarding clusters 20 eV are connected with impacts of Ar atoms compressing the film and knocking out Cu atoms.

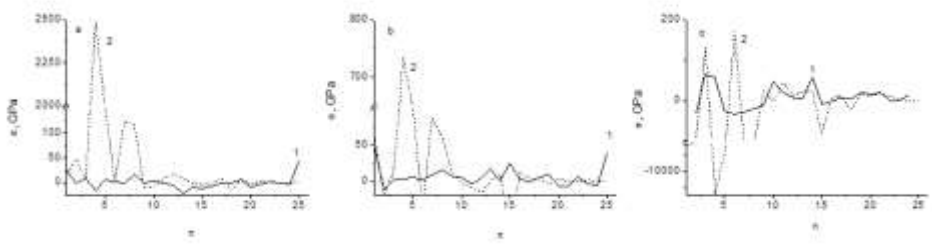

Fig. 5. Stresses of metal film: (a) σ_{zx}, (b) σ_{zy}, (c) σ_{zz} in xoy plane at bombardment by clusters at incident angle 0° and energy: (1) 10 eV, (2) 20 eV.

Stresses distribution in graphene between the rows in the "chair" direction (at Ar_{13} cluster energies 10 and 20 eV) is shown in Fig. 6. Because of strong shot-interacting bonds in graphene there are no essential differences between stresses values of σ_{zx}, σ_{zy} and σ_{zz} for serious of cluster bombarding with energies 10 and 20 eV. The σ_{zx} and σ_{zy} stresses are uniformly distributed in the plane of the graphene sheet. For both energies the maximum σ_{zz} stress in this area of graphene sheet exceeds in 4-7 times the maximum values of σ_{zx} and σ_{zy} stresses. It is connected with impulses transmitted to graphene from Cu atoms which they get as a result of impacts with Ar atoms.

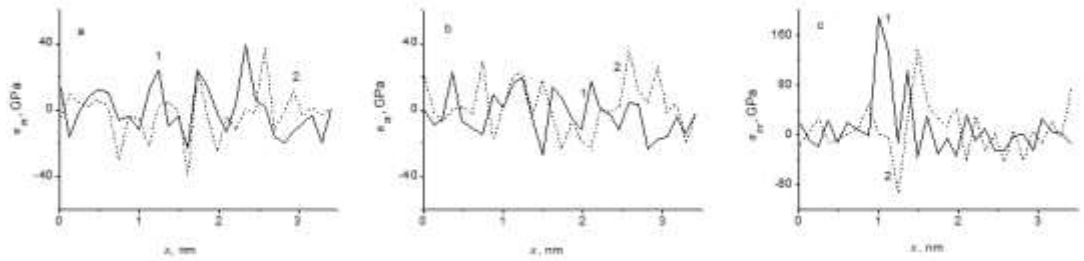

Fig. 6. Stresses distribution: (a) σ_{zx}, (b) σ_{zy}, (c) σ_{zz} in the graphene sheet by the rows of carbon atoms along the "chair" direction for bombarding serious by Ar_{13} clusters with energies: (1) 10 eV, (2) 20 eV.

Roughness R_a of the graphene sheet rises nonmonotonically as the number of Ar_{13} clusters impacts with a target grows (Fig. 7). When the clusters energy is 10 eV the increase of R_a is a slow process with low amplitudes. There are considerable fluctuations of $R_a(n)$ function especially in the values range of $10 \le n \le 25$ when energies are 20 and 30 eV. The decrease of initial growth of roughness in the case of energy 20 eV is connected with the reduction of final R_a value because of smoothing effect. At the final step of bombarding the Ar_{13} cluster flies rather lower over graphene surface and "polishes" it not meeting Cu atoms.

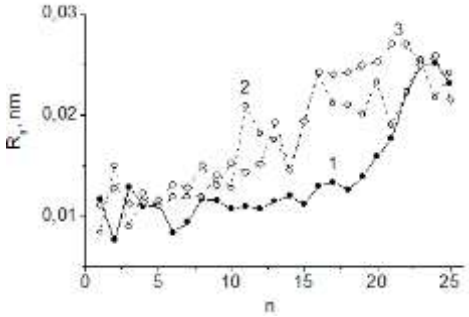

Fig. 7. Roughness of graphene surface at bombarding of "metal film on graphene sheet" system by Ar_{13} clusters with energy: (1) 10 eV, (2) 20 eV, (3) 30 eV.

4. Conclusion

The simulation of graphene cleaning of copper with Ar_{13} clusters is executed in this work. The clusters have incident angles θ = 90º, 75º, 60º, 45º and 0º and energies 5, 15, 20 and 30 eV. The bombarding with incident angle of 0º has not given the desirable result. There is no graphene cleaning of copper even at energy 20 eV. The remained copper atoms on the graphene surface form a "column". Dependently upon the energy the "column" is vertical or has an inclination in relation to the graphene sheet. Incline bombarding (at angles θ = 45º, 60º, 75º) gives positive result only at the angle 45º and Ar_{13} clusters energy 20 and 30 eV. Graphene has been cleaned of copper at such energies but it is damaged drastically. Its edges are bent and lost a few carbon atoms. The total amount of Cu atoms are removed from graphene at the angle θ = 45º and with clusters kinetic energy 30 eV. In the case of energy 20 eV the remained copper film over graphene is removed at motion of graphene sheet vertically

down or in parallel direction. Bombardment in the direction parallel to the graphene sheet (incident angle 90°, the "nap of the earth" flight) is the most effective cleaning method. At the "nap of the earth" flight the total cleaning is obtained with the clusters energy 20 and 30 eV. The strong stresses especially caused by vertical forces appeared in the copper film during initial bombarding. There are no considerable stresses in the graphene sheet. There is a weak dependence of stresses in the graphene plane on the energy of clusters. Stresses in graphene caused by vertical forces are much lower here (in several times) comparing to any other incline bombarding. The deformation of the graphene sheet during parallel bombarding is minimal.

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