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Functionalization of *low-k* surfaces with low-energy Ar ions

© A.A. Solovykh[1], A.A. Sycheva[2], E.N. Voronina[1,2]

[1] Moscow State University, Moscow, Russia
[2] Skobeltsyn Institute of Nuclear Physics, Moscow State University, Moscow, Russia
E-mail: sycheva.phys@gmail.com

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In this work low-energy Ar impacts on *low-k* surfaces were simulated with ab initio density functional theory method. The obtained results reveal the mechanism of CH_3-group removal under Ar atom/ion irradiation; the threshold energy of this process was estimated.

Keywords: *low-k* dielectrics, functionalization, simulation, diffusion barriers, methyl groups.

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Nanoporous organosilicate films with ultralow permittivity k (*low-k* dielectrics) based on amorphous SiO_x matrices are now used widely to insulate copper conductors in interlayer connections of modern very-large-scale integration circuits [1]. However, this technology is fraught with problems, and one of them is related to the diffusion of Cu atoms deeper into a *low-k* film and the associated deterioration of dielectric material properties. In order to prevent this, ultrathin (up to 5 nm) barriers made from refractory metals [1,2] are deposited onto the surface of narrow trenches produced in *low-k* films. This procedure is made difficult by the complex morphology of *low-k* dielectrics: their low k values are achieved by introducing pores coated with hydrophobic CH_3 groups into their structure. In order to enhance the adhesion between metal atoms and a dielectric material, one needs to perform preparatory treatment (i.e., functionalization) of a thin near-surface layer of *low-k* materials with the purpose of removing CH_3 groups from it. This treatment performed in plasma may result in deterioration of the properties of *low-k* films under the influence of chemically active radicals and vacuum ultraviolet radiation. Therefore, low-energy (no higher than 20 eV) ions, which have the capacity to remove methyl groups both from the bottom and from the side walls of trenches [3] and do not cause any significant damage to the lower-lying dielectric layers, are planned to be used to functionalize the surfaces of these materials.

The aim of the present study is to examine the influence of low-energy (below 20 eV) Ar atoms and ions on a *low-k* dielectric and determine the conditions under which methyl groups may be removed from its surface. The quantum-mechanical density functional theory (DFT) method is used to achieve these goals. The steady-state DFT method differs from the Hartree–Fock method in that the total ground-state energy of the system is presented not in the form a functional of a many-electron wave function, but as a functional of the electron density of the system [4]. This method is not just more efficient in terms of computational costs; it often provides more accurate results due to the introduction of an approximate functional characterizing the exchange and correlation effects. In the present study, the exchange–correlation PBE functional within the generalized gradient approximation (GGA) was applied. It provides a correct description of the interaction of atoms and ions of inert gases with various chemical elements in a wide energy range [5]. Dynamic DFT calculations with molecular dynamics algorithms were carried out in the plane wave basis with PAW pseudopotentials [6] in Vienna Ab Initio Simulation Package (VASP) [7] at the supercomputer complex of the Moscow State University [8]. A POSS (polyhedral oligomeric silsesquioxanes) molecule with an attached methyl group, which is characterized by formula $Si_8O_{12}H_7-CH_3$ (Fig. 1), was chosen as a model of a *low-k* dielectric to reduce computational costs. Such simplified molecular models containing Si−O and Si−C bonds, which are typical of *low-k* dielectrics, are used widely to study reactions on the surface of these materials [9]. Initial energy $E_0 = 5-20$ eV of incident particles and the angles between the initial Ar velocity direction and the Si−C bond line were varied in dynamic calculations, and different impact parameters (with respect to a C atom) were considered. Lower boundary E_0 of the energy interval was determined based on the results of preliminary steady-state calculations of the Si−C bond energy in a POSS molecule. The obtained value (4.4 eV) agrees closely with the available experimental data (see, e.g., [10]). The time step was set to 0.1 fs, and the duration of a single trajectory was 0.5−1.0 ps. The VMD package was used to visualize and analyze calculated data [11].

The results of dynamic simulations revealed that threshold energy E_{th} of an ion (i.e., the energy needed to remove the CH_3 group) depends to a considerable extent on the interaction geometry. The minimum value of $E_{th} = 11$ eV was obtained when Ar approached the C atom directly at an angle of 90° to the Si−C bond (Fig. 1). Having analyzed the calculated data, we identified the key features of the mechanism of methyl group removal. Figure 2, *a* presents the successive changes in positions of atoms in

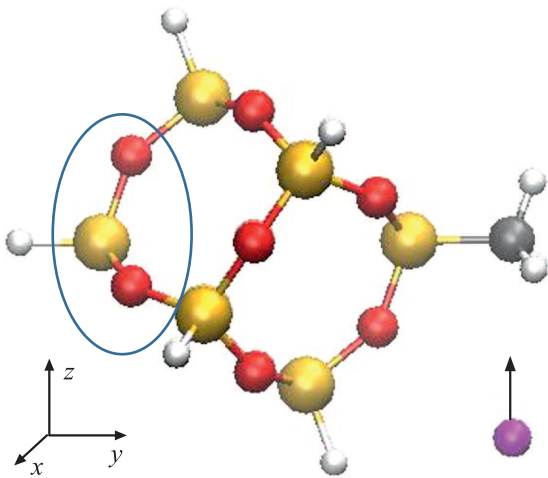

Figure 1. Mutual arrangement of the POSS molecule model and an incident Ar atom/ion corresponding to the minimum threshold energy value. The direction of motion of the incident particle is indicated by an arrow. The atoms enclosed in an oval were fixed to prevent translational and rotational motion of the molecule.

the POSS molecule and the incident Ar atom for one of the calculated trajectories in the case when the CH_3 radical was ejected, and Fig. 2, *b* shows the temporal dependences of the kinetic energy of the Ar atom and the radical at different values of initial energy E_0. It can be seen that Ar atoms lose a major fraction ($\sim 80\%$) of their initial energy E_0 in the interaction with the POSS molecule (curves *1–3* in Fig. 2, *b*) and deviate from the initial direction by angle $\sim 35{-}40^\circ$, which decreases as E increases. A significant fraction ($\sim 50{-}60\%$) of energy transferred to the molecule is converted into kinetic energy E_{CH_3} of the methyl group that increases rapidly after the impact, but then starts decreasing and approaches a certain asymptotic value (curves *4–6* in Fig. 2, *b*). If the transferred energy is not sufficient to break the Si–C bond, oscillations of the methyl group are observed. They decay slowly in the process of molecule relaxation (curve *6* in Fig. 2, *b*). In the contrary case, the CH_3 radical is ejected. The force of attraction acting between this radical and the POSS molecule at relatively small separation distances reduces the kinetic energy of CH_3. The resulting asymptotic value of E_{CH_3} is roughly equivalent to the difference between the energy transferred to the methyl group and the Si–C bond energy (curves *4* and *5* in Fig. 2, *b*).

When the angle of particle incidence or the impact region change, the threshold energy increases (e.g., E_{th} grows to ~ 17.5 eV in the case of incidence at an angle of 60° to the Si–C bond). The fraction of energy transferred to the CH_3 group then decreases to $\sim 40\%$, and marked oscillations of atoms around the Ar motion trajectory are seen in the POSS molecule. These oscillations induce a more substantial deformation of the molecular structure than the impact delivered perpendicular to the Si–C bond. The population analysis (see its results in the table) and calculations of the spatial distribution of the spin electron density (see the insets in Fig. 2, *a*) were performed in order to identify changes in the electronic structure of the POSS molecule induced by its interaction with a neutral Ar atom. It is evident that the positive charge magnitude at the Si atom in the POSS molecule decreases after the methyl group removal, and the spin density is localized at this Si atom and the CH_3 radical. Thus, the obtained results demonstrate that the impact mechanism plays a leading part in the interaction between an incident neutral Ar atom and a methyl group, and the structural changes in the POSS molecule are insignificant.

The above data were obtained by simulating the interaction between a neutral Ar atom and the POSS molecule. Owing to the specifics of implementation of the DFT method in VASP, the charge was set for the system as a whole in subsequent studies into the interaction with a positively charged Ar ion. The results of dynamic simulations presented in Figs. 2, *c, d* and in the table illustrate clearly the differences between the interaction mechanisms of an ion and a neutral atom. In contrast to the previous case, an impact alters significantly the POSS molecule geometry: the Si atom shifts toward the center of the molecule, thus changing the length of Si–O bonds and valence angles O–Si–O (see the table). It follows from the analysis of the temporal dependences of the kinetic energy for an Ar ion (Fig. 2, *d*) that the total energy transferred by it to the CH_3 group does not decrease after the ejection of the group (i.e., CH_3 is not attracted to the molecule). This is the reason why the E_{th} value decreases significantly: the methyl group is removed under the influence of an Ar ion with an initial energy of ~ 5 eV. The calculated data suggest that the interaction of an ion with the methyl group results in neutralization of this ion and the emergence of a defect (with an excess positive charge localized at it) in the POSS molecule. This is confirmed by the calculated values of fractional charges at atoms (see the table). The discovered charge defect may be neutralized quickly by an incident electron flux at the bottom of trenches, but is likely to be preserved for a much longer time on the side walls.

Significantly, the above values of threshold energy E_{th} were determined for the optimum parameters of interaction with argon. However, since the surface of *low-k* dielectrics is not perfectly smooth, the interaction of incident irradiating particles with CH_3 groups on the side walls of trenches may occur at different angles to the Si–C bond. This contributes to an increase in E_{th}. It should also be noted that additional energy may be released in the process of ion neutralization near the surface; therefore, more accurate *ab initio* methods are needed to calculate the exact value of E_{th} of an ion needed to remove the methyl group.

Thus, the obtained simulated data revealed that Ar atoms and ions incident on the surface of a *low-k* dielectric may break the Si–C bond and thus induce subsequent removal of the CH_3 group. The threshold energy of an Ar atom needed for the CH_3 group to be ejected

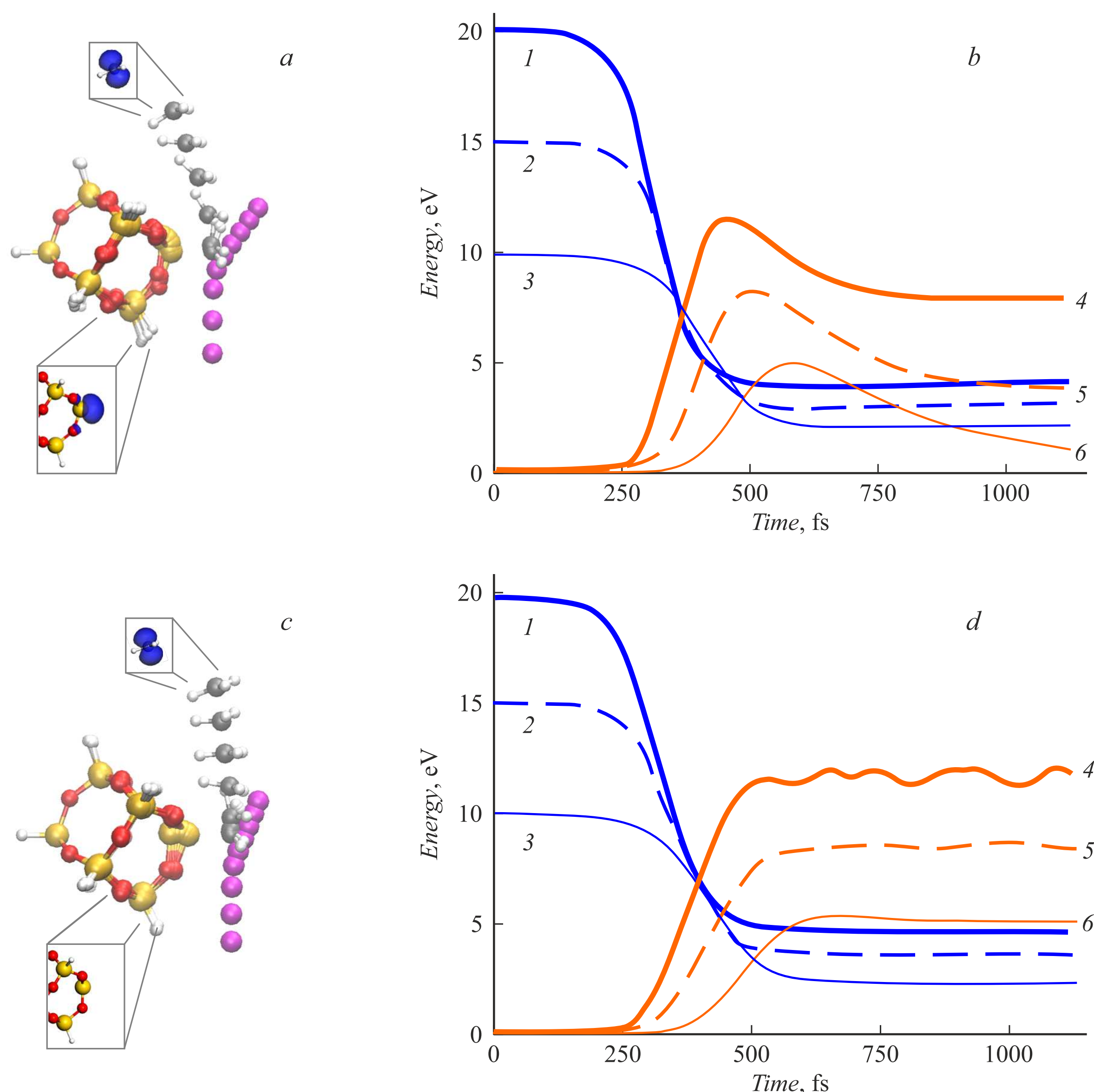

Figure 2. *a*, *c* — Successive changes in positions of atoms in the POSS molecule and the incident Ar ($E_0 = 12.5$ eV) without (*a*) and with (*c*) regard to charge, which were registered every 10 fs within the first 140 fs of simulation. The spatial distributions of spin electron density (for 0.05 $Å^{-3}$) in the POSS molecule and the CH_3 radical are shown in blue in the insets (see the color version of this figure in the online version of the paper). *b*, *d* — Temporal dependences of the kinetic energy of Ar (*1–3*) and the escaping CH_3 radical (*4–6*) for $E_0 = 10$ (*3, 6*), 15 (*2, 5*), 20 eV (*1, 4*) without (*b*) and with (*d*) regard to charge.

Parameters of the POSS molecule prior to and after the incidence of Ar (R is the bond length, α is the valence angle, Q is the fractional atom charge, and BO is the value of the overlap integral characterizing the bond strength)

		R, Å		α, deg		Q, e		BO		
		Si–O	C–H	O–Si–O	H–C–H	Si	O	Si–O	Si–C	C–H
Before interaction	–	1.65	1.10	109.35	108.3	+1.77	−0.93	0.58	0.81	0.73
After the CH_3 group ejection	Without charge	1.65	1.10	109.67	120.0	+1.35	−0.91	0.81	–	0.73
	With charge	1.58	1.10	119.92	120.0	+1.75	−0.87	0.76	–	0.73

assumes a minimum value of $\sim 11\,eV$ in the case when the impact is delivered to the C atom at an angle of 90° to the Si–C bond. When the incident particle is positively charged, the methyl group is removed even at an energy of 5 eV (if the interaction trajectory is optimal). Thus, Ar ions with an ultralow energy of 5–20 eV have the capacity to remove hydrophobic CH_3 groups from the surface layer of *low-k* films. The obtained results may help develop a technique for preparatory functionalization of the surface of *low-k* dielectrics by low-energy ion fluxes with the purpose of subsequent formation of diffusion barriers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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