

Mechanisms of fluorocarbon film destruction during atomic layer etching of silicon dioxide

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This paper describes the results of quantum-mechanical DFT modeling of elementary physical and chemical processes of fluorocarbon film damage and removal during plasma-assisted atomic layer etching of silicon dioxide. The energy parameters of the chemical reactions involved are determined, which has important practical implications for improving VLSI manufacturing technology.

Keywords: plasma, atomic layer etching, fluorocarbon film, ions, radicals, modelling.

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As the manufacturing process for very large scale integrated circuits improves, the need for precision control of the surface of processed materials at the atomic layer level grows. During etching, such control can be achieved by using atomic layer etching (ALE), which is based on self-limiting reactions [1]. The sequences of these reactions are selected accounting for the surface properties of a particular material and can differ drastically for different materials, which ensures high selectivity of such etching. The ALE process can be divided into two main stages, which are repeated many times:

- 1) surface modification by creating a thin modified layer by gas-phase particles (including through film deposition);
- 2) further removal of this layer.

Particular interest is attracted to plasma-enhanced ALE (PE-ALE), in which it is possible to ensure anisotropy of etching due to ion irradiation in the second stage. However, when implementing PE-ALE in low-temperature gas discharge plasma, it is necessary to carefully control the discharge parameters in order to minimize the sputtering of the material under treatment and the defect accumulation in its surface layers. At the same time, the implementation

of PE-ALE technological process requires ensuring reproducibility of the etching conditions and the thickness of the removed layer in each cycle [2].

Currently, an active search is underway for ALE „recepies“ i.e., a detailed description of the process stages, including reaction sequences, composition of gas mixtures, discharge parameters, temperature conditions, etc., for specific materials, taking into account already known technological solutions. Thus, conventional ion-assisted etching of silicon dioxide (SiO₂) often involves the use of fluorocarbon plasma. An important role in this process is played by CF_x film formed on the surface of the material, which serves as a source of radicals necessary for etching SiO₂ surface layers [3,4]. In existing implementations of PE-ALE SiO₂ [4–6], the first stage involves film deposition („surface modification“) without bias voltage ($V = 0$), and the second stage involves bombardment with Ar ions with energies up to 150 eV, which „activate“ chemical reactions both in the film and in the thin surface layer of SiO₂, which ultimately leads to the removal of this layer. In order to minimize damage to the material by ions, a three-stage PE-ALE process was implemented at SINP MSU (a detailed description is given in the works [7,8]):

- 1) film deposition in plasma C₄F₈/Ar: $V = 0$, power $P = 200$ W, flow rate $v(\text{Ar}) = 834$ sccm (similar for three stages), $v(\text{C}_4\text{F}_8) = 27$ sccm, pressure 3 Pa, time 15 s;
- 2) irradiation with low-energy Ar ions: $P = 400$ W, ions energy $E_{\text{Ar}} \sim 50$ eV, 15 s;
- 3) cleaning of material surface in plasma O₂/Ar: $V = 0$, $P = 500$ W, $v(\text{O}_2) = 166$ sccm, 20 s.

It should be noted that at the third stage, the chamber walls are also cleaned of fluorocarbon compounds, which made it possible to ensure a virtually identical thickness (~ 0.5 nm) of the removed SiO₂ layer throughout the entire etching process.

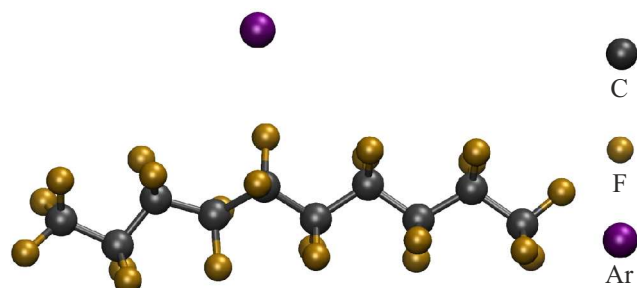


Figure 1. Image of the model of C₁₀F₂₂ molecule and flowing Ar ion.

Table 1. The most probable processes of Ar and O₂ ions interaction (at E_0 up to 50 eV) with a non-defect molecule C₁₀F₂₂, resulting in the escape of hot radicals

Process	Ion		Radical		
	E_{th} , eV	E_X/E_0 , %	E_{com}/E_0 , %	E_{sum}/E_0 , %	θ , deg
Ar ion					
F atom knock-out without breaking of C–C bond	15	up to 20	up to 50	–	5–25* 45–65**
Escape of F atom with breaking of C–C bond	20	up to 10	up to 20	–	50–60
Escape of two atoms of F	30	up to 30	20–30 5–10	30–35	up to 10 50–60
Escape of CF radical	30	up to 5	up to 30	up to 35	25–40
Escape of CF ₂ radical	20	8	10–25	15–35	to 25
Breaking of C–C bond (without escape of radical)	15	up to 10	–	–	–
O ₂ ion (without dissociation)					
F atom knock-out without breaking of C–C bond	15	up to 30	up to 30	–	up to 60
Escape of F atom with breaking of C–C bond	20	5–10	up to 5	–	80–90
Escape of two atoms of F	25	up to 15	20–25 5	up to 25–30	10 60
Escape of CF	25	up to 20	19	20	up to 15
Escape of CF ₂ radical	20	up to 5	15	40	30
Breaking of C–C bond (without radical escape)	20	up to 20	–	–	–

*When hitting an F atom directly.

**When the ion hits the area near C–C bond or C atom.

To improve the proposed implementation of PE-ALE process, including finding the optimal range of ion energies, a detailed understanding of the defect formation mechanisms in CF_x film and knowledge of the energy parameters of the volatile products formed during this process are critical. Therefore, in this work, a modeling of elementary physical and chemical processes occurring in such films due to impacts of plasma particles was performed.

Film models were developed accounting for the available experimental data on the structure of similar films: looseness and low density (about 1.0–1.5 g/cm³) [3,4,9], prevalence of single bonds C–F and C–C and low concentration of double bonds C=C [3], as well as groups CF_x ($x = 1, 2, 3$), among which CF₂ groups prevail [3,6]. It is generally accepted that film growth occurs due to the addition of CF₂ radicals to radical sites that arise in it as a result of ion bombardment. Therefore, the film can be considered as a set of long branched fluoropolymer chains with the chemical formula (–CF₂–CF₂–)_{*n*}, fragments of which are connected to the surface of SiO₂ and other chains. It should be emphasized that the described mechanism of film growth due to chemisorption of CF₂ radicals does not reduce the number of radical sites, since each adsorbed radical becomes such a site.

For modeling, the quantum method of density functional theory (DFT) was chosen rather than the classical method of molecular dynamics, since the interatomic potentials developed for this method do not yet allow a reliable description of the formation and breaking of chemical bonds impacted by low-energy ions (see, for example, [10]). As a film model C_{*n*}F_{2*n*+2} molecule was selected at $n = 10$ (Fig. 1). DFT calculations were performed within the generalized gradient approximation (GGA) with the exchange-correlation functional PBE in the basis of plane waves with PAW pseudopotentials in the VASP software [11] on „Lomonosov-2“ supercomputer of the Shared Research Facilities using ultra-high-performance computing resources of Moscow State University [12]. In the calculations, the particles initial energy of $E_0 = 5–50$ eV and the approach angles were varied; the time step was chosen within 0.01–0.1 fs depending on E_0 . The analysis of the calculated trajectories of 0.5–5.0 ps was carried out using VaspReader package developed by A.A. Solovykh, and VMD [13] program was used to display the calculated data.

DFT-modeling demonstrated that Ar ions with an energy of $E_0 = 15–50$ eV are capable of breaking both, C–F, and C–C bonds (energy of these bonds is equal ~ 5.1 and 3.8 eV respectively) in CF_x-film, thus, triggering the escape of chemically active F-containing radicals. Table 1 contains a

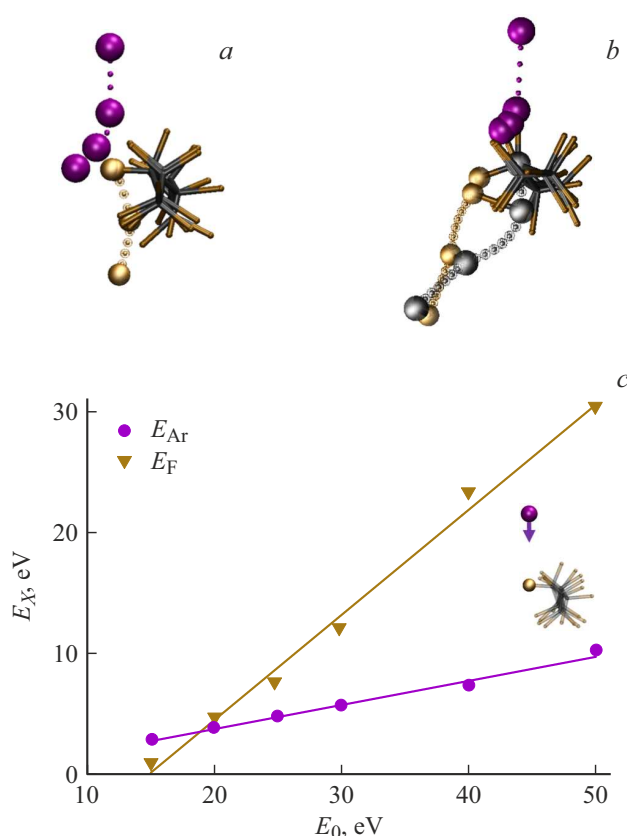


Figure 2. *a, b* — successive changes in positions of atoms involved in the process of F atom (*a*) and CF radical (*b*) elimination when hit by Ar ion with an energy of 25 (*a*) and 50 eV (*b*) per molecule C₁₀F₂₂. *c* — dependencies of kinetic energy of F (E_F) and Ar (E_{Ar}) atoms after hitting from the initial energy of E_0 ion for the impact geometry shown in the Figure.

list of the most frequently encountered elementary processes in our calculations, which occurred quickly (less than 1 ps) and led to the emission of hot radicals F, CF and CF₂ with energy of 5–30 eV, as well as to the breaking of C–C bond. The specific parameters of the analyzed processes are also given there: the process threshold energy E_{th} , the escape angle and volatile products energy in relation to the initial energy of the ion E_0 (E_{sum} ion and E_{com} denote the total kinetic energy of the particle and the energy of its translational motion). Much slower processes were also observed: e.g., if an ion impact affected several atoms at once, intense vibrations arose in the molecule, which could lead to its division into two fragments or breaking of the end groups (C₂F₅ or CF₃).

An important result of the calculations is the confirmation of the formation of reactive radicals F and CF with high kinetic energy (Fig. 2, *a, b* and Table 1). Such radicals may penetrate through CF_x-film into the near-surface layer SiO₂ [4,14]. In order to determine the threshold energy of E_{th} ion required to knock the F atom out of the film, we performed calculations in the impact geometry, when Ar ion moved perpendicular to C–F bond in the molecule and entered the immediate vicinity of F atom (Fig. 2, *a*). An

analysis of the calculated trajectories revealed close to linear dependences of kinetic energy of the knocked-out F atom and Ar atom after the impact on the initial energy of E_0 ion (Fig. 2, *c*) and made it possible to estimate the threshold energy: $E_{th} \approx 13$ eV (Table 2). For this configuration, the escape angle of F atom (relative to the direction of the initial ion velocity) lay within 5–25°, going down with the rise of E_0 . The CF radical formation, accompanied by breaking of two C–C bonds at once, was demonstrated in our analysis at a significantly higher energy of the incident Ar ion ($E_{th} \sim 30$ eV) and a certain direction of its movement (almost parallel to the C–F bond, as in Fig. 2, *b*). Therefore, at E_0 less than 30–40 eV the formation of such radicals seems unlikely, however, with an increase in E_0 the probability of CF escape may increase significantly.

Thus, at the second stage of ALE, Ar ions with an energy of 40–50 eV can knock out hot F atoms and CF_x radicals from the fluorocarbon film, which are capable of penetrating into the surface layer of SiO₂ and initiating successive breaking of Si–O [14] bonds and formation of various surface groups up to the appearance of volatile products, i.e., the actual etching of SiO₂ [4,8]. In CF_x film, fragmentation of (–CF₂–CF₂–)_n chains and their depletion of fluorine occurs, which is in good agreement with the experimentally observed decrease in F/C concentration ratio in the second stage of PE-ALE [4–7]. Defluorination of the film leads to the appearance of radical centers and the subsequent formation of double bonds –C=C– in the chains [4]. However, the IR spectra of such films after irradiation with Ar ions with energies up to 50 eV contain intense peaks corresponding to CF_x groups and significantly weaker peaks characteristic of double bonds between C [4] atoms. Therefore, it can be assumed that the defects formed by ions are “healed” slowly.

At the third stage of ALE, as follows from the experimental data [7], there occurs a complete removal of the residues of the defluorinated CF_x film and the cleaning of the surface of the material from etching products under the action of Ar/O₂ plasma. The main particles in the gas discharge mode are Ar⁺ and O₂⁺ ions with an average energy of ~ 20–25 eV and highly reactive O atoms with the flux density two to three orders of magnitude higher than the ion flux density [8].

As demonstrated from dynamic DFT analysis, during the interaction of O atoms with energies up to 0.5 eV

Table 2. The coefficients of the linear dependences of the kinetic energy of the ion and the escaping F atom after hitting of the ion initial energy

Ion	X	k_X	$E_X(0)$, eV
Ar	Ar	0.20	–0.19
	F	0.87	–12.8
O ₂	O _{2 com}	0.21	0.99
	O _{2 sum}	0.25	1.08
	F	0.64	–12.8

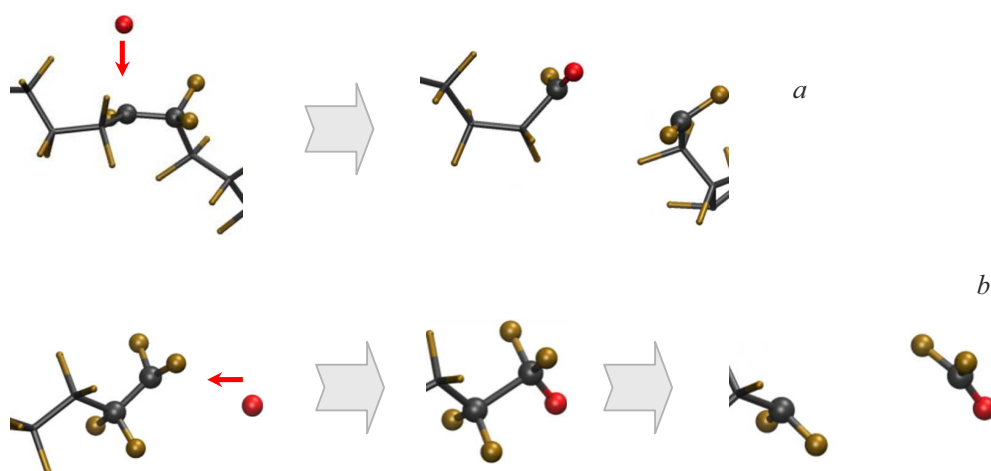
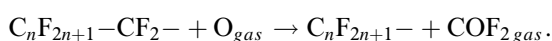


Figure 3. Splitting of $C_{10}F_{21}$ molecule with a defect into two fragments after breaking of C–C bond by a thermal O atom (a) and the addition of O atom to the radical end group of CF_2 with the formation of the carbonyl fluoride molecule COF_2 (b).

with defect-free C_nF_{2n+2} molecules, scattering of incident particles predominates due to their intense repulsion from F atoms. This result is in good agreement with the high resistance of F-containing films to impacts of even hot O atoms with energies up to 4 eV [15]. However, the presence of defects in such fluorocarbon chains drastically changes the interaction pattern: now thermal O atoms easily attach to the defect (Fig. 3, a), which causes a rapid rupture of one of the adjacent C–C bonds and the division of the molecule into two parts with terminal groups $FC=O$ and CF_2 on the left and right fragments, respectively. The second of the resulting groups is radical and can actively participate in reactions with thermal O atoms with the formation of C-containing volatile products, e.g. carbonyl fluoride (COF_2) (Fig. 3, b):



This exothermic ($\Delta E = -5.8$ eV) reaction observed in our dynamic analysis at $E_0 = 0.1$ eV, contains two stages: first, O atom is attached to the radical group of CF_2 ($\Delta E = -5.6$ eV), and then a volatile COF_2 molecule ($\Delta E = -0.2$ eV is formed, with the energy barrier for COF_2 separation $E_{act} = 0.2$ eV [16]). The important peculiarity of this reaction is reproduction of the radical group CF_2 , due to which the reaction may be repeated with the next attacking O atom. Thus, the removal of carbon from the fluorocarbon chains $(-CF_2-CF_2-)_n$ by thermal O atoms is a multi-stage process that involves the sequential breaking of chemical bonds by several O atoms, and the key condition for this process to occur is the presence of defects in such chains.

Molecular ions O_2 with an energy of 15–40 eV are also capable of breaking C–C or C–F bonds (Table 1), initiating the chain breaking into two fragments and the formation of volatile products (mainly hot radicals F and CF_2), however, in the specified range of E_0 , no dissociation of O_2 occurred. As for Ar ions, a linear dependence of energy of the escaped F atom on E_0 was revealed, as well as the kinetic energy

of the O_2 molecule after the impact on the initial energy of the ion (Table 2 and Fig. 4, which also shows the relative positions of O_2 ion and F atom after hitting). The presence of a defect in $C_{10}F_{22}$ molecule (e.g., due to the removal of one F atom) drastically increases the probability of dissociation of the molecular ion even at $E_0 = 15$ –20 eV, and the hot O atoms formed in this case with an energy above 4–5 eV are capable, as noted above, of initiate rapid destruction of the film.

Thus, the performed dynamic DFT-modeling showed that the effect of Ar ions with an energy of 15–50 eV leads to fragmentation of CF_x film and its defluorination, which is consistent with the experimentally observed decrease in F/C concentration ratio [4–7]. Hot F atoms and CF radicals generated by ion impacts penetrate the loose CF_x film quite easily and reach the SiO_2 surface with high kinetic energy,

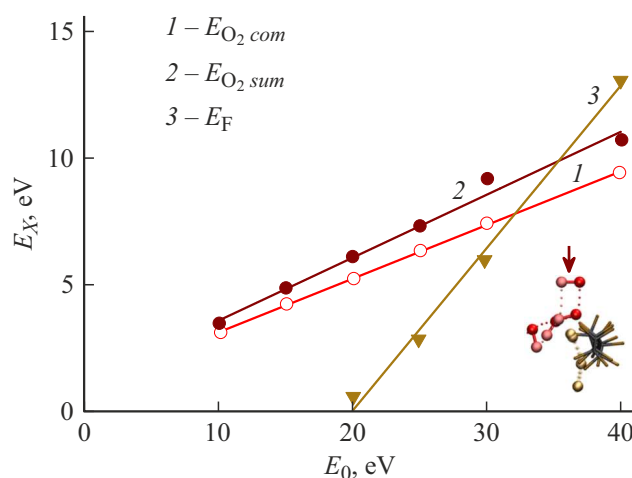


Figure 4. Dependences of the total kinetic energy of O_2 ($E_{O_2, sum}$) molecule, the energy of its translational motion ($E_{O_2, com}$) and the kinetic energy of the escaping F atom (E_F) on the initial energy of E_0 ion. Also, the successive changes in position of O_2 ion and knocked out F atom were demonstrated.

whereby they can initiate chemical reactions that cause etching of the material. Thus, CF_x -film acts as a source of hot F-containing radicals, which modify the SiO_2 surface layer [3,8,14]. Complete destruction of the film and its removal from the surface of the material occurs at the third stage of PE-ALE in O_2/Ar plasma mainly due to thermal highly reactive O atoms, but the presence of defects in CF_x -film, which are formed at the second stage of PE-ALE under irradiation with Ar ions, is critically important.

Analysis of the calculated data made it possible to estimate the threshold energies of elementary physical and chemical processes and revealed a linear dependence of the energy of knocked-out F atoms on the initial energy of the impacting ion. The found parameters and dependencies are important for the development of kinetic models used to optimize modern and develop new methods for implementing PE-ALE SiO_2 in fluorocarbon plasma.

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Conflict of interest

The authors declare that they have no conflict of interest.

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