# Elastic Scattering of Neutral Fluorine on Si, O, C, and H Atoms in the Range of the Relative Kinetic Energies of 2–200 eV

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**Abstract**– Binary interatomic potentials F–F, F–Si, F–O, F–C, and F–H are calculated from the first principles (ab initio) on the basis of the multi-configuration method of self-consistent field (CAS-SCF) with a basic set of atomic wave functions aug-pp-AV6Z and are used to calculate phase shifts and cross sections of elastic scattering of atoms in the range of relative kinetic energies of 2–200 eV. It is expected that the obtained elastic scattering cross sections will be useful for a description of sputtering and etching of porous organosilicate films with ethylene bridges used in modern nanoelectronics.

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In the coming years, the semiconductor industry may reduce the requirements to the dielectric constant of films in the interconnect technology for the first 4 layers from 2.5 to 2.7–3.2 due to the use of air gaps in even layers and ultra-thin diffusion barriers [1, 2]. One of the main reasons for this trend is the low value of Young's modulus of highly porous films. This creates problems in the manufacturing of final products and reduce their reliability. Therefore, simultaneously with the reduction of porosity, the possibility of improving the mechanical film properties by introducing carbon bridges, for example, ethylene groups  $(-CH_2-CH_2-)$  [3], in the matrix of organosilicate glasses [4, 5] is studied.

The most successful technology of film etching is still the use of beams of neutral Cl atoms [6] in twochambers etching setup. This approach makes it possible to obtain a deep trench form, close to ideal, because the influence of dielectric charge up by plasma and UV radiation in the etching process is excluded. Chlorine, however, is a poisoning gas, so the question of its replacement is extremely appropriate. Fluorine is one of candidates to replace it.

To describe sputtering of films, either the Monte Carlo (MC) method or the molecular dynamics (MD) approach are usually used, if the elastic scattering cross sections [7] or interatomic interaction potentials are known [8]. Using the method of MD allows not only to calculate the energy and angular distributions of sputtered and reflected atoms, but also to obtain such important parameters as the volume and surface binding energies of atoms in a solid. The use of the MD method to real problems of nanoelectronics is limited by high requirements to computer resources, and the MC approach is still the main one in modeling of nanodevices. The aim of this work is to compute interatomic potentials and quantum-mechanical cross sections of elastic scattering of atomic pairs involved in sputtering of porous organosilicate films by atomic fluorine, i.e., F–H, F–C, F–O, F–F, and F-Si pairs, for their subsequent use in the MC method [9].

As the interaction potentials of F–H, F–C, F–O, F–F, and F–Si atomic pairs, the corresponding molecular terms in the ground state of molecules were used, i.e.  ${}^{1}\Sigma^{+}$ ,  ${}^{2}\Pi$ ,  ${}^{2}\Pi$ ,  ${}^{2}\Pi$ , and  ${}^{1}\Sigma^{+}$ , respectively. We have calculated these terms on the basis of the multi-configuration Hartree–Fock method (CAS-SCF) for interatomic distances from 0.4 to 20 a.u. All calculations were performed with the software package MOLPRO 2010.1 [10] with a set of basic atomic wave functions aug-pp-AV6Z [11].

Figure 1 shows the potentials used in this work for F–H, F–F, F–C, F–O, and F–Si atomic pairs. It is clearly seen that all five potentials have the regions of attraction with wells of different depths: from the minimum value of -0.42 eV for F–F pair to the maximum one of 5 eV for F–H molecule. The equilibrium distances vary from 0.9 Å for the F–H molecule to 1.59 Å for the F–Si atomic pair.

The phase shifts  $\delta_l(E)$  were determined by analyzing the solution of the radial Schrödinger equation in



Fig. 1. The potential energy of F–H, F–F (a) and F–C, F–O, and F–Si (b) atomic pairs used to desribe sputtering of  $SiO_2C_xH_y$  films.

the asymptotic region for the relative kinetic energy *E* of atoms in the range of 2–200 eV. Phase shift calculations were limited by 0.001 radian, that for the energy value of 200 eV corresponded to the maximum orbital quantum numbers  $l_{max} = 90$  for F–H,  $l_{max} = 814$  for F–F,  $l_{max} = 2907$  for F–C,  $l_{max} = 2655$  for F–O, and  $l_{max} = 7203$  for F–Si pairs. The obtained values of the phase shifts  $\delta_l(E)$  were then used to calculate the differential and integral sections of the elastic scattering.

For heterogeneous atomic pairs, the differential scattering cross-section in the center-of-mass (CM) system was calculated on the base of the equation:

$$\frac{d\sigma_{cm}}{d\Omega}(E,\theta) = \left|\sum_{l=0}^{\infty} \frac{(2l+1)}{k} e^{i\delta_l(E)} \sin \delta_l(E) P_l(\cos \theta)\right|^2, (1)$$

where  $P_l(\cos \theta)$  is the *l*-th Legendre polynomial,  $k = \{2\mu E/\eta^2\}^{1/2}$  is the wave vector,  $\theta$  is the scattering angle in the system of the center of mass of a heterogeneous molecule,  $\mu$  is the reduced mass of the molecule, *E* is the kinetic energy of the relative motion of the atoms of the pair.

The differential cross section (DCS) of the scattering of homogeneous atomic pairs, in our case F-F, in the CM system was calculated on the basis of the equation [12]:

$$\frac{d\sigma_{cm}}{d\Omega}(E,\theta) = 2 \left| \sum_{l=0,2,4...}^{\infty} \frac{(2l+1)}{k} e^{i\delta_l(E)} \sin \delta_l(E) P_l(\cos\theta) \right|^2,$$
(2)

where  $k = \{2\mu E/\eta^2\}^{1/2}$  is the wave vector,  $\theta$  is the scattering angle in the system of the center of mass of homogeneous molecules,  $\mu$  is the reduced mass of the homogeneous molecule, *E* is the kinetic energy of the relative motion of the atoms of the pair.

Integral cross-sections were calculated using analytical formulas obtained by integrating expressions (1)-(2) over all polar and azimuthal angles.

The differential cross sections of F-C (a) and F-F (b) atomic pairs for the relative kinetic energy of 10 eV depending on the scattering angle in the system of the center of mass of the atomic pair are presented on Fig. 2. In the case of identical atoms, Fig. 2b, it is seen that the DCS has the mirror symmetry with respect to the angle of 90°. For both cases, the maximums at rainbow angles (close to 30° and 15°) corresponding to the position of the singularity in the classical DCS are clearly visible. For the F-C pair, the rainbow angle is 35°, and the DCS decreases almost monotonically with a further increase in the scattering angle.

The integral cross sections (ICS) of the elastic scattering of atomic pairs F–C, F–O, and F–Si (a), F–F and F–H (b) are shown on Fig. 3 as a function of the relative kinetic energy. The main feature of the obtained ICS is the presence of well-recognized Glory maxima, the number of which [13] is equal to the number of bound states supported by the potential under study. In the case of F–Si, F–O, F–C, F–F, and F–H pairs, the numbers of such states are 67, 18, 58, 12, and 14, respectively. It is seen from Fig. 3 that



Fig. 2. The differential cross section of F-C (a) and F-F (b) atomic pairs for the relative kinetic energy of 10 eV as a function of the scattering angle in the center of mass of the atomic pairs.



Fig. 3. The dependence of the integral cross section of the elastic scattering of atomic pairs on the relative kinetic energy.

only a part of such maxima are shown for all five potentials.

The authors expect that interatomic potentials and elastic scattering cross sections obtained for the F–Si, F–O, F–C, F–F, and F–H atomic pairs will be used to describe sputtering, either by the MC or MD method for typical plasma processing energies, i.e., 2–200 eV. All phase shifts and elastic scattering cross-sections were calculated using programs developed at SINP MSU. The obtained potentials, phase shifts and cross sections can be provided by A.P. upon request.

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## CONFLICT OF INTEREST

The authors state that they have no conflict of interest.

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