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Elastic scattering of ruthenium atoms from Si and O atoms in the range of relative kinetic energies of 2−200 eV

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Interconnector technologies of a new generation involve the use of ruthenium. The high cost of experimental study of sputtering and etching of trenches in Ru leads to the need to optimize it by modeling that requires knowledge of the cross sections of elementary processes of interaction of plasma particles with Ru. In this work, the binary interatomic potentials of Ru-Ru and Ru-Si pairs tested by the molecular dynamics method, and the Ru-O one calculated by the method of multi-reference configurational interaction MRCI/AV5Z were used to calculate the elastic scattering cross sections of the atomic pairs in the energy range typical of plasma etching chambers.

Keywords: ruthenium, elastic scattering, cross sections, sputtering, binary potential.

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Ruthenium is one of the main candidates for replacing copper in the technique for creating next-generation interconnectors [1]. The rutheniuḿs advantages over copper are, first, a lower nanoscale electrical resistance and, second, the absence of necessity to use a barrier layer in dielectrics, which allows (at least partially) applying lower-cost techniques developed for aluminum, i.e., prior to emergence of the copper-based interconnectors [2].

Direct etching of ruthenium is performed in plasma of argon, oxygen and chlorine; as a result, ruthenium gets fully removed, mainly in the form of volatile compound RuO_4 [3]. As a mask, silicon compounds are used, for instance, SiO_2 [4]. While the $Ar/O_2/Cl_2$ plasma has been already modeled [5], literature does not offer etching models accounting for both the ruthenium sputtering in such a plasma and chemical etching itself.

To describe the sputtering process with the Monte-Carlo method, it is necessary to know differential and integral cross sections of the atomsélastic scattering (DCSES and ICSES, respectively); the first ones are used to describe variations in the particle motion direction after the collision, the second ones are for determining the pre-collision mean free path of a particle. The goal of this work was to calculate quantum-mechanics DCSES and ICSES for atomic pairs consisting of Ru, Si and O.

Parameters of binary potentials in equation (1) for the Ru−Ru and Ru−Si pairs [7]

Atomic pair	D_o	S	R	D	β	R_o
Ru−Ru	3.5739	1.3923	4.7770	0.2617	1.4795	2.1189
Ru−Si	4.0886	1.8837	1.8818	0.7751	1.7812	2.1769

For this purpose, we use the binary part of empirical three-particle potentials which have confirmed their reliability in describing by the molecular dynamics method the properties of silicon carbide films with embedded ruthenium atoms [7]. In this work, the ruthenium trajectories were described using binary potentials of atomic pairs Ru−Ru and Ru−Si

$$V(r) = \frac{D_o f}{S-1}\Big\{\exp\big(-\beta\sqrt{2S}(r-R_o)\big) - S\exp\big(-\beta\sqrt{2/S}(r-R_o)\big)\Big\},$$

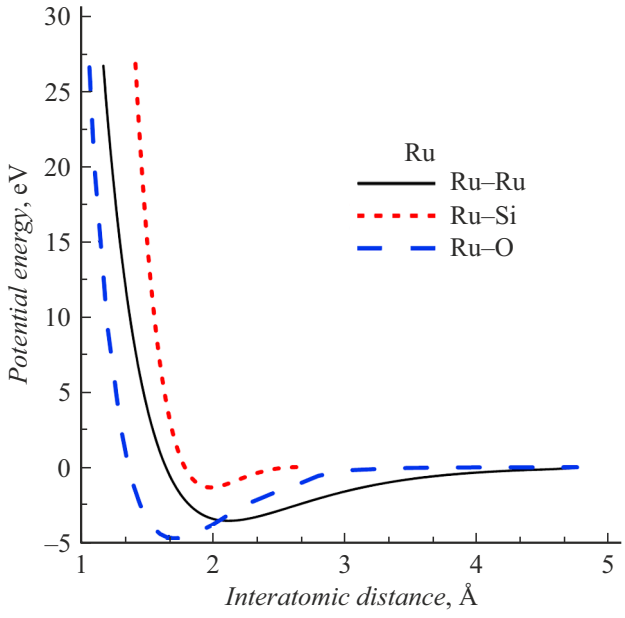

Figure 1. Potential energies of atomic pairs Ru−Ru, Ru−Si and Ru−O versus interatomic distance.

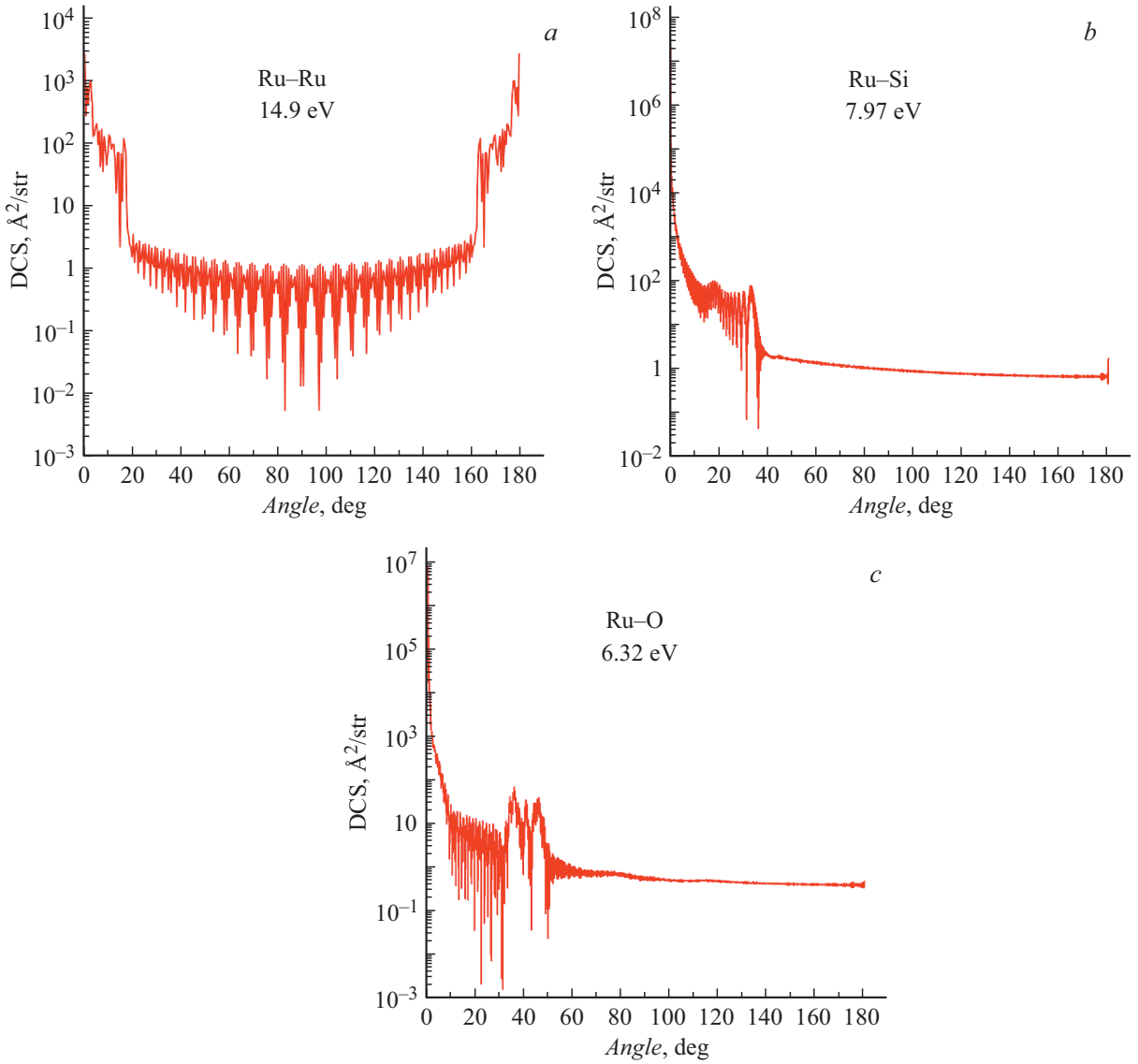

Figure 2. DCSES of atomic pairs Ru−Ru (a), Ru−Si (b) and Ru−O (c) versus θ for $E = 14.9$, 7.97 and 6.32 eV, respectively.

$$f = \begin{cases} 1, & r \leqslant R - D, \\ 0.5\left(1 - \sin\left(\dfrac{\pi}{2}\dfrac{r-R}{D}\right)\right), & |R - r| \leqslant D, \\ 0, & R + D < r, \end{cases} \quad (1)$$

where parameters D_o, S, R, D, β and R_o are presented in the table. The potential is expressed in eV, the distance is given in Å.

As for the Ru−O pair, we used the molecule RuO ground state $X^5\Delta$ calculated based on the method of multi-reference configurational interaction (MRCI) with the basis set aug-cc-pV5Z-PP (Ru) and aug-cc-pV5Z (O) [8]. Fig. 1 presents the potentials used in this work for pairs Ru−Ru, Ru−Si and Ru−O. All the three potentials are of the attractive type with wells of different depths and different equilibrium states R_e: 3.574 eV and $R_e = 2.123$ Å for pairs Ru−Ru, 1.352 eV and $R_e = 1.984$ Å for pairs Ru−Si, 4.734 eV and $R_e = 1.703$ Å for pairs Ru−O.

Phase shifts $\delta_l(E)$ were precisely calculated by the variable phase method [9,10] for atomsrelative kinetic energies $E = 2-20$ eV and by the WKB approximation for energies of 20−200 eV. The calculations were stopped at reaching $\delta_l(E) = 0.001$ rad which corresponded to the maximal orbital quantum numbers $l_{\max} = 10\,787$ for pairs Ru−Ru, $l_{\max} = 3721$ for pairs Ru−Si, and $l_{\max} = 4539$ for pairs Ru−O for the upper energy limit of 200 eV. Then DCSES and ICSES were calculated based on the obtained phase shifts $\delta_l(E)$.

In the center-of-mass (CM) system, DCSES of atomic pairs Ru−O and Ru−Si were calculated as follows [11]:

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

Here $P_l(\cos\theta)$ is the lth Legendre polynom, θ is the scattering angle in the CM system of the Ru−O molecule,

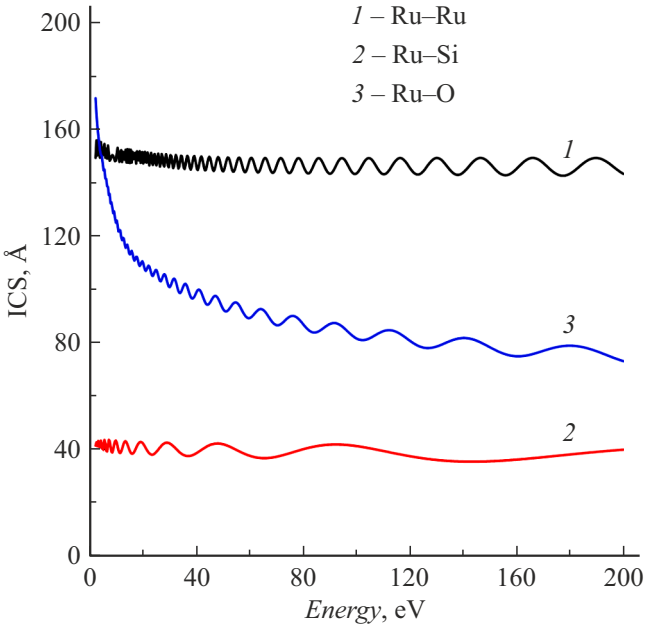

Figure 3. ICSES of atomic pairs Ru−Ru, Ru−Si and Ru−O versus E.

E is the relative kinetic energy of atoms Ru and O, with corresponding wave vector $k = \{2\mu_{\mathrm{RuO}}E/\hbar^2\}^{1/2}$ (μ_{RuO} is the molecule Ru−O reduced mass). Similar calculations were performed for the Ru−Si molecule.

Scattering of pairs of identical atoms (Ru−Ru) was simulated in the CM system using the following expression [11]:

$$\frac{d\sigma_{CM}}{d\Omega}(E,\theta) = 2\left|\sum_{l=0,2,4\ldots}^{\infty}\frac{2l+1}{k}e^{i\delta_l(E)}\sin\delta_l(E)P_l(\cos\theta)\right|^2, \quad (3)$$

where designations E, k, θ and μ are of the same meaning as in equation (2). ICSES is the integral of (2), (3) over the polar $(0, \pi)$ and azimuthal $(0, 2\pi)$ angles.

Fig. 2 presents DCSES of atomic pairs Ru−Ru (a), Ru−Si (b) and Ru−O (c) versus θ for $E = 14.9$, 7.97 and 6.32 eV, respectively. Characteristic features of the calculated DCSES are the right-angle mirror symmetry in the case of identical atoms (Ru−Ru in Fig. 2, a) and local maxima in Fig. 2, $a-c$ at rainbow angles of 10−50° corresponding to the DCSES singularity positions in classical mechanics.

Fig. 3 demonstrates ICSES of atomic pairs Ru−Ru, Ru−Si and Ru−O versus E. Generally, the calculated ICSES exhibit only one remarkable feature, i. e., glory-oscillations whose number corresponds to the number of potential bound states of atomic pairs Ru−Ru, Ru−Si and Ru−O, namely, 185, 91 and 75, respectively. Other ICSES characteristic features, for instance, shape resonances, are not visible in the figure because energies they occur at are considerably lower than the lower limit of the range under consideration.

In summary, notice that the obtained DCSES and ICSES values may appear to be awfully useful in simulating sputtering of ruthenium films with the typical plasma ion energies of $\sim 2-200$ eV.

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Conflict of interests

The author declares that he has no conflict of interests.

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