

Article

Contamination of Amorphous Carbon Thin Films: Modelling the Transport of Atoms in Gases During Deposition

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Abstract

Monte Carlo simulations of the transport of atoms in gases related to the deposition process and the contamination of amorphous carbon thin films during deposition in magnetron discharges have been performed. These films are of interest in accelerator technology due to their low secondary electron yield when their structures are dominated by sp² carbon. Two codes, which practically share the same algorithm, are introduced: TAGs 1 simulates the transport of sputtered atoms from the target to the substrate, and TAGs 2 simulates the transport of atoms from the plasma towards the target and the substrate. The similar results of TAGs 1 and the well-established SIMTRA for the same input parameters imply the algorithm's accuracy. The codes were used to model the transport of different atoms (C, H, O, D) in a magnetron Ar discharge. The simulations reveal that the operating pressure should be higher than 1 Pa for a sample-target distance of 90 mm to secure sp² carbon formation. The contamination mechanisms of amorphous carbon coatings were then studied by merging the results obtained with both programs. Preliminary comparisons with experiments suggest that the combined results of TAGs 1 and 2 agree very well with the experiments.

Keywords: magnetron sputtering; Monte Carlo simulation; a-C thin films; secondary electron emission

1. Introduction

Electrons accelerated in RF fields towards chamber walls can be multiplied in the process of secondary electron emission. If the secondary electron yield (SEY) is too high, this can lead to the formation of electron clouds in accelerators of positively charged particles, thereby limiting their performance through the increased heat load in the cryogenic parts of the system, a rise in pressure, and beam instabilities [1–3]. The formation of electron clouds can be efficiently suppressed by coating the inner walls of accelerator tubes with a low-SEY material. Amorphous carbon (a-C) coatings have been successfully used for that purpose in the Super Proton Synchrotron at CERN (European Organisation for Nuclear Research, Geneva, Switzerland) [4]. The same material is also being considered

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as a solution for the High-Luminosity upgrade of the Large Hadron Collider (CERN) and the Electron-Ion Collider (Brookhaven National Laboratory, Upton, New York, USA) [5,6].

The SEY of a-C coating is strongly influenced by the film structure and various impurities that are incorporated during deposition [7–9]. In particular, the presence of hydrogen increases SEY. In recent studies, we have investigated the deposition of amorphous carbon coatings by magnetron sputtering in the presence of different amounts of deuterium in Ar to reveal the mechanisms of deuterium incorporation [10,11]. The ultimate goal of that work was to develop mitigation strategies for preserving the low SEY of the a-C coatings produced in the presence of hydrogen precursors in the discharge gas.

Given the presence of H₂ in the residual gas, there are generally two major mechanisms of hydrogen poisoning, both initiated by the formation of H atoms in the discharge by electron-impact dissociation:

1. Direct transport of hydrogen atoms from the plasma to the substrate (direct poisoning);
2. Target poisoning by atomic hydrogen, followed by resputtering and subsequent deposition onto the substrate together with carbon atoms (poisoning via target contamination).

Other mechanisms, such as the implantation of H₂⁺ and, in particular, H⁺ ions into the target, followed by resputtering, are significantly less probable [10]. In the case of other hydrogen precursors that are commonly present in the residual gas (e.g., H₂O or CH₄), electron-impact dissociation rate constants are significantly higher than the formation rates of molecular or atomic ions in magnetron discharges, which typically exhibit electron temperatures in the 1–10 eV range. Therefore, dissociation, followed by film contamination—either directly or via target poisoning—should also represent the dominant contamination mechanisms.

Equivalent processes occur in the presence of deuterium in the discharge gas. Previous results have indicated that, under the studied conditions [10], the dominant mechanism for deuterium contamination is target poisoning. It is, however, not clear which fraction of D atoms generated in the discharge reaches the substrate directly and is incorporated into the growing film. Another important detail to be understood is which of the two mechanisms dominates at a particular target–substrate distance and operating pressure, and how the total contamination level varies with these parameters. Addressing these questions through simulations requires programs that can model the transport of two kinds of atoms in gases: those sputtered from the target and the atoms generated in the plasma by the dissociation of the precursors.

A detailed model of a magnetron sputtering has to encompass all relevant aspects of the process: the magnetic field distribution, the magnetron discharge itself, particle–target interactions yielding ion sputtering of target atoms and secondary electron emission, particle transport in the gas phase, and film growth on the substrate [12]. An example of such a comprehensive simulation is DSMC/PICMC (Direct Simulation Monte Carlo/Particle in Cell Monte Carlo), which represents a kinetic plasma and transport simulation for coating processes at low pressure, developed at the Fraunhofer Institute for Surface Engineering and Thin Films [13], as well as the more recent Pantera code [14]. Execution of such simulations requires high-performance computing, which is not suitable for rapid tests. Another approach is the separate modelling of the key steps in the deposition process. Apart from the ion–target interaction, which determines the sputtering yield and the energy and angular distribution of sputtered particles, their transport from the target to the substrate also has a significant influence on the deposition rate, composition, and structure of the deposit.

A few Monte Carlo simulations have been developed to model the transport of sputtered atoms [15–19]. A comprehensive review of this topic can be found in [20]. After the appearance of the program SIMTRA [21], which gained widespread use due to its user-friendly interface, the ability to model complex geometries, and free availability, further interest in developing similar codes largely diminished, although occasional studies continue to appear (e.g., [22]). Nevertheless, we are not aware of Monte Carlo simulations capable of modelling the transport of atoms generated in the gas phase freely available to the research community. This latter point motivated us to develop such a code, based on an algorithm very similar to the one used in SIMTRA and other equivalent simulations. Since SIMTRA cannot model the transport of sputtered hydrogen atoms—which we identified as one of the contamination steps of a-C films—a separate code for modelling the transport of sputtered particles was also developed. The major difference between the two codes lies in the initial conditions assigned to the atoms tracked during their transport through the gas.

In this work, we investigate the contamination of a-C films during the deposition process. To this end, two Monte Carlo simulation programs were developed to model atom transport in gases during magnetron sputtering. TAGs 1 (Transport of Atoms in Gases simulation) simulates the transport of sputtered atoms from the target to the substrate and is, therefore, equivalent to the well-established SIMTRA code, while TAGs 2 simulates the transport of atoms from the plasma towards both the target and the substrate. Both programs can simulate transport through multi-component gases. After presenting details of the algorithm shared by the two programs, we compare the results obtained with SIMTRA and TAGs 1 for the transport of sputtered carbon atoms through Ar to validate the accuracy of TAGs 1. We then analyse how variations in input parameters and the introduced approximations may affect the simulation results. The central part of the work consists of simulations of the transport of carbon, oxygen, hydrogen and deuterium atoms to the substrate as a function of pressure and target–substrate distance. Selected results are then used to estimate the deposition rates of deuterium and carbon under the experimental conditions reported in [10], enabling direct comparison with the experimental data. Finally, the results were used to predict the contamination trends as a function of pressure and target–substrate distance for two different magnetron sources.

2. The Algorithm of TAGs

The general simulation strategy is similar to that employed in other test-particle Monte Carlo simulations describing the motion of particles in a gas [15–21] or in solid phase (e.g., SRIM [23]). In the development of TAGs 1, we mainly followed the approach used in SIMTRA ver. 2.2.0, which corresponds to the authors' publication [21]. The current version of TAGs 1 is suitable for simulating particle transport between a planar disc-shaped target and a planar substrate oriented parallel to the target surface. Other geometries can be modelled after relatively simple modifications of this code. The present version of TAGs 2 models the transport of atoms from toroidal plasma located just above the target, towards both the target and the substrate.

Atoms begin their trajectories either from the target surface (TAGs 1) or from a point within the toroidal plasma (TAGs 2). The initial velocity vectors are randomly chosen according to predefined distributions. While inside the chamber, emitted atoms undergo elastic collisions with gas atoms, resulting in linear momentum transfer and changes in velocity direction. Interatomic interactions are modelled within the binary collision approximation using an interaction potential selected according to the projectile energy. The distance between two successive collisions is randomly chosen based on the previously calculated mean free path. Each sputtered particle trajectory is followed until the particle

reaches the chamber walls, the magnetron source surface, or the substrate; particles impacting a solid surface are assumed to stick. The algorithm's details are provided below.

The initial particle conditions, selected using the Monte Carlo principles, include the emission point, initial energy, and initial velocity direction. In TAGs 1, sputtered particles of mass m are emitted from an axially symmetric plasma track with a radial distribution corresponding to the etching profile of the target. The latter can be measured using a profilometer or defined by the user and expressed as two-column, radius vs. depth, within an input ASCII file. The energy distribution of sputtered particles follows the Thompson distribution,

$$Y_T(E_0) = \frac{E_0}{(E_0 + E_{SB})^3} \cdot \left(1 - \sqrt{\frac{E_0 + E_{SB}}{E_{max}}}\right), \quad (1)$$

where E_0 is the initial energy of a sputtered particle in vacuum and Y_T is the sputtering yield. The distribution depends on two parameters: the surface binding energy E_{SB} and the maximum energy of sputtered particles E_{max} . In the present version of the code, the angular distribution of sputtered particles, $dY_T/d\Omega$, is proportional to $\cos^a(\theta)$. The initial direction in the spherical coordinate frame is determined by the azimuthal and polar angles, chosen as $\varphi = 2\pi \cdot R_\varphi$ and $\theta = \arcsin(R_\theta^{1/(1+a)})$, where R_φ and R_θ are random numbers uniformly distributed in the interval $[0, 1]$. Other energy and angular distributions of sputtered particles can be easily implemented. Atoms formed in the plasma (TAGs 2) are uniformly distributed within the discharge volume and have velocities following a Maxwell distribution determined by the discharge gas temperature.

From the known gas composition and the total gas pressure, the collision partner and the exact position of the next collision are determined using the Monte Carlo approach from the partial pressures of the gas atoms and the corresponding collision cross sections. The distance between two subsequent collisions is calculated as $d = -\lambda \cdot \ln R$, where λ is the mean free path between two collisions and R is a random number uniformly distributed in the range $[0, 1]$. The mean free path is calculated as

$$\lambda = \frac{1}{\sum_{i=1}^n (n_i \sigma_i)} \cdot \frac{v_p}{\langle v_{rel} \rangle}, \quad (2)$$

where n_i is the concentration of the i -th atomic species in the gas, σ_i is the total scattering cross section of the projectile on gas atom i , which depends on the projectile energy E , v_p is the projectile speed and $\langle v_{rel} \rangle = \langle |\vec{v}_p - \vec{v}_g| \rangle$ is the mean value of the projectile speed relative to the gas atoms.

As in SIMTRA, atomic collisions are calculated using three different approaches depending on the projectile velocity relative to the most probable speed of a gas atom, $v_{g0} = (2kT/M)^{1/2}$, where k is the Boltzmann constant, T is the absolute gas temperature, and M is the mass of a gas atom. For multicomponent gases, an average value of the most probable gas speed is used, calculated using the gas stoichiometry. The same holds for the average speed of gas atoms, $v_{g1} = (8kT/(\pi M))^{1/2}$, which is also used in the simulation. Depending on the projectile speed, the following three approaches are used to simulate the collision events:

1. For projectile speeds higher than $7 v_{g0}$, we can safely neglect the motion of gas atoms and model the collisions as an interaction of the projectile with a gas atom at rest. This choice of the velocity limit ensures relative errors below 1%. (SIMTRA uses a less restrictive limit of $5 v_{g0}$ [20]).
2. For projectile speeds below $7 v_{g0}$, the velocity of the gas atom is included. Collisions are treated in the gas atom reference frame after randomly choosing gas atom velocities from a Maxwell distribution, $[v_{gx}, v_{gy}, v_{gz}] = (kT/M)^{1/2} [R_{n1}, R_{n2}, R_{n3}]$, where R_{ni} ($i = 1, 2, 3$) are normally distributed random numbers with unit standard deviation. In

the new reference frame, the scattering events are modelled using approach 1 if the projectile kinetic energy exceeds $E_{min} = 3kT/2$, or approach 3 otherwise. Apart from the alteration of the projectile velocity, gas atom motion also affects the total scattering cross-section, as described below.

3. Projectiles with kinetic energies $E < E_{min}$ in the gas atom reference frame are treated as thermal, and their interactions with gas atoms are described within a hard-sphere model. Most collision events in TAGs 2 fall within this regime.

In this type of simulations, the most complex task is the calculation of the scattering angle from the known interaction potential, impact parameter and projectile energy, which implies solving the scattering integral of the form

$$\Theta = \pi - 2p \cdot \int_{r_{min}}^{\infty} \frac{dr}{r^2 \cdot \left[1 - \frac{U(r)}{E} - \frac{p^2}{r^2} \right]} \quad (3)$$

in the centre of mass coordinate frame [24]. Here, E is the total energy of the system, $U(r)$ is the interaction potential of the collision partners at distance r between the two nuclei, and p is the impact parameter. This integral has analytical solutions only for the simplest potentials, such as the hard sphere model (case 3). For more realistic interaction potentials, including screened Coulomb potentials that are suitable for 1 eV–100 keV energies (including cases 1 and 2), the integral in Equation (3) must be solved numerically.

An efficient way to reduce the time necessary for the scattering angle calculation is to form a 2D mesh of scattering angles for each atomic species i in the gas, in the centre of mass frame, as a function of the projectile energy and the impact parameter $\Theta_{ijk}(E_j, p_k)$ [25] (index i defines the gas atom species). Energies are equidistant in the range from E_{min} to E_{max} (with a typical energy step of 1 eV for TAGs 1 and 50 meV for TAGs 2), while impact parameters span from 0 to the energy-dependent value p_{max} , where the scattering angle is negligible, i.e., smaller than a value Θ_{min} , being an input parameter. Having in mind the character of the scattering angle dependence on the impact parameter, the p -axis uses a logarithmic scale with 20 values per decade. Scattering angles $\Theta_{ijk}(E_j, p_k)$ are computed by solving the integral in Equation (3) using the Chebyshev–Gauss quadrature [26]. Then, during simulations, the scattering angle of the projectile on the gas atom i , $\Theta_i(E, p)$, is obtained by 2D linear interpolation of the pre-calculated values of the $\Theta_{ijk}(E_j, p_k)$ mesh.

Similarly, for each projectile energy, in the considered range, the scattering angle $\Theta_{ij}(p)$ is also calculated for equidistant values of $p \leq p_{max}(E_j)$, to determine the differential cross-section $(d\sigma/d\Omega)_{CM} = p/\sin \Theta \cdot |dp/d\Theta|$. These values are then transformed to the laboratory frame $(d\sigma/d\Omega)_L$ by the relation [24]

$$\left(\frac{d\sigma}{d\Omega} \right)_L = \left(\frac{d\sigma}{d\Omega} \right)_{CM} \cdot \frac{\left[\left(\frac{m}{M} + \cos \Theta \right)^2 + \sin^2 \Theta \right]^{3/2}}{1 + \frac{m}{M} \cos \Theta}, \quad (4)$$

and integrated over the solid angle to obtain the total scattering cross-sections for each combination of the gas atoms i and projectile energies j . During the simulations, the $\sigma_i(E)$ values, used to calculate the mean free path λ (Equation (2)), are obtained by the linear interpolation from the previously calculated total cross-sections $\sigma_{ij}(E_j)$.

In case 3 ($E < E_{min}$), the scattering angle is given by $\Theta = 2 \cdot \arccos(p/(r_p + r_g))$, where r_p and r_g are the projectile and gas atom radii in the hard sphere model, respectively [24]. In our simulations, $r_p + r_{gi} = (\sigma_i(E_{min})/\pi)^{1/2}$, and the total cross section σ_i used in Equation (2) equals $\sigma_i(E_{min})$.

Assuming the velocity of gas atoms follows the Maxwell distribution, the average value of the projectile speed relative to the gas atoms can be expressed as [27]

$$\langle v_{rel} \rangle = v_{g1} \cdot \left[\left(s + \frac{1}{2s} \right) \frac{\sqrt{\pi}}{2} \operatorname{erf}(s) + \frac{1}{2} e^{-s^2} \right] \quad (5)$$

where $s = v_p/v_{g0}$. When the projectile speed is sufficiently high, $v_p > 7v_{g0}$, the average of the relative speed of the projectile practically equals v_p . Equation (2) then reduces to $\lambda = 1/(n\sigma)$, which is exact only for the target atoms at rest. Otherwise, the mean free path shortens with decreasing of v_p .

In both simulations, the chamber pressure is constant. In TAGs 2, the plasma region temperature differs from the rest of the chamber. The input files for TAGs 1 and TAGs 2 differ slightly, as the latter additionally requires information about the size and shape of the discharge region. Their examples can be found in the Supplementary Material S1. Both programs support several screened Coulomb interaction potentials [24]: Thomas–Fermi with Molliere screening length (TFM), Ziegler–Biersack–Littmark potential with the universal screening length (ZBL), Thomas–Fermi–Molliere with the correction introduced by O’Connor and Biersack (OCB) [28], and Kr–C potential with universal screening length.

3. Results

The TAGs codes, initially developed in Scilab, were converted into Python (ver. 3.12.7), enabling the application of parallel computing and speeding up execution. For instance, when run on a current mid-range PC (Intel Core i7 13700H processor, Intel Corporation, Santa Clara, CA, USA), the execution of TAGs 1 for 10^6 carbon atoms at 1 Pa of Ar and a target–sample distance of 90 mm lasts approximately 3–4 min. The execution is not as fast as that of SIMTRA, which requires about 1 min on the same hardware for identical input parameters. However, one clearly does not need high-end performance hardware to execute the codes within a reasonable time while maintaining statistical accuracy. All TAGs simulations presented in this work were performed with 10^6 projectiles. The equivalent SIMTRA simulations were executed with 5×10^6 projectiles. All other parameters were kept identical.

3.1. The Benchmarking Study of TAGs 1 and SIMTRA

To test the algorithm of the TAGs 1 code, its results were compared with those of SIMTRA using identical input parameters. We simulated the transport of carbon atoms sputtered in an Ar discharge from a planar graphite target, based on an existing experimental setup [29]. The target has the form of a disc with a diameter of 25.4 mm, mounted on the Torus 1” HV cylindrical magnetron source from Kurt Lesker, schematically presented in Figure 1a. The carbon atoms are deposited onto a square $10 \times 10 \text{ mm}^2$ substrate situated 90 mm from the target surface, inside a cylindrical chamber with a diameter of 100 mm. The centres of the target and substrate surfaces are located on the chamber axis. The pressure was varied in the range from 0.01 to 3 Pa, and the temperature was fixed at 300 K. The ion energy was assumed to be $E_0 = 500 \text{ eV}$, which is an input parameter of SIMTRA used to calculate the maximum energy of sputtered particles. The maximum energy of sputtered particles in TAGs 1 was estimated from the corresponding SRIM simulations, yielding a value of $E_{max} = 125 \text{ eV}$. The surface binding energy was set to 7.41 eV, corresponding to the sublimation energy of graphite [30]. In the simulations performed with TAGs 1, a trajectory simulation of sputtered atoms terminates when their trajectory intersects the side walls of the vacuum chamber, as well as the target or substrate surface planes. The latter condition reduces the execution time with a modest impact on the accuracy (see Section 3.2.3. for details). The radial distribution of the emission points of sputtered particles, shown in Figure 1b, represents the measured radial profile of the plasma track on the graphite target used in our experiments. The TAGs 1 and SIMTRA

simulations were performed using the TFM interaction potential, as recommended in the SIMTRA manual. The gas diffusion option was turned off in SIMTRA to make the simulation conditions closer to those in TAGs 1. The simulation conditions are summarised in Table 1.

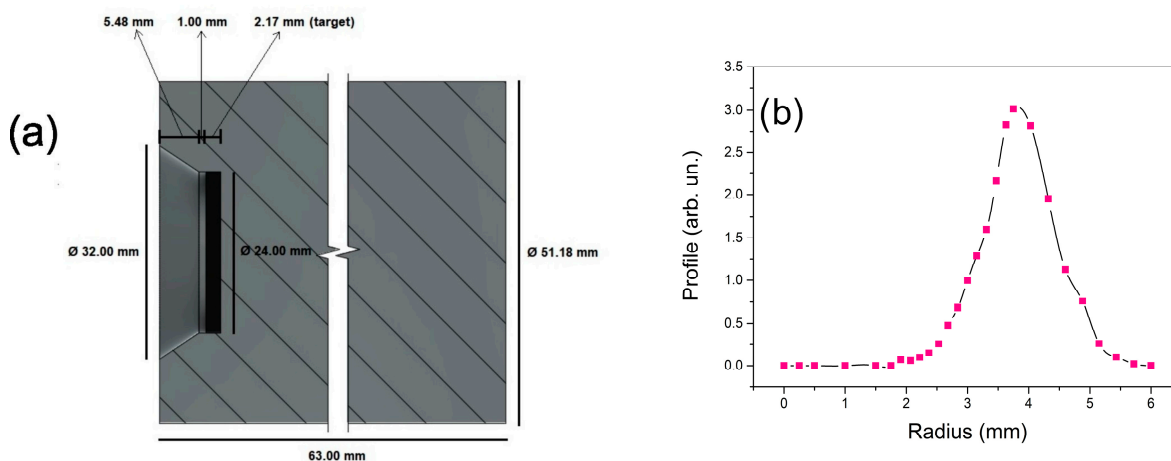


Figure 1. (a) Schematic of the magnetron source used in the simulations; (b) experimental profile of a plasma racetrack of a 1" graphite target used in the magnetron source in (a).

Table 1. Summary of the simulation parameters in TAGs 1, performed with 10^6 atoms.

p (Pa)	Substrate Target Distance	Chamber	Simulation Volume
0.01–3	10–90 mm	Cylindrical, D = 100 mm	Between the substrate and the target
$dY/d\Omega$	dY/dE	Interaction potential	Boundary conditions
$\cos\theta$	Thompson, $E_{SB} = 7.41$ eV, $E_{max} = 125$ eV	TFM	Sticking probability = 1

The uncertainty of the results was estimated by performing 20 consecutive simulations for different numbers of particles. The corresponding results are presented in Supplementary Material S2, Figure S1. For a sufficiently large number of particles in the simulation, the relative uncertainty of each parameter can be well approximated by

$$u_{rel} = \frac{200}{\sqrt{N_s}} \%, \quad (6)$$

where N_s is the number of atoms arriving at the substrate surface. The relative uncertainty determined in this way corresponds to two standard deviations of a Poisson distribution, which is expected to be applicable in this case, as it corresponds to stochastic, discrete rare events. Therefore, the absolute uncertainty of all parameters obtained using the TAGs 1 simulations is taken as the product of the relative uncertainty given by Equation (6) and the simulation result. The only parameter that may exhibit a slightly higher uncertainty is the average collision number (cf. Figure S1 in the Supplementary Material), which is of limited relevance. The error bars in the figures correspond to $\pm u_{rel}$, which should cover about 95% of possible values.

The comparison of the pressure dependences of the probability of sputtered atoms arriving at the substrate, F_s , their average arrival energies, E_{av} , and the average number of collisions, N_{col} , they encountered is presented in Figure 2. The results show the same trends, i.e., a decrease in F_s and E_{av} and an increase in N_{col} with increasing pressure.

Moreover, the average number of collisions appears to be very similar (although one should note that this scale is semi-logarithmic), as is the probability F_s at pressures up to 0.5 Pa and the average arrival energy at higher pressures. The values of E_{av} at lower pressures obtained using SIMTRA are about 30% higher. This discrepancy suggests that the definitions of the initial energies and directions may differ between the two codes.

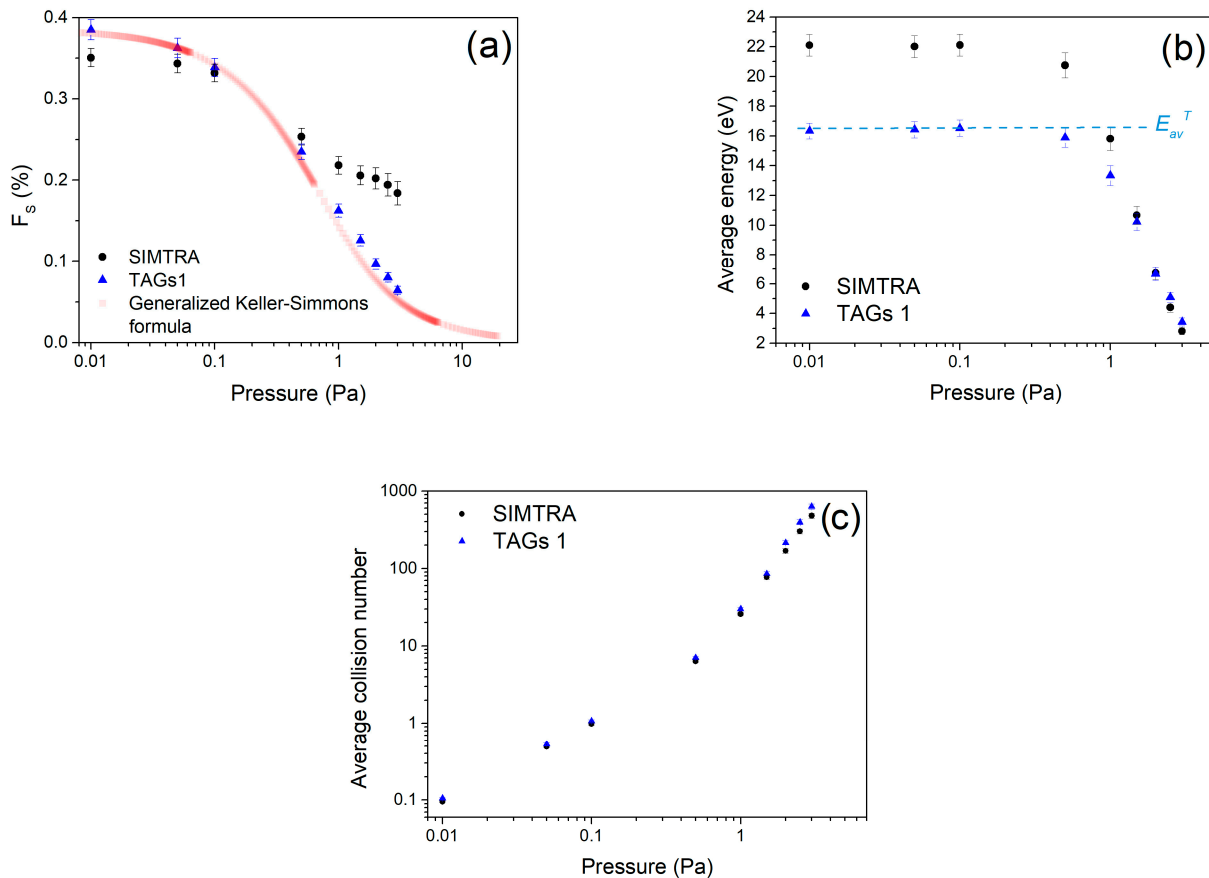


Figure 2. Simulations of the transport of sputtered carbon atoms to the substrate by SIMTRA and TAGs 1—pressure dependence: (a) F_s ; (b) E_{av} ; (c) N_{col} (see the text for details). The translucent red line in (a) is the generalised Keller–Simmons formula normalised to $F_s = 0.385\%$. The dashed line in (b) corresponds to the average energy of C atoms leaving the target, as calculated from the Thompson distribution with $E_{SB} = 7.41$ eV and $E_{max} = 125$ eV.

To test this hypothesis, Figure 3 compares the energy distributions of sputtered particles in TAGs 1 and SIMTRA with the Thompson distribution with $E_{max} = 125$ eV (Equation (1)), used as the input parameter in TAGs 1. While the TAGs 1 distribution practically overlaps with the Thompson distribution, the one generated by SIMTRA has a somewhat different shape and a comparable energy cut-off (around 93 eV). The average energy of the SIMTRA distribution is 22.2 eV, which perfectly matches the average energy of particles arriving at the substrate surface at very low pressures. Similarly, the value of E_{av} obtained with TAGs 1 at low pressures is practically equal to the average energy of the Thompson distribution $E_{av}^T = 16.5$ eV, calculated using the analytical Equation (1) (the same result was reported in [31]). Therefore, both codes yield average energies consistent with the energy distributions used, indicating that sampling of the initial energy of sputtered particles is performed correctly.

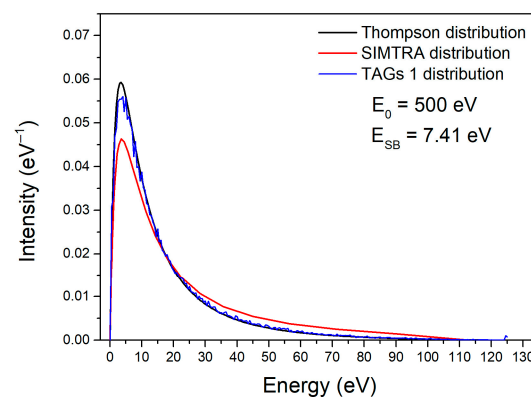


Figure 3. Comparison of the energy distribution of sputtered atoms used in the simulations.

Low-pressure conditions are also suitable to test the angular contribution of particles emitted from a point source at the chamber axis. For the cosine angular distribution, the probability of atoms reaching a square $10 \times 10 \text{ mm}^2$ substrate situated along the chamber axis at a distance z from the target surface and oriented parallel to it can be calculated as

$$F_s = \frac{z^2}{\pi} \cdot \iint_{x_{\min}, y_{\min}}^{x_{\max}, y_{\max}} \frac{dx dy}{(x^2 + y^2 + z^2)^{3/2}} \quad (7)$$

yielding 0.392% for $z = 90 \text{ mm}$ ($x_{\max} = y_{\max} = 5 \text{ mm}$, and $x_{\min} = y_{\min} = -5 \text{ mm}$). The TAGs 1 simulation resulted in $F_s = 0.390 \pm 0.005\%$ at $p = 0.01 \text{ Pa}$, while SIMTRA yielded F_s about 8% lower, namely 0.358%, under the same conditions.

A more significant discrepancy between the SIMTRA and TAGs 1 results was obtained for F_s at pressures above 0.5 Pa, where the TAGs 1 result decreases monotonically with pressure. At the same time, that of SIMTRA tends to saturate at approximately 0.2%. The pressure dependence of the deposition rate has been the subject of experimental investigation for some time, yielding an empirical expression from Keller and Simons [32]. Several years ago, a generalised Keller–Simons formula was proposed, which successfully describes this dependence and shows very good agreement with experimental data obtained using magnetron sputtering [33]. The implementation of this formula is explained in Appendix A. This dependence, normalised to the value $F_s = 0.385\%$ and shown in Figure 2a, agrees much better with the TAGs 1 dependence than with that of SIMTRA. A closer inspection of the results reveals that the average number of collisions of C atoms impinging on the substrate surface is approximately 25% higher in TAGs 1 than in SIMTRA at higher pressures, while E_{av} remains almost the same. Although similar, the treatment of collisions is not identical in the two codes, which may be responsible for the discrepancy observed at higher pressures. The same type of simulation was performed for a square substrate with an area of 4 cm^2 (Appendix A), confirming excellent agreement between TAGs 1 and the analytical expression, while the results obtained with SIMTRA are somewhat closer to the other two. This possibly suggests a higher consistency of the TAGs 1 results compared to those of SIMTRA, although a comparison with experiments would be necessary for a final conclusion. It should also be noted that, according to [33], the validity of the generalised Keller–Simons formula in this case is limited to pressures of about 0.7 Pa, i.e., precisely where the SIMTRA results stop following it (and TAGs 1). Therefore, additional experimental data would be required to compare the accuracy of the two codes in more detail.

The results indicate that the algorithm used in the TAGs 1 and TAGs 2 simulations was implemented correctly, knowing that the two codes share the same general algorithm. The results using TAGs 1 and SIMTRA are, generally, very similar. The minor differences

observed at higher pressures should be the subject of a separate study. At this stage, TAGs 1 and 2 appear to be suitable tools for studying the transport of atoms in a discharge gas during deposition.

3.2. Influence of the Input Parameters and Introduced Assumptions on the Accuracy and Precision

Several input parameters used in the simulations were chosen based on certain assumptions or, frequently, by following approaches adopted by other researchers. Here we analyse how these choices affect the simulation results and discuss possible consequences of the introduced approximations.

3.2.1. Initial Conditions of the Sputtered Atoms

First, the influence of the energy and angular distribution of sputtered particles is considered. For that purpose, a set of TAGs 1 simulations of the transport of C atoms towards the substrate, located 90 mm from the target, was performed for different Ar pressures. Different values of the surface binding energy E_{SB} , the maximum energy of sputtered atoms E_{max} , and the exponent of the angular distribution, α , were used. Only one parameter was varied at a time, while the others were fixed to the values listed in Table 1.

Sigmund's sputtering theory predicts an angular distribution $dY/d\Omega \sim \cos^\alpha(\theta)$, where α takes values between 1 and 2 [34]. However, surface roughness introduced during target sputtering blurs this dependence, which is why a simple cosine distribution is usually assumed [20]. The simulations were performed for α equal to 1, 1.5 and 2. The pressure dependences of F_s , the average energy, and the average collision number of atoms reaching the substrate surface, presented in Figure S3 of the Supplementary Material S3, reveal a secondary influence of α compared to that of the energy distribution parameters. This influence is mainly visible at very low pressures and tends to disappear as the pressure increases, owing to collisions that progressively diminish its effect.

The choice of the surface binding energy mainly influences the energy distribution of arriving atoms at low pressures, as shown in Figure 4a, while the other two output magnitudes (N_{col} and F_s) are much less affected (these results are presented in the Supplementary Material, Figure S4). The maximum energy E_{max} also influences the average energy E_{av} over the entire pressure range considered (Figure 4b). It should be noted that the range over which the parameter E_{max} was varied is relatively large (85–133 eV). As in the case of E_{SB} , the influence on N_{col} and F_s is minor (Supplementary Material S3, Figure S5). The rather wide range of considered surface binding energies of carbon atoms reflects the strong influence of surface contamination on this parameter, as will be elaborated below. Additionally, the rather wide range of E_{SB} and E_{max} considered in these simulations was chosen knowing that the Thompson formula may not be the best model for the energy distribution of sputtered atoms [20]. It appears, however, that the choice of the energy distribution model does not strongly influence the simulation results as long as the number of collisions of sputtered particles is not too small.

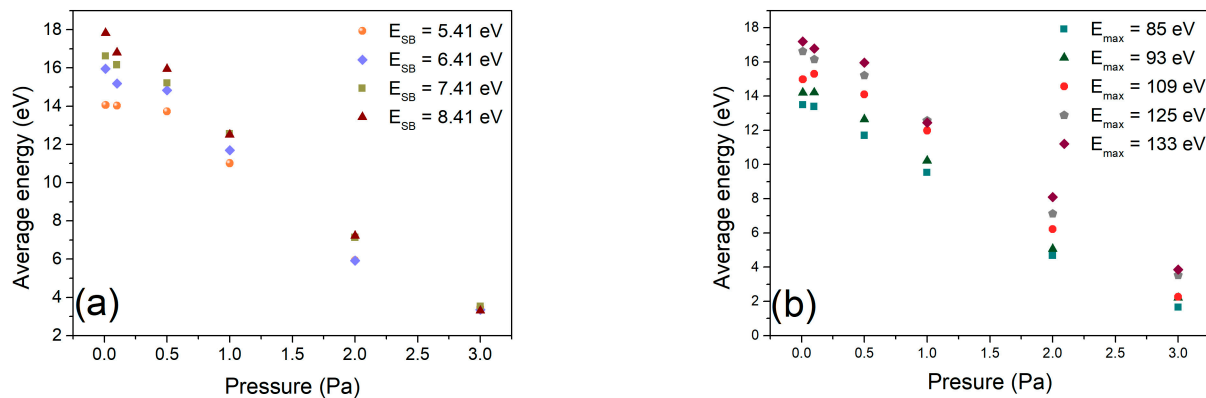
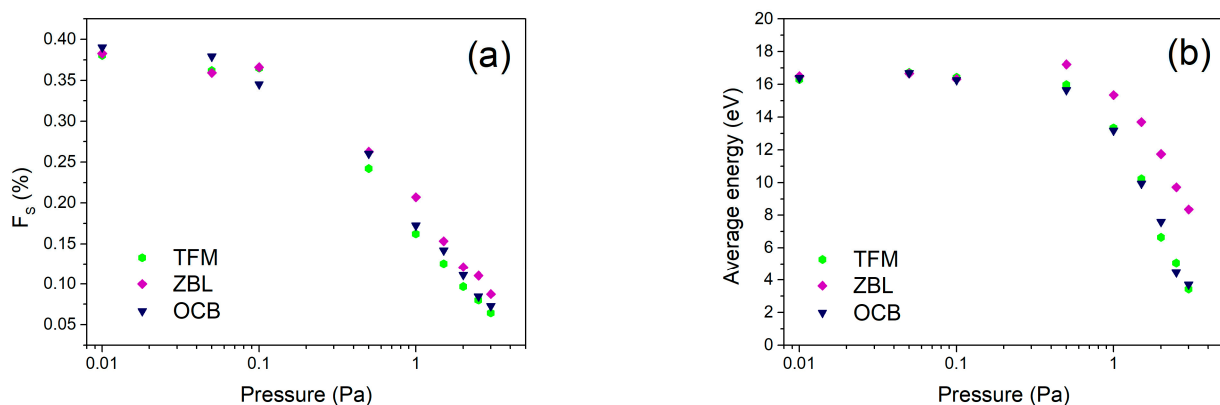


Figure 4. TAGs 1 simulations: Pressure dependence of the average arrival energy of carbon atoms obtained for (a) different values of E_{SB} and (b) different values of E_{max} .

3.2.2. The Choice of the Interaction Potential

The choice of the interaction potential is not trivial, since the precision of a given model depends on both the energy and the collision partners. Over a wide energy range, the ZBL potential demonstrates the highest accuracy [28]. However, at larger inter-nuclear distances, corresponding to lower energies and smaller scattering angles, and particularly for larger atoms, the ZBL interaction potential becomes too strong [24]. That is a possible reason why SRIM, which uses ZBL potential, is much less accurate in modelling the ion sputtering, as compared to TRIDYN and SDTrimSP, which employ the Kr-C potential [35]. A similar issue arises with the TFM potential, which is why its screening length is often multiplied by a correction factor smaller than one. Its value strongly depends on the collision partners [36] and, in particular, on the projectile energy, being smaller at the lowest energies [28]. The OCB potential is identical to the TFM potential down to the energy of 10 eV, while at lower energies, a correction factor dependent on the atomic numbers of the collision partners is introduced. This correction enormously improves its accuracy in the low energy range [28]; however, potential limitations at higher energies may persist for some collision partners.

The dependencies of the arrival probability of sputtered C atoms, the average arrival energy, and the average collision number on Ar pressure, obtained by simulations, using TFM, ZBL, and OCB interaction potentials, are presented in Figure 5. The target–substrate distance was fixed at 90 nm.



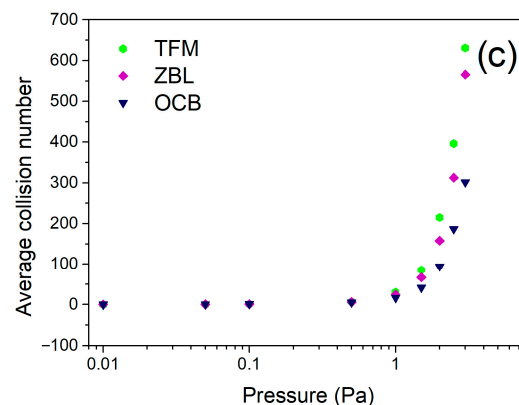


Figure 5. TAGs 1 simulations of C atoms in Ar for the target–sample distance of 90 mm: pressure dependence of (a) F_s , (b) E_{av} , (c) N_{col} obtained using different interaction potentials.

While the arrival probability of sputtered particles is practically unaffected by the choice of interaction potential, the average arrival energy is significantly higher for the ZBL potential (particularly at high pressures), and the average collision number is considerably lower in the case of the OCB potential. The latter result is clearly a consequence of the reduced cross-section within the hard-sphere model for the OCB potential. Given that the OCB potential is much more accurate than the TFM potential, the ZBL potential is also too strong at low energies, contributing to an overestimated cross-section within the hard-sphere model. At the same time, the average arrival energies using the OCB and TFM potentials are very similar, revealing that low-energy collisions do not have a strong impact on E_{av} . The significantly higher average energies obtained with the ZBL potential, together with its known inadequacy at lower energy range, suggest that it is probably the worst of the three for the considered energy range and impact parameters. It should be stressed, however, that this estimation considers only this case. At the same time, the OCB potential appears to be the most accurate of the three, motivating its use in the forthcoming sections.

3.2.3. Limits of the Simulation Volume

Terminating the simulation for all particles that leave the volume between the target surface and substrate surface planes significantly reduced the computational time, but also introduced a systematic error. The arrival probabilities at the substrate surface are somewhat underestimated, as some atoms may backscatter from gas atoms behind the substrate plane, then again in front of the plane, and finally impinge on the substrate surface. A conservative estimate was performed for thermal atoms, which have the largest scattering cross-section. For carbon atoms transported in the chamber with 1 and 3 Pa of Argon, the simulations show that the probability of atoms reaching the substrate surface increases by 0.7% and 1.3%, respectively. The introduced error is therefore well below other sources of uncertainty in the system and remains within the uncertainty margin of simulations performed with 10^6 particles.

3.2.4. Temperature Distribution

The temperature distributions adopted in the simulations are extremely simple: they are uniform and equal to the ambient temperature in TAGs 1, with two uniformly distributed temperatures for TAGs 2 (one corresponding to the gas in the plasma and the other

in the rest of the chamber). The mean free path of sputtered carbon atoms with an average initial energy of 17 eV is approximately 1.5 cm at 1 Pa. Considering the size of the toroidal plasma in the modelled reactor and its relatively low power (below 100 W), only a few collisions are expected within this region. Consequently, the assumption used in TAGs 1, which is widely adopted in simulations of this type, appears reasonable. In TAGs 2, the mean free path and the velocity of gas particles are calculated according to the local temperature, depending on whether the atom is inside or outside the plasma. The assumption of a uniform gas distribution in and out of plasma is an approximation that may reduce accuracy. However, determining the temperature profile in the chamber would require a significantly more complex approach, well beyond the scope of the present model. Moreover, the assumption of a constant gas temperature in low-power magnetron discharges is sometimes used in dedicated plasma models of magnetron discharge and provides reasonable agreement with the experiments [37]. The uncertainties introduced by these assumptions are expected to be much smaller than those, not related to the model, that arise when combining the simulation results with other parameters to estimate, e.g., deposition rate of sputtered particles (see Section 4 for details).

3.2.5. Distribution of the Generation Rate of Active Species Inside the Discharge

The assumption used in TAGs 2 that chemically active species are generated uniformly within the toroidal discharge is not strictly correct. Secondary electrons emitted from the target are accelerated into the discharge, thus increasing both the electron concentration and the electron temperature near the target [37]. As a result, the generation rate of active species (e.g., atomic hydrogen, H^+ and H_2^+) is significantly enhanced in that region. However, the mean free path of these species at kinetic energies corresponding to the local gas temperature is only a few millimetres (e.g., 5.6 mm for a H atom in 1 Pa of Ar at 500 K), which is comparable to the diameter of the toroidal plasma in the simulations (cf. Section 3.4). Consequently, variations in the generation position within the plasma hardly affect collision processes in this region. Moreover, since the concentrations of electrons, atoms and other active species in the discharge are several orders of magnitude smaller than that of the neutral gas, interaction between transported atoms passing through and plasma species can be safely neglected. On the other hand, the preferential formation of hydrogen atoms closer to the target increases target contamination due to geometric reasons. Nevertheless, the generation rate in the simulation is kept uniform within the plasma due to the lack of information concerning its distribution in this case. As in the case of the temperature distribution, we are convinced that this approximation is much less significant than other uncertainties introduced when estimating the deposition rates.

3.2.6. Sticking Probability

The sticking probability of atoms impinging on the chamber walls can strongly influence the transport of atoms. Typically, the sticking probability of sputtered particles is assumed to be unity, although its actual value strongly depends on the deposited material, discharge parameters and system geometry. Depending on the system, sticking probabilities in the range from 0.02 to 1 have been reported [38–40]. Both experiments and simulations reveal the influence of sputtered particles' energy and incident angle on the sticking probability [38,40–42]. To test its possible influence, the TAGs 2 code was modified to include variable sticking probability: if an atom does not stick to the surface, it is elastically reflected from the chamber walls. Reducing the sticking probability on the chamber walls to 0.75 already increases the arrival probability at the substrate surface by almost 50%. However, one should have in mind that the sticking probability at the substrate surface

can also be less than 1. Moreover, the sticking coefficient of any surface in the system can change during an experiment due to passivation by previous adsorptions (e.g., by hydrogen). When considering the possible influence of energy and impinging angle, the sticking probability remains the most relevant parameter, with a potentially large uncertainty.

3.3. Transport of Sputtered H and C Atoms During the Deposition of Amorphous Carbon

The simulation results presented in this section are obtained mainly with the input parameters presented in Table 1, using $N = 10^6$ atoms in each simulation, and the OCB potential, which we find to be more accurate than TFM. The surface binding energy value chosen for H atoms sputtered from a contaminated graphite surface was 3.5 eV, corresponding to the average C-H bond strength [30]. The maximum energy of sputtered hydrogen contaminant was determined from SRIM simulations as $-E_{max}^H = 55$ eV. The simulation conditions are summarised in Table 2.

Table 2. Summary of the simulation parameters in TAGs 1 presented in Section 3.3.

Interaction Potential	E_{SB}^C	E_{max}^C	E_{SB}^H	E_{max}^H	$dY/d\Omega$	N
OCB	7.41 eV	125 eV	3.5 eV	55 eV	$\cos\vartheta$	10^6

Simulations of this type are used to provide access to the relative fluxes of sputtered particles, which manifest as variations in sample composition with pressure and target–substrate distance, or as thickness distributions on large-area substrates [15–21], frequently demonstrating discrepancies within 10% from the experiments. In this case, a simulation will be used to estimate the flux of incorporated carbon atoms during the deposition of amorphous carbon. In previous work [10], this flux was determined to be $1.88 \cdot 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$. The deposition was performed by magnetron sputtering of a 2'' graphite target in 2 Pa of argon, with a target–substrate distance of 90 mm. The discharge power was 30 W, corresponding to a discharge current of 55 mA, and a potential difference of approximately 550 V between the plasma and the target. The sputtering yield of carbon atoms by 550 eV Ar^+ ions, calculated by the empirical formula of Matsunami and co-workers [43], is 0.3034. The probability of the carbon flux reaching a substrate of 1 cm^2 area, calculated using TAGs 1, is 0.1074%. Finally, according to the molecular dynamics simulations [44], the sticking probability of carbon on amorphous carbon at 300 K is estimated to be 0.12. Together, these values allow us to estimate the flux of atoms deposited on the substrate as $1.33 \cdot 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$, which is about 29% lower than the experimental value ($1.88 \cdot 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$).

The comparison with the experiment given above cannot serve as a reliable test of the accuracy of the TAGs 1 code, owing to the high uncertainty associated with several parameters used in estimating the flux of incorporated carbon atoms. The sputtering yield was calculated under the assumption of an ideal, pure graphite surface. The graphite sublimation energy was used for E_{SB} , which represents only a first approximation of this important parameter. If instead $E_{SB} = 6.67$ eV, obtained from the model of Kudriavtsev and co-authors [45], is used, the relative discrepancy could be reduced to 11%. More importantly, the a-C film produced in that experiment contained 11% hydrogen, indicating that the target was poisoned (see below). This can also considerably reduce E_{SB} [46] and, consequently, increase the sputtering yield. Particularly questionable is the choice of the sticking probability, as already discussed in Section 3.2.6. While the proposed value of only 0.12 was obtained from simulation of thermal atoms, it is well known that the sticking coefficient increases with the arrival energy (unless the energy is sufficiently high to induce backscattering or even resputtering of previously deposited atoms). On the other hand, two effects may lead to a reduction in the calculated flux of incorporated carbon

atoms: (a) the rate of positive ions impinging on the target was overestimated by neglecting the contribution of secondary electrons emitted from the target; and (b) possible interactions of ions with gas atoms in the cathode dark space could reduce the sputtering yield due to the reduced energy of the impinging atoms. A simple model was proposed in [10] to estimate this effect for a graphite electrode at an Ar pressure of 2 Pa and a plasma potential of 500 V. It appears that a reduction in the sputtering yield of about 20%, relative to that of the 500 eV Ar ions, occurs in the case of the 5 mm thick dark cathode space. Taking all these factors into account, the level of agreement obtained suggests that TAGs 1 provides reasonable predictions.

The pressure dependences of the landing probabilities, F_s , and the average collision number, N_{col} , for sputtered carbon and hydrogen atoms are presented in Figure 6. The sample–target distance was fixed at 90 mm. Both atomic species exhibit the same expected trends. The average collision number is significantly lower for H atoms, owing to their smaller scattering cross section. Consequently, the landing probability of H is systematically higher than that of carbon. The relative difference in F_s increases with pressure (and N_{col}), as expected, reaching approximately 30% at 3 Pa. This relatively small discrepancy may appear surprising at first sight, since H undergoes six times fewer collisions than C at this pressure. However, much lighter H atoms tend to change their direction in these collisions more abruptly than carbon atoms, although the kinetic energy transfer should be more efficient in the latter case.

Figure 7 compares the average initial and arrival energies of sputtered H and C atoms that reach the substrate as a function of Ar pressure. As in the previous case, the distance between the target and the substrate is 90 mm. Practically the same pressure dependence of the arrival energy of carbon atoms is observed as that shown in Figure 2b. An additional piece of information is the increase in the average initial energies of carbon atoms with increasing pressure, which can be interpreted as follows. Pressure growth increases the number of collisions. During these collisions, sputtered atoms lose their energy and change direction, contributing to a decrease in their landing probability. Higher initial energy reduces the scattering cross section, meaning that more energetic particles undergo fewer collisions and, therefore, have a higher probability of reaching the substrate surface. While the same trend was obtained in simulations of sputtered oxygen atoms (see Figure S6 in the Supplementary Material S4 for details), the situation is clearly different for hydrogen at pressures below 2 Pa: the initial energy increases with pressure, as for the heavier projectiles, and the final energy follows this trend owing to the small number of collisions and inefficient momentum transfer. It should also be noted that the energy scales in Figure 7a,b are different and that the uncertainties in the latter case are much more relevant. At higher pressures, the average energy exhibits the same trend as for the heavier projectiles, owing to the more pronounced interaction with the gas.

The influence of target–substrate distance on the probability of H and C atoms arriving at the substrate for a fixed Ar pressure of 1 Pa is presented in Figure 8. The synergy of two effects is responsible for the exponential increase in F_s with decreasing distance: (a) an increase in the solid angle within which sputtered particles should be emitted to reach the substrate, assuming low-pressure conditions; and (b) a shorter distance implies fewer collisions, which is equivalent to the increase in F_s observed with decreasing pressure (cf. Figure 6). The difference between the F_s values for hydrogen and carbon is relatively small, as expected from the result in Figure 6. At 1 Pa and a distance of 90 mm, the probability of hydrogen atoms is about 16.6% higher than that of carbon. With further reduction in the distance, corresponding to the reduced number of collisions, this difference can only decrease further. Equivalent simulations performed for oxygen atoms yield trends

very similar to those observed for carbon atoms. These results are presented in Figure S7 of the Supplementary Material S4.

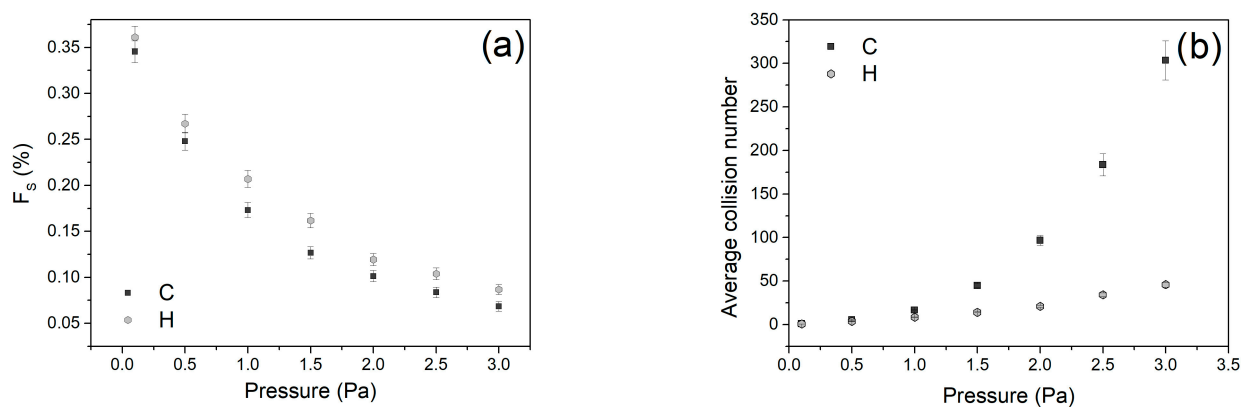


Figure 6. TAGs 1 simulation of the transport of C and H sputtered atoms to the substrate: (a) the probability of atoms arriving at the substrate surface; (b) average collision number of the atoms from (a).

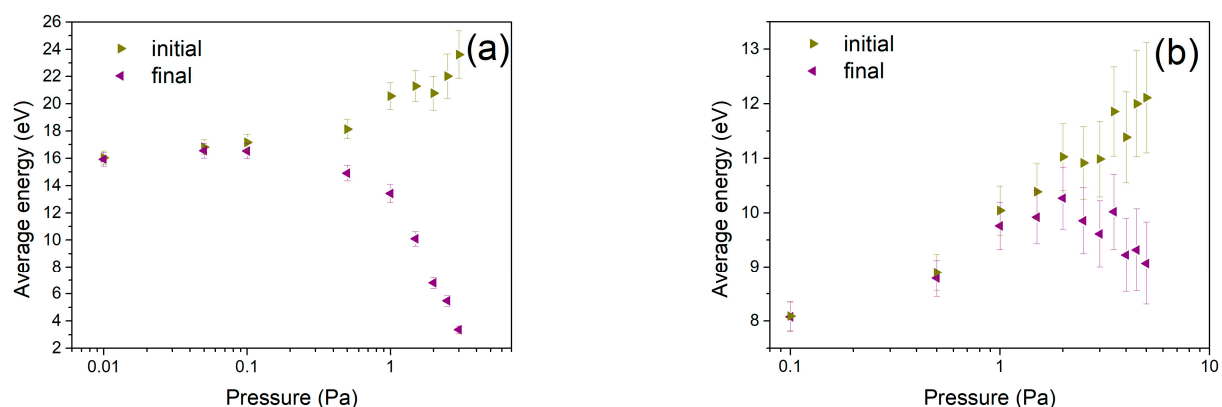


Figure 7. Average initial and final energies of the sputtered atoms that reached the substrate surface of (a) Carbon and (b) Hydrogen.

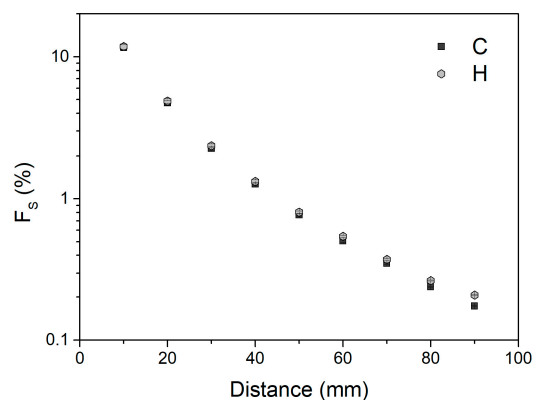


Figure 8. The probability of sputtered C and H atoms arriving at the substrate at 1 Pa of argon as a function of substrate–target distance.

3.4. Transport of H and O Atoms from the Discharge Towards the Target and the Substrate

In the context of film contamination by atoms originating from the discharge, it is of interest to study the transport of these atoms both towards the substrate and towards the target. In the simulations performed using TAGs 2, the substrate was modelled as a $20 \times 20 \text{ mm}^2$ square in order to improve the statistics. The discharge was assumed to have a toroidal shape, with inner and outer diameters of 12 and 19 mm, respectively, as estimated from the size of the plasma track (cf. Figure 1b). The central plane of the plasma was located 5 mm above the target surface. The gas temperatures in the plasma T_{pl} and in the rest of the chamber T_g were fixed at 500 K and 293 K, respectively. The atoms in the discharge follow the Maxwell distribution $f(E, \Omega)$, corresponding to the temperature T_{pl} , and are generated uniformly within the plasma. The number of particles in each simulation was $N = 10^6$. The most relevant simulation parameters are summarised in Table 3.

Table 3. Summary of the TAGs 2 simulation parameters presented in Section 3.4.

Interaction Potential	$f(E, \Omega)$	T_g	T_{pl}	Generation Rate	Substrate Size	N
OCB	Maxwell	293 K	500 K	uniform	$20 \times 20 \text{ mm}^2$	10^6

As in the case of the TAGs 1, the uncertainty of the simulation results was obtained by performing 20 consecutive simulations for different particle numbers. The corresponding result is presented in the Supplementary Material S2, Figure S2. The conclusion is the same, i.e., the uncertainty of each magnitude can be determined by multiplying the obtained value by the relative uncertainty calculated using Equation (6). In this case, the number N_s denotes the number of atoms arriving at the substrate surface, or the plasma track of the target. Given the large number of the latter, the corresponding uncertainties are negligible owing to the excellent statistics.

Simulation results for the transport of hydrogen and oxygen atoms from plasma to the substrate and to the target as a function of Ar pressure are presented in Figure 9. The gas temperatures in the plasma region and in the rest of the chamber were fixed at 500 K and 293 K, respectively. The probabilities of hydrogen and oxygen atoms reaching the substrate from the plasma, F_{sp} , and their average number of collisions as a function of pressure are shown in Figure 9a,b, respectively. The target–substrate distance was fixed at 90 mm. As in the case of sputtered particles, interaction with the gas reduces the probability that particles reach the substrate, owing to the more pronounced interaction with gas atoms. Hydrogen atoms undergo significantly fewer collisions and therefore traverse the gas more efficiently at higher pressures, compared with oxygen atoms. This behaviour is due to the lower collision cross-sections of hydrogen and the less efficient momentum transfer resulting from the larger mass ratio. At lower pressures, collisions are less frequent, leading to a weaker dependence of F_{sp} on the atomic species. The pressure rise also enhances the probability of atoms originating from the plasma reaching the plasma track, F_{Tp} , as shown in Figure 9c. This effect is caused by the backscattering of light O and H atoms from heavier Ar atoms and is slightly more pronounced for O than for H owing to its higher mass and larger scattering cross-section. The ratio of the atomic fluxes reaching the substrate surface, ϕ_s , and at the plasma track surface, ϕ_T , is equal to the ratio of the corresponding arriving probabilities, $F_{sp}:F_{Tp}$. The pressure dependence of the flux ratio ϕ_s/ϕ_T for hydrogen and oxygen is dominated by the strong decrease in ϕ_s (i.e., in F_{sp}) as shown in Figure 9d.

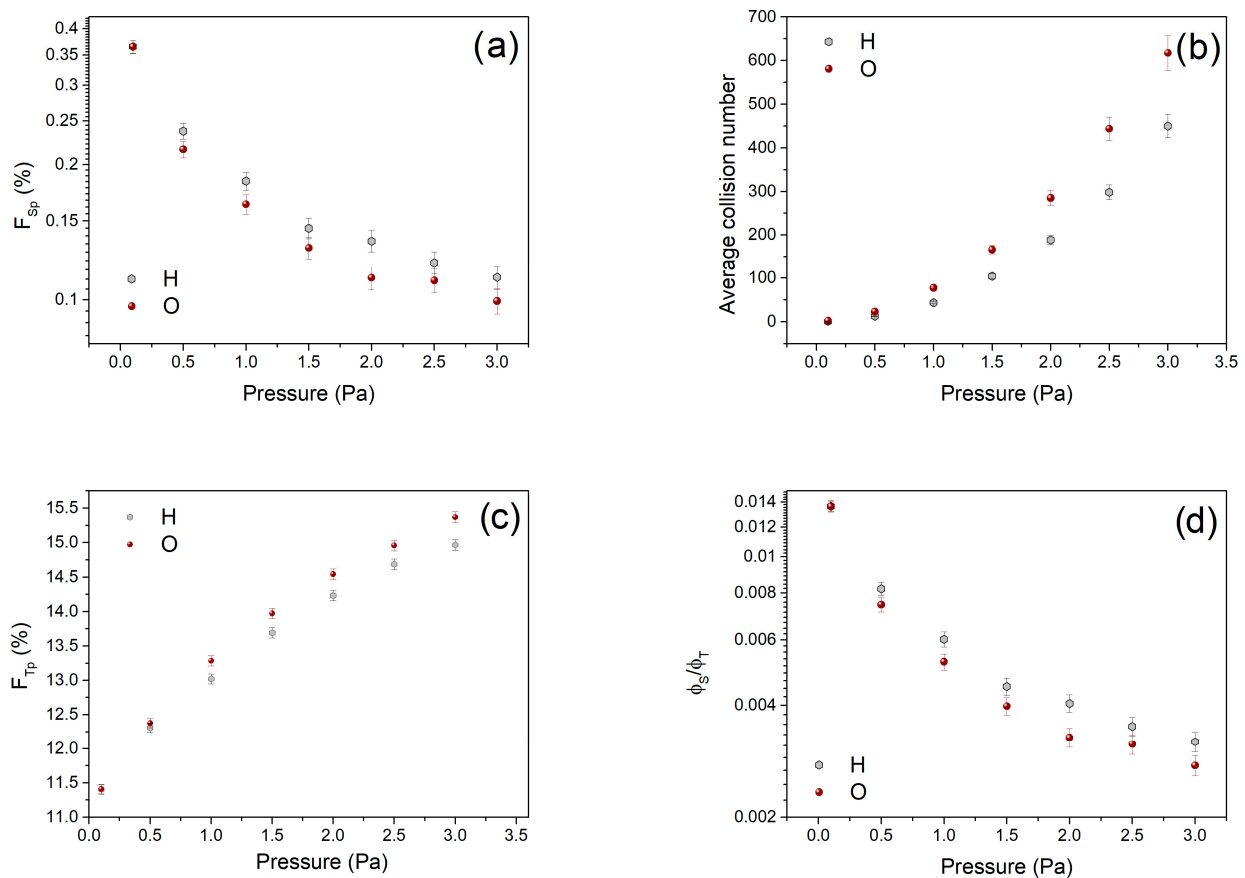


Figure 9. Transport of O and H atoms from plasma towards the target and the substrate as a function of Ar pressure: (a) the probability of atoms reaching the substrate surface; (b) the average number of collisions from (a); (c) the probability of atoms reaching the target surface; (d) the ratio of fluxes of atoms reaching the substrate and the target surface.

Reducing the distance between the target and the substrate increases the probability that both sputtered carbon atoms and contaminants reach the substrate surface. The probabilities of O and H atoms reaching the substrate surface, as well as the ratio of their fluxes from the plasma to the substrate and to the plasma track surfaces, ϕ_s/ϕ_t , as functions of the substrate–target distance, are shown in Figure 10. At a distance of 90 mm and a pressure of 1 Pa, the ratio ϕ_s/ϕ_t is only about 2.5% and remains close to 10% down to a distance of 50 mm. A further reduction in the distance leads to a rapid increase in the normalised probability ϕ_s , which becomes equal to ϕ_t at a distance of 10 mm. The change in the flux ratio corresponds to the change in the flux ϕ_s , while ϕ_t remains constant within the statistical uncertainty.

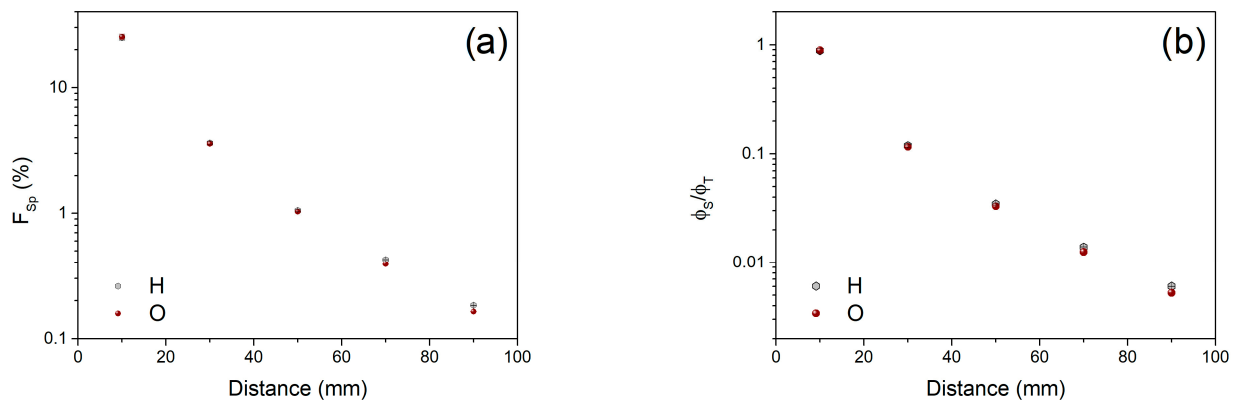


Figure 10. Transport of O and H atoms from plasma towards the target and the substrate as a function of distance: (a) the probability of atoms reaching the substrate surface; (b) the ratio of atomic fluxes from plasma reaching the substrate and the plasma track surface. The Ar pressure is 1 Pa.

The gas temperature in the discharge is a rather unknown parameter in magnetron discharges. To evaluate its impact, we simulated the transport of atoms from the plasma to the substrate and the target when the gas temperature increases from 400 K to 700 K. The simulations reveal that the probability of atoms reaching the substrate, F_{sp} , increases by about 20%, while the average number of collisions is reduced by roughly the same amount (see details in the Supplementary Material S5, Figure S8). This effect is overcompensated for by the decrease in the particle concentration, assuming that the pressure is constant in the chamber and that the dissociation rate of precursors is constant. In total, the contamination rate should be reduced by about 30% as the gas temperature in the plasma region increases from 400 K to 700 K.

3.5. Contamination of the a-C Films by Hydrogen

Contamination of a-C films by hydrogen in the presence of hydrogen precursors begins with their dissociation in the discharge. Let us consider a simple case of H_2 dissociation and the corresponding H production rate, R_H . As already discussed in the Introduction, hydrogen contamination occurs via two pathways: H atoms reaching the substrate directly from the discharge, and resputtered H atoms that have previously poisoned the target surface.

The flux of hydrogen atoms reaching the substrate directly from the plasma is equal to $R_H \times F_{sp}$. The probability F_{sp} can be obtained from a TAGs 2 simulation of the corresponding system (i.e., the gas pressure and the experiment geometry). The flux of H atoms attached to the target surface is given by $R_H \times F_{Tp} \times S_{Tp}$, where S_{Tp} is the sticking coefficient of thermal atoms at the target, and F_{Tp} can be obtained from the same TAGs 2 simulation. Target poisoning takes place during the intense bombardment by Ar^+ ions, which permanently creates dangling bonds that H atoms readily occupy [46]. Similar reasoning was applied in [47] when modelling reactive magnetron sputtering. Therefore, we assume that $S_{Tp} = 1$. The equilibrium between the resputtering rate and the deposition rate determines the concentration of hydrogen atoms at the target surface. The diffusion of H atoms into the bulk is not considered here, under the assumption that their in-depth concentration gradient in the equilibrium is very small and that the corresponding diffusion flux is negligible compared with the other two. Under these assumptions, the flux of resputtered atoms reaching the substrate surface is equal to $R_H \times F_{Tp} \times F_s$, where the probability F_s of sputtered hydrogen atoms reaching the substrate can be obtained from a TAGs 1

simulation of the same system. The total rate of hydrogen atoms reaching the substrate surface is therefore equal to $R_H \times F_H$, where F_H is the total probability for hydrogen atoms generated in plasma to reach the substrate surface:

$$F = F_{Sp} + F_{Tp} \cdot F_S \quad (8)$$

To determine the contamination rate, one should also consider the sticking probability of H atoms impinging on the surface, which strongly depends on the deposited surface and on the energy of the incoming atoms.

Figure 11 presents the ratio of the probabilities of hydrogen atoms reaching the substrate via mechanism 1, $F_1 = F_{Sp}$, and mechanism 2, $F_2 = F_{Tp} \times F_S$, as a function of (a) Ar pressure at a fixed target–surface distance of 90 mm, and (b) the target–substrate distance at a fixed Ar pressure of 1 Pa. The simulation results for two magnetron sources operating with 1" and 2" targets are shown. The latter magnetron source was used in our previous experimental studies [10,11]. In the TAGs 2 simulation of transport from the 2" target, the discharge has a toroidal shape with inner and outer diameters of 12 and 37 mm, respectively (as estimated from the size of the corresponding plasma track). A square substrate with a 1 cm² area was used for both sources. The probability ratio $F_1:F_2$ does not depend strongly on pressure and decreases monotonically with the distance. The relative contribution of mechanism 2 is approximately two times lower for the smaller target, which "captures" fewer hydrogen atoms on the plasma track owing to its smaller size. It should be noted that the results presented in Figure 11 do not provide complete insight into the ratio of efficiencies of the two contamination mechanisms, since the sticking coefficient typically increases with the energy of impinging particles [38]. From this perspective, contamination mechanism 2 is expected to prevail over direct contamination from the plasma for the larger target, as anticipated in [10]. Apart from making a considerable (if not dominant) contribution to overall film contamination by hydrogen, particularly for larger targets, mechanism 2 also plays an essential role in the deposition process: it increases the sputtering yield of carbon atoms and the ion-induced secondary electron yield from the target. The latter modifies the plasma properties, thereby influencing the current-voltage characteristics of the discharge, the gas temperature, and the dissociation and ionisation rates.

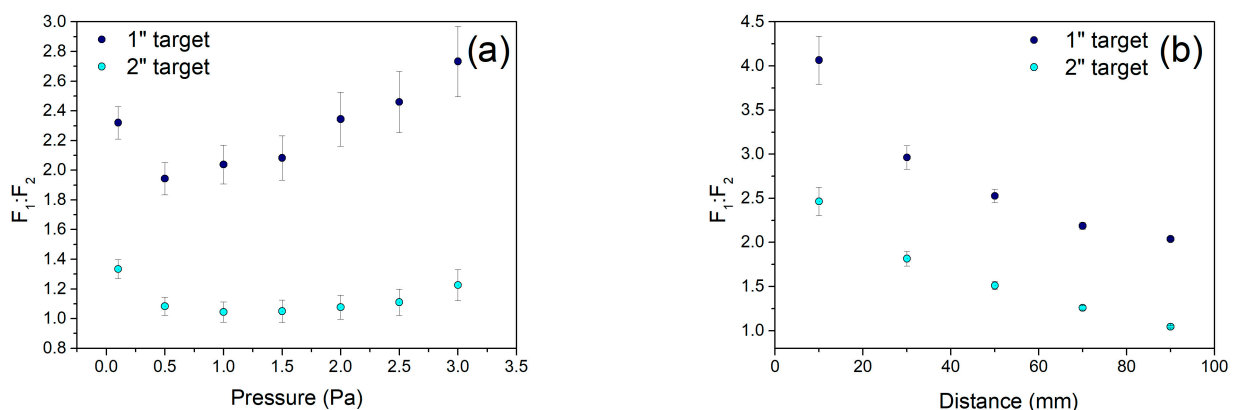


Figure 11. The ratio of probabilities of hydrogen atoms arriving at the substrate surface directly from the plasma and via target poisoning for 1" and 2" targets: (a) pressure dependence; (b) distance dependence.

The hydrogen percentage in the film, c_H , increases with the ratio of hydrogen to carbon fluxes deposited at the substrate surface according to: $c_H = \phi_H/\phi_C/(1 + \phi_H/\phi_C) \times 100\%$. This flux ratio is proportional to the ratio of the probabilities of H and C atoms arriving at the substrate, $F^H:F^S_C$, which is shown in Figure 12 as a function of Ar pressure and target–substrate distance for 1" and 2" targets. It appears that the system employing the 2" target is more sensitive to contamination, owing to the larger target surface area from which hydrogen atoms can be resputtered. The probability of hydrogen atoms was calculated by summing the probabilities for both mechanisms, F_1 and F_2 . Figure 12a suggests that higher pressure favours the incorporation of hydrogen relative to carbon and thus enhances the contamination.

The dependence of the ratio $F^H:F^S_C$ on distance, presented in Figure 12b, is substantially different for the two targets: for the 2" target, the ratio decreases monotonically with the distance, whereas it remains practically constant for the 1" target. This result can be readily explained by geometrical considerations, given that the diameters of the plasma track and the toroidal plasma of the 2" target are larger than the substrate size. At larger distances, this effect becomes less significant due to collisions with Ar atoms which “blur” the angular distribution of sputtered carbon atoms. However, as the distance decreases, the probability of carbon atoms reaching the substrate decreases for the 2" target relative to the 1" target, owing to the cosine angular contribution of the sputtered particles and the reduced number of collisions that would otherwise average their direction and diminish the importance of the initial angular distribution.

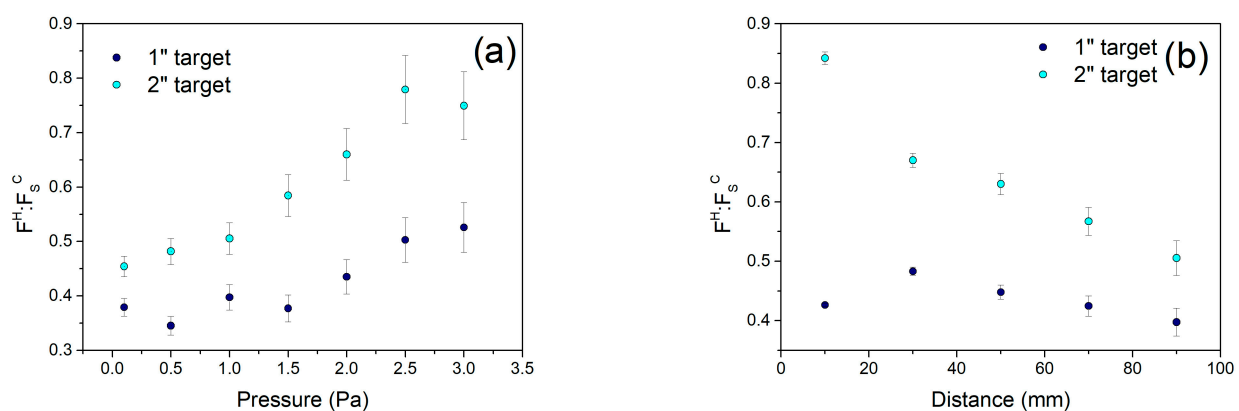


Figure 12. The ratio of probabilities of hydrogen atoms and sputtered carbon atoms arriving at the substrate for the 1" and the 2" target: (a) pressure dependence for 90 mm distance; (b) distance dependence for 1 Pa pressure.

Deuterium contamination of a-C films was quantified in [10] using Ion Beam Analysis, which provided the deposition rate of deuterium atoms, R_D^{dep} , as a function of the D_2 partial pressure (Table 4). In that experiment, performed by a 2" target, the total pressure was 2 Pa, the discharge power was 30 W, and the relative amount of D_2 in the discharge gas was varied in the range 0.19–10.1%. The intensity of the peak corresponding to D_2 in the mass spectrum measured by a differentially pumped residual gas analyser decreased upon plasma ignition due to the dissociation of the deuterium molecule in the plasma. This signal drop was used to calculate the dissociation rate of D_2 , i.e., the production rate of deuterium atoms, R_D , by the discharge, as listed in Table 4. The measured maximum secondary electron yields and the percentages of deuterium in the films are also given.

Table 4. Comparison of the experimental deposition rate from [10] with the flux of D atoms impinging on the substrate calculated from the experimental generation rate R_D [10] and the TAGs simulation results. The maximum SEY and relative deuterium content c_D [10] are also presented.

p_{D_2} (Pa)	$R_{D^{dep}}$ ($10^{12} \text{ cm}^{-2}\cdot\text{s}^{-1}$)	R_D (10^{16} s^{-1})	$R_D \times F_D$ ($10^{12} \text{ cm}^{-2}\cdot\text{s}^{-1}$)	SEY_{max}	c_D (%)
0.0038	3.12	0.347	2.44	1.03	9.6
0.0102	9.58	0.855	6.01	1.15	23.7
0.026	24.9	1.74	12.23	1.38	39.9
0.22	21.8	8.01	56.30	2.03	50.4

The flux of D atoms impinging on the substrate surface can be expressed as $R_D \cdot F_D$, where the probability F_D of deuterium atoms reaching the substrate surface can be obtained from the corresponding TAGs 1 and TAGs 2 simulations using an expression equivalent to Equation (8). This probability should not be strongly affected by the small D_2 content in the discharge gas, since D– D_2 collisions are relatively rare. The probabilities F_{Sp} and F_{Tp} for deuterium atoms obtained from the TAGs 2 simulations for pure Ar gas at 2 Pa and for the geometry in the experiment in [10] are 0.0361% and 25.9%, respectively. The probability F_s obtained from the TAGs 1 simulations is 0.132%, yielding a total value of $F_D = 7.03 \times 10^{-4}$. The flux of deuterium atoms reaching the target is compared with the experimentally measured deposition rate of deuterium in Table 4. The calculated rate of deuterium atoms approaching the surface, $R_D \cdot F_D$, agrees with the experimental deposition rate, $R_{D^{dep}}$, within a few tens of percentage points, which is already a good result considering both the complexity of the physical phenomenon involved and the relative simplicity of the model. The calculated values are systematically lower than the experimental ones, except at the highest D_2 partial pressure. These discrepancies are discussed in some detail in the following section.

4. Discussion

The very good general agreement between the TAGs 1 and SIMTRA results, the latter being a well-established simulation tool, gives some credibility to the results obtained using the codes introduced in this study. While the minor differences observed should be a subject of a separate investigation, here we focus on the outcomes of TAGs 1 and TAGs 2 related to the growth and contamination of a-C carbon films, the latter being a task that cannot be addressed using SIMTRA.

The results presented in Section 3 clearly demonstrate a decrease in the probability of atoms reaching the substrate, whether originating from the target or from the plasma, with increasing pressure. It was also demonstrated that the energy of sputtered atoms arriving at the substrate surface depends on both pressure and target–substrate distance. More energetic carbon atoms can promote the formation of a diamond-like carbon phase, whereas lower-energy arriving atoms predominantly yield graphitic carbon structures with low SEY. Energetic atoms can penetrate the first atomic layer, implant into interstitial sites, and form a metastable sp^3 configuration with increased density [48,49]. The optimal energy range for this process lies between 15 and 70 eV [50]. Deposition under clean conditions (very low base pressure) and at low operating pressures should therefore ensure high-purity a-C films at increased deposition rates. However, under such conditions, a considerable fraction of sputtered atoms may reach the substrate with sufficient energy to form an unfavourable sp^3 phase. Consequently, deposition should be carried out at elevated pressures to slow down sputtered atoms on their way to the sample and to provide conditions more favourable for the formation of the sp^2 -rich carbon. For the same reason, the target–substrate distance should not be too small. While the simulations performed

using both TAGs 1 and SIMTRA can be used to determine the minimum pressure required for a given distance, the results may depend strongly on the energy distribution of sputtered particles [51]. One of the first improvements planned for the TAGs 1 code is, therefore, to provide the ability to choose between different energy distributions, e.g., those of Stepanova, Falcone, or Kenmotsu (cf. [20,51] and references therein).

Considering that, at low pressures, carbon atoms reach the substrate with enough energy to promote the sp^3 phase and thus a higher SEY, the simulation results indicate the existence of a relatively narrow optimal pressure range. At excessively low pressures, the high energy of sputtered carbon atoms favours sp^3 phase formation, whereas too-high pressures favour hydrogen contamination. Notably, this result complies with our experimental findings, revealing that the coatings with the lowest SEY are produced at Ar pressures of approximately 1–2 Pa [29].

The primary motivation for the development of TAGs 1 and TAGs 2 was to obtain a more complete insight into the transport of atoms during the deposition of amorphous carbon by magnetron sputtering in Ar, including the effect of oxygen and hydrogen originating from different residual-gas precursors such as water vapour, hydrocarbons, CO, H₂, etc. The presence of hydrogen, in particular, deteriorates the secondary electron emission properties of the deposited film (see Table 4 for details).

A similar experimental rate of the deuterium incorporated in a-C films to the calculated rate of deuterium atoms impinging on the surface (which also encompasses the experimental generation rate of D atoms in the discharge) is an encouraging result. It suggests that the dominant contamination mechanism has been correctly identified and that the deuterium transport was modelled with reasonable accuracy. The largest discrepancy occurs at the highest deuterium partial pressure (cf. Table 4), where the experimental deposition rate is more than twice smaller than the impinging rate. This discrepancy was already explained in [10] using mass spectrometry measurements. Under these conditions, C_xD_y species, formed in the process of chemical sputtering [46], were detected. Being volatile, the corresponding fraction of deuterium was pumped away. In addition, the thin film produced with a deuterium partial pressure of 0.22 Pa exhibits a combined deuterium and hydrogen relative content of approximately 47%, therefore approaching the theoretical maximum of 67% for long-chain saturated aliphatic hydrocarbons. From the deposition perspective, this implies a reduction in the deuterium sticking coefficient due to the limited number of available adsorption sites.

At lower deuterium partial pressures, the calculated impinging rate is systematically lower than the deposition rate. The calculated incorporation rate should be lower than the impinging rate because of the sticking probability below 1 and the possible diffusion of deuterium atoms into the bulk of the target. Moreover, C_xD_y molecular species will likely be resputtered from the contaminated target [46], and these species have very low sticking probabilities at arriving energies below 20 eV [52]. All these effects would further increase the underestimation of the incorporation rate of deuterium. One possible explanation for this systematic deficiency of the calculated deposition rate might be the consideration of the implantation of D⁺ and D₂⁺ ions into the target, which would enhance contamination via target poisoning. The ratio of the generation rates of these ions to that of atomic deuterium equals the ratio of the corresponding rate constants. It was demonstrated in [10] that the ratio of D and Ar⁺ production rates for different gas compositions is consistent with the assumption that the electrons in the discharge are Maxwellian with an electron temperature of 5 eV. Assuming that the generation rate of deuterium ions equals the incorporation rate of deuterium atoms into the target via D⁺ and D₂⁺ implantation, this effect will increase the target surface concentration of D by approximately 17.4%. In this estimation, we used the previously determined probability of $F_{Tp} = 25.9\%$ for D atoms from the

plasma to reach the plasma track on the target surface, as obtained from the TAGs 2 simulations. Accounting for this increased target surface concentration of D atoms raises the impinging rate of D atoms for the lowest D_2 partial pressure to $2.67 \cdot 10^{12} \text{ s}^{-1}$, thereby reducing the relative discrepancy with the experimental incorporation rate to only 14.4%. The remaining discrepancy at low p_{D_2} may be attributed to the oversimplified assumption that Ar^+ ions impinge exclusively on the plasma track of the target, which does not correspond to the experimental observations. X-ray Photoelectron Spectroscopy of the used graphite targets reveals implanted Ar both within the plasma track and in the central region of the target disc, with nearly identical intensities of the Ar 2p line relative to that of the C 1s line. This implies that deuterium is also captured in target areas outside the plasma track. Widening the area from which D atoms are resputtered would increase the overall impinging rate of deuterium atoms on the surface.

Nevertheless, none of these effects can explain the increase in discrepancy in Table 4 in the D_2 partial pressure under the assumption that the electron temperature remains independent of p_{D_2} (the latter agreeing with the ratio of the Ar^+ and D atom generation rates).

In general, the growing discrepancy between the experimentally measured D deposition rate and the calculated impinging rate with increasing deuterium partial pressure may have its origin in a change in the discharge properties and/or the transport properties. The former could be associated with changes to the electron energy distribution: an increased abundance of energetic electrons would increase the fraction of D atoms reaching the target surface via ion implantation, and thus the impinging rate of D atoms onto the substrate surface. While this assumption is inconsistent with the experimental observation that the electron temperature is independent of p_{D_2} , it should be noted that the electron energy distribution in magnetron discharges is not strictly Maxwellian [53,54]. Therefore, we still cannot exclude the possibility of the influence of deuterium in the discharge gas on the electron energy distribution. To further explore this possibility, more experimental data related to the plasma properties, particularly electron concentrations and their energy distribution, would be required.

Collisions with D_2 molecules are highly unlikely to affect the transport of D and C atoms towards the substrate due to the very small deuterium partial pressure involved. Nevertheless, one secondary effect significantly influencing the transport properties might appear. As already mentioned in Section 3.2.6, the assumption that the sticking probability of D atoms on the chamber walls equals 1 is a clear oversimplification: regions of the chamber surface that are not bombarded by Ar^+ ions will gradually become saturated with deuterium atoms and become chemically inert. The efficiency of this process increases with the deuterium atom generation rate, that is, with the deuterium partial pressure increasing. Both D and C atoms impinging on these saturated parts of the chamber wall will continue their trajectories after reflecting off them and will thus increase their probability of reaching the sample. As reported in [10], the ratio of the D to C incorporation rates is directly proportional to R_D . Therefore, both the D and C incorporation rates grow faster than R_D as we increase the deuterium partial pressure. The saturation of the chamber walls by deuterium, which should be more efficient at higher partial pressures, reduces the sticking probability of both D and C atoms. This effect could therefore explain both the experimental observations and the increasing underestimation of the calculated impinging rate at higher deuterium partial pressure.

5. Conclusions

A novel Monte Carlo simulation for modelling the transport of atoms in gases has been presented, encompassing two codes: TAGs 1, which models the transport of

sputtered atoms from the target to the substrate surface, and TAGs 2, which simulates the transport of atoms from the plasma towards both the target and the substrate. These codes were applied to study the contamination of a-C thin films by hydrogen.

When comparing with the well-established code SIMTRA ver. 2.2.0 for the simulation of the transport of sputtered C atoms in argon at different pressures, TAGs 1 produces very similar results. Additionally, the C atom deposition rate obtained using TAGs 1 agrees very well with the experimental results in [10].

Simulations of the transport of sputtered carbon, hydrogen, and oxygen atoms using TAGs 1, as well as of H and O atoms originating from the plasma using TAGs 2, provide important insight into the contamination mechanisms of a-C films. Modelling film contamination by deuterium shows good agreement with the experimental results of [10], while also implying the presence of additional processes not included in the current model, whose influence increases with the deuterium partial pressure. Possible reasons for this discrepancy were identified as changes in the electron energy distribution with the deuterium partial pressure and passivation of the chamber walls by previously adsorbed D atoms. This is an excellent example of the true value of simulations: when very good agreement with experiments is achieved, they can be used to predict the dependencies of experimental parameters and plan new experiments, and when discrepancies are observed, simulations serve as guidelines for identifying their possible origins, which may lie beyond the applied physical model. This can potentially reveal new effects that can be used for further refinement of the simulations.

The presented results clearly suggest that both programs can provide useful insights towards a deeper understanding of deposition processes in magnetron discharges. However, further comparisons with experimental results are necessary to explore their full potential. The programs can be readily modified to introduce additional functionalities (e.g., different energy distribution of sputtered atoms) and adapted to other geometries. The authors are open to collaboration with colleagues who would like to test the codes for modelling other deposition systems or experiments involving the transport of atoms in rarefied gases.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/c12010013/s1>, S1: Examples of the TAGs 1 and TAGs 2 input files; S2: Uncertainty analysis of the TAGs 1 and TAGs 2 simulations; S3: Influence of the energy and angular distribution of sputtered atoms on the results in TAGs 1 simulations; S4: Simulations of the transport of sputtered oxygen atoms; S5: Simulations of the transport of oxygen atoms from plasma to the substrate by TAGs 1—temperature dependence.

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Appendix A

Keller–Simmons’ Generalised Formula and Comparison with the Program Outputs

The generalised Keller–Simmons formula, which was used as a comparison model for SIMTRA and TAGS 1, has the following form [33]:

$$\Phi = \eta(d, R) \Phi_0 \frac{(pd)_0}{pd} \left(1 - e^{-\frac{pd}{(pd)_0}} \right) \quad (A1)$$

where Φ and Φ_0 are the fluxes of deposited and sputtered atoms, respectively. $\eta(d, R)$ is the geometric factor, which depends on the target radius R , and the target–substrate distance, d ; p is the pressure inside the chamber, and $(pd)_0$ is the characteristic pressure–distance product for a specific deposition condition, evaluated as:

$$(pd)_0 [Pa \cdot cm] = \frac{0.107 \left(\frac{m_1}{m_2} \right)^{0.69} \left(0.62 + 0.23 \ln \left(7736.4 \frac{E_{SB}}{T} \right) \right)}{(r_1 + r_2)^2} \cdot T \quad (A2)$$

where m_1 and m_2 are the masses of the sputtered and gas atoms, respectively, E_{SB} is the surface binding energy in eV, T is the gas temperature in K, and r_1 and r_2 are the radii of the sputtered and gas atoms in Å. This equation was obtained by finding the universal correcting factor that would conjugate the analytical dependencies with experimental data.

The parameter $(pd)_0$ was computed for sputtered carbon atoms interacting with the Argon gas. We used a binding energy of 7.41 eV and room temperature (293 K), since the interaction occurs primarily outside the plasma. The atomic radii were calculated from the total cross section in the hard-sphere approximation, computed within TAGs 1. This choice is consistent with [33], as the denominator in Equation (A2) has to correspond to the cross/section of thermal atoms. With these considerations, the resulting $(pd)_0$ for our system is 0.639 Pa·cm. The expression was normalised to the maximum value of F_s obtained in TAGs 1 simulations. The factor $\eta(d, R)$ does not depend on the pressure, so it will disappear in the process of normalisation.

The results of this treatment are presented in Figures 2a and A1a, for substrates of 10×10 and 20×20 mm² square, respectively, using a fixed target–substrate distance of 90 mm. In both cases, TAGs 1 simulation data clearly agrees with the work in [30]. However, the original author highlights an important limitation: the generalised formula in the expression A1 was experimentally validated only for pressures below $10 \cdot (pd)_0/d$, which corresponds to 0.7 Pa in our case. At higher pressures, the flux of deposited atoms decreases, and a Monte Carlo simulation method of the sputtered atoms is requested. Despite the uncertainty of applying the formula at higher pressures, our simulation data matches the predicted curve well.

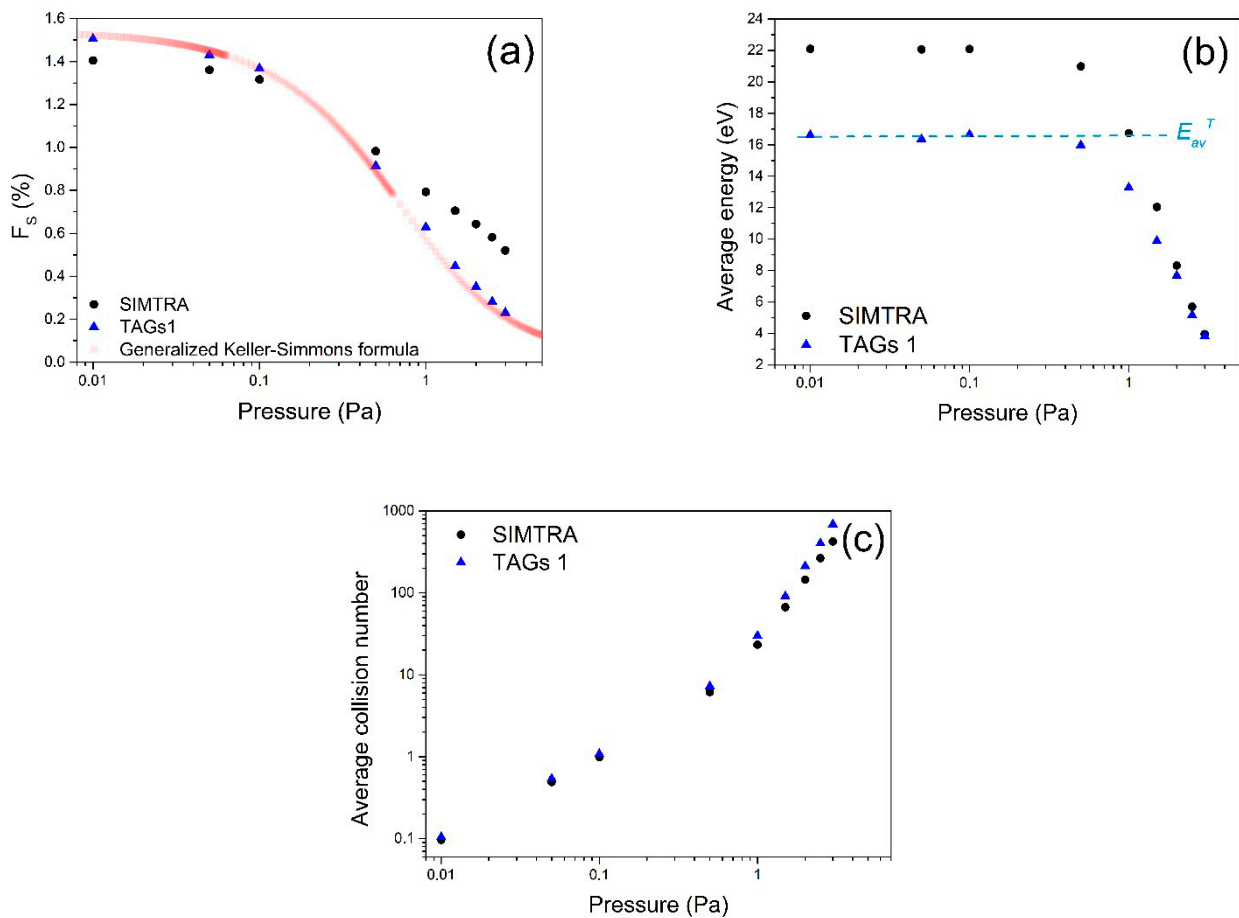


Figure A1. Simulations of the transport of sputtered carbon atoms to the substrate by SIMTRA and TAGs 1—pressure dependence: (a) probability of carbon atoms reaching the substrate; (b) average energy of arriving atoms; (c) average collision number of arriving atoms. The translucent red line in (a) is the denormalized expression A1 for a substrate of 20×20 mm² square. The dashed line in (b) corresponds to the average energy of the carbon atoms leaving the target, as calculated from the Thompson distribution with $E_{SB} = 7.41$ eV and $E_{max} = 125$ eV.

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