

Article

Total and Differential Sputtering Yields Explored by SRIM Simulations

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Abstract: Total sputtering yield and spatial distributions of sputtered atoms are important for numerous deposition techniques. We performed SRIM (Stopping and Range of Ions in Matter) simulations to analyze the total sputtering yield and angular distribution of sputtered atoms for a range of single-element target materials. The simulations were conducted for normal argon ion incidence in the 300–1200 eV range and at an oblique angle for selected ion energies. We examined the total and differential sputtering yields for the transition metals in the periods 4–6 and groups 4–6 (Ti, V, Cr; Zr, Nb, Mo; Hf, Ta, and W) and group 11 (Cu, Ag, and Au) of the periodic table, and other materials that are relevant to sputtering (B and C; Al and Si). For the transition metals, the total sputtering yield increases with the group of the periodic table. The elements in group 4 (i.e., Ti, Zr, and Hf) have the lowest sputtering yield, while the elements in group 11 (i.e., Cu, Ag, and Au) exhibit the highest sputtering yield. The angular distribution of the sputtered atoms shows a cosine distribution for the transition metal atoms. The angular distribution of the sputtered atoms for the oblique ion incidence is more asymmetric for the lower ion energies, while for the higher ion energies, the atoms are sputtered more symmetrically. The symmetry also depends on the group of the periodic table and the atomic mass of the target material. The elements in group 11 show the most symmetric distribution, while the elements in group 4 experience the most asymmetric distribution. Furthermore, in an individual group, the distribution becomes more symmetric with heavier target elements. We also examined in detail the influence of the surface binding energy, atomic mass, and ion energy on the total sputtering yield. These parameters were analyzed with regard to the simplified analytical formula for the total sputtering yield, which was derived by Sigmund. This formula was modified by introducing a power fitting parameter, which accounts for the non-linear sputtering yield dependence on the ion energy. The equation provided good estimates for the total sputtering yield of the transition metals that were sputtered by argon ions with energies up to 1200 eV.

Keywords: sputtering; total sputtering yield; differential sputtering yield; SRIM simulations; spatial distribution of sputtered atoms



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1. Introduction

Sputter deposition and ion etching techniques are important technological processes that require a good estimation of the sputtering yield. Sputtering occurs when an energetic ion impinges onto a surface and propagates through the solid. In the process, a series of collisions occur between the ion and the atoms in the solid, which results in a so-called collision cascade. Some of these cascades are directed toward the surface. If the energy of the last recoiled atom traveling towards the surface is larger than the surface binding energy, then the atom is ejected from the material. The stochastic nature of collisions results in the emission of various amounts of atoms into various directions. The distribution of these atoms depends on the energy, mass, and angle of the impacting ion as well as on the properties of the target material [1,2].

Sputtering is a line-of-sight process where sputtered atoms travel in straight trajectories from the source to the substrate (i.e., if collisions with residual gas atoms are neglected). The spatial distribution of the atoms arriving on the substrate is important because it affects the uniformity of the growing thin film in terms of the film thickness and its structural, physical, and chemical properties. The atom flux directionality can also have a considerable influence on the film growth even with the use of a sophisticated substrate rotation. In the industrial magnetron sputtering systems, typically four or sometimes six magnetrons are arranged around the central substrate table. The table rotates around several axes, which is similar to a planetary rotation framework, to ensure the uniformity of the deposition [3]. In such a source–substrate arrangement, the direction and intensity of the atom flux onto the substrates vary with the rotation, which affects the deposition rate and energy of the arriving atoms. These variations should average out with the multi-axis substrate rotation, nevertheless, it has been reported that in the reactive deposition, the varying ratio between the metal flux and reactive species flux can cause the unintentional growth of the Cr_2N phase within CrN [4].

The directionality of the atom flux should be also considered in the laboratory-type magnetron sputtering systems. In these systems, a different source–substrate arrangement is typically used. The substrate table rotates around a single central axis, or it is stationary, and several magnetrons are orientated toward the center of the table (either at the top or at the bottom of the vacuum chamber). In this arrangement, the flux of atoms on the substrate arrive from a narrower spatial angle than they do in the deposition systems with the planetary type of rotation. Scaling thin film production from the laboratory to the industrial systems is thus, not a trivial task. These difficulties can be to a large extent attributed to the different spatial and energy distributions of the sputtered atoms that are encountered in the laboratory and industrial systems. A good estimation of the sputtering yield as well as the energy distribution of the atoms are, therefore, required for the precise control of the deposition process. Furthermore, they are needed for the accurate modeling of the sputtering process and the magnetron discharges in general [5–9].

Spatial and energy distributions of the sputtered flux are also an important subject of research in the areas where ion etching plays a central role. For example, a great deal of effort is dedicated to understanding and predicting the sputtering in fusion research [10–16], where energetic ions from the plasma cause a degradation of the first wall material. Similar studies can be found in astrophysical planetary science [17], the electric propulsion of spacecrafts [18], the focused ion beam technique [19,20], secondary ion mass spectroscopy [21] and other areas where sputtering is the central phenomenon or is a part of the technological process.

There are plenty of experimental data that are available for the total sputtering yields of single-element materials which are sputtered by various ions. Nevertheless, the data are missing for several ion–target combinations. Furthermore, the measurements for specific ion–target combinations can differ significantly between various authors. Many measurements were performed decades ago, and more up-to-date measurements are needed. A large collection of total sputtering yields is provided in the book by Behrisch and Eckstein [22] and the earlier collections by Yamamura and Tawara [23], and Matsunami et al. [24,25]. The measurements of the differential sputtering yields are less common in the literature and are only reported for specific ion–target combinations [26–31].

Sputtering yields can be calculated analytically. The most comprehensive theoretical description of the sputtering process can be found in the early works by Thompson [32–34] and Sigmund [35–37]. In both of the treatments, a linear collision cascade model is assumed in which the ions propagate through the solid and cause a series of binary collisions. Sigmund's work provides the most general expression for the sputtering yield. Over the years, improvements have been made to the Sigmund equation in the form of semi-empirical relations [23,38–40] to better fit to the experimental values of the total sputtering yield. In the original works by Thompson and Sigmund, a simple cosine distribution was

assumed for the angular distribution of the sputtered atoms. Several new expressions have been developed for the angular dependence of the sputtering yield as well [39,41–43].

The theoretical models for describing sputtering and evaluating the total and differential sputtering yields have limitations. Nowadays, computer simulations offer a better approach to study the sputtering process. In practice, two types of simulations are used. The first method, which is called the molecular dynamics simulation, is a deterministic approach where the motion of all of the particles in the system is calculated using Newton's equation of motion [44]. The forces between the particles are modeled by the inter-atomic potential, and therefore, a precise evolution of the system can be simulated [45–48]. Such simulations offer a very accurate insight into the atom dynamics as the ion propagates through the solid, but they are less useful for calculating the sputtering parameters such as the sputtering yield. They are computationally demanding and therefore, only a limited number of impinging projectiles can be simulated, thus providing modest sputtering statistics. The second type of sputtering simulation is based on the binary collisions approximation (BCA), which takes into account only the interactions between the particles that are involved in the collisions [44]. This simulation approach is simpler and less computationally demanding; as a result, it enables calculations of a large number of impinging projectiles and thus, provides better statistics.

Several codes have been developed which are based on the binary collision approximation. One of the earliest and most often used codes is called TRIM (TRansport of Ions in Matter). A program package called SRIM (Stopping and Range of Ions in Matter) utilizes the TRIM code. The SRIM program was developed by Ziegler et al. [49,50]. It calculates in detail all of the kinetic phenomena that are associated with the propagation of the particles, including the target damage, the energy losses of the propagating particles, sputtering and others. For sputtering, the output of the program provides data on the total sputtering yield and the average atoms energies. There have been several improvements to the TRIM code; new programs such as TRIDYN [51] and SDTrimSP [52] have been developed. These programs include surface morphology changes that are due to successive ion bombardment in contrast to SRIM, which assumes a flat and pristine surface for each ion impingement. Nevertheless, the SRIM program is still commonly used for simulating sputtering parameters due to its open access, relative simplicity, and a user-friendly interface.

In this work, we performed SRIM (2013) simulations for argon ion incidence in the 300–1200 eV energy range. Such parameters were chosen to be comparable to the typical ion energies in the sputtering techniques such as DCMS (direct current magnetron sputtering), HiPIMS (high-power impulse magnetron sputtering), triode sputtering and ion-beam sputtering. A comparative study was performed for a wide range of target materials which are typically used for the sputter deposition of thin films. The SRIM parameters were modified to obtain a good agreement with the experimentally reported sputtering yields. The goal of the study is to provide the total and differential sputtering yields that are derived from the combination of simulated and theoretical data along with the published collections of the experimental data. These data and optimization parameters should be useful for engineers and scientists who are working with sputter deposition or ion etching techniques to obtain accurate estimations of the spatial distribution of sputtering. This study can be also used for a quick estimation of the sputtering yield for energies that are below 1200 eV.

2. SRIM Simulation Details

The SRIM code is based on the binary collisions approximation (BCA) which employs the Monte Carlo method for choosing random variables that are associated with the stochastic particle collisions. The BCA approach takes into account only the interactions between the two particles which are directly involved in a collision event. The motion and energy of the particles (ion projectile or target atoms) are determined by the nuclear and electronic interactions that are described in detail in [44]. The particles lose energy in discrete amounts during nuclear collisions and by electron excitation or ionization. They also

dissipate energy continuously due to their interaction with electron gas in the solid. The nuclear and electronic energy losses or the stopping powers are assumed to be independent. The particles travel in straight trajectories between the collisions, while for other particles, it is assumed that they are undisturbed. The trajectories of the particles are calculated from the conservation of momentum and energy.

The SRIM program monitors the trajectories of all of the particles that are involved in the collisions (the ion and the recoiled atoms) until the energy of the moving particle drops below the threshold that is needed to cause the atom displacement or until the particle leaves the target surface. It records the locations and energies of the particles and also the location, direction, and energy of the sputtered atoms. In SRIM, it is assumed that the target material is amorphous with the atoms at random locations—the directional properties of the crystal lattice are disregarded. The average quantities, such as the total sputtering yield or average atom energy can be determined by simulating numerous incident ions. The different distributions, such as the energy and angular distributions of the sputtered atoms can also be calculated by data post-processing. The physics of the SRIM code is presented in the textbook by the authors of the program [50]. The BCA simulation approach is also described in detail in the book by Eckstein [44].

In this work, SRIM simulations were made for a range of single-elements from the periodic table to explore, methodologically, the differences in the sputtering yields. We performed a series of simulations for the target materials that are typically used in the sputter deposition (Figure 1). In particular, we analyzed the sputtering of elements that are lighter than the bombarding argon ion ($Z = 18$)—including B and C; Al, and Si (i.e., $Z = 5, 6, 13$, and 14 , respectively), and elements that are heavier than argon—specifically, the transition metal elements from groups 4, 5, 6, and 11 (i.e., Ti, Zr, and Hf; V, Nb, and Ta; Cr, Mo, and W; Cu, Ag, and Au). Such material selections allowed us to explore the differences in the elements of the same group or period of the periodic table. For each material, we performed more detailed simulations for the argon ion energies of 300 eV, 600 eV, and 1200 eV to evaluate the differential sputtering yields. Such energies were chosen to be roughly comparable to the typical ion energies which are encountered in DC magnetron sputtering (DCMS), high-power impulse magnetron sputtering (HiPIMS), and triode sputtering.

		group																18	
period	1	2											13	14	15	16	17	18	
	1	H	2																He
	2	Li	Be											B	C	N	O	F	Ne
	3	Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	Xe
	6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Figure 1. Target materials investigated by SRIM simulations sputtered by Ar ions.

For the simulations, we used the version SRIM-2013. The number of impinging argon ions was set to 10^6 , which generated several hundred thousand to a million sputtered atoms, depending on the target material and the ion energy (i.e., the sputtering yield). Such numbers provided adequate statistics for the evaluation of the differential sputtering yields. The “detailed calculation with full damage cascades” type was chosen for the calculation. The default stopping powers that were provided by the program were used. We focused mainly on the evaluation of the sputtering yield for a normal ion impingement, however, several off-axis simulations were also performed.

2.1. SRIM Set-Up Parameters and Experimental Data

Several parameters which influence the sputtering yield can be adjusted in the SRIM program. These parameters include: the surface binding energy, the displacement energy, the lattice binding energy, and the mass density of the target material. The surface binding energy presents the potential energy barrier for removing an atom from the surface. It has the greatest influence on the sputtering yield. The displacement energy is defined as the minimum energy that is required to knock a target atom far away from its lattice site so that it does not immediately return to the original position [50]. This results in the formation of a Frenkel pair, i.e., a single vacancy and a nearby interstitial atom. If the atom does not move more than one lattice spacing, it is assumed that it returns to its original position and gives up the energy to the phonons. The typical values of the displacement energy are around 15 eV for semiconductors and 25 eV for metals. The lattice binding energy is defined as the minimum energy that is needed to remove an atom from a lattice site [50]. Hence, this energy is required to break the electronic bonds and displace an atom from a lattice site. The atom which leaves the lattice site loses this energy. The lattice binding energy is always smaller than the displacement energy is, with the typical values being around 1–3 eV.

The roles of these parameters on the total sputtering yield for the selected materials are presented in the Supplementary Materials. The surface binding energy (SBE) has the largest effect on the sputtering yield, while the other two parameters (the displacement energy and the lattice binding energy) have only a minor effect on this (a few percent). The SRIM program uses the heat of sublimation (per atom) for the approximation of the surface binding energy. However, these two quantities are not necessarily the same since the energy threshold for the atoms leaving the surface also depends on the surface morphology, composition, and other factors as discussed in [50].

To obtain sputtering yields in line with the measured values, we modified the SBE in a similar way as in [53]. The displacement energy and the elastic binding energy parameters were not changed from the default SRIM values since the sensitivity analysis showed that they had a small effect on the sputtering yield (see Supplementary Materials). The surface binding energy was modified in such a way to obtain a good fit between the simulated and the experimental yields in the 300–1000 eV range. For the experimental data, we used the total sputtering yields that are reported in the collection by Behrisch and Eckstein [22]. In some cases, we also compared the simulated values to the experimental data that are in the study by Matsunami et al. [24,25] and other more recent measurements [54]. We chose those SBE values, for which the simulated yields were closer to the experimental data rather than the fitted curves that are provided in the collections.

For the sputtering of carbon by argon ions, more recent sputtering yield data from Kolasinski et al. [55] were used. The experimental yields for the boron sputtering by argon ions were not available. In this case, we relied on the experimental and simulation yield data for the sputtering of boron nitride. Chen et al. [56] found that simulated sputtering yields best agree with the experimental values for boron nitride if a surface binding energy of 2–3 eV is used for boron. In our simulation, we use the value 2.8 eV, which is closer to 3 eV and is proportionally reduced from the default SBE by a similar amount as in the case of carbon. Furthermore, when performing the simulations using $E_{sb} = 2.8$ eV, we obtained a relatively good agreement with the experimental data for boron self-sputtering which are reported in [22]. Nevertheless, the error between the simulated and real yields in the case of boron was expected to be larger. Overall, we aimed to obtain yields which were within the 10–20% error of the measured values for the 300–1200 eV range. However, due to the measurement and simulation uncertainties, larger errors were likely to occur.

The parameters that were used in the simulations are collected in Table 1. Note, that the modified SBE for the light elements (i.e., B, C, Al, and Si) had to be decreased significantly from the default SBE values which are used by the SRIM program (i.e., the heat of sublimation). For the transition metals, particularly for the heaviest elements (e.g., Hf, Ta, W, and Au), we had to increase the SBE by a significant amount. In some cases (e.g.,

V and Ag) the modified SBEs were similar to the default values in the SRIM program. The lattice binding energy was 3 eV for all of the simulated elements, except for the silicon, for which it was 2 eV. The displacement energy for carbon was 28 eV, for silicon, it was 15 eV, and for all of the other elements, it was 25 eV.

Table 1. Parameters used for SRIM simulations. Z —atomic number, M —atomic mass, ρ —mass density, E_{sb} —surface binding energy used in SRIM (i.e., the heat of sublimation), E_{msb} —modified surface binding energy. References point to the experimental data that were used for simulation of the total sputtering yield from which the modified surface binding energy was obtained.

Elem.	Z	M (amu)	ρ (g/cm ³)	E_{sb} (eV)	E_{msb} (eV)	Ref.
B	5	10.81	2.35	5.73	2.8	[56]
C	6	12.01	2.25	7.41	3.6	[55]
Al	13	26.98	2.70	3.36	2.8	[22]
Si	14	28.08	2.32	4.70	3.8	[22]
Ti	22	47.85	4.52	4.89	5.2	[22]
V	23	50.94	5.96	5.33	5.5	[22]
Cr	24	52.00	7.20	4.12	4.9	[22]
Cu	29	63.55	8.92	3.52	4.3	[22]
Zr	40	91.22	6.49	6.33	8.3	[22]
Nb	41	92.91	8.57	7.59	9.0	[22]
Mo	42	95.95	10.21	6.83	10.0	[22]
Ag	47	107.87	10.47	2.97	3.2	[22]
Hf	72	178.49	13.31	6.31	9.5	[22]
Ta	73	180.95	16.60	8.10	13.5	[22]
W	74	183.84	19.35	8.68	14.0	[22]
Au	79	196.97	19.31	3.80	5.5	[22]

2.2. Total and Differential Sputtering Yield Evaluation

The total sputtering yield (Y) is independent of the spatial direction and is defined for the entire spatial area into which the atoms are sputtered (i.e., a hemisphere). It is defined as the number of sputtered atoms divided by the number of impinging ion projectiles:

$$Y = \frac{N}{N_i}, \quad (1)$$

where N is the number of sputtered atoms and N_i is the number of impinging ions. The total sputtering yield in the SRIM program was evaluated using the above equation, and this was obtained directly from the SRIM interface.

The evaluation of the differential sputtering yield requires the processing of the SRIM output data. The file contains information on the energy, position, and direction of sputtered atoms. The position and direction are provided in the Cartesian coordinate system, and therefore, these data were first converted into a spherical system. The schematic of the geometry that was used for the evaluation of the differential yields is shown in Figure 2. In the coordinate system of the SRIM program, the surface normal axis is labeled as x , and it is pointing inwards into the target material. In this work, we analyzed the sputtered atoms, and therefore, the x -axis positions in the direction of the surface normal.

For the atoms that were sputtered into a particular solid angle of a sphere ($d\omega = \frac{d\Omega}{r^2}$), the differential sputtering yield Y_d is defined as [2,22]

$$Y_d(\theta, \varphi) = \frac{d^2Y}{d^2\omega} = \frac{1}{N_i} \frac{d^2N}{d^2\omega}. \quad (2)$$

The integration of the differential sputtering yield over the full polar (θ) and azimuthal (φ) angles (i.e., the whole hemisphere) gives the total sputtering yield

$$Y = \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi/2} Y_d(\theta, \varphi) d\omega = \int_0^{2\pi} \int_0^{\pi/2} Y_d(\theta, \varphi) \sin\theta d\theta d\varphi. \quad (3)$$

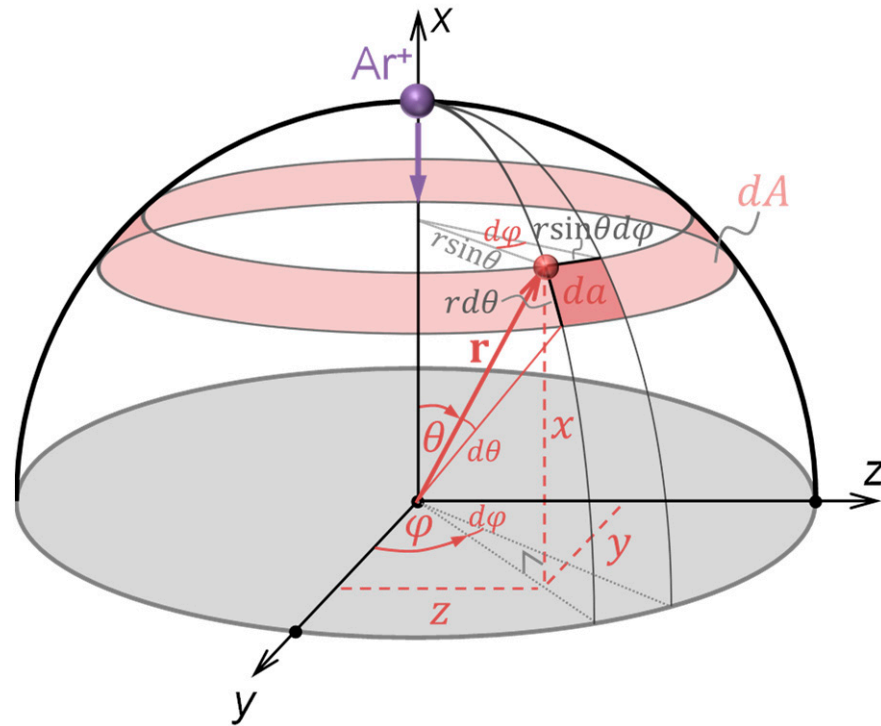


Figure 2. Schematic of the geometry in the evaluation of the SRIM data. Ions impact the target surface and cause the emission of sputtered atoms in different spatial directions.

Here, we considered that the differential solid angle in the spherical coordinates is equal to $d\omega = \sin\theta d\theta d\varphi$. The spatial area da which determines the solid angle is marked by the dark red square in Figure 2. The spatial area dA and corresponding solid angle $d\Omega = \frac{dA}{r^2} = 2\pi \sin\theta d\theta$, which is integrated over the azimuth, is also marked in the figure. For a normal ion incidence, sputtering is azimuthally isotropic (i.e., the number of sputtered atoms does not depend on the azimuthal direction), therefore, we can integrate Equation (3) over the azimuthal angle and write:

$$Y = 2\pi \int_0^{\pi/2} Y_d(\theta) \sin\theta d\theta. \quad (4)$$

The derivative of Equation (4) provides the differential sputtering yield in the dependence of the polar angle

$$Y_d(\theta) = \frac{1}{2\pi \sin\theta} \frac{dY}{d\theta} = \frac{1}{2\pi N_i \sin\theta} \frac{dN}{d\theta}. \quad (5)$$

To evaluate the polar distribution, we define a constant differential sputtering yield for the particular polar interval, i.e., $\bar{Y}_d[\theta_1, \theta_2]$. From Equation (5), it then follows that the number of atoms that are sputtered into the polar angle interval can be calculated by the integration from θ_1 to θ_2 :

$$N_d[\theta_1, \theta_2] = 2\pi N_i \bar{Y}_d \int_{\theta_1}^{\theta_2} \sin\theta d\theta = 2\pi N_i \bar{Y}_d (\cos\theta_1 - \cos\theta_2). \quad (6)$$

Note that when it is integrated over the whole hemisphere (i.e., $\theta_1 = 0$ and $\theta_2 = \frac{\pi}{2}$) we get $\bar{Y}_d[0, \frac{\pi}{2}] = Y/2\pi$ since $N_d[0, \frac{\pi}{2}] = N$. The polar differential yield is defined as $Y_d(\theta) = \frac{d^2Y}{d^2\Omega}$ and therefore, it is normalized by the factor 2π .

The average differential sputtering yield into a specific polar angle interval $[\theta_1, \theta_2]$ can be rewritten from Equation (6) as:

$$\bar{Y}_d[\theta_1, \theta_2] = \frac{1}{2\pi(\cos\theta_1 - \cos\theta_2)} \frac{N_d[\theta_1, \theta_2]}{N_i}. \quad (7)$$

Hence, the differential yield is not simply $\frac{N_d}{N_i}$, instead it needs to be normalized by the geometrical function $2\pi(\cos\theta_1 - \cos\theta_2)$. This function represents the azimuthal surface area on the hemisphere, which changes with the polar emission angle (see Figure 2). When counting the number of atoms for the azimuthally isotropic case, one needs to normalize the number of atoms by this surface area. The units for $\bar{Y}_d[\theta_1, \theta_2]$ are atoms/ion $\times$ sr⁻¹.

For the azimuthally isotropic sputtering, the sum of the polar differential yields into each solid angle $\Delta\Omega_j$ provides the total sputtering yield:

$$Y = \sum_{j=1}^n \bar{Y}_{d,j} \cdot \Delta\Omega_j = \sum_{j=1}^n \bar{Y}_{d,j} \cdot 2\pi(\cos\theta_j - \cos(\theta_j + \Delta\theta)) = \sum_{j=1}^n \frac{N_{d,j}}{N}. \quad (8)$$

Here, we considered that $\Delta\Omega_j = 2\pi \int_{\theta_j}^{\theta_j + \Delta\theta} \sin\theta d\theta = 2\pi(\cos\theta_j - \cos(\theta_j + \Delta\theta))$. The summation number j ranges from 1 to $n = \left(\frac{\pi/2}{\Delta\theta}\right) - 1$ with the polar angle interval $\Delta\theta$ (e.g., 10°). To calculate the total sputtering yield from the average differential sputtering yields, which are presented in Section 3.2, one needs to multiply the values on the graph by the solid angle factors $2\pi(\cos\theta_j - \cos(\theta_j + \Delta\theta))$.

In the evaluation of the differential sputtering yield, we also considered the assumption that the atoms are refracted as they cross the surface plane due to the surface binding energy. This refraction is evaluated in the original works by Thompson, Sigmund, and others [1,32,35]:

$$\sin\theta_1 = \sqrt{\frac{E_0}{E_0 - E_{sb}}} \sin\theta_0. \quad (9)$$

Here, θ_1 is the angle of an atom as it crosses the surface potential barrier and enters the space (vacuum), θ_0 is the initial incident angle of the atom, E_0 is the incident energy, and E_{sb} is the surface binding energy. The surface potential barrier causes the largest atom refraction for the low-energy atoms that are directed under a large angle with respect to the surface normal.

After the transformation that is related to atom refraction, the number of atoms sputtered into a specific polar angle interval was counted. The data were first rearranged by the polar angle, then, the number of atoms that were sputtered into a polar interval $[\theta_1, \theta_2]$ was counted for all of the azimuthal angles. The differential sputtering yields were calculated according to Equation (7). The data were evaluated for the 10° polar intervals. The smaller polar intervals of 5° and 3° were also considered, but they provided essentially the same distributions. We also verified that the total sputtering yield that was obtained from the SRIM interface was the same as the one which was obtained by summing all of the average differential sputtering yields using Equation (8).

3. Results of SRIM Simulations

3.1. Total Sputtering Yield

The simulations for the total sputtering yield were performed for all of the sputtering-relevant elements as discussed in Section 2. For each element, the incident ion energies

were taken from 200 eV to 1200 eV with a step size of 100 eV. The energy dependence was fitted to a power-law equation using the modified surface binding energy:

$$Y = a \left(\frac{E_i}{E_{msb}} \right)^b, \quad (10)$$

where a and b are the fitting parameters. The results are presented in Table 2. For most of the elements, the data are best fitted with $b \approx 0.66$, which somewhat deviates from the square function, whereas for the lightest elements (boron and carbon), a close-to-linear function best fit the data. The coefficient of determination R^2 was in all of the cases, better than 0.98. The total sputtering yields at three different energies are also presented in Table 2.

Table 2. Fitting parameters for the sputtering yield (a and b) and the coefficient of determination R^2 together with the atomic number Z , the energy transfer factor Λ , and the simulated sputtering yields at three different energies.

Elem.	Z	Λ	a	b	R^2	Y (300 eV)	Y (600 eV)	Y (1200 eV)
B	5	0.670	0.0024	0.831	0.985	0.28	0.52	0.85
C	6	0.711	0.0011	0.904	0.987	0.17	0.38	0.64
Al	13	0.962	0.0104	0.699	0.983	0.55	0.97	1.40
Si	14	0.970	0.0045	0.744	0.988	0.30	0.54	0.85
Ti	22	0.992	0.0126	0.616	0.993	0.42	0.66	0.98
V	23	0.985	0.0153	0.608	0.992	0.49	0.77	1.10
Cr	24	0.983	0.0201	0.644	0.993	0.77	1.27	1.88
Cu	29	0.948	0.0319	0.658	0.993	1.34	2.22	3.29
Zr	40	0.847	0.0145	0.603	0.993	0.44	0.73	1.04
Nb	41	0.841	0.0135	0.621	0.996	0.48	0.73	1.08
Mo	42	0.830	0.0137	0.628	0.995	0.50	0.78	1.15
Ag	47	0.789	0.0429	0.639	0.993	1.64	2.67	3.86
Hf	72	0.598	0.0113	0.655	0.992	0.47	0.77	1.15
Ta	73	0.593	0.0059	0.724	0.996	0.37	0.62	0.99
W	74	0.587	0.0064	0.721	0.995	0.39	0.67	1.06
Au	79	0.561	0.0191	0.715	0.993	1.12	1.90	2.94

Figure 3 presents simulations of the total sputtering yield together with the fitting curves. The elements from groups 11, 13, and 14 are shown in Figure 3a, while elements from groups 4–6 are presented in Figure 3b with an identical scale to perform easier comparisons. In the latter case, an inset is given at an enlarged scale. An alternative presentation of the sputtering yield data is shown in the Supplementary Materials. The behavior of the total sputtering yield of various elements can be compared at different energies. The power parameter is similar for the evaluated elements, with the exception of boron and carbon, therefore, the relative values of the sputtering yield are comparable regardless of the ion energy. In the forthcoming description, we only discuss the values at 1200 eV.

For the group 11 elements, the total sputtering yields are larger than they are for the elements of the other analyzed groups. They are in the range from 3.0 (Au) to 4.0 (Ag). Surprisingly, the remaining elements in groups 4–6 have very similar sputtering yields, with values that are close to 1.0; the outlier is chromium, which has a sputtering yield of 1.9. The lightest elements (groups 13 and 14) have, in general, lower sputtering yields than the transition metals do, with exception of aluminum, which has a sputtering yield of about 1.4. Carbon has the lowest sputtering yield among the studied elements at 0.64. Carbon and boron have close-to-linear dependence, while other elements show a parabolic-like dependence on the energy of the ion.

The descriptions so far have been limited to the perpendicular impact of the impinging ions. In some situations, the sputtering is also performed under non-perpendicular incidence angles. Figure 4 presents the total sputtering yield at 600 eV at 10-degree steps

from the perpendicular angle (0°) to the glancing angle of incidence (89.9°). Though the absolute sputtering yield values are important for the sputter deposition (Figure 4a,b), it is more revealing to analyze the relative values with respect to the perpendicular ion impact in order to extract the dependence for the different elements (Figure 4c,d). This is further discussed below.

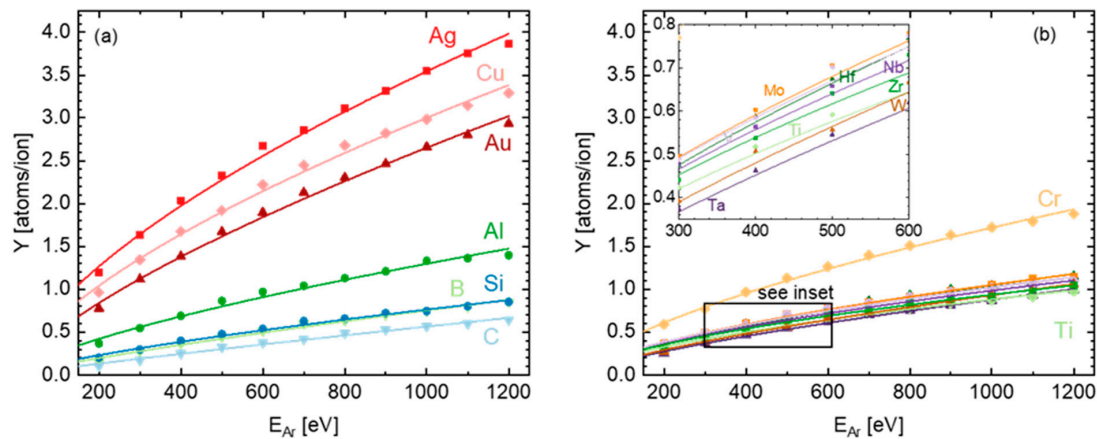


Figure 3. The total sputtering yield in dependence of Ar ion energy simulated by the SRIM program for different elements for normal ion impingement. For clarity, the elements are shown in two separate graphs at identical scales: (a) elements from groups 11, 13, and 14; (b) elements from groups 4–6. Due to minor differences, an inset is shown at an enlarged scale.

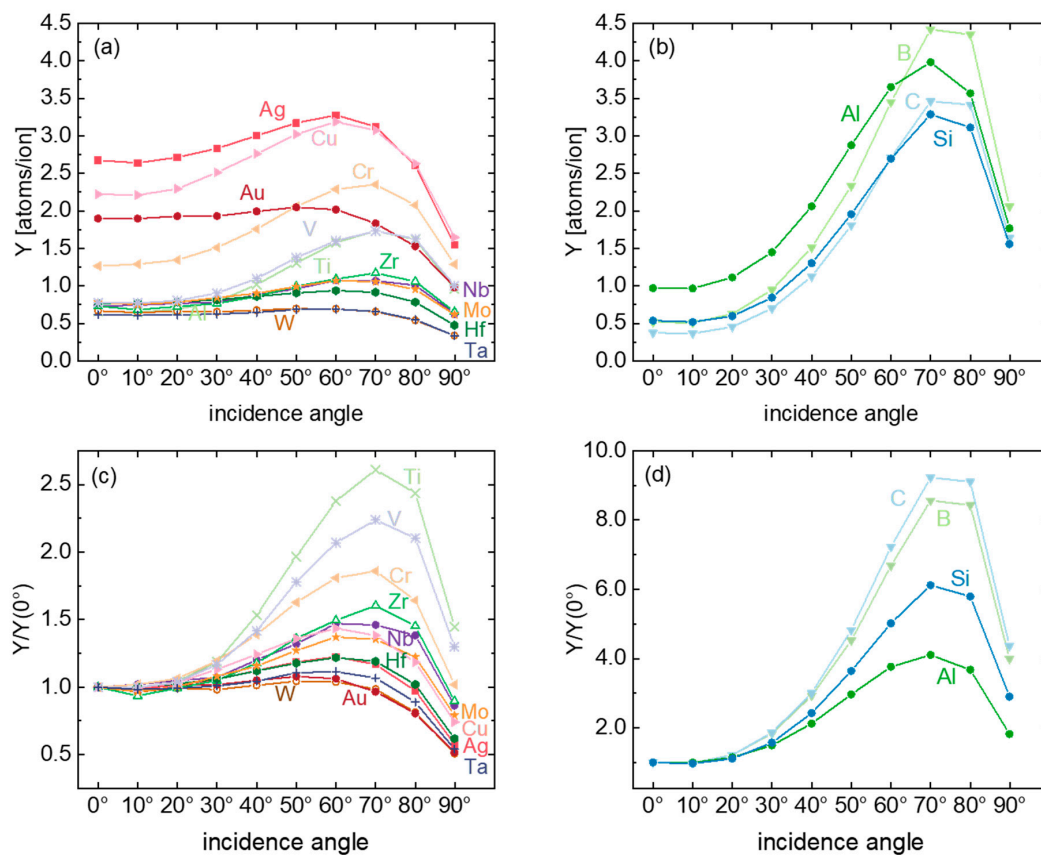


Figure 4. Total sputtering yield in dependence of ion incidence angle for (a) selected transition metals and (b) selected elements with $Z \leq 14$. Normalized values against the normal ion impingement for the same elements are shown in graphs (c,d). Calculations were made by SRIM using Ar ions with 600 eV.

For the transition metals (Figure 4a), the total sputtering yield is essentially unchanged for an incident angle that is below about 30° , while for the lighter elements $Z \leq 14$ (Figure 4b), this angle is about 20° . After the plateau, the sputtering yields start to increase with the incident angle up to around 70° , where the maximum peak is reached for most of the elements. With further increases of the incidence angle, the total sputtering yield decreases for all of the elements.

In the central region (i.e., about 50 – 80°), the largest differences that are between the elements can be observed. In contrast to the absolute values (Figure 4a,b), the main parameter that influences the normalized values (Figure 4c,d) is the atom mass rather than the group in the periodic system. For the elements with $Z \geq 22$ (Figure 4c), it can be seen that the lighter elements (Ti, V, and Cr) experience a marked peak of the sputtering yield that is up to about 2.6-times larger than it is at the perpendicular incidence. This is followed by the heavier elements in the next period (Zr, Nb, and Mo), which have no more than 1.6-times larger sputtering yields. In the case of the last period (Hf, Ta, and W), there is hardly any difference when it is compared to the perpendicular incidence. The group 11 elements follow a similar pattern though with a slight shift. The lighter elements (Figure 4d) show significantly larger variations in the total sputtering yield with the ion incidence angle than the transition metals do. The lightest two elements (B and C) show the largest variations, and these are followed by Si and Al. According to the simulations, more than eight times larger sputtering yields are observed for B and C at the 70° ion incidence angle than those which are observed for the normal ion incidence. In the absolute terms, the elements with $Z \leq 14$ (Figure 4b) have higher sputtering yields at 70° than the transition metal elements do, including the elements in the group 11 which have the highest sputtering yields (Figure 4a).

3.2. Differential Sputtering Yield

The differential sputtering yield data were processed from the SRIM data as described in Section 2.2. The analysis was made for three ion energies: 300 eV, 600 eV, and 1200 eV, which roughly correspond to the typical ion energies in DCMS, HiPIMS, and triode sputtering.

Here, the differential sputtering yield represents the polar differential sputtering yield or the polar distribution of the sputtered atoms if they are multiplied by the number of impinging argon ions (10^6). The points in the polar graphs present the intervals in the 10-degree steps. The value at 5° thus encompasses the emission of the target atoms in a predominantly normal direction, i.e., in the interval that is below 10° .

Figure 5 presents the differential sputtering yields for each of the studied transition metal elements. They are arranged in the same way as they are in the periodic table. If the individual values are integrated over the polar and azimuthal angles, then we can obtain the total sputtering yield at the respective energy as shown in Figure 3. In line with the results from Figure 3 and the accompanying discussion, the absolute values of the differential sputtering yield for the group 4–6 elements are very similar. Titanium experiences somewhat lower values, and chromium experiences higher ones; however, the values for the group 11 elements are substantially higher. At least visually, the angular dependence does not show any particular difference between any element.

Regarding the light elements from groups 13 and 14, the results are not straightforward (Figure 6). For silicon, the results appear to be comparable to the angular distribution that is observed in the transition metals. On the other hand, the other three light elements (B, C, and Al) show unusual distributions. For the lower sputtering angles, i.e., those towards a perpendicular direction, the simulated differential sputtering yield is far higher than that which would be anticipated. This is especially the case for angles that are below 10° , with results that are as high as 2.09 sr^{-1} (for boron at 1200 eV), 2.54 sr^{-1} (for Al at 600 eV), and even 3.70 sr^{-1} (for Al at 1200 eV). These unreasonably high values are discussed in more detail in Section 4.2.

While the polar graphs in Figures 5 and 6 are informative, the sputtering angle dependence can be better extracted from the standard cartesian graphs. Figure 7a presents

the metallic elements from groups 4–6 and 11. As in the total sputtering yield, the group 11 elements have a far higher differential sputtering yield in comparison to those from groups 4–6. Aside from Cr (higher) and Ti (slightly lower), all of the remaining elements from these three groups essentially behave in an identical way, with negligible differences between them. The angular dependence is monotonously decreased, with a slight change of slope at around 40° . Among the light elements (Figure 7b), silicon has a similar angular dependence as the group 4–6 elements do. However, for B, C, and Al (Figure 6), the simulations gave unexpectedly high values of the differential sputtering yield in the sputtering angles that were below 40° . While one can accept the somewhat higher values at 35° and 25° (possibly also at 15°), the values at 5° are not realistic. Thus, the results that are presented in Figure 7b should be taken as an output of the simulation only, rather than a verified conclusion.

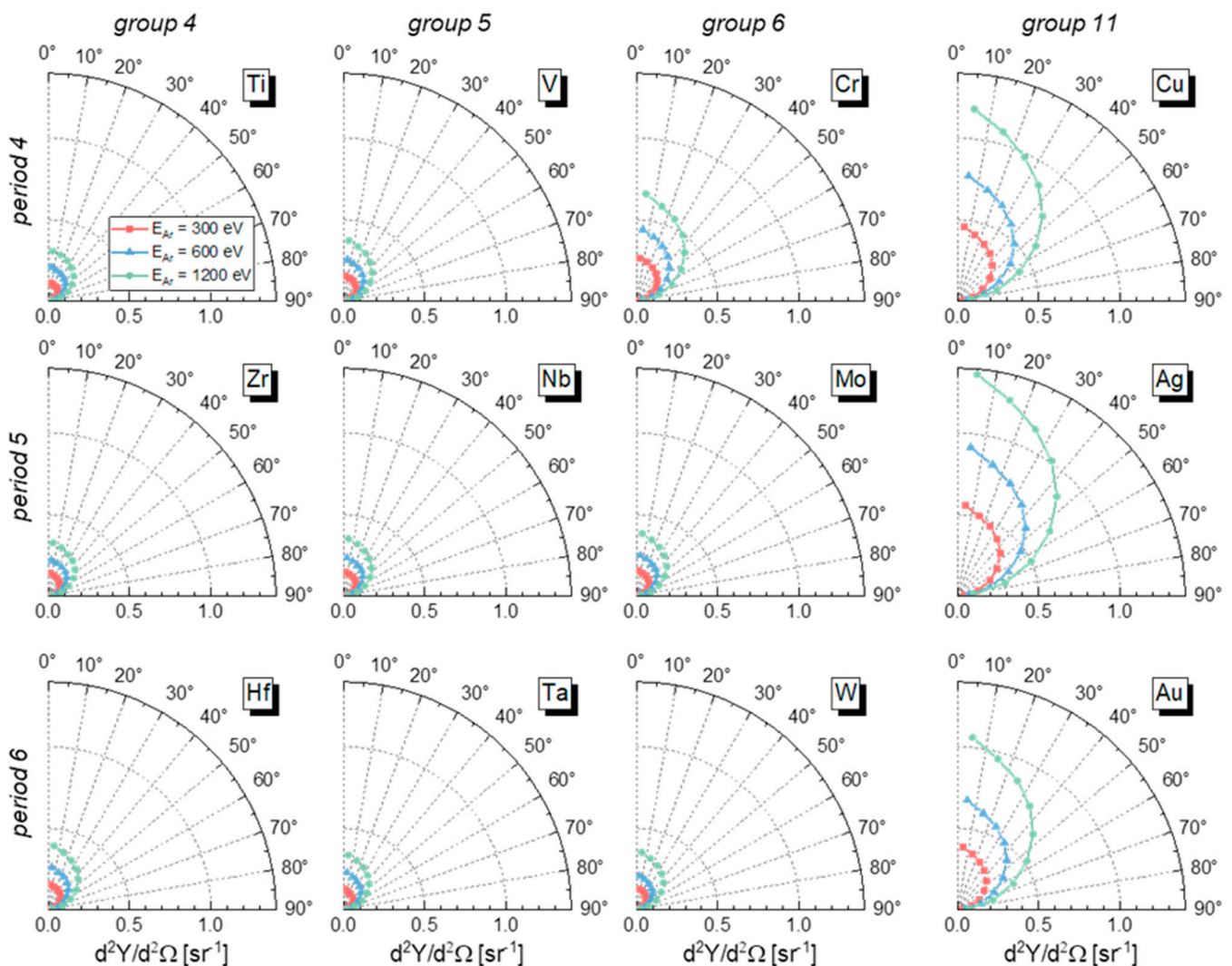


Figure 5. Angular distribution of sputtered metallic elements (groups 4–6 and 11) with 300 eV (red), 600 eV (blue), and 1200 eV (green) energy argon ions at perpendicular incidences. The graphs show the number of sputtered atoms in a particular polar angle interval.

Another way of presenting the angular dependence of the sputtered atoms is to divide the differential sputtering yields by the total sputtering yield of the respective element. For the transition metals, these results are shown in Figure 7c. Surprisingly, all of the studied elements, including group 11, essentially follow the same curve. There are only slight variations among them, thus, only the lowest (V) and the highest (Ta) ones are marked. This suggests that the sputtering angle dependence of the differential sputtering yield is

the same regardless of the metal type. Normalizing the already questionable differential sputtering yields of the light elements does not make much sense; nevertheless, even silicon appears to be quite off in comparison to the metals (Figure 7d). Therefore, we believe that even the results for silicon should be taken with reservation.

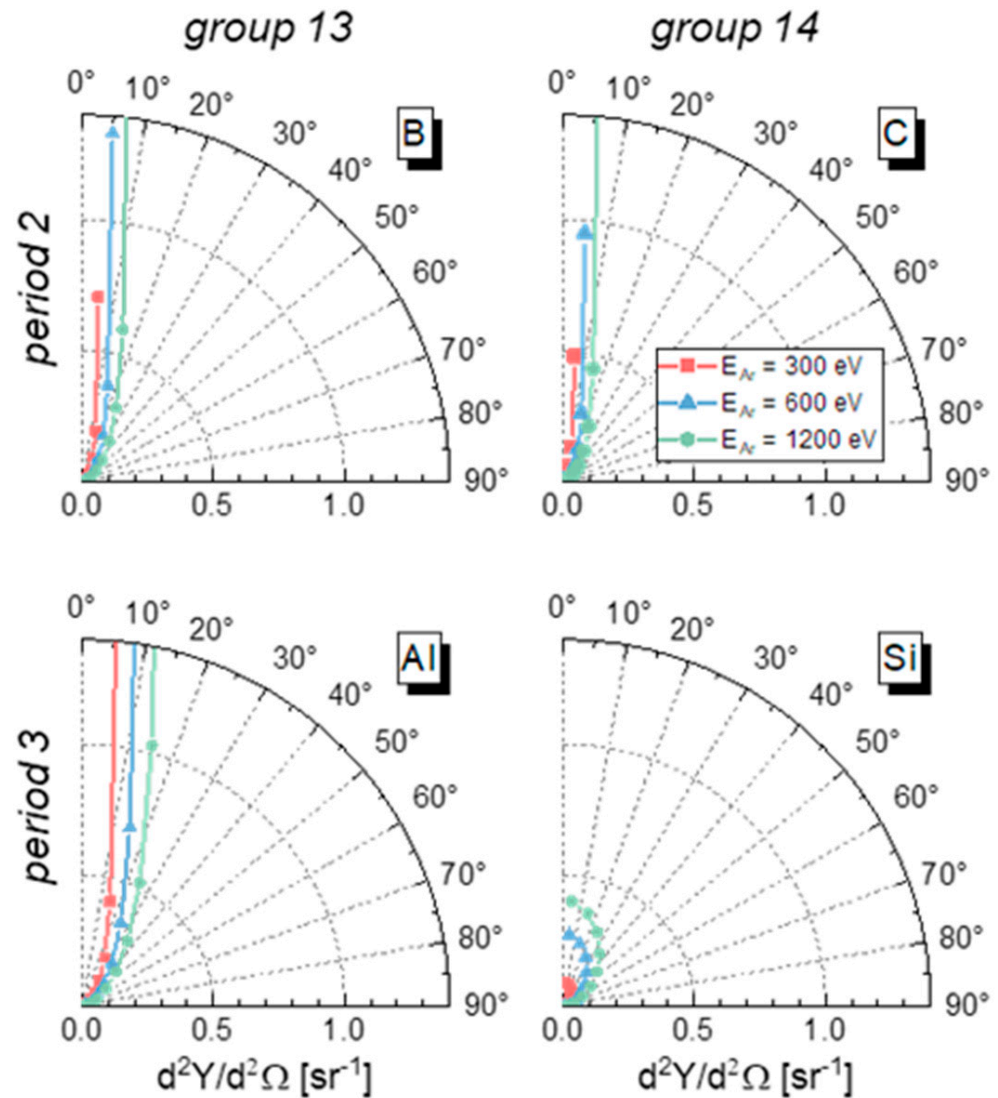


Figure 6. Angular distribution of sputtered light elements (groups 13 and 14) with 300 eV (red), 600 eV (blue), and 1200 eV (green) energy argon ions at perpendicular sputtering directions. The graphs show the number of sputtered atoms in a particular polar angle interval.

The differential sputtering yields were also fitted according to the cosine law:

$$\frac{1}{Y} \frac{d^2Y}{d^2\Omega} = A \cos^y \theta, \quad (11)$$

where A and y are the fitting parameters. The results are given in Table 3. In line with the results from Figure 7, there is not much variation between the elements.

The discussion on the differential sputtering yield has so far been limited to a perpendicular incidence of the bombarding ions. In the following, we discuss the results of the simulations for the oblique ion incidence angles. In Figure 8, we present the polar graphs of the sputtered atoms, which is similar to Figures 5 and 6. While yet another parameter (incidence angle) to the existing ones (element and energy) would further increase the complexity of the topic, we limited our work to one incidence angle (60°). At these conditions,

we analyzed the angular distribution for the selected elements at one ion energy (600 eV) and three different ion energies of sputtering Cr as a single selected element.

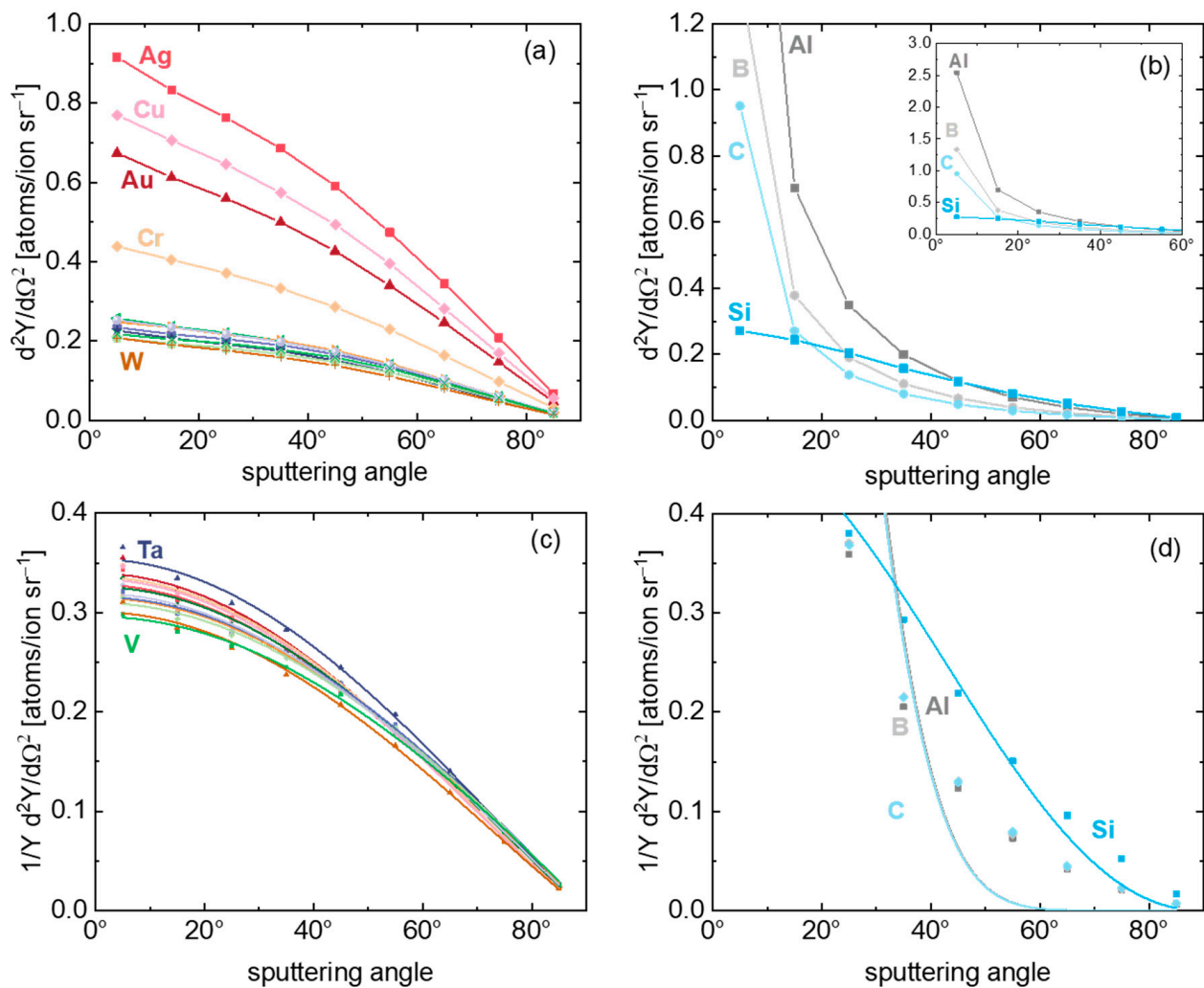


Figure 7. Polar distribution of the differential sputtering yield for metallic elements (a) and light elements (b). Normalized distributions for the two collections are given in (c,d). Graphs for both collections have identical scales; in the case of light elements, the inset also shows excessively high values at low sputtering angles.

Table 3. Fitting parameters for cosine approximation of the differential sputtering yield curves; the coefficient of determination R^2 is also given.

Element	A	y	R^2
Si	0.487	2.172	0.989
Ti	0.308	0.973	0.998
V	0.319	1.035	0.998
Cr	0.336	1.116	0.997
Cu	0.333	1.132	0.996
Zr	0.296	0.951	0.998
Nb	0.316	0.980	0.998
Mo	0.315	1.004	0.999
Ag	0.328	1.101	0.995
Hf	0.326	1.060	0.998
Ta	0.329	1.077	0.997
W	0.325	1.087	0.997
Au	0.340	1.141	0.995

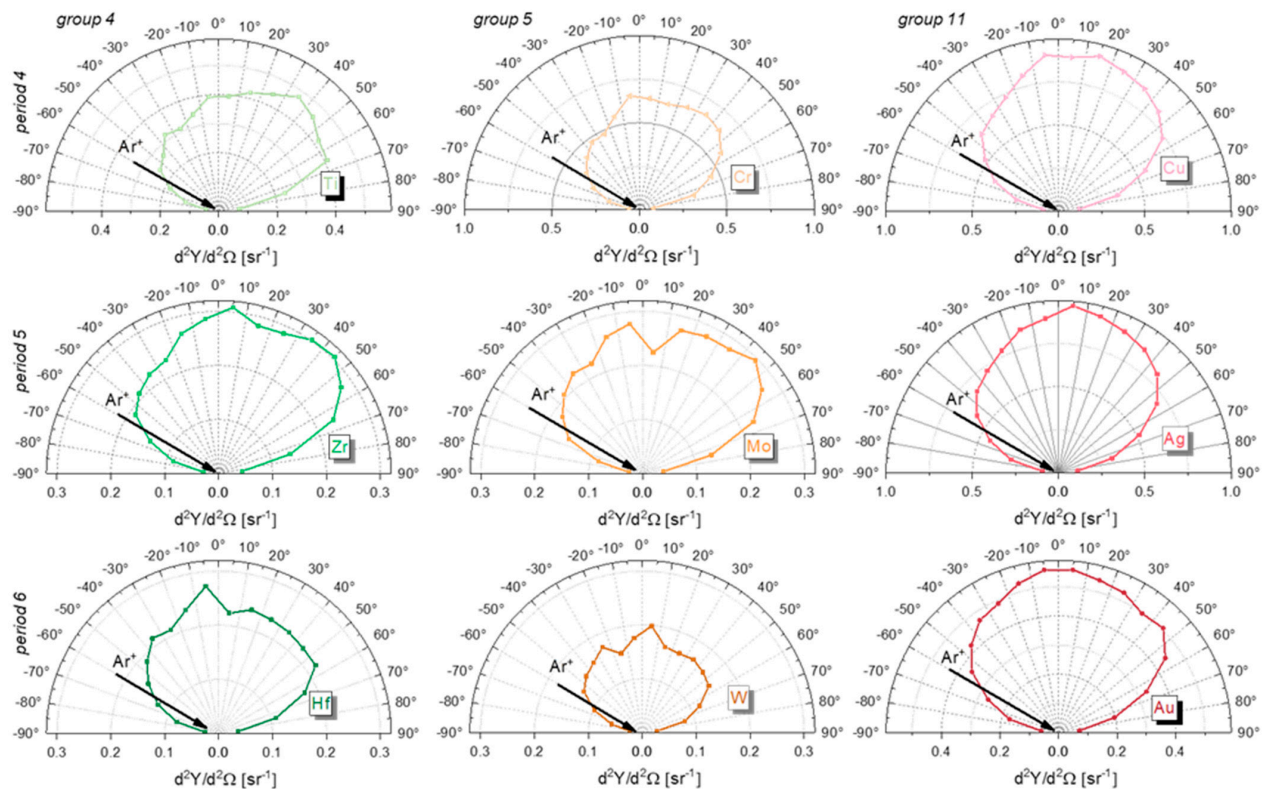


Figure 8. Angular distribution of sputtered atoms for selected elements (Ti, Cr, and Cu; Nb, Mo, and Ag; Hf, W, and Au) bombarded by argon ions at 60° angle and energy of 600 eV.

The polar graphs in Figure 8 show the different elements (groups 4, 6, and 11) at the ion energy of 600 eV. At least some asymmetry of enhanced forward sputtering can be observed in all of the graphs. The asymmetry increases with the group of the periodic table, and it decreases with the period. Thus, the most expressed forward sputtering is observed in Ti, and the least of this is observed in Au. Due to statistical noise, it is not meaningful to look for any higher-order effects.

Finally, we looked at the situation of the same element (Cr) at three different energies. Figure 9a shows the absolute values of the differential sputtering yield. As these values substantially depend on the energy, the angular asymmetry is more visible if the values are normalized at the total sputtering yield. This is shown in Figure 9b, where it can be observed that the symmetry increases with the ion energy, i.e., the sputtering at lower ion energies causes a more asymmetric distribution of the atoms than it does at higher energies.

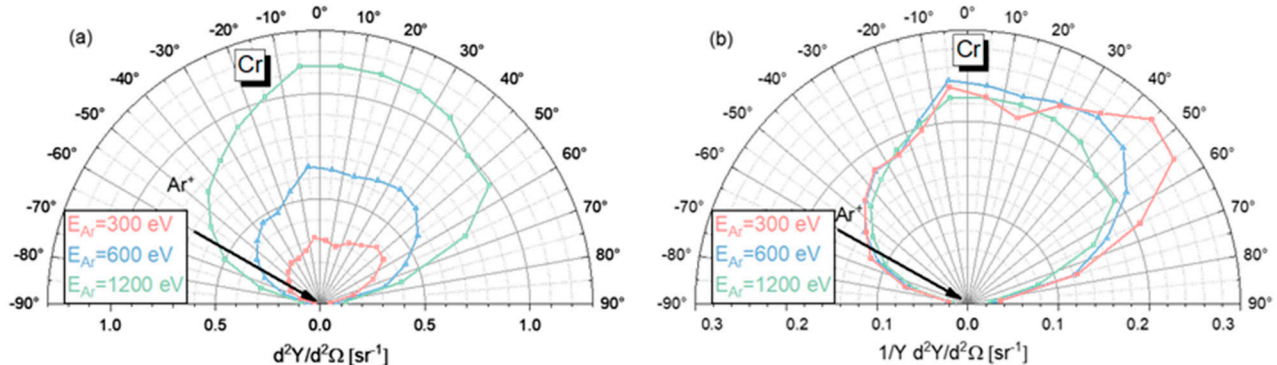


Figure 9. (a) Angular distribution of Cr atoms sputtered by Ar ions at 60° ion incidence for different ion energies. (b) Angular distribution normalized with the total sputtering yield.

4. Discussion

4.1. Total Sputtering Yield

The total sputtering yield depends on several parameters that are related to the impinging ion and the sputtered target material. An insight into the influence of these parameters can be obtained from the analytical equation for the sputtering yield. The analytical expressions that are most often used for the calculation of the total sputtering yield were derived by Sigmund in his seminal work on the theory of sputtering [35]. For a perpendicular ion impact in the linear cascade regime, Sigmund derived the following expression for the total sputtering yield:

$$Y = 0.042 \frac{\alpha}{E_{sb}} S_n, \quad (12)$$

where E_{sb} is the surface binding energy and α is a dimensionless function which depends on the ion-target atomic mass ratio and the ion incidence angle, but it does not depend on the ion energy. In Equation (12), the nuclear stopping cross section S_n is a complex function of the ion and the target atomic masses and the ion energy

$$S_n = 4\pi a_l \frac{e^2}{4\pi\epsilon_0} Z_i Z_s \frac{M_i}{M_i + M_s} s_n, \quad (13)$$

with Z and M corresponding to the ion atomic number and mass (index i) and the solid atomic number and mass (index s), respectively. The a_l factor is the Lindhard screening length. Further complexity in Equation (13) arises from the reduced nuclear stopping power s_n . In practice, different forms of the reduced nuclear stopping power are used, which are based on the particular interatomic potential between the interacting atoms. Often a Thomas–Fermi or Krypton–Carbon potential is utilized [57]. For the Thomas–Fermi potential, the reduced nuclear stopping power is:

$$s_n^{TF} = \frac{3.441 \sqrt{\epsilon} \ln(\epsilon + 2.718)}{1 + 6.35 \sqrt{\epsilon} + \epsilon(6.882 \sqrt{\epsilon} - 1.708)}, \quad (14)$$

while for the Krypton–Carbon potential, it is:

$$s_n^{KC} = \frac{0.5 \ln(1 + 1.2288\epsilon)}{\epsilon + 0.1728 \sqrt{\epsilon} + 0.008\epsilon^{0.1504}}, \quad (15)$$

where the reduced energy ϵ is defined as:

$$\epsilon = \frac{a_l}{Z_i Z_s} \frac{4\pi\epsilon_0}{e^2} \frac{M_s}{M_i + M_s} E_i. \quad (16)$$

The nuclear stopping cross section S_n is the only term in Equation (12) which depends on the ion energy (E_i).

Over the years, the general equation for the total sputtering yield has been modified to achieve a better agreement with the experimental data (particularly at lower ion energies). An overview of various semi-empirical equations for the total sputtering yield can be found in Table 2 of [18]. Several authors have performed different modifications to Equation (12). Bohdansky [38] and Yamamura [23] introduced corrections for low-energy sputtering using very light or heavy ions (also at grazing incident angles). The correction factor that they introduced decreased the sputtering yield near the threshold energy. Eckstein et al. [39] proposed a different empirically based correction factor for low-energy sputtering, whereas Wilhelm [40] considered sputtering near the sputtering threshold by employing the quantum statistical approach of three-body sputtering. In the latest attempt, Shang et al. [58] included a factor that is related to electronic energy loss for low-energy sputtering. They modified the equation of Zhang [59], which is based on Yamamura's semi-empirical formula.

The SRIM program uses the specific nuclear stopping power function to evaluate the propagation of the ions and the atoms through the solid. The authors of the program (Ziegler, Biersack, and Littmark) proposed the nuclear stopping power, which is derived from the so-called universal atomic potential, which is more often referred to as the ZBL potential. This interatomic potential was found to agree well with the experimentally determined interatomic potentials for numerous atomic pairs [60]. The reduced nuclear stopping power in SRIM is calculated from the function:

$$s_n(\varepsilon) = \frac{0.5 \ln(1+a\varepsilon)}{\varepsilon + b\varepsilon^c + d\varepsilon^{1/2}}; \quad \varepsilon \leq 30$$

$$s_n(\varepsilon) = \frac{\ln(\varepsilon)}{2\varepsilon}; \quad \varepsilon > 30$$
(17)

where $a = 1.1383$, $b = 0.01321$, $c = 0.21226$, and $d = 0.19593$ are the best fit factors for the experimental data. The ZBL potential is an improvement of the Krypton–Carbon potential. Note that there are similarities between Equations (15) and (17). It should be emphasized that SRIM does not calculate the total sputtering yield from Sigmund's equation, Equation (12). It uses the nuclear stopping power to determine the strength of the interactions (i.e., forces) between the particles that are involved in the binary collisions. The total sputtering yield is determined from the ratio between the number of sputtered atoms and the number of impinging ions. The SRIM program simulates the particle collisions with the stochastic Monte Carlo approach, which follows the path of all of the interacting atoms (and the impinging ions) and counts the number of atoms that leave the surface.

The general sputtering yield equation, Equation (12), should provide the most accurate data for the total sputtering yields; however, it is not very convenient for practical calculations due to the complexity of the S_n function. Furthermore, it does not provide a clear relationship between the target and the ion-related parameters (e.g., mass and energy) and the sputtering yield. For this reason, Sigmund attempted to derive a simpler expression for the total sputtering yield. He considered the Thomas–Fermi potential for the nuclear stopping cross section and made several simplifications for the ion energies that are below 1 keV (i.e., energies typical for the sputter deposition). He derived a simple relation for the total sputtering yield [35]:

$$Y \approx \frac{3}{4\pi^2} \frac{\alpha \Lambda E_i}{E_{sb}} \text{ for } E_i \gg E_{sb}. \quad (18)$$

This equation depends only on a few target and ion parameters: the energy transfer factor $\Lambda = 4M_s M_i / (M_s + M_i)^2$, the dimensionless factor α (which is a function of the target-to-ion mass ratio), the surface binding energy E_{sb} , and the incident ion energy E_i .

Sigmund analyzed the factor α for different sputtering conditions and proposed a general function in dependence of the target-to-ion mass ratio (i.e., M_s/M_i). The α function is presented in Figure 13 of [35]. By extracting the data from the figure and fitting a linear function (see graph in the Supplementary Materials), we can find a very good fit to the following function:

$$\alpha \approx k \left(1 + \frac{M_s}{M_i} \right), \quad (19)$$

where constant k is approximately 0.15. By inserting Equation (19) into Equation (18), we obtain a very simple expression for the total sputtering yield:

$$Y \approx \frac{0.45}{\pi^2} \frac{M_s}{M_s + M_i} \frac{E_i}{E_{sb}}. \quad (20)$$

Note that this more elegant equation depends only on two target parameters (the atomic mass and the surface binding energy) and two ion parameters (the atomic mass and the ion energy). The total sputtering yield, according to this equation, is linearly dependent on the ratio between the target atomic mass and the sum of target and ion masses. It also depends on the ratio between the ion energy and surface binding energy. In

general, this equation should be useful for calculating sputtering yields of different ion-target combinations for ion energies that are up to 1200 eV. However, the accuracy of the calculated values in many instances differs significantly from the experimental sputtering yield data. Nevertheless, Equation (20) provides a very useful insight into the relations between the total sputtering yield, and the ion and the target properties.

In the following chapters, we examine the sputtering yields that were simulated by the SRIM program, which were optimized to be close to the experimental values. We compared them with the simplified expression, Equation (20). From this comparison, we attempted to draw some general trends and relations between the sputtering yield, and target- and ion-related properties as well with the order of elements in the periodic table.

4.1.1. Surface Binding Energy

The surface binding energy (SBE) is the energy that is needed for a particle in the solid to overcome the lattice bonding and leave the target material. This results in the ejection of the atoms from the surface (i.e., sputtering). The SBE is a crucial sputtering parameter. It appears in analytically derived sputtering yield equations and in the modeling of the sputtering process. Experimentally, the SBE values are not well established, therefore, in the majority of works (including the SRIM program), the heat of the sublimation is used as an approximation for the SBE. However, in the SRIM program, the surface binding energy is not defined as a simple chemical binding energy for the surface atoms; instead, the parameter also includes all of the surface non-linearities such as those which are produced by radiation damage, surface relaxation, surface roughness, and other effects as discussed by the authors of the program [50]. The surface binding energy in SRIM is, therefore, a free input parameter, whereas the heat of sublimation is used as the default value for SBE.

The goal of this work was to obtain simulated total sputtering yields which are close to the experimental values. For this reason, we modified the SBE since it is not accurately defined in SRIM and because it has the strongest influence on the sputtering yield among the free parameters. We aimed to achieve a good agreement with the experimental sputtering yields in the 200–1200 eV range, which is the most relevant energy range for the sputter deposition techniques. Figure 10a shows the modified SBE, and Figure 10b shows the default SBE values that were used by SRIM (i.e., the heat of sublimation) in the dependence of the atomic number (Z) of the investigated materials. From the comparison it can be seen that for some materials, the SBE had to be modified significantly from the heat of sublimation values. The largest corrections had to be made for the lightest elements (i.e., B and C), where we had to decrease the value of SBE (e.g., for C, this was from 7.4 eV to 3.6 eV) and for the heaviest elements, where the values had to be increased (e.g., for W, this was from 8.7 eV to 15.0 eV). Smaller modifications were made for Cr, Cu, Zr, Mo, and Au, while the values for Ti, V, and Ag were close to the heat of the sublimation values.

In general, the increase in the atomic number is correlated with a larger SBE, whereas this is not the case for the heat of sublimation. A nearly linear relationship is observed for elements in the groups 4, 5, and 6, and for the lightest four elements (B, C, Al, and Si). For the heat of sublimation, the data are more scattered, and no clear trend was observed. It should be noted that if the heat of sublimation values were used in the simulations, then in some cases, the simulated values would differ significantly from the experimental values (sometimes even for a factor of two). The use of the modified SBE in the SRIM program was necessary and it was the only option to get a good agreement between the simulated and experimental data.

Before the development of the sputtering theory, it was already established experimentally that the total sputtering yield correlates with the reciprocal value of the heat of sublimation [61]. Sigmund's theoretically derived general equation for the total sputtering yield, Equation (12), and its simplified form, Equation (20), demonstrate such inverse proportionality. Hence, the sputtering yield is lower when the atoms are strongly bound near the surface (i.e., a larger SBE), and it is higher when they are weakly bound (i.e.,

a smaller SBE). Figure 11a shows the sputtering yields that were calculated using SRIM for different target materials in dependence of the modified surface binding energies.

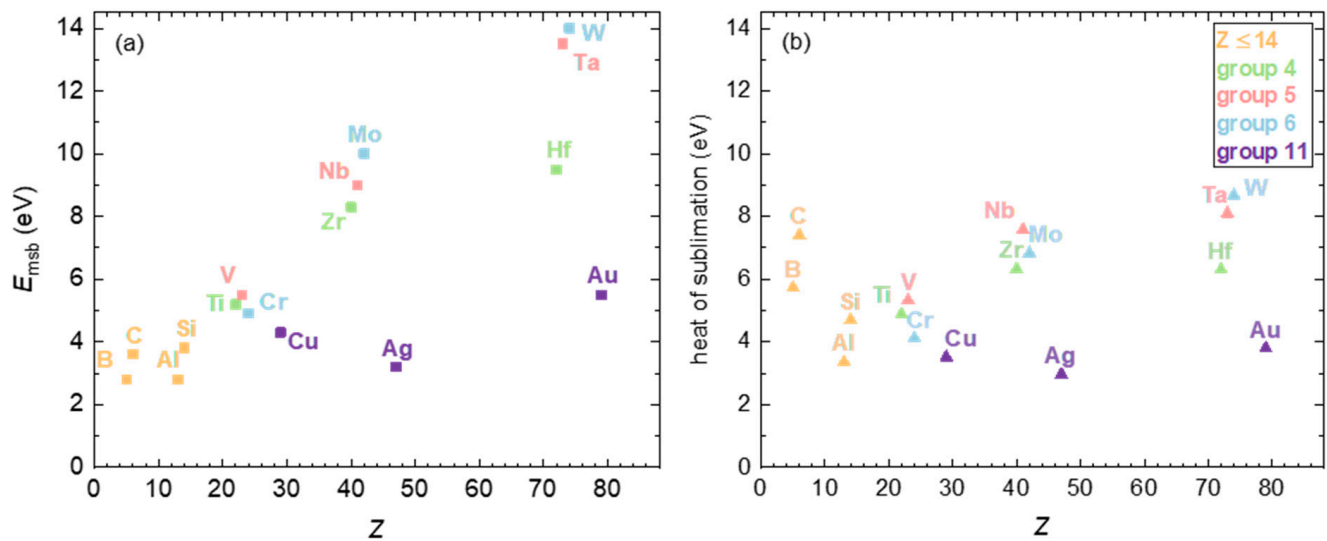


Figure 10. (a) The modified surface binding energy in dependence of the atomic number used in our SRIM simulations. (b) The heat of sublimation, which is used in SRIM as the default value for SBE, in dependence of the atomic number.

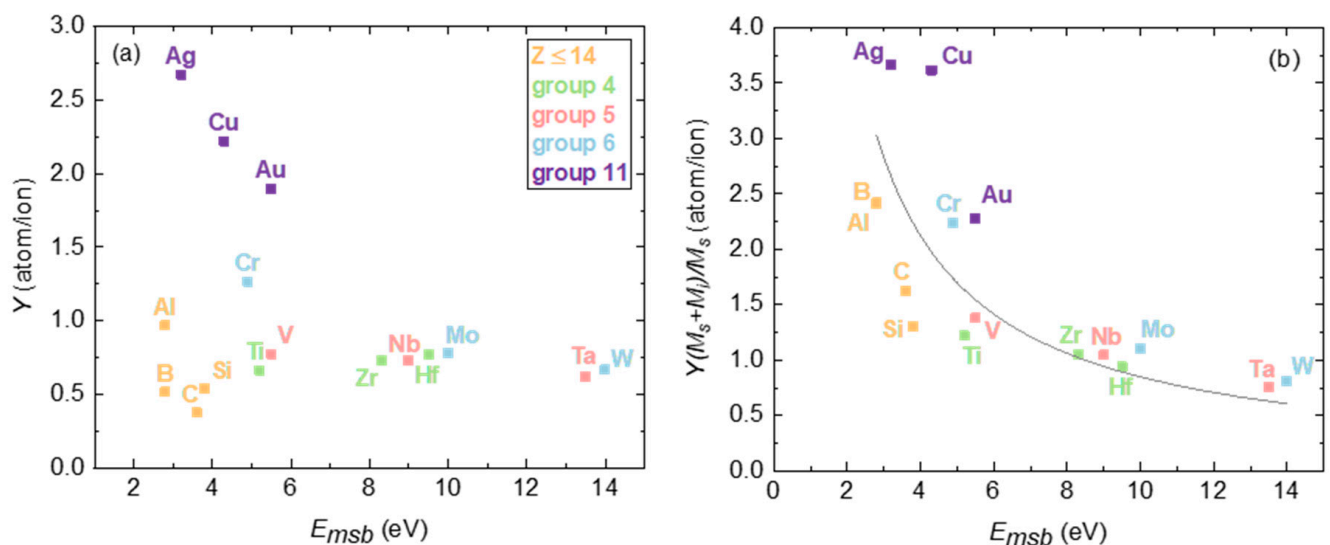


Figure 11. (a) The sputtering yield and (b) the sputtering yield divided by the target-to-ion mass ratio for different elements in dependence of the modified surface binding energy. The $1/E_{msb}$ trend is found in the case of $Y/\left(\frac{M_s}{(M_s+M_i)}\right)$, which is in accordance with the simplified sputtering yield formula, Equation (20). The total sputtering yields were calculated by SRIM using Ar ions impinging normally to the surface with an energy of 600 eV.

It can be seen that the sputtering yield is not simply an inverse function of the modified SBE. The belief that a smaller SBE results in a higher sputtering yield is not entirely correct. For example, the sputtering yield of the elements in group 11 (Ag, Au, and Cu) is much higher than the yield of the light elements (B, C, Al, and Si) and Ti, V, and Cr despite them having a very similar SBE. Many transition metals in the groups from 4 to 6 have similar sputtering yields (e.g., Ti, V, Zr, Nb, Mo, Hf, Ta, and W), although they have very different SBE values. The lowest sputtering yield was observed for the light elements (B, C, and Si), which also have low SBE values. The approximate inverse proportionality with the

modified SBE can be seen for the elements within the same group of the periodic table. This is true for elements in the groups 5 and 6, but not for elements in group 4 where Y slightly increases with the SBE. In group 11, there is also a discrepancy in the trend. Hence, there is an inconsistency in the relationship between the sputtering yield and SBE.

This inconsistency in the inverse proportionality can be understood by analyzing Equation (20), which shows that the total sputtering yield also depends on the target-to-ion atomic mass ratio. If the sputtering yield is normalized by $M_s/(M_s + M_i)$ and plotted as a function of the modified SBE (Figure 11b), then the data decrease much closer to the $1/E_{msb}$ trend. For some elements, the values deviate from this trend, therefore, it can be concluded that other factors which are contained in the complex general equation for total sputtering yield (Equation (12)) must contribute to the deviations from the fitting function.

In the literature, it was reported that the total sputtering yield also correlates with the filling of the d -shells [62]. Namely, the elements with filled s and d outer shells have the highest sputtering yield—these are the elements in group 12 (Zn, Cd, and Hg). The elements in group 11 (Cu, Ag, and Au) have a similar shell filling (with one missing electron in the d -shell). This effect, together with a low SBE, can explain the large sputtering yields that were observed among the elements of group 11.

4.1.2. Mass Ratio

The atomic masses of the impinging ion and the target material also influence the total sputtering yield. A simplified view suggests that the sputtering yield is higher when the atomic mass of the ion is close to the atomic mass of the target material. The difference between the masses of the two colliding particles is described by the energy transfer factor $\Lambda = 4M_s M_i / (M_s + M_i)^2$. For similar atomic masses, the Λ is close to one and for very different masses, it is significantly below one (typically closer to 0.5 when using argon ions). For example, in the case of sputtering a Ti target by Ar ions, the energy transfer factor Λ is 0.992 (i.e., $M_{Ti} = 47.88$ and $M_{Ar} = 39.95$, similar masses), while the sputtering W target it is 0.587 (i.e., $M_W = 183.84$, different masses). In the case of sputtering with the same ions as the target material (i.e., self-sputtering $M_i = M_s$), the energy transfer factor equals one.

The total sputtering yield in the dependence of the energy transfer factor is shown in Figure 12a. It can be seen that having similar masses for the impinging argon ion and the target material does not necessarily result in a higher total sputtering yield; for instance, the yields for Si, Ti, and V have a similar Λ . Hence, the proximity of the atomic masses is not the best indicator for higher sputtering yields. Furthermore, there is no obvious trend between the total sputtering yield and the energy transfer factor. For the elements in group 6, the sputtering yield increases with Λ , but not in the other groups. The opposite trend was observed in group 4 (i.e., Y slightly decreases when Λ approaches 1), while in group 12, there is no clear trend. The reason for the absence of trends can be understood by examining Equation (18) where Y also depends on the factor α , which is a function of the target-to-ion mass ratio as well as of SBE (as was discussed in Section 4.1.1).

The product of the energy transfer factor Λ and the factor α is approximately: $\Lambda\alpha \approx \frac{M_s}{(M_s + M_i)}$. According to Equation (20), the total sputtering yield linearly depends on the $\frac{M_s}{(M_s + M_i)}$. Hence, for a given ion, the heavier elements should in general have a higher sputtering yield than the lighter elements do. Figure 12b shows the total sputtering yield for the investigated target materials in the dependence of the $\frac{M_s}{(M_s + M_i)}$ ratio for the sputtering by argon ions with 600 eV. The trend of the sputtering yield increasing with the atomic mass is more obvious than in Figure 12a, however, the relationship is not unambiguous. For example, the sputtering yield increases for the elements with $Z \leq 14$ and the elements in group 11, but it decreases for the elements within groups 5 and 6. This inconsistency is a result of the surface binding energy, which strongly influences the sputtering yield. For this reason, in Figure 12c, we present YE_{msb}/E_i in the dependence on the $\frac{M_s}{(M_s + M_i)}$ as suggested by Equation (20). A relatively good linear trend can be observed in this case. It should be noted that the quantities on the y -axis are related to the SRIM simulations (i.e., Y and E_{msb}), while the values on the x -axis correspond to the material properties. The

plot shows that the simple sputtering yield equation that is presented (Equation (20)) can provide a reasonable estimate for the total sputtering yield, however, the influence of the ion energy should be analyzed as well (see Section 4.1.3).

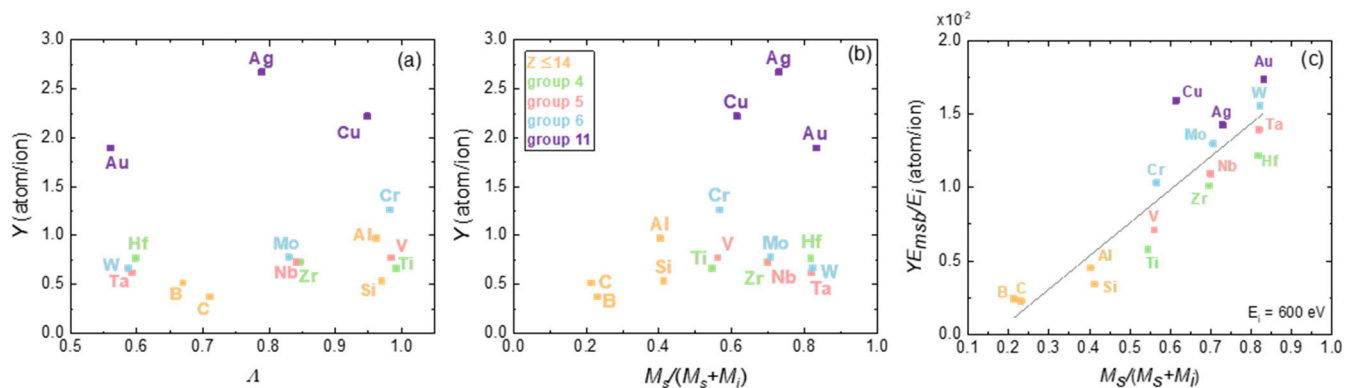


Figure 12. Sputtering yields (a) in dependence of the energy transfer factor $\Lambda = 4M_s M_i / (M_s + M_i)^2$ and (b) in dependence of the $M_s / (M_s + M_i)$, which is a product of the energy transfer factor and the dimensionless factor α . (c) Sputtering yield normalized by the E_i / E_{msb} ratio in dependence of the $M_s / (M_s + M_i)$ with a near-linear relation. Sputtering yields were calculated by SRIM using Ar ions with an energy of 600 eV.

The total sputtering yield for sputtering under an oblique angle also significantly depends on the atomic masses of the ion and the target material. In Figure 4a, the total sputtering yield for the target material is the highest for the oblique angles between 60° and 70° . The largest differences between the sputtering yield at the 70° ion incidence angle and the perpendicular ion sputtering are observed for the lightest elements B, C, Al, and Si (see Figure 4d). Among the transition metals, the lighter elements (Ti, V, and Cr) show the largest relative sputtering yields when they are sputtered by argon ions under a 70° incidence angle (see Figure 4c). On the other hand, in the case of the heaviest transition metals (i.e., Au, W, and Ta), we can observe that the total sputtering yield stays almost flat up to the incidence angle at around 60 – 70° —there is practically no increase in the sputtering yield under the larger incidence angles. At angles that are above 70° , the sputtering yield starts to drop sharply in all of the materials.

Hence, the atomic mass of the target material significantly influences the total sputtering yield for the oblique ion sputtering. To analyze this influence further, we show in Figure 13 the relative sputtering yield $Y(70^\circ)/Y(0^\circ)$ in the dependence of $\frac{M_s}{(M_s + M_i)}$. A clear inverse proportionality can be observed, i.e., the $Y(70^\circ)/Y(0^\circ)$ ratio decreases with mass ratio. Figures 4 and 13 demonstrate that the lighter elements sputter more substantially under the oblique ion angles than they do at the normal ion incidence. This difference becomes smaller with the increasing atomic mass of the target material, and it practically disappears for the heaviest elements. Hence, a viable approach to increase the sputtering yield of the lighter elements, which in general have the lowest sputtering yields at a normal ion incidence, is to sputter them under higher angles or to use targets with a large surface roughness.

The experimental sputtering yield data for ion bombardment under an oblique angle are rather scarce. In the collection by Behrisch and Eckstein [22], the data are available for several elements that were analyzed in this work (Al, Ti, Cu, Zr, Ag, Ta, W, and Au) which were sputtered by 1.05 keV argon ions. In the Supplementary Materials, we show a comparison between the simulated and empirical data for the selected elements. In general, the agreement is good for most of the materials except for Al and Ti, where larger deviations from the experimental data are observed. Overall, the simulated data show the same trends with regard to the ion incidence angle as the experimental data do. For example, the experimental data also demonstrate that the heavier elements have much smaller variations in the dependence of the ion incidence angle than the lighter elements

do. Furthermore, the highest experimental values for the sputtering yield are also observed between the 60° and 70° incidence angles, as demonstrated by the SRIM simulations.

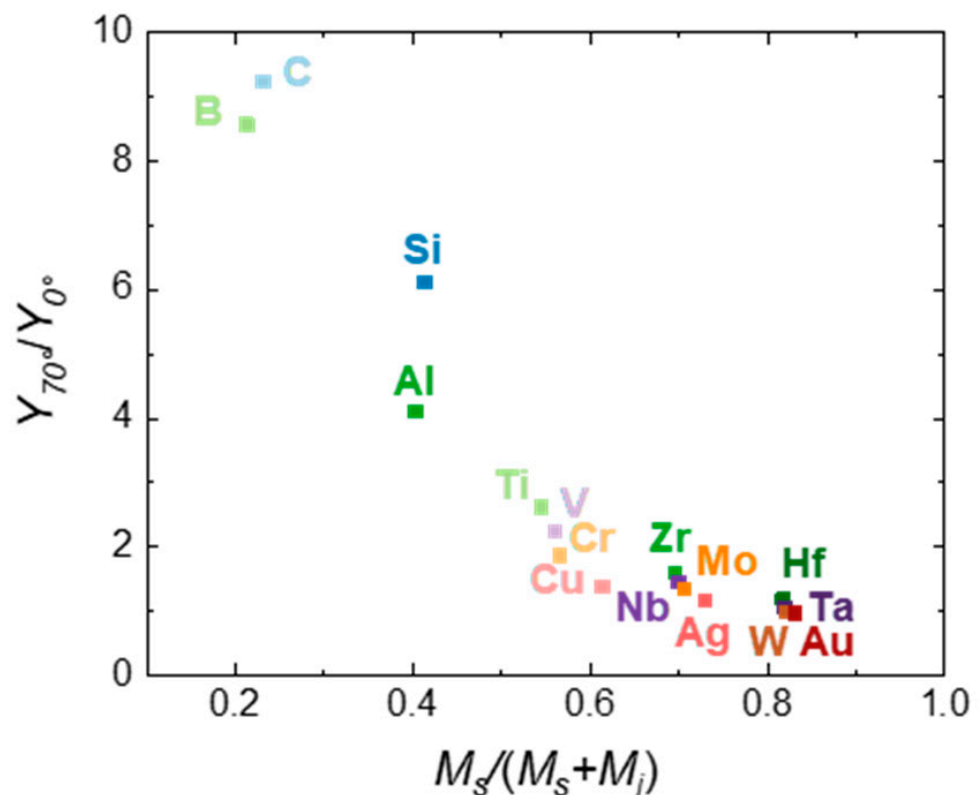


Figure 13. The sputtering yield at 70° argon ion incidence normalized by the perpendicular sputtering yield in dependence of the $M_s/(M_s + M_i)$ ratio.

The sputtering yield at a normal incidence is usually considered to be the most reliable value, and it is generally used to obtain information on the sputtering yields at an oblique incidence using semi-empirical models. Rather complicated algebraic formulas are used to describe the angular dependence of the total sputtering. The reader that is interested in the evaluation of the sputtering yields under an oblique angle can find an overview of the semi-empirical fitting equations in Table 3 of [18].

4.1.3. Ion Energy

The number of sputtered atoms strongly depends on the energy of the impinging ions. Higher ion energies in general result in larger sputtering yields. The energy of the ions is of particular interest for the sputter deposition techniques since the ion energy can be adjusted to a large degree. In magnetron sputtering, the energy of the ions is controlled by the cathode potential. The typical cathode voltages in the DCMS regime are between 250 V and 400 V, in HiPIMS, these are between 450 V and 600 V, and in triode sputtering, these are around 1000 V or more. In the ion beam deposition, the energy of the ions is determined by the ion beam source, and it is also in the range of 1000 eV.

The simplified Sigmund Equation (20) suggests that Y increases linearly with the ion energy. However, the results of the SRIM simulations that are presented in Figure 3 show that Y in the low-energy range (i.e., 200–1200 eV) deviates from the linear relationship. The same is observed in the experimental data [22]. When calculating the sputtering yield values using Equation (20) and comparing them to experimental values, a large overestimate of the sputtering yield is found for most of the elements.

In order to account for the deviation from the linear relation with the ion energy, we fitted the simulated sputtering yields to the power-law Equation (10) using the parameters

a and b . In Section 3.1, we used both of the free parameters to obtain the best fit with the simulated data. Here, we use only the power parameter b as a fitting parameter, while parameter a was obtained from the analytical Equation (20). From the comparison of Equations (10) and (20) it follows that:

$$a = \frac{0.45}{\pi^2} \frac{M_s}{(M_s + M_i)}. \quad (21)$$

This approach reduces the number of fitting parameters and makes the allometric Equation (10) fall more in line with the sputtering theory that was developed by Sigmund. In Table 4, we present the factor a , the power coefficient b , and the coefficient of determination R^2 . The comparison of R^2 in Tables 2 and 4 shows that the new fitting approach still provides a good agreement with the simulated data. The coefficient of determination is above 0.97 for most of the materials, and it is somewhat lower for C, Cu, and Ag. In [63], a similar fitting approach was used as described in Section 3.1. Both of the fitting parameters a and b were free parameters, however, their values differ from the ones in this work due to there being a few differences. In this work, we used the modified SBE values (instead of the heat of the sublimation) and considered the power equation $\left(\frac{E_i}{E_{msb}}\right)^b$ as opposed to E_i^b . Furthermore, we fitted the data to a lower energy range (up to 1200 eV). Hence, the coefficients a and b that are provided in Table 2 should be more in line with the experimental sputtering yield values.

Table 4. Parameter a calculated from Equation (21), power parameter b for fitting the sputtering yield in dependence of ion energy, and coefficient of determination R^2 .

Element	Z	a	b	R^2
B	5	0.0097	0.7381	0.978
C	6	0.0105	0.7031	0.957
Al	13	0.0184	0.7248	0.982
Si	14	0.0188	0.6623	0.980
Ti	22	0.0249	0.6806	0.987
V	23	0.0256	0.7116	0.975
Cr	24	0.0258	0.7707	0.973
Cu	29	0.0280	0.8627	0.943
Zr	40	0.0317	0.7103	0.974
Nb	41	0.0319	0.7317	0.977
Mo	42	0.0322	0.7611	0.970
Ag	47	0.0333	0.8169	0.952
Hf	72	0.0373	0.7183	0.987
Ta	73	0.0373	0.7342	0.996
W	74	0.0375	0.7748	0.984
Au	79	0.0379	0.8192	0.982

The fitting approach with the a values which were calculated from Equation (21) and using b as the fitting parameter is physically more reasonable. By combining the allometric Equation (10) and the simplified analytical equation, which was derived by Sigmund, we can modify the sputtering yield equation to account for the non-linear behavior with the ion energy:

$$Y \approx \frac{0.45}{\pi^2} \frac{M_s}{M_s + M_i} \left(\frac{E_i}{E_{msb}} \right)^b. \quad (22)$$

This equation should provide more accurate results for the total sputtering yield than the linear Equation (20) can. It is valid for argon ion energies that are up to 1 keV. This semi-empirical relation depends on two empirical parameters: the modified surface binding energy which was derived from SRIM simulations (fitted to the experimental yield data) and the power coefficient b which was derived from fitting the energy-dependent sputtering yields (simulated by SRIM using modified SBE). The power coefficient b depends

on the particular target material and the ion type. For a specific target material, the same value of b cannot be used for the other types of ions because the sputtering yield as a function of energy depends on the mass of the ions. The experimental data and SRIM simulations show a more linear-like relationship for the sputtering by heavier ions (e.g., Kr and Xe) and a more parabolic one for the sputtering by lighter elements (e.g., He and Ne). The power coefficient clearly depends on the ion mass. The usefulness of Equation (22) should be verified for other types of ions by making the same fitting approach which was performed for the argon ions in this work.

If we analyze the parameter b , we can observe some interesting trends which demonstrate the soundness of the second fitting approach. In Figure 14, we present the fitting parameter b in dependence of the atomic number Z (a similar graph is obtained if it is plotted against the $\frac{M_s}{(M_s + M_{Ar})}$ ratio). Surprisingly, a sequential trend can be observed for the transition metal elements. The parameter b increases practically linearly along the individual periods of the periodic table. For example, in period 4, the parameter b changes from 0.68 (Ti) to 0.86 (Cu), while in period 5, it changes from 0.71 (Zr) to 0.82 (Ag). On the other hand, very similar values of the parameter b are found within the individual groups of the periodic table. The elements in group 6 have values of b that are close to 0.77. In group 5, a slightly increasing trend is observed, although the values of b are close to 0.73. Thus, the elements in group 4 show the most parabolic behavior with the ion energy, while the elements in group 11 show the least parabolic behavior (see Equation (10)). Hence, for the transition metals, the trend shows a linear-like increase with the group number. However, for the lightest elements in groups 13 and 14 with $Z \leq 14$, the opposite trend is observed—the value of b for the elements in an individual group decreases with the atomic number (e.g., the values for B and C are different for those of Al and Si).

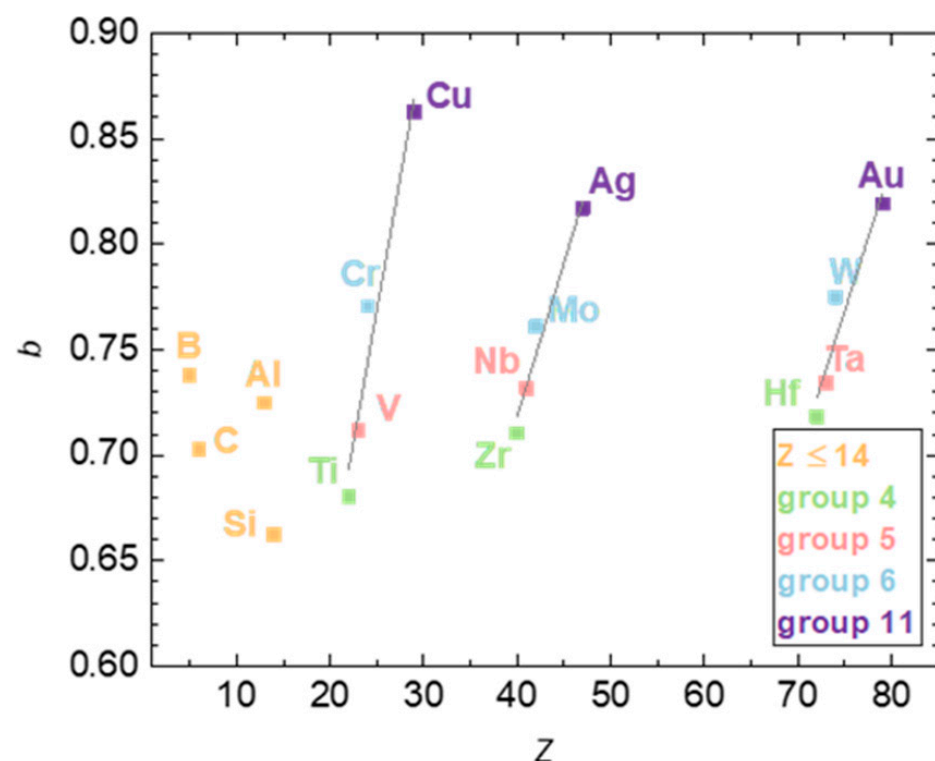


Figure 14. Fitting parameter b calculated from Equation (22) in dependence of atomic number.

The sequential linear increase in the parameter b for the transition metals gives us the confidence to estimate the fitting parameters for other elements of the periodic table that have not been studied in this work. From the linear increase of b with respect to Z within the individual periods, we can calculate the values of b for all of the elements of the individual period. For example, according to the trend in the period 4: Mn, Fe, Co, and Ni

must have values that are between those of Cr and Cu (one should note the fitted linear curves in Figure 14 for periods 4, 5, and 6). In the Supplementary Materials, we provide the calculated values of the total sputtering yield for the transition metals and several other elements. The parameter a was evaluated from Equation (21), and the fitting parameter b was extrapolated from the linear functions in the individual periods that are shown in Figure 14. By comparing the calculated sputtering yields with the experimental values, we can find a fairly good agreement for most of the elements. The transition metals which have not been investigated in this work (i.e., Mn, Fe, Co, Ni, and Zn; Ru, Rh, Pd, and Cd; Re, Os, Ir, and Pt) indeed show a relatively good agreement between the calculated data and experimental data, where they are available. The agreement is good for all three of the analyzed energies (i.e., 300 eV, 600 eV, and 1000 eV). This means that valuable sputtering yields could be also obtained for other ion energies.

The above results demonstrate that the simple semi-empirical Equation (22) is useful for a quick evaluation of the total sputtering yields using argon ions with energies that are up to 1200 eV. We should note that the simplified Sigmund's equation for the total sputtering yield (Equation (20)) was derived from the Thomas–Fermi potential, which is too high at lower ion energies. However, with the use of the power parameter b for the ion energy, we can compensate for this discrepancy. In the derivation of Equation (18), it is assumed that sputtering occurs in the linear cascade regime. This is true for higher ion energies where the ion penetrates deeper into the solid and causes many collisions, which then result in the emission of atoms.

For the lower ion energies (e.g., those that are below 300 eV), the surface atoms are often sputtered through a single knock-on collision as demonstrated in the simulations by Biersack and Eckstein [64]. For this reason, it can be expected that the sputtering yield values that were simulated using SRIM and calculated using Equation (20) could differ more significantly at lower ion energies than they might at higher ones. The single knock-on regime becomes even more important when the material is bombarded at higher incidence angles. Under an oblique ion sputtering, the α function also depends on the ion incidence angle [59], which means that the Equation (18) cannot be simply reduced to Equation (20). For all of the above-mentioned reasons, noteworthy deviations between the calculated and experimental values can be expected, especially at lower ion energies. Further deviations can be attributed to the uncertainties that are related to the parameters in the SRIM simulations and the experimental methods that were used for measuring the sputtering yield.

The semi-empirical Equation (22) has many limitations, and it does not capture all of the complex relations that are contained in the general sputtering yield Equation (12). The most accurate approach for the evaluation of the total sputtering yields is therefore to use a general equation that was derived by Sigmund with corrections for the lower ion energy sputtering which are provided by the other authors.

4.2. Differential Sputtering Yield

The total sputtering yield is an important parameter in the theory of sputtering, however, for practical applications, the differential sputtering yield is often more relevant. The growth of thin films is determined by the deposition rate, which linearly depends on the differential sputtering yield [65]. The atom flux from the sputtering sources, which is directed onto a specific region of the substrate, defines the film growth process. All of the target and ion properties that are discussed in the previous Section 4.1 also influence the differential sputtering yield, but they are not discussed in detail in this chapter. Instead, we discuss the general trends in the differential sputtering yield of the investigated elements.

The angular distribution of the sputtered atoms is presented in Figures 5 and 6, where the graphs are arranged in the same way as they can be found in the periodic table. The elements in the same column in the figure belong to the same group of the periodic table, meaning that they have the same valence shell electron configuration. In all of the investigated materials, the sputtered flux is the highest in the direction that is perpendicular

to the target surface. According to simulations, the lightest elements seem to be sputtered predominantly near the normal direction (Figure 6). This unusual angular distribution is discussed later in this paper.

In the theory of sputtering, Sigmund assumes that the angular distribution of the sputtered atoms is a cosine function [35,36]. Such a dependence is attributed to the isotropic flux inside the amorphous target material [1]. A perfect cosine distribution is often not observed experimentally, especially when measuring at very low or very high ion energies. The angular distribution of the sputtered material is often fitted using the power fitting parameter y [66]:

$$\frac{1}{Y} \frac{d^2Y}{d^2\Omega} \propto \cos^y \theta. \quad (23)$$

Our simulations of angular distribution (Section 3.2) show that the fitting parameter y is close to one for the majority of the investigated materials. Therefore, the SRIM simulations show essentially a cosine angular distribution of the sputtered atoms. The exception is Si, where the y was 2.172, while for elements B, C, and Al, we could not determine the power fitting factor because the simulations show a highly directed flux near the surface normal. Such an unrealistic atom distribution for the elements with $Z < 14$ was also observed by other authors.

Several possible reasons were suggested as the source of an error. Shulga [67] suggested that directed atom emission in the light elements results from errors in the calculations of particle trajectories within the material. Wittmaack [68] identified several problems in the earlier versions of the SRIM program (specifically, the 2000 and 2003 versions). The author attributed the sputtering yield artifacts to an incorrect approximation of ion-target scattering and too low electronic stopping power in the low-energy range. Furthermore, they identified the differences between the detailed and quick calculation mode, which are still present in the latest version of SRIM. Wittmaack also suggested that the problems in simulations might be caused by the assumed non-random atom spacing in the solid. As a result, the simulated sputtering yields that were achieved by earlier SRIM versions were compared to experimental values, and they were too large for $Z_i/Z_s < 0.7$ and too small for $Z_i/Z_s > 2$.

In our work, we compensated for any differences between the calculated and the experimental values by modifying the surface binding energy parameter. Other authors proposed additional sources of error in the SRIM, such as the algorithm for searching the collision partners when an ion approaches the surface [69] or ignoring the extremely small scattering angles [70]. We examined the collision cascades in the SRIM simulations for all of the investigated target materials, but we did not find any preferential direction for sputtering in the case of the elements with $Z < 14$. The nuclear stopping powers which are essential in the SRIM simulation are uncertain for lower ion energies, and this could be the source of the error in the simulation. We cannot identify the specific source of the error in SRIM, which results in highly directed atom emission in the case of the light elements.

In the literature, under-cosine, over-cosine, and cosine angular distributions of sputtered material are reported. In one of the earliest reports, Wehner and Rosenberg [71] measured the angular distribution of Ni, Ge, Fe, Mo, and Pt for normal Hg^+ ion bombardment with energies that were between 100 eV and 1 keV. Their experiments demonstrate an under-cosine angular distribution with more material which was ejected to the sides than that which was demonstrated in the direction that was normal to the target. Tsuge et al. [26] also measured an under-cosine distribution for the Au, Al, and NiFe targets, which were bombarded by 1 keV argon ions. They related the under-cosine spatial distribution to the crystallographic orientation. Oyarzabal et al. [29,72] performed measurements of an angular distribution for a very low ion energy range (75–225 eV) by analyzing the sputtering of C and Mo. Their measurements show a heart-like distribution. The differential sputtering yields which were measured for several metals using heavier ions (Kr and Xe) also showed a heart-like distribution [73]. Turner et al. [74] measured the angular distribution for Cu which was sputtered by argon ions with an energy of

510 eV. The distribution differed from the cosine distribution as more particles were sputtered near the target normal (between -10° and 10°) and at approximately 45° . Surla et al. [75] measured an under-cosine distribution for Mo which was sputtered by argon ions with an energy of 750 eV. Chini et al. [76] analyzed the sputtering of a Ge target with argon ions between 600 eV and 4000 eV. The authors found the distribution best fits with an over-cosine function, with the power parameters that were between 1.25 and 1.32.

Computer simulations that were performed by Yamamura et al. [66] using the Monte Carlo simulation program ACAT showed that the degree of the over-cosine distribution depends on the energy of the incident ions. By analyzing an Fe target, they simulated over-cosine angular distributions for higher ion energies (above 2000 eV) and under-cosine angular distributions for lower ion energies (below 500 eV). They claim that the over-cosine angular distribution is due to the geometrical asymmetry near the surface. The authors explain the under-cosine distribution for low ion energy sputtering by an anisotropic velocity distribution of the cascade near the surface. Feder et al. [77] measured and simulated the sputtering of Ag with argon ions. The shape of the angular distribution also qualitatively agreed with their simulations. The same authors sputtered Ge with argon and xenon ions and compared the measurements with the simulations that were performed using the TRIM.SP code [31]. They measured a cosine-like angular distribution for 1 keV argon ions and an under-cosine distribution for the sputtering with 1 keV xenon ions. Hence, very different angular distributions were observed experimentally and by simulations. According to the SRIM simulations that were performed in this work, the angular distributions of the sputtered atoms are cosine for all of the elements (except for the elements with $Z < 14$), and they do not change with an increasing ion energy in the 300–1200 eV range.

It should be noted that the sputtering is also influenced by the roughness, composition, and crystallinity of the target material [64], however, these parameters are not included in the SRIM program, but they often cannot be avoided in the experimental studies. Recent measurements and simulations by Cupak et al. [15] show that when rather rough surfaces were bombarded by ions under large incidence angles, a more-or-less uniform distribution of the atoms resulted around the normal of the surface. On the other hand, the earlier simulations where the atomic-scale surface roughness had been implemented in the TRIM code show that the roughness significantly affected the total sputtering yield for the low ion energies and the non-normal angles of incidence [78]. Similarly, Yamamura et al. [66] stress the importance of roughness. Based on their sputtering simulations, they concluded that the roughness reduces the degree of the over-cosine distribution since the rougher surfaces have a larger effective surface area in comparison to the flat surfaces. Schlueter et al. [79] found that polycrystalline metals with randomly oriented grains do not sputter with the same sputtering yield as an amorphous material does. They explained that the key reason for this is attributed to the linear collision sequences rather than the channeling effect. All of the above-discussed effects can influence the significant discrepancies between the experimentally determined angular distributions and the ones that are simulated by the SRIM program.

Several trends can also be recognized for the sputtering at oblique ion incidence angles. Figure 8 shows the angular distribution for the sputtered elements in groups 4, 5, and 6 by argon ions impinging at a 60° angle with an energy of 600 eV. It can be seen that the symmetry of the atom distribution depends on the group of the periodic table. The elements in group 4 (Ti, Zr, and Hf) appear to have a more asymmetric distribution than the elements in group 5 (Cr, Mo, and W) do despite them having similar masses (i.e., for the elements in the same period). The most symmetric distribution is expressed by the elements in group 11 (Cu, Ag, and Au). However, the distribution also depends on the atomic mass of the target material. Within an individual group of elements, the lightest elements show the most asymmetric distribution (cf. columns in Figure 8). For example, the lightest element in group 4 (i.e., Ti) experienced the largest asymmetry, while the most symmetric distribution can be observed in the heaviest element (Hf). Similar observations

are valid for the other two analyzed groups of elements. The most symmetric distribution is observed in the sputtering of the heaviest analyzed element (Au). On the other hand, the asymmetry of the distribution does not appear to be associated with the surface binding energy. For example, Ti and Au have similar surface binding energies, but very different angular distributions of their sputtered atoms.

When analyzing the angular distribution for oblique sputtering with respect to the energy of the ions, we can see that distribution is more asymmetric at lower ion energies. Figure 9 shows an example of the Cr distribution when it was sputtered by argon ions at a 60° angle at 300 eV, 600 eV, and 1200 eV. The atom distribution is the least symmetrical at 300 eV and the most symmetrical at 1200 eV. The sputtering by higher energy ions clearly causes a more symmetrical distribution of the sputtered atoms. This trend could be explained by the deeper penetration of the ions when a solid is bombarded by ions of a higher energy. Higher-energy ions cause more collisions in the solid, which results in a more uniform distribution of the collision cascades, while the lower-energy ions cause fewer cascades with a more asymmetric distribution, and consequently, an asymmetric emission of the atoms from the surface.

Lautenschläger et al. [80] measured the angular distribution of Ti. They sputtered the target material perpendicularly and at 30° and 60° with 1 keV Ar. They also performed measurements and simulations for different Ar ion energies. They showed that sputtering is more isotropic for higher energies of incident ions and for lower incidence angles of the ions. Such sputtering enables more collisions along the ion and atom path inside the solid material. This leads to fully developed collision cascades which results in a more isotropic distribution of the sputtered particles.

5. Conclusions

The SRIM program (Stopping and Range of Ions in Matter) was used to simulate the total sputtering yield and the angular distribution of the sputtered atoms for the transition metals in groups 4, 5, 6, and 11 of the periodic table and for the selected lighter materials that were relevant to the sputter deposition (i.e., B, C, Al, and Si). The sputtering yield was analyzed using argon ions in the 300–1200 eV energy range for normal ion impingement and oblique ion incidence at selected ion energies. To obtain the best agreement between the simulated and the experimental sputtering yield data, we modified the surface binding energy, which is a free parameter in SRIM, and it significantly influences the sputtering yield. In this way, we obtained realistic total sputtering yields in the typical energy range for the sputter deposition techniques (i.e., below 1 keV).

The simulations demonstrate that the total sputtering yield for the transition metals increases with the number of the group of the periodic table. The elements with the lowest total sputtering yield are in group 4 (i.e., Ti, Zr, and Hf), while with the highest yields are in the group 11 (i.e., Cu, Ag, and Au). The lighter elements in group 13 (B and Al) and group 14 (C and Si) have, in general, much lower sputtering yields than the transition metals do (except for Al). The transition metals show a cosine angular distribution of their sputtered atoms. On the other hand, the SRIM simulations predict that the atoms with the atomic number $Z < 14$ (i.e., B, C, and Al) are predominantly sputtered in the spatial region near the surface normal. A cause for the highly directed emission is not understood. It is assumed to be an artifact of SRIM simulations since it is not observed in experiments, and there is no clear physical reason for such a highly directed sputtering. Hence, the differential sputtering yields that were simulated using SRIM for the elements with $Z < 14$ cannot be trusted, while the simulations can still provide useful data for the total sputtering yields.

We also examined the angular distribution of the sputtered atoms for an oblique ion incidence. A more asymmetric distribution was observed for the lower ion energies, and it was more symmetric for the higher ion energies. The symmetry also depends on the group of the periodic table and the atomic mass of the element within the group. The elements in group 4 show the largest asymmetry in the sputtered flux, while elements in group 11

show the most symmetric distribution. Within individual groups, the heavier elements show a more symmetric atom distribution than the lighter elements do.

The influence of the target and the ion properties on the total sputtering yield was further investigated by using the analytical expression for the total sputtering yield which was derived by Sigmund. The simplified equation, which is valid for the ions with an energy that is up to 1 keV, depends on the surface binding energy, target-to-ion mass ratio, and ion energy. We compared the sputtering yields that were simulated using SRIM with Sigmund's simplified equation. Relatively good trends were observed between the simulated values and the simplified expression using the modified surface binding energies. A reasonable trend was also observed when comparing the dependence of the target-to-ion mass ratio, as suggested by Sigmund's formula, with the simulated values. The largest deviations were observed in the dependence of the ion energy.

Sigmund's simple equation predicts a linear dependence of the total sputtering yield with the ion energy, while the simulated and experimental data show a parabolic dependence. For this reason, we introduced a power factor for the ratio between the ion energy and the modified surface binding energy. Such a modification to the simple Sigmund equation provides a promising agreement with the experimental sputtering yields for the sputtering by argon ions with energies up to 1 keV. A linear relationship between the power fitting coefficient and the atomic number was found for the transition metals. This allowed us to estimate the total sputtering yields for the other transition metal elements that were not analyzed in this work. A reasonable agreement was found between the calculated and experimental yield values. The modified equation could be also used for other ion types if the appropriate power coefficients are obtained from the procedure that is described in this work. Nevertheless, the best approach for the estimation of the total sputtering yield is to perform SRIM simulations for specific ion-target combinations using modified surface binding energies.

In the future, we plan to investigate the angular energy distributions of the sputtered atoms and the influence of the different parameters on the energy distribution. Furthermore, we will analyze the average energies of the sputtered atoms in the different spatial directions for the same target elements that are investigated in this paper and various ion energies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12101541/s1>, Figure S1: The influence of (a) the displacement energy E_d , (b) the lattice binding energy E_l and (c) the surface binding energy E_{sb} on the total sputtering yield. SRIM simulations were made using a Zr target sputtered by Ar ions at different energies. In each chart, we varied one parameter and used the default SRIM values for the other two parameters (shown in the legend). The surface binding energy has the largest influence on the total sputtering yield; Figure S2: The total sputtering yield in dependence of ion energy for investigated target materials; Figure S3: The total sputtering yield in dependence of Ar ion energy simulated by the SRIM program for investigated target materials: (a) graph shown at the full scale and (b) at an enlarged scale; Figure S4: The α function in dependence of the target-ion mass ratio. The red line shows original data from Sigmund and black line the fitted function (Equation (S1)); Figure S5: The total sputtering yield for sputtering under an oblique angle using Ar ions with the energy 1050 eV. The experimental data was taken from the collection of Behrisch and Eckstein [1]; Table S1: The experimental and theoretical values of the total sputtering yield sputtered by Ar ions with energy 300 eV, 600 eV and 1000 eV.

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