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Peak amplitude of target current determines deposition rate loss during high power pulsed magnetron sputtering

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Abstract

Film growth rates during DCMS and HIPIMS sputtering in Ar are measured for ten technologically-relevant elemental target materials: Al, Si, Ti, Cr, Y, Zr, Nb, Hf, Ta, and W, spanning wide range of masses, ionization energies, and sputter yields. Surprisingly, the ratio of power-normalized HIPIMS and DCMS rates α decays exponentially with increasing peak target current density J_T^{max} for all metals. The effect of J_T^{max} on α is dramatic: $\alpha \approx 1$ in the limit of lowest J_T^{max} values tested (0.04 A/cm²) and decreases to only 0.12 with $J_T^{max} \sim 3$ A/cm². With the exception of Al and Si, $\alpha(J_T^{max})$ curves overlap indicating that the debated rate loss in HIPIMS is to large extent determined by the peak amplitude of the HIPIMS target current for all tested metals. Back attraction of ionized target species is responsible for such large variation in α .

Keywords: HIPIMS; growth rate; deposition rate; magnetron sputtering, ionized PVD

High power pulsed magnetron sputtering (HIPIMS or HPPMS)¹ is a valuable addition to magnetron-sputtering-based PVD techniques.^{2,3,4,5} HIPIMS is particularly attractive for the growth of transition metal (TM) nitride layers for two main reasons: (i) the ability to ionize up to 90% of the sputtered metal flux with an option to control the ionization degree by varying the peak target current density,^{6,7} and (ii) the time separation of metal- and gas-ion fluxes from the target.⁸ The former effect is ascribed to the effective electron-impact ionization in the high-density plasma region⁹ formed, for a short period of time, 20-100 μ s, in front of the sputtering target operated in HIPIMS mode. The latter effect, caused by a strong gas rarefaction taking place during the high-power pulse^{10,11,12} allows the control of metal-ion momentum and energy arriving onto a growing film, through the synchronization of the substrate bias pulse to the metal-ion rich part of the sputter-deposited flux,^{13,14} with decisive influence on film nanostructure, phase content, and stress state.^{15,16}

It was postulated early that the benefits of HIPIMS in terms of high ionization of the target material come at the expense of a lowered deposition rate,^{17,18,19,20} implying worse process economics which is currently a perceived obstacle for industrial implementation. Numerous phenomena have been proposed to account for this behavior including (i) the so-called “return effect” - an effective capturing of the ionized portion of the sputter-ejected flux by the cathode field,^{21,22} (ii) an enhanced azimuthal ion transport (across the magnetic field lines),²³ (iii) a “yield effect” since usually HIPIMS operates at higher target voltage V_T than in conventional DC magnetron sputtering (DCMS) one may expect lower power-normalized rate due to the fact that sputter yields are not directly proportional to V_T ,²⁴ and (iv) “species effect” related to the change of effective sputter yield once gas ions are replaced with the back-attracted target ions in the later phase of the pulse.²⁵

The reported values for the loss of power-normalized HIPIMS deposition rate $\bar{R}_{HIPIMS}$ show large spread even for the same material system. For example, if referred to the power-

normalized DCMS rate $\bar{R}_{DCMS}$, the ratio $\bar{R}_{HIPIMS}/\bar{R}_{DCMS}$ varies from 15% to 75% for Ti, and from 37% to 80% in the case of Cu.^{2,26} This may be due to different HIPIMS settings and prevents systematic comparisons between material systems, as well as, identification of key parameters for the here contested effect of HIPIMS rate loss.

We performed film growth rate measurements under identical conditions for ten elemental targets representing widely different masses, melting temperatures, sputtering yields, ionization potentials, and secondary electron emission yields during HIPIMS and DCMS in Ar atmosphere. The HIPIMS peak target current density J_T^{max} is varied by two orders of magnitude, from 0.04 to 3 A/cm², by means of changing the average power settings at constant pulsing frequency. We find that materials that are prone to high target current densities during HIPIMS discharge have second ionization potential IP_T^2 lower than the first ionization potential of Ar IP_{Ar}^1 . This results in higher concentrations of doubly-ionized sputter-ejected species that, in turn, enable effective potential emission of secondary electrons during the metal (self-sputtering) phase and, hence, enhanced ionization of sputtering gas. For all materials, the ratio of power normalized HIPIMS and DCMS rates α decays exponentially with increasing peak target current density J_T^{max} . Surprisingly, with the exception of Al and Si, $\alpha(J_T^{max})$ curves overlap indicating that the rate loss in HIPIMS is to large extent determined by the peak amplitudes of the HIPIMS target currents.

Aluminum, Si, Ti, Cr, Y, Zr, Nb, Hf, Ta, and W films are grown in a CC800/9 CemeCon AG magnetron sputtering system using rectangular 8.8×50 cm² targets that are virgin to exclude possible influence of the target history. The same magnetron is used in the experiments to ensure the same magnetic field strength and distribution. Prior to film growth each target undergoes a sputter-in sequence consisting of (1) DCMS operation with the average power $\langle P \rangle_T$ increasing from 1 to 8 kW in steps of 1 kW and 5 min per step, followed by (2) 1 h DCMS with $\langle P \rangle_T = 4$ kW, and (3) HIPIMS with average power set to 2 kW and a frequency f of 1000 Hz

resulting in rather low target current density values which increase as f is gradually decreased to 500, 300, 200, and 100 Hz. Finally, frequency is set to 200 Hz (as for the film growth) and $\langle P \rangle_T$ is scanned from 0.4 to 4 kW during less than 15 min in order to assure stable operation in a wide current density range.

Si(001) substrates, $2 \times 1 \text{ cm}^2$, are cleaned sequentially in acetone and isopropyl alcohol, and mounted at a distance of only 6 cm from the target to minimize the influence of gas scattering.²⁷ The growth chamber is degassed prior to deposition during a 2-h-long heating cycle so that the system base pressure is 2.3×10^{-6} Torr (0.3 mPa). Targets are operated in pure Ar with the gas flow f_{Ar} set at $420 \text{ cm}^3/\text{min}$, resulting in the total pressure of 3 mTorr (0.4 Pa). The substrate temperature is 400 °C.

Two multilayer films are grown for each material system, one in HIPIMS and one in DCMS mode, with the average target power $\langle P \rangle_T$ varied from 0.4 to 4 kW in steps of 0.4 kW. During HIPIMS experiments the pulsing frequency f is fixed at 200 Hz, thus variation in $\langle P \rangle_T$ corresponds to changing the pulse energy E_p from 2 to 20 J in steps of 2 J ($\langle P \rangle_T$ and E_p are related by $\langle P \rangle_T = f \times E_p$). While the preset pulse length T_{ON} is 200 μs , the effective pulse length τ , defined here as the time period during which $J_T(t) > 0.1 \times J_T^{max}$, may vary depending on $\langle P \rangle_T$ and target material. Resulting film thickness of individual layers is in the range from 350 to 650 nm. A 50-nm-thick TiN marker layers are deposited after each step in order to facilitate the layer thickness determination by cross-sectional scanning electron microscopy (XSEM) analyses. For the TiN growth in mixed Ar/N₂ atmosphere, the target is protected by cathode shutters to avoid cross-contamination from the neighboring cathode equipped with Ti target. All tested targets are pre-sputtered behind close shutters to remove possibly formed surface nitride layer following each TiN deposition step. A negative dc substrate bias, $V_s = -60$ V is used during DCMS film growth, while pulsed bias voltage with the same amplitude and 4 % duty cycle, synchronized with the HIPIMS pulse, is used for HIPIMS experiments.^{13,14}

Target current $I_T(t)$ and target voltage $V_T(t)$ waveforms (in which T stands for the target material) during film growth are recorded with a Tektronix 500 MHz bandwidth digital oscilloscope. The target current density $J_T(t)$, a more generic quantity, is obtained by dividing $I_T(t)$ with the entire target area $A = 440 \text{ cm}^2$.

Figures 1(a-d) show $J_T(t)$ and $V_T(t)$ waveforms recorded with the pulse energy $E_p = 18 \text{ J}$ during the HIPIMS operation of different metal targets in Ar. Data presented reveal large differences with respect to current-voltage performance between the materials. Based on the appearance of $J_T(t)$ and $V_T(t)$ curves as well as their evolution with E_p (not shown) the target materials can be divided into two categories. The first category, including Ti, Zr, Nb, and Y (Figs. 1(a) and 1(c)), is characterized by narrow, high-amplitude current pulses, and relatively short triangular voltage waveforms that possess low amplitudes towards the end of the HIPIMS pulse.²⁸ For materials in the second category (Si, Cr, Hf, Ta, and W), current pulses are relatively broad with low-amplitudes, while $V_T(t)$ traces are characterized by higher voltage values towards the end of the pulse. Al target constitutes an intermediate case between category I and II metals. Trends outlined here are independent of the average power setting.

In the case of category I metals the peak target current density J_T^{max} reaches 2.4 A/cm^2 for Zr and Nb, 3 A/cm^2 for Ti, and 3.4 A/cm^2 for Y. The effective pulse lengths τ is in the range from 51 to 59 μs . As a consequence of these extremely high currents PS capacitors get almost completely emptied resulting in low V_T values towards the end of the pulse (cf. Fig. 1(c)). Materials in this category are characterized by rather low second ionization potential IP_T^2 values (cf. Tab.1), all satisfying the criterion $IP_T^2 < IP_{Ar}^1$ ($IP_{Ar}^1 = 15.76 \text{ eV}$)²⁹ meaning that there is a significant electron population in the discharge with energies in the range $IP_T^2 < E_e < IP_{Ar}^1$, i.e., too low to ionize Ar, yet high enough to produce doubly-ionized target ions.³⁰ This is of key importance in HIPIMS plasmas, since the primary ionization mechanism is by electron impact. As pointed out by Anders et al.³¹ the presence of higher charge state species is essential

for the secondary electron emission during the metal-dominated (self-sputtering) phase of the HIPIMS pulse, when concentrations of inert gas ions is lowered due to rarefaction effects.^{10,11,12} For relatively low ion energy used in sputtering, secondary electrons are predominantly ejected by potential emission, which requires that the condition:³²

$$0.39IP > \phi_T \quad (1)$$

in which ϕ_T is the target work function,³³ is satisfied. It follows from data presented in Table 1 that all IP_T^1 values are too low to fulfill Eqn.(1) and doubly-charged species are necessary for the potential emission to set in, in the absence of gas ions. Eqn.(1) is readily satisfied in the case of category I metals, for which higher concentrations of doubly-ionized species are indeed expected, leading to effective secondary electron emission during the metal (self-sputtering) phase, resulting in thorough ionization of the working gas (diluted due to rarefaction) and high target current densities.

In distinct contrast, for category II metals operation with $E_p = 18$ J results in relatively low J_T^{max} values, from 0.9 A/cm² for W to 1.3 A/cm² for Ta target. Pulses become broader with τ values 78-79 μ s for Cr and Ta, to 84, 105, and 106 μ s with Si, Hf, and W, respectively. In addition, $J_T(t)$ waveforms exhibit a more complex form (in opposite to category I metals) characterized by a fast rise of the current density during the first 10 μ s followed by a short, ~ 5 μ s, plateau-like period (best visible for W, Hf, and Cr) after which $J_T(t)$ continues to rise until the J_T^{max} is reached. Materials Cr, W or Hf $J_T(t)$ also exhibit a pronounced shoulder at $t \sim 60$ μ s. Capacitors do not get fully discharged due to lower target current, hence V_T stays relatively high towards the end of the HIPIMS pulse (cf. Fig. 1(d)). Contrary to category I metals, the majority of category II metals has IP_T^2 either greater or similar to IP_{Ar}^1 , hence lower concentrations of doubly-ionized species are expected. The secondary electron emission is thus predominantly due to noble gas ions. Once the Ar^+ concentration decreases due to rarefaction

so does the electron emission, hence the resulting target current density gets seriously limited during the self-sputtering phase.

Target current density is surprisingly high for the Al target that possesses highest IP_T^2 in the whole set (see Tab. 1) resulting in negligible Al^{2+} fluxes.³⁴ One reason may be relatively low melting point (660 °C) of Al, such that the target surface is at the onset of evaporation during most energetic phase of HIPIMS discharge.³⁵ The film growth rate measurements presented below are in favor of this interpretation.

HIPIMS film growth rates are commonly compared to corresponding DCMS rates obtained at the same average target power.²⁵ Therefore, in Figure 2 the ratio $\alpha = \bar{R}_{HIPIMS}/\bar{R}_{DCMS}$ of power-normalized rates is plotted as a function of peak target current density for all target materials tested. Clearly, the loss of deposition rate with increasing J_T^{max} takes place for each metal, irrespective of target ability to produce high current densities (category I vs. category II metals). In the limit of lowest J_T^{max} values, $\alpha(J_T^{max})$ curves approach unity indicating nearly-DCMS sputter efficiency, which means that pulsing itself has no effect on the rate drop. With increasing peak target current density α exhibits nearly exponential decay for all materials. Interestingly, with the exception for Al and Si, all $\alpha(J_T^{max})$ curves nearly overlap such that for any J_T^{max} value the spread in α is only +/- 5%, and even less than that in the high current limit, $J_T^{max} > 1.5 \text{ A/cm}^2$ (category I). This shows that the rate loss in HIPIMS is to a large extent determined by the peak amplitude of the HIPIMS target current in a wide J_T^{max} range spanning nearly two orders of magnitude, from 0.04 to 3 A/cm². There is no apparent difference between category I and category II metals in this respect.

In order to evaluate the potential contribution of the “yield effect”²⁴ to the observed loss of deposition rate we calculated the ratio of time-averaged power-normalized deposition rates $\overline{\langle R \rangle}_{HIPIMS}/\overline{\langle R \rangle}_{DCMS}$ accordingly to³⁶

$$\overline{\langle R \rangle}_{HIPIMS} / \overline{\langle R \rangle}_{DCMS} = \frac{1}{T_{ON}} \frac{\int_{t=0}^{t=T_{ON}} dt J_T(t) V_{HIP}^{b-1}(t)}{\int_{t=0}^{t=T_{ON}} dt J_T(t)} / V_{DC}^{b-1} \quad (2)$$

in which b is a constant for the target material obtained by fitting sputter yield $\gamma_{Ar \rightarrow M}$ values calculated for a range of incident ion energies E_i using TRIM (Transport of Ions in Matter) software package,^{37,38} with an allometric function of the form aE_i^b . Eqn.(2) was evaluated for each power setting and target material using the recorded current density and voltage functions and the results compared with the experimental observations in Fig.2. We find that $\overline{\langle R \rangle}_{HIPIMS} / \overline{\langle R \rangle}_{DCMS}$ ranges from 0.75 for Cr to 0.97 for Nb and shows only a weak dependence on J_T^{max} . Thus, the “yield effect” does not account for the observed exponential decay in α , which decreases to values as low as 0.1 in the limit of highest J_T^{max} .

Potential influence of the “return effect”, as well as, the “species effect” on α is treated explicitly by the target materials pathway model²¹. Within this approach

$$\alpha = \frac{1 - \beta + \beta(1 - \sigma)\eta_T}{1 + \beta\sigma(\gamma_{Ar \rightarrow M} - \gamma_{M \rightarrow M})} \quad (3)$$

in which β is the ionized fraction of the sputtered flux, σ is the fraction of the ionized metal species that gets captured by the magnetron and directed to the target for sputtering, η_T is the fraction of sputtered species that is available for deposition (assuming that the transport from the target to the substrate is the same as during DCMS), finally $\gamma_{Ar \rightarrow M}$ and $\gamma_{M \rightarrow M}$ are sputtering and self-sputtering yields. While it is unknown how σ and η_T vary with increasing J_T^{max} , it is commonly accepted that the ionization of the sputtered flux (hence β) increases with increasing peak target current density due to higher probability for electron-impact ionization.⁹ Thus, the straightforward interpretation of results shown in Fig. 2 is that, α decreases with increasing J_T^{max} for all metals due to increasing β . In the limit of the lowest J_T^{max} , $\beta \rightarrow 0$ (no or little ionization) and $a \rightarrow 1$ ($\bar{R}_{HIPIMS} \sim \bar{R}_{DCMS}$), as indeed observed. For the highest J_T^{max} values, $\beta \rightarrow 1$ and Eqn.(3) becomes

$$\alpha_{\beta \rightarrow 1} = \frac{(1-\sigma)\eta_T}{1+\sigma(\gamma_{Ar \rightarrow M} - \gamma_{M \rightarrow M})}. \quad (4)$$

In the case of $\sigma \approx 1$ (100% capturing efficiency) $\alpha_{\beta \rightarrow 1} \approx 0$ (HIPIMS rate approaches zero), which clearly does not take place in our experiments, where $0.1 < \alpha_{\beta \rightarrow 1} < 0.15$ (see Fig. 2).

The main explanations for significantly higher α values observed for Al and Si targets are (1) the short plasma transit time of the relatively low-mass sputter-ejected Al and Si atoms that decreases the probability for electron-impact ionization events resulting in lower ionization (lower β in Eqn.(3) implies higher α), and (2) Al and Si have $\gamma_{Ar \rightarrow M} < \gamma_{M \rightarrow M}$ (see Tab.(1)), by which the sputtering rate should increase as the discharge transforms into the metallic phase (assuming constant β and σ) with a positive effect on α .

In conclusion, Ti, Y, Zr, and Nb yield very high peak target current densities during HIPIMS discharge, not achievable with other targets. This is because their second ionization potentials IP_T^2 are significantly lower than the first ionization potential of Ar IP_{Ar}^1 , leading to higher concentrations of doubly-ionized sputter-ejected species in the plasma that cause effective secondary electron emission during the metal (self-sputtering) phase and enhanced ionization of sputtering gas diluted due to rarefaction. For all metals included in this study, the ratio of power normalized HIPIMS and DCMS rates α decays exponentially with increasing peak target current density from $\alpha = 1$ in the limit of lowest J_T^{max} tested to $\alpha \sim 0.1$ with $J_T^{max} \sim 3 \text{ A/cm}^2$. Surprisingly, with the exception for Al and Si, all $\alpha(J_T^{max})$ curves overlap indicating that the rate loss in HIPIMS is to large extent determined by the peak amplitude of the HIPIMS target current. The “return effect”, i.e., back attraction of ionized target species, is the only mechanism that can account for such large variation in α . Hence, the choice of HIPIMS working condition for a particular application, should be based on an optimization between required ionization degree and loss of deposition rate by taking advantage of a wide process parameter space.

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Figure and Table Captions

Fig. 1. (a-b) Target current density $J_T(t)$, and (c-d) target voltage $V_T(t)$ waveforms recorded during HIPIMS process with pulse energy of 18 J for Al, Si, Ti, Cr, Y, Zr, Nb, Hf, Ta, and W targets.

Fig. 2. The ratio of HIPIMS and DCMS power-normalized film growth rates $\alpha = \bar{R}_{HIPIMS}/\bar{R}_{DCMS}$ as a function of peak target current density J_T^{max} for Al, Si, Ti, Cr, Y, Zr, Nb, Hf, Ta, and W targets operated in HIPIMS mode. Category I and category II metals are indicated in the legend.

Tab. 1 Target material parameters relevant for HIPIMS and DCMS sputtering. Atomic mass m , bulk density ρ , homologous temperature T_s/T_m , first and second ionization potential IP_T^1 and IP_T^2 ,²⁹ as well as work function ϕ_T .³³ Sputter yield for 1 keV Ar ions $\gamma_{Ar \rightarrow M}$ as well as self-sputtering yield for 1 keV ions $\gamma_{M \rightarrow M}$ are calculated using TRIM software.³⁸

REFERENCES

- ¹ V. Kouznetsov, K. Macak, J. M. Schneider, U. Helmersson and I. Petrov, *Surf. Coat. Technol.* 122 (1999) 290
- ² K. Sarakinos, J. Alami, S. Konstantinidis, *Surf. Coat. Technol.* 204 (2010) 1661–1684
- ³ A. Anders, *Surf. Coat. Technol.* 257 (2014) 308
- ⁴ A. Anders, *Surf. Coat. Technol.* 204 (2010) 2864
- ⁵ A. Anders, *Surf. Coat. Technol.* 205 (2011) S1–S9
- ⁶ J. Böhlmark, J. Alami, C. Christou, A.P. Ehasarian, U. Helmersson, *J. Vac. Sci. Technol. A* 23 (2005) 18
- ⁷ G. Greczynski, J. Jensen, L. Hultman, *Thin Solid Films* 519 (2011) 6354–6361
- ⁸ K. Macak, V. Kouznetsov, J. Schneider, U. Helmersson and I. Petrov, *J. Vac. Sci. Technol. A* 18 (2000) 1533
- ⁹ J.T. Gudmundsson *Journal of Physics: Conference Series* 100 (2008) 082013
- ¹⁰ S. M. Rosnagel, *J. Vac. Sci. Technol. A* 6, 19-24 (1988).
- ¹¹ G. Greczynski and L. Hultman, *Vacuum* 84 (2010) 1159–1170
- ¹² D. Lundin, N. Brenning, D. Jadernas, P. Larsson, E. Wallin, M. Lattemann, M. A. Raadu and U. Helmersson. *Plasma Sources Sci. Technol.* 18 (2009) 045008
- ¹³ G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 206 (2012) 4202
- ¹⁴ G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 86 (2012) 1036
- ¹⁵ G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *J. Vac. Sci. Technol. A* 30 (2012) 061504
- ¹⁶ G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *Thin Solid Films* 556 (2014) 87
- ¹⁷ J. A. Davis, W. D. Sproul, D. J. Christie, and M. Geisler, in *Proceedings of the 47th Annual SVC Technical Conference*, Dallas (TX), 2004, p. 215
- ¹⁸ D. A. Glocker, M. M. Romach, D. J. Christie, and W. D. Sproul, in *Proceedings of the 47th Annual SVC Technical Conference*, Dallas (TX), 2004
- ¹⁹ W. D. Sproul, D. J. Christie, and D. C. Carter, in *Proceedings of the 47th Annual SVC Technical Conference*, Dallas (TX), 2004
- ²⁰ M. Samuelsson, D. Lundin, J. Jensen, M.A. Raadu, J.T. Gudmundsson, U. Helmersson, *Surf. Coat. Technol.* 205 (2010) 591
- ²¹ D. J. Christie, *Journal of Vacuum Science and Technology A* 23 (2005) 330.
- ²² J. Vlcek, P. Kudlacek, K. Burcalova, and J. Musil, *Journal of Vacuum Science and Technology A* 25 (2007) 42
- ²³ D. Lundin, P. Larsson, E. Wallin, M. Lattemann, N. Brenning, and U. Helmersson, *Plasma Sources Sci. Technol.* 17 (2008) 035021
- ²⁴ J. Emmerlich, S. Mraz, R. Snyders, K. Jiang, and J. M. Schneider, *Vacuum* 82, (2008) 867.
- ²⁵ A. Anders, *J. Vac. Sci. Technol. A* 28 (2010) 783
- ²⁶ U. Helmersson, M. Lattemann, J. Böhlmark, A. P. Ehasarian, and J. T. Gudmundsson, *Thin Solid Films* 513 (2006) 1
- ²⁷ with the experimental conditions used here the average sputtered atoms mean free paths are between 3 and 6 cm, see e.g. W.D. Westwood *J. Vac Sci Technol.* 1978;15:1.
- ²⁸ in the case of HIPIMS in the industrial-size cathodes the amount of energy stored in the capacitor bank of the HIPIMS power supply is often not high enough to sustain a constant voltage during the entire pulse period due to high $I_T(t)$ values. In such a case, a drop in $V_T(t)$, that occurs with the rate directly proportional to the amplitude of the target current density, $J_T(t) = C/A \times dV_T(t)/dt$ (in which C is the size of the capacitor bank) takes place resulting in a triangular pulse form.
- ²⁹ David R. Lide (ed), *CRC Handbook of Chemistry and Physics, 84th Edition*. CRC Press. Boca Raton, Florida, 2003; Section 10, Atomic, Molecular, and Optical Physics; Ionization Potentials of Atoms and Atomic Ions
- ³⁰ G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 116 (2015) 36
- ³¹ A. Anders *Appl. Phys. Letters* 92 (2008) 201501
- ³² R. A. Baragiola, E. V. Alonso, J. Ferron, and A. Oliva-Florio, *Surf. Sci.* 90 (1979) 240
- ³³ all ϕ_r values from: CRC Handbook of Chemistry and Physics version 2008, p. 12–114
- ³⁴ G. Greczynski, J. Lu, J. Jensen, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 257 (2014) 15
- ³⁵ See for instance: E. P. Vaulin, N. E. Georgieva, and T. P. Martinenko, *Sov. Phys. Solid State* 19, 827 (1977)
- ³⁶ to derive Eqn.(3) we used the fact that the sputter yield γ can be fitted with an allometric function of the form aE_i^b where a and b are fitting parameters and ion energy $E_i \cong q_n V_T$ (no
- ³⁷ J. F. Ziegler, J. P. Biersack, U. Littmark, "The Stopping and Range of Ions in Solids," vol. 1 of series "Stopping and Ranges of Ions in Matter," Pergamon Press, New York (1984).

³⁸ www.srim.org; accessed on 2015-06-28.

Target Element	m [amu]	ρ [g/cm ³]	T_s/T_m	IP_T^1 [eV]	IP_T^2 [eV]	$\gamma_{Ar \rightarrow M}$ ($E_i = 1$ keV)	$\gamma_{M \rightarrow M}/\gamma_{Ar \rightarrow M}$ ($E_i = 1$ keV)	ϕ_T [eV]
Al	26.98	2.70	0.72	6.01	18.89	1.08	1.32	4.1-4.3
Si	28.09	2.33	0.4	8.15	16.35	0.57	1.42	4.6-4.9
Ti	47.87	4.51	0.35	6.85	13.62	0.98	0.85	4.3
Cr	52.0	7.19	0.31	6.79	16.54	2.10	0.89	4.5
Y	88.91	4.47	0.37	6.24	12.27	1.30	0.77	3.1
Zr	91.22	6.52	0.31	6.66	13.21	1.20	0.80	4.1
Nb	92.91	8.57	0.24	6.78	14.35	1.20	0.76	4.0-4.9
Hf	178.49	13.31	0.27	6.85	14.98	1.62	0.86	3.9
Ta	180.95	16.69	0.2	7.91	15.60	1.58	0.88	4.0-4.8
W	183.34	19.25	0.18	8.01	17.68	1.63	0.82	4.3-5.2

Tab. 1

Fig. 1

Fig. 2