

**Selfsputtering runaway in high power impulse magnetron sputtering:
The role of secondary electrons and multiply charged metal ions**

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Abstract

Selfsputtering runaway in high power impulse magnetron sputtering is closely related to the appearance of multiply charged ions. This conclusion is based on the properties of potential emission of secondary electrons and energy balance considerations. The effect is especially strong for materials whose sputtering yield is marginally greater than unity. The absolute deposition rate increases $\sim Q^{1/2}$, whereas the rate normalized to the average power decreases $\sim Q^{-1/2}$, with Q being the mean ion charge state number.

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High power impulse magnetron sputtering (HIPIMS) is an emerging coatings technology characterized by ionization of the sputtered material and significant selfsputtering of the target. The pulsed power density of the magnetron discharge is enhanced by typically two orders of magnitude compared to the power density used in conventional sputtering. This implies a relatively small pulse duty cycle of 5% or less to avoid overheating, which could lead to target melting and/or damage of the magnets. The production of ionized sputtered material offers an elegant approach to self-ion-assisted deposition of thin films and nanocomposites.^{1,2}

As the HIPIMS pulse length is increased from the typical 10-100 μs to 400 μs ,^{3,4} and even into the millisecond regime,⁵ the fraction of sputtered atoms and ions in the plasma is increased, and the fraction of the sputter gas, usually argon, is reduced. One may define the selfsputtering parameter as

$$\Pi = \alpha\beta\gamma_{ss}, \quad (1)$$

where α is the probability for a sputtered atom to become ionized, β is the probability for the ion to return to the target, and γ_{ss} is the yield of selfsputtering. The greater the power density of the discharge, the more and faster the sputtered metal becomes ionized and contributes to the discharge current. When the power density is high (typically $> 1 \text{ kW/cm}^2$) and the discharge is sufficiently long (typically $> 100 \mu\text{s}$), the parameter Π may exceed unity, implying that selfsputtering accelerates, i.e. runs away. The current will increase until either the power supply reaches its design or arc suppression limit, or, if enough power is supplied, the discharge is allowed to rapidly develop into a new, high-current steady state in which ionization and loss processes are balanced. Then, $\Pi = 1$ if

self-sputtering is relying on ionized metal only,⁶ or $\Pi < 1$ but very close to unity if gas (argon) ions are still participating.

A key feature for any magnetron discharge is the existence of a thin sheath adjacent to the target (cathode). A large portion of the applied voltage, V , drops in the sheath, determining the ion energy gain

$$\Delta E_{kin} = Qe\Delta V_{sheath} \sim QeV, \quad (2)$$

where Q is the ion charge state number, e is the elementary charge, and ΔV_{sheath} is the sheath voltage.

Apart from generating sputtered atoms, the impact of ions also generates secondary electrons. The yield γ_{SE} of this process depends on the material, its surface conditions, as well as on the kinetic and potential energy of the impacting ion. Secondary electrons travel through the sheath (opposite to the direction of positive ions), gain energy from the electric field, and enter the plasma as energetic (“hot”) electrons. The electron motion is “bound” to the magnetic field lines via gyration in the magnetic field. Additionally, due to the geometry of the electric and magnetic fields of a magnetron, electrons are subject to $\mathbf{E} \times \mathbf{B}$ and other drifts.

Secondary electrons are the “engines of the discharge.” They take energy from the electric field of the sheath and transfer it to the plasma. Without secondary electrons, the electron temperature will drop, ionizing collisions will be reduced, and ion generation will be diminished to a point where the discharge may cease. Therefore, when considering how HIPIMS can operate as the plasma changes from gas sputtering to self-sputtering, a discussion of secondary electron emission is needed.

One generally distinguishes between kinetic and potential electron emission. For clean surfaces, *kinetic emission* (KE) is dominant for projectile energies exceeding about 300 eV/amu^{7,8} and is observed down to an apparent threshold in the ~10 eV/amu region.⁹ For “dirty” or technological surfaces, the threshold is reduced by about one order of magnitude and the yields can vary greatly depending on the specifics of the surface.¹⁰

For the relatively low kinetic energies of HIPIMS ions, we need to consider the emission determined by the potential energy of the arriving ion projectiles (*potential emission*, PE). PE is produced mainly above and at the surface due to resonance- and Auger electron transitions, whereas KE can only originate from collisions at and below the target surface.⁹ Experimental data of the secondary emission yields for various ions satisfy the fit¹¹

$$\gamma_{SE} = 0.032(0.78 E_{pot} - 2\phi). \quad (3)$$

In order for any PE to occur, the condition

$$0.78 E_{pot} > 2\phi \quad (4)$$

needs to be fulfilled. A closer look at the work functions and first ionization energies of metals shows that (4) is not fulfilled for any singly charged ion of any metal! Table I gives some examples illustrating this statement. In contrast, the first ionization energy of argon is high enough to satisfy (4). Figure 1 shows this situation for gold: the electron emission from Au⁺ is practically zero, while the potential emission from Au²⁺ and Au³⁺ are considerably higher.⁹

As we increase the (peak) power to the magnetron and start ionizing the sputtered atoms, the flux of argon ions to the target is not only reduced by rarefaction,¹² but replaced by ions of the sputtered material.¹³ The HIPIMS pulse may enter its sustained

self-sputtering (SSS) phase with $\Pi = 1$, and the discussion in the remainder of this contribution focuses on this phase. For selected materials (e.g. Cu and Ag), SSS has been demonstrated even for *continuous* operation at relatively moderate power densities.^{6,14}

As shown in the example of Fig. 1, *singly* charged metal ions (in their ground state) cannot create the necessary secondary electrons. Therefore, *one should expect that doubly charged, and perhaps even higher charged ions are present* when the system is at the runaway threshold. From an energetic point of view, that should be possible because the second ionization energy of metals is about the same as, or only slightly greater than, the first ionization energy of argon (Table I).

Since $\alpha < 1$ and $\beta < 1$, the condition $\gamma_{ss} > 1$ is necessary but not sufficient to reach $\Pi > 1$ (runaway) and $\Pi = 1$ (SSS). If $\gamma_{ss} > 1$ by a large margin, e.g. for copper, silver, and gold (Fig. 2), the system can operate in the SSS phase with a moderate degree of ionization and relatively small presence of doubly charged ions. Large amounts of metal neutrals leads to a high probability for electrons to make collisions. Therefore, the electron temperature is lower in those cases, and relatively less doubly and higher charged ions are produced. Conversely, one should expect a higher electron temperature and higher mean ion charge for materials that only marginally satisfy $\gamma_{ss} > 1$.

An estimate for the minimum fraction of doubly charged ions can be derived from the energy balance in the SSS phase

$$I_{SE}V = \int_S \sum_Q \Phi_Q E_Q^{cum} dS + P_e + P_n + P_{rad}, \quad (5)$$

where the integral is over the surface that encloses the plasma, Φ_Q is the flux (loss) of ions of charge state Q flowing through the boundary area S , E_Q^{cum} is the cumulative

ionization energy of ions of charge state Q (tabulated e.g. in ref.¹⁵), P_e , P_n , and P_{rad} are the losses associated with the flow of electrons, heated neutrals, and radiation through the boundary area. If we assume that only singly and doubly charged ions are produced, equation (5) can be simplified to

$$I_{SE} V = \gamma_{SE,Q=2} I_2 V > \int_S (\Phi_1 E_{0 \rightarrow 1} + \Phi_2 (E_{0 \rightarrow 1} + E_{1 \rightarrow 2})) dS. \quad (6)$$

The integral over S can be split into two sub-areas: one considering the return flux to the target area, A , and the rest of the flux through the area $S - A$. The return probability β can be used to express the integral over A , and furthermore we can use the relationship between flux and current density $\Phi_Q = j_Q / Qe$ to obtain

$$\gamma_{SE,Q=2} I_2 V > \beta \left(\frac{I_1}{e} E_{0 \rightarrow 1} + \frac{I_2}{2e} (E_{0 \rightarrow 1} + E_{1 \rightarrow 2}) \right) \quad (7)$$

which, when rearranged, gives a ratio of currents of doubly and singly charged ions:

$$\frac{I_2}{I_1} > \frac{\frac{\beta}{e} E_{0 \rightarrow 1}}{\gamma_{SE,Q=2} V - \frac{\beta}{2e} (E_{0 \rightarrow 1} + E_{1 \rightarrow 2})}. \quad (8)$$

A necessary condition (to make the r.h.s. positive) is

$$V > \frac{\beta}{2e \gamma_{SE,Q=2}} (E_{0 \rightarrow 1} + E_{1 \rightarrow 2}). \quad (9)$$

Let us consider the example of gold, assuming $\beta \approx 0.9$, $\gamma_{SE,Q=2} = 0.075$ (from Fig. 1), with the ionization energies from Table I. At a voltage of 1000 V we obtain $I_2/I_1 > 0.135$. The relatively high value of β seems reasonable given that the electric field extends beyond the sheath of the target because the plasma is magnetized.

Most transition metals have γ_{ss} that is not much greater than unity for typical voltages of 600 V – 1000 V.³ Therefore, $\Pi = 1$ implies that α and β must be very high. In those cases, we have *two* reasons to expect significant amounts of multiply charged ions, namely: (i) the necessity to produce secondary electrons to maintain the energy supply to the plasma, (ii) the necessity for ions to gain enough kinetic energy from the sheath to obtain a sufficiently high sputtering yield. The system is self-consistent: by producing large amounts of multiply charged ions, more energy is supplied to the plasma via secondary electrons, and by having more energy supplied, the electron temperature is high enough to produce multiply charged ions.

Doubly charged metal ions have indeed been detected in HIPIMS plasmas.^{1,3,4,16} Contrary to the general treatment in the literature, they should not be considered as a side effect but as crucial, and they indeed facilitate that the HIPIMS discharge can evolve into the SSS phase.

Experimental quantification of multiply charged ions arriving at the target is challenging. Optical emission spectroscopy should be done in the ultraviolet where the strong lines of the ions can be found. Charged particle spectrometry is typically done at some distance from the target in order to not disturb the magnetron discharge. However, charge exchange reactions $M^{Q+} + M \rightarrow M^{(Q-1)+} + M^+$ are likely in the presence of a high metal neutral concentration, which reduce, or may even prevent, the detection of multiply charged ions at those distances for high γ_{ss} materials.

Multiply charged ions gain more energy in the sheath and therefore contribute to the deposition rate more than their fraction in the plasma. Sputtering yields can be approximated by fit functions of the type

$$\gamma_i = a_i E_{kin}^{b_i}, \quad (10)$$

where a_i is material dependent and $b_i \equiv b \approx 1/2$ is an acceptable approximation (Fig. 2).

The energy (i.e., charge state and voltage) depending sputter yields of ions of type i are therefore

$$\gamma_i(Q_i V) \approx a_i (Q_i V)^{1/2}. \quad (11)$$

For materials with $\gamma_{SS} \sim 1$ at voltages $V = 600-1000$ V, the appearance of multiply charged metal ion may actually be the trigger for $\Pi > 1$.

To estimate the effect of multiply charged ions on the deposition rate we see that the rate is about proportional to $Q^{1/2}$ due to the yield dependence (11). However, the rate is generally normalized by the time-averaged power, which in turn is approximately proportional to Q because the ion current is proportional to Q . Therefore, the deposition rate, normalized by the time-averaged power, is reduced when the charge states is increased,

$$R/\bar{P} \sim Q^{-1/2}. \quad (12)$$

This is a consequence of the less than proportional increase of the sputter yield with energy and the choice of normalization, and it is not related to the reduction of the rate by the return effect. In an analog manner,¹⁷ the normalized deposition rate is reduced by the higher voltage of HIPIMS operation, $R/\bar{P} \sim V^{-1/2}$.

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TABLE I. Workfunction, and first and second ionization energies for selected materials.

	ϕ (eV)	$E_{0 \rightarrow 1}$ (eV)	$E_{1 \rightarrow 2}$ (eV)
<i>Ar</i>	<i>n/a</i>	<i>15.76</i>	<i>27.63</i>
Ti	4.3	6.82	13.58
Cr	4.5	6.77	16.49
Cu	4.9	7.73	20.29
Nb	4.2	7.67	14.32
Au	5.3	9.23	20.50

Figure Captions

Fig. 1 (Color online) Measured yield of secondary electrons, γ_{SE} , versus kinetic energy of gold ions impacting polycrystalline gold, with the gold ion charge state as a parameter (data from ref. 9, the lines are polynomial fit curves).

Fig. 2 (Color online) Sputtering yield as a function of target (sheath) voltage and kind (incl. charge state) of impacting ions; SRIM calculations.

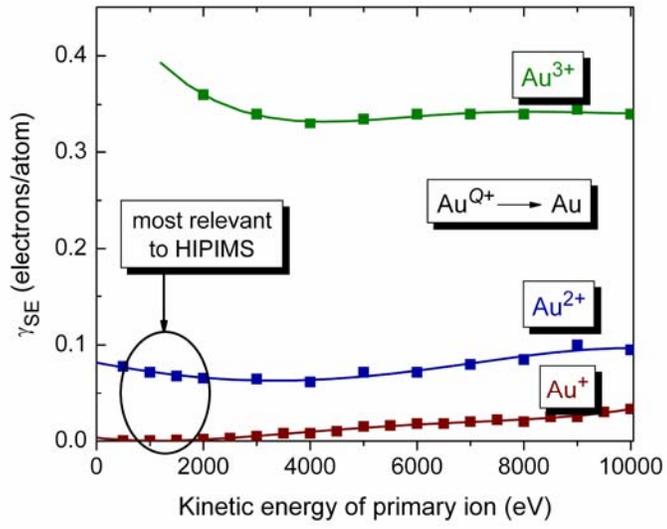


Fig. 1

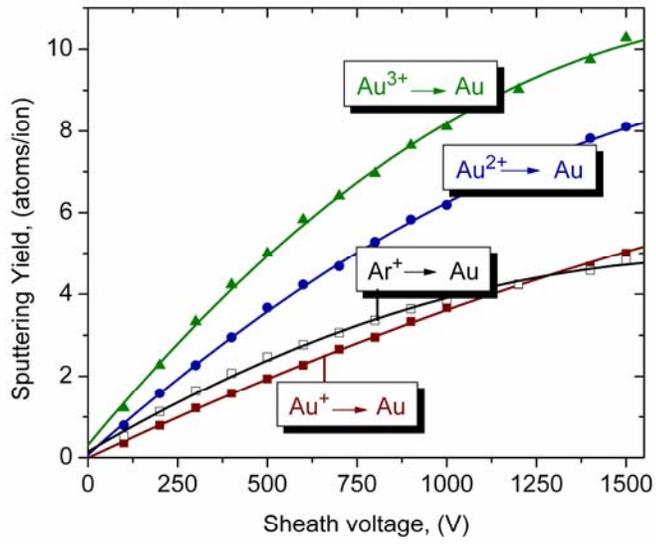


Fig. 2