

# FUNDAMENTALS OF SPUTTER DEPOSITION

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## REVIEW ARTICLE



### Review Article: Tracing the recorded history of thin-film sputter deposition: From the 1800s to 2017

J. E. Greene<sup>a)</sup>

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Professor of Materials Science, National Taiwan University Science and Technology, Taipei City, 106, Taiwan

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[10.1116/1.4998940](https://doi.org/10.1116/1.4998940)

View online: <https://doi.org/10.1116/1.4998940>

526 references; open access

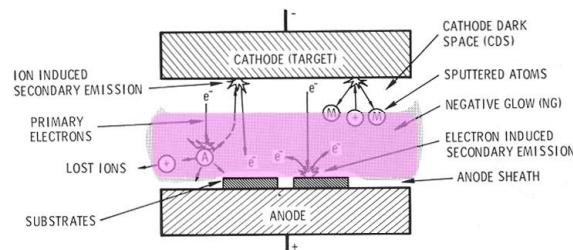
## D. Conclusions

It seems perfectly safe to predict that sputter-deposition of thin films will remain a vibrant and active field of human endeavor incorporating fundamental scientific research, process development, deposition-system design, and new-product manufacturing for periods far into the future.

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## Sputter deposition



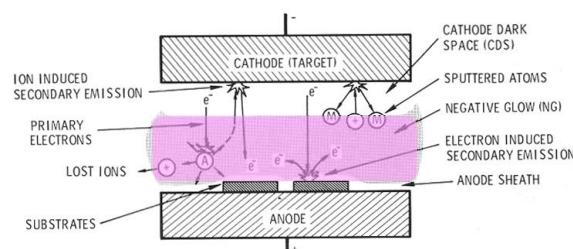
Basics:

- A voltage is applied across a rarified gas in a vacuum.
- Breakdown of the gas forms a glow discharge plasma.
- Positive ions from the plasma strike the negative electrode (cathode/target).
- Energy from the ions is transferred to target atoms.
- A few of these may escape from the target surface (they are sputtered).
- Sputtered atoms undergo collisions in the gas phase
- Some of the sputtered atoms reach the substrate
- The sputtered atoms condense on the substrate forming a film.

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## Sputter deposition



Important processes:

- Ion-solid interactions on the target.
- Plasma generation and discharge maintenance
- Collisions in the gas phase – ionization, scattering.
- Nucleation and film growth on the substrate.
- Use of ion solid interactions to modify film growth

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## Part 1. Fundamentals of Sputter Deposition

### 1.1 Elements of kinetic theory of gases

- Gas laws
- mean free path
- gas impingement rate

### 1.2 Elements of plasma physics

- Plasma probes
- Sheath width
- Penning ionization
- Electron energy distribution functions

### 1.3 Glow discharge maintenance

- Secondary ion-electron emission
- Electron ionization cross-sections

### 1.4 Sputtering yield

- Linear cascade model
- Correction for threshold effects
- Sputtering efficiency
- Energy of sputtered atoms
- Other energetic particles: backscattered ions and negative oxygen ions

### 1.5 Transport in the gas phase

- Thermalization
- Deposition rate calculation

### 1.6 Sputtering systems

- Magnetron sputtering
- Reactive sputtering

### 1.7 HIPIMS

- Source of metal ions
- Time separation between gas and metal ions
- High energy ions
- Lower deposition rates
- Bipolar HIPIMS
- Control of doubly charged ions

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## Elements of Kinetic Theory of Gases

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For gas phase transport we need some basic formulas from the **kinetic theory of gases**

Mean free path       $\lambda = \frac{1}{\sqrt{2} n \sigma}$

Gas density       $n = \frac{p}{kT}$

Average velocity       $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$

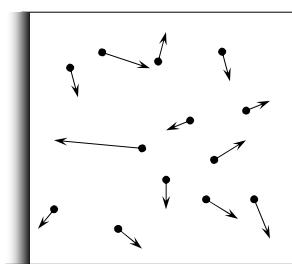
Impinging gas flux on the walls       $J_g = \frac{n\bar{v}}{4} = \frac{p}{\sqrt{2\pi m kT}}$

Modifications of these expressions are used in plasma physics

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## Kinetic theory of gases

provides microscopic picture of gas laws



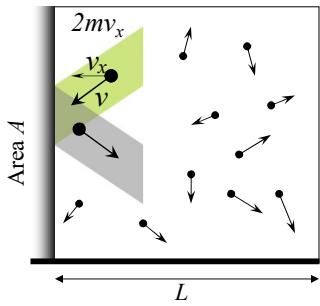
### Assumptions:

- A gas consists of a large number of molecules;
- separations are large compared to molecule size
- Molecules move randomly with a distribution in velocities which remains constant
- Molecules obey Newton laws of motion.
- Elastic collisions between the molecules and between molecules and the walls; no forces otherwise.

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## Pressure of gas molecules



$$n = \frac{N}{V}$$

$p = F/A$  units [N/m<sup>2</sup>] or [Pa]

Momentum change in one collision –  $\Delta p = 2 m v_x$

Time between collisions –  $\Delta t = 2L/v_x$

Force by one molecule –  $\Delta p/\Delta t = m v_x^2/L$

Force by N molecules –  $N m v_x^2/L$

Pressure –  $p = N m v_x^2/L A = n m v_x^2$

However, the average kinetic energy in x

$$E = \frac{1}{2} m v_x^2 = \frac{1}{2} kT$$

$$p = n k T$$

Ideal gas laws:

Boyle:  $p \sim 1/V$

Charles:  $V \sim T$

Gay-Lussac:  $p \sim T$

$N$  - number of molecules

$V$  - volume (=  $L \times A$ )

$p$  - pressure

$T$  - absolute temperature

$m, v$  - mass and velocity of molecules

$k$  - Boltzmann constant =  $1.38 \cdot 10^{-23}$  [J/K]

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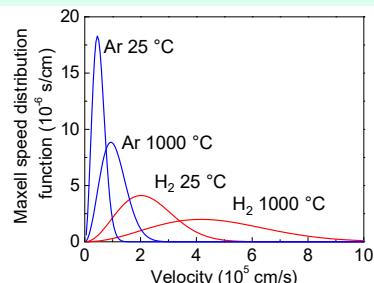
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## Velocity and energy distribution of gas molecules

### Maxwell-Boltzmann distribution

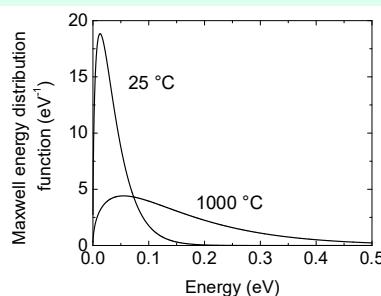
#### Velocity

$$f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp(-\frac{m}{2kT}v^2) v^2$$



#### Energy

$$f(e) = 2\pi \left( \frac{1}{\pi kT} \right)^{\frac{3}{2}} \exp(-\frac{e}{kT}) \sqrt{e}$$



**average**

$$v_{av} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{kT}{m}}$$

**root-mean-square**

$$v_{rms} = \sqrt{3} \sqrt{\frac{kT}{m}}$$

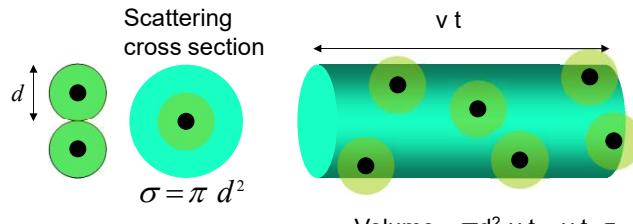
**most probable**

$$v_p = \sqrt{2} \sqrt{\frac{kT}{m}}$$

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## Collisions and mean free path



$$\text{Mean free path} \gg \frac{\text{travelling distance}}{\text{number of collisions}} = \frac{v t}{n \pi d^2 v t} = \frac{1}{n \sigma}$$

More accurate expression:  
 (with relative motion of all gas molecules)  $l = \frac{1}{\sqrt{2} n \sigma}$

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## Some useful formulas from kinetic theory of gases

Mean free path  $\lambda = \frac{1}{\sqrt{2} n \sigma}$

Gas density  $n = \frac{p}{kT}$

Average velocity  $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$

Impinging gas flux on the walls  $J_g = \frac{n\bar{v}}{4} = \frac{p}{\sqrt{2\pi mkT}}$

Deposition flux  
 growth rate R [cm/s]  
 films density  $n_{dep}$  [at/cm³]  $J_{dep} = R n_{dep}$

Note: from the bottom two expressions one can calculate the expected contamination of the films due to residual gases from the background pressure and the deposition rate  $J_g/J_{dep}$

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## Examples

	$\lambda$		$J$ ( $\text{cm}^{-2} \text{s}^{-1}$ )		$t_{\text{ML}}$
	25°C	1000°C	25°C	1000°C	25°C
1 atm ( $10^5$ Pa)	100 nm	400 nm	$2.4 \times 10^{23}$	$1.2 \times 10^{23}$	4 ns
1 Torr (133 Pa)	70 $\mu\text{m}$	300 $\mu\text{m}$	$3.2 \times 10^{20}$	$1.6 \times 10^{20}$	3.0 $\mu\text{s}$
1 mTorr (0.133)	7 cm	30 cm	$3.2 \times 10^{17}$	$1.6 \times 10^{17}$	3.0 ms
$10^{-6}$ Torr	70 m	300 m	$3.2 \times 10^{14}$	$1.6 \times 10^{14}$	3.0 s
$10^{-11}$ Torr	7,000 km	30,000 km	$3.2 \times 10^9$	$1.6 \times 10^9$	84 hours

$\lambda$ : mean free path

$J$ : flux of the atoms on sample/walls

$t_{\text{ML}}$ : time to form a monolayer (ML) at sticking probability of 1

diameter of a gas atom  $\sim 3 \times 10^{-8}$  cm; area of a gas atom  $\sim 10^{-15}$   $\text{cm}^2$   
 one monolayer  $\sim 10^{15}$  atoms  $\text{cm}^{-2}$

For comparison: Ti growth with 1  $\mu\text{m}/\text{h}$        $J_{\text{Ti}} = 1.6 \times 10^{15}$  ( $\text{cm}^{-2} \text{s}^{-1}$ )

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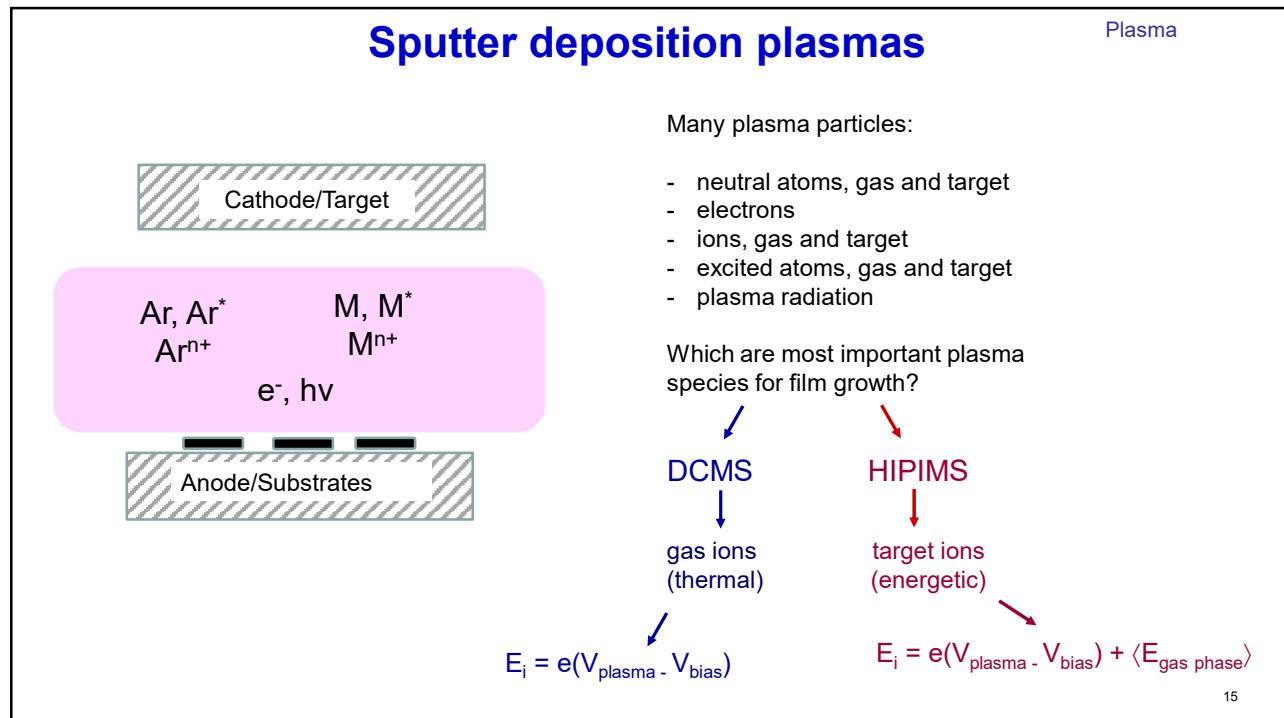
## Elements of Plasma Physics

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## Sputter deposition plasmas

Plasma

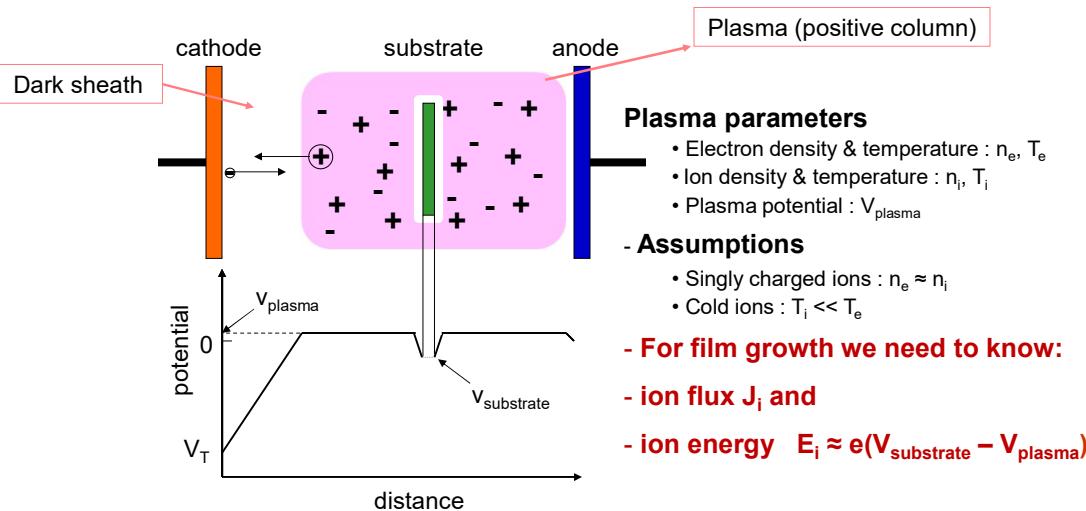


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## Plasma characterization by electrostatic probes

Plasma



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## Why is the dark sheath dark?

Because electron leave the cathode with energy well above the maximum of the excitation cross section

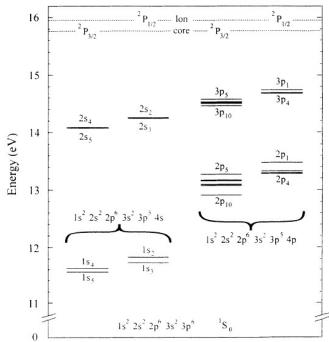


FIG. 1. Energy-level diagram of the argon atom. The Paschen notation ( $1s_2$ ,  $1s_1$ ,  $1s_4$ , and  $1s_3$ , and  $2p_1$ ,  $2p_2$ , ...,  $2p_{10}$ ) is used to label the energy levels associated with the  $1s^2 2s^2 2p^6 3s^2 3p^1 4s$  and the  $1s^2 2s^2 2p^6 3s^2 3p^1 4p$  configurations.

PHYSICAL REVIEW A

VOLUME 50, NUMBER 1

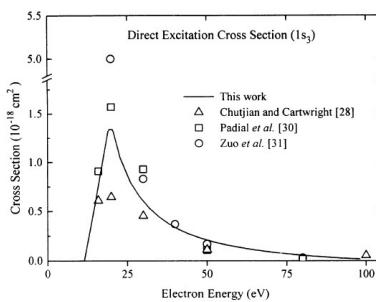
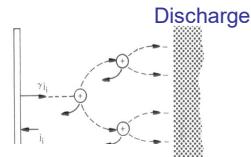


FIG. 13. Comparison of experimental and theoretical results for the energy dependence and magnitude of the direct excitation cross section for the  $1s_3$  ( $J=0$ ) metastable level.

JULY 1994

### Measurements of cross sections for electron-impact excitation into the metastable levels of argon and number densities of metastable argon atoms

R. Scott Schappe, M. Bruce Schulman,\* L. W. Anderson, and Chun C. Lin

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

(Received 20 December 1993)

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## Sheath width between the plasma and a negatively biased electrode (target or substrate)

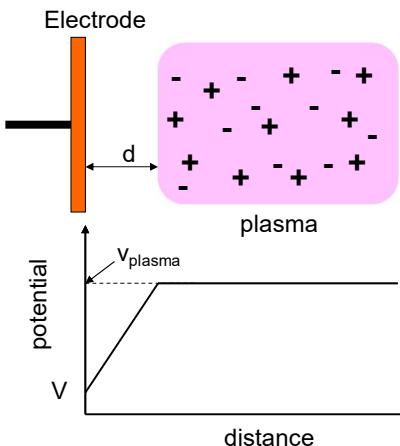
Child-Langmuir formula

$$d^2 = \frac{4\epsilon_0}{9} \left( \frac{2e}{m} \right)^{1/2} \frac{V^{3/2}}{j}$$

$V$  – bias voltage  
 $j$  – ion current density  
 $m$  – ion mass

$$\text{for } Ar^+ \longrightarrow d^2[m^2] = \frac{4 \times 8.854 \times 10^{-12}}{9} \left( \frac{2 \times 1.6 \times 10^{-19}}{40 \times 1.66 \times 10^{-27}} \right)^{1/2} \frac{V^{3/2}[V]}{j \left[ \frac{A}{m^2} \right]} = 8.64 \times 10^{-9} \frac{V^{3/2}}{j}$$

Plasma



$$\text{Mean free path } \lambda = \frac{1}{\sqrt{2} n \sigma}$$

We use this expression to compare the sheath width with the ion mean free path and evaluate the energy of the impinging ions on the electrode (target or substrate)

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### Plasma parameters

- Electron density & temperature :  $n_e, T_e$
- Ion density & temperature :  $n_i, T_i$
- Plasma potential :  $V_{\text{plasma}}$

#### - Assumptions

- Singly charged ions :  $n_e \sim n_i$
- Cold ions :  $T_i \ll T_e$

#### - For film growth we need ion flux $J_i$ and ion energy

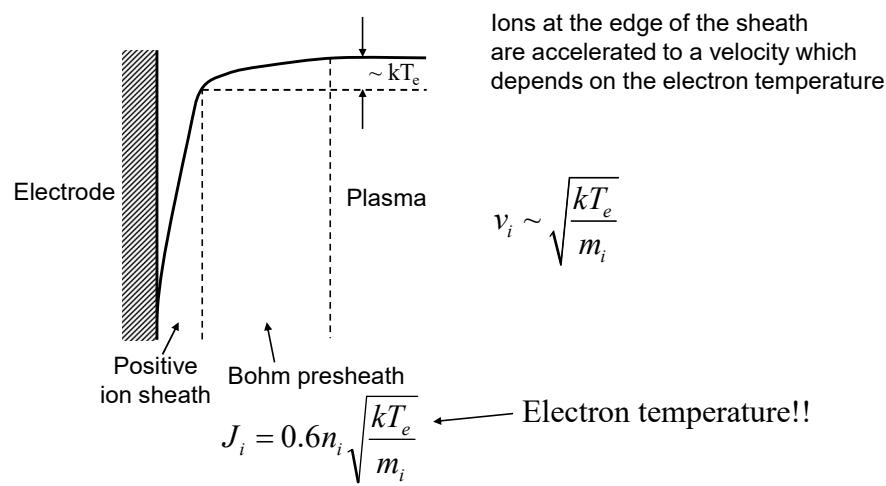
$$E_i \sim e(V_{\text{substrate}} - V_{\text{plasma}})$$

#### - Fluxes (in analogy with the kinetic theory of gases)

$$J_{i,e} = \frac{n_{i,e} \sqrt{v_{i,e}}}{4} = \frac{n_{i,e}}{4} \sqrt{\frac{8kT_{i,e}}{\pi m_{i,e}}} = 0.4n_{i,e} \sqrt{\frac{kT_{i,e}}{m_{i,e}}}$$

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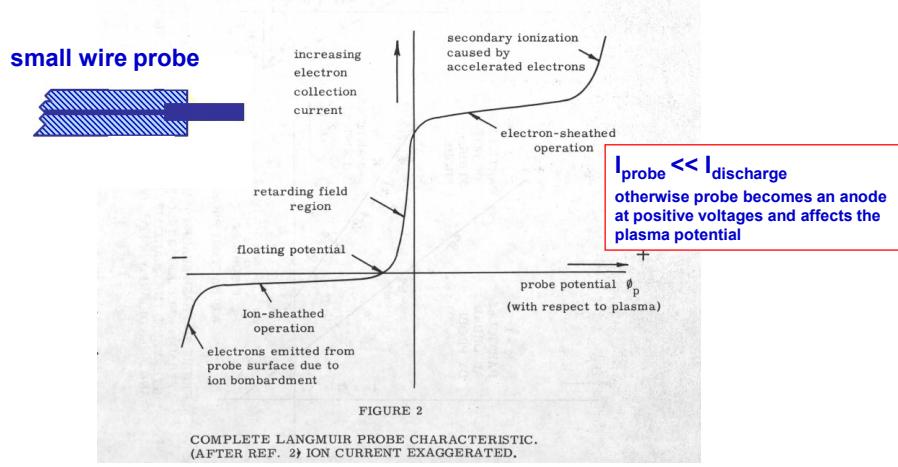
### Bohm presheath



Ion flux is a function of the electron temperature  $T_e$ , not  $T_i$

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## Langmuir Probe Characteristics

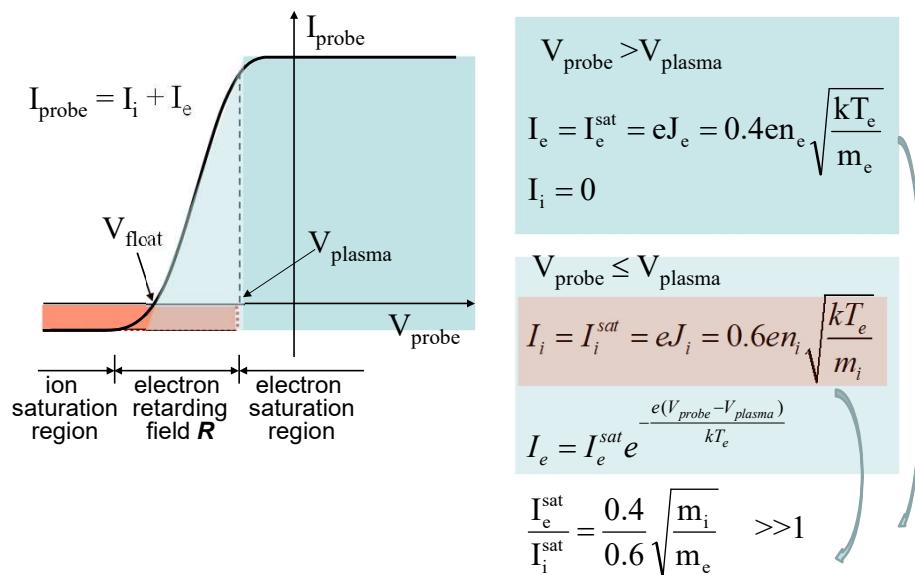


Laframboise, J.G.  
University of Toronto, Institute of Aerospace Studies, Report No 100

Available to download - Google it.

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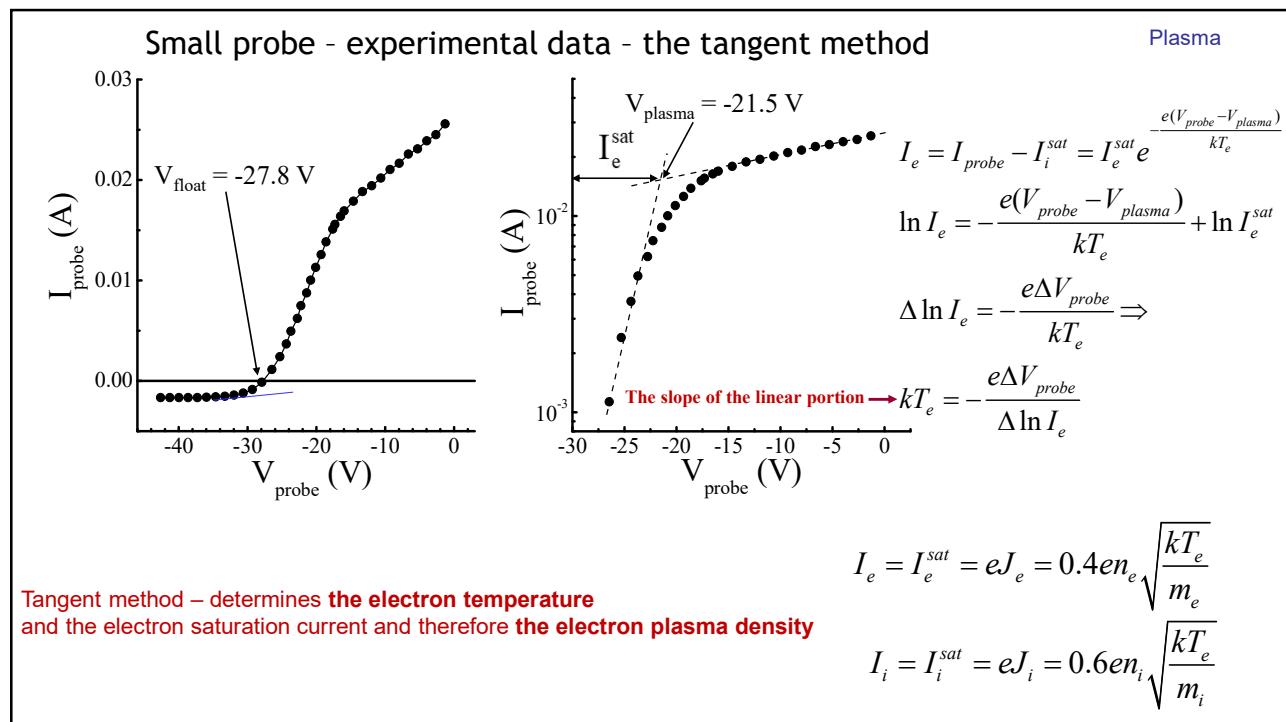
## Idealized Probe Characteristics



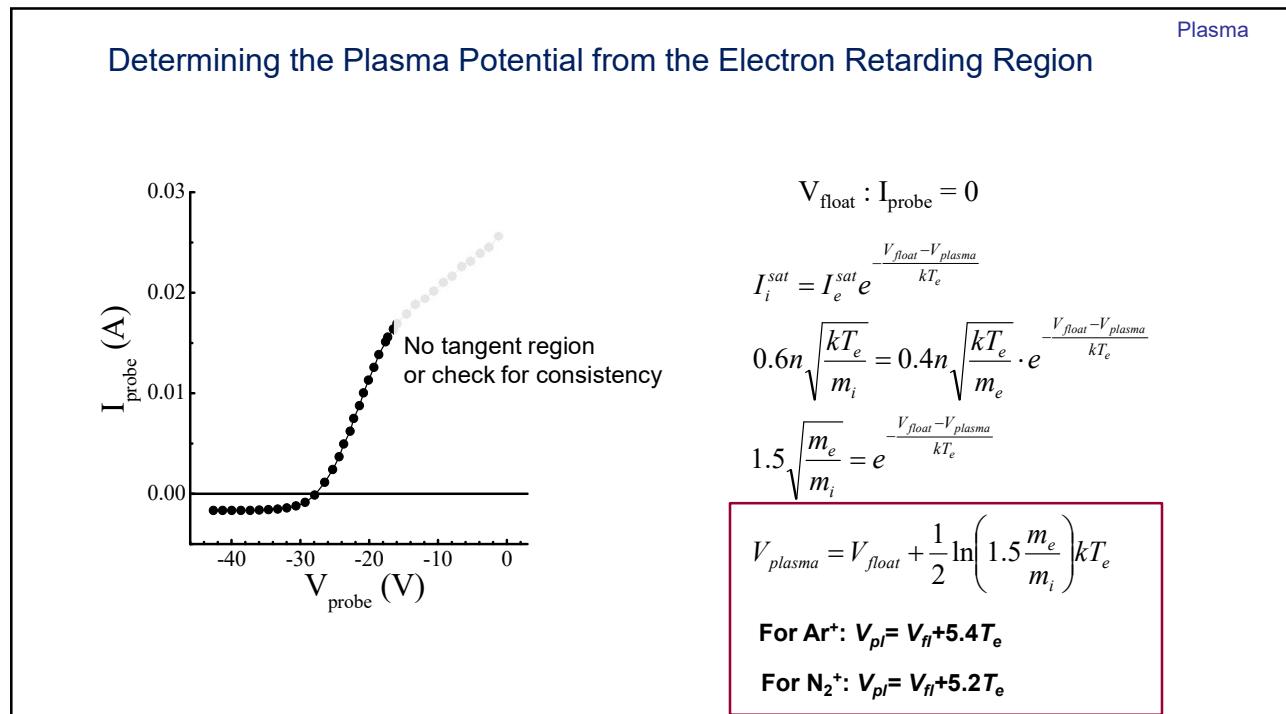
Electrons much lighter; for Ar<sup>+</sup> the ratio is ~ 200

NB; magnetic field affects the motion of the electrons and this ratio could be smaller

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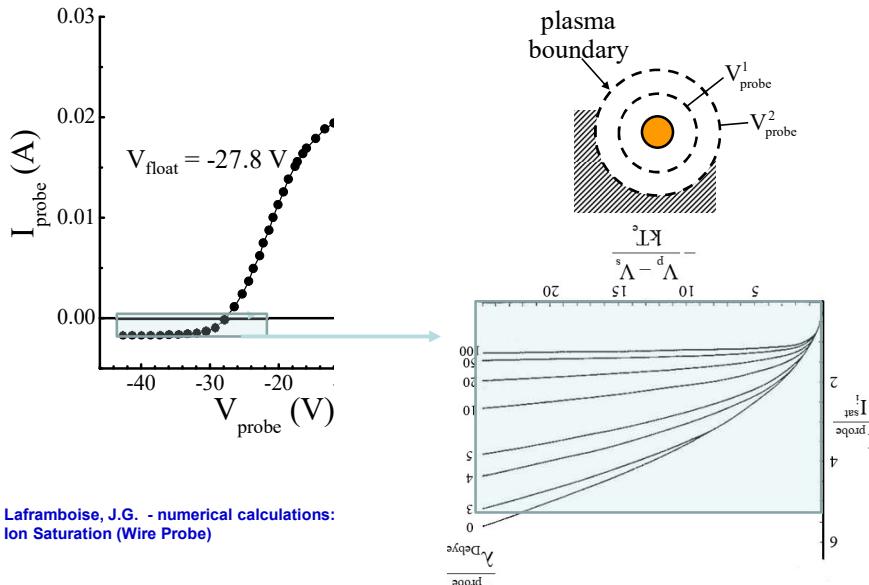


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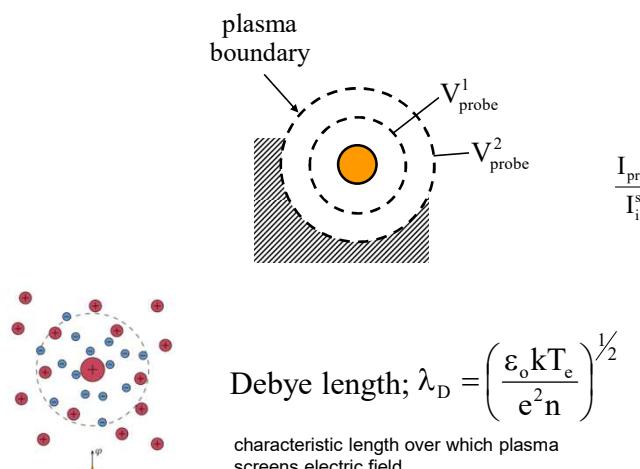
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**Small probe - experimental data**  
**The ion saturation region - how can we use it? difficult**

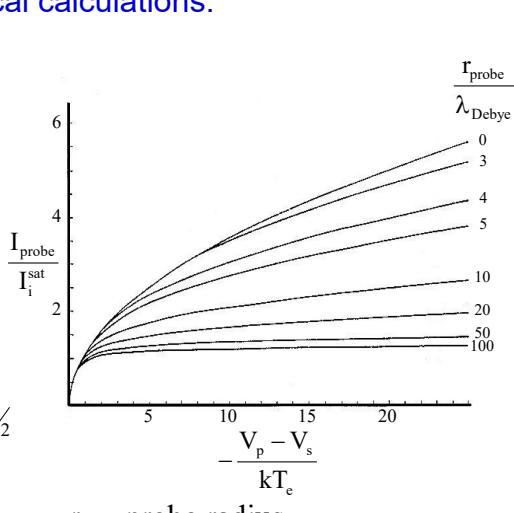


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**Laframboise, J.G. - numerical calculations:**  
**Ion Saturation (Wire Probe)**



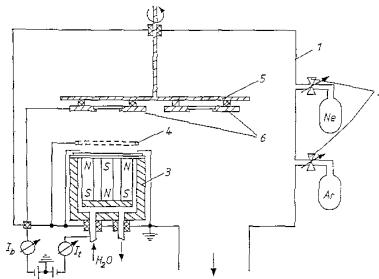
**$T_e, n_i, V_s$  needed - iterations**



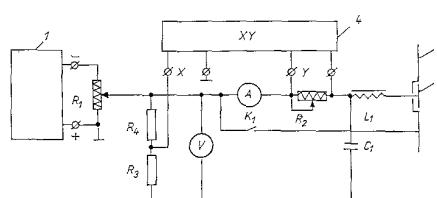
**Complicated procedure to determine ion fluxes from wire probe characteristics**

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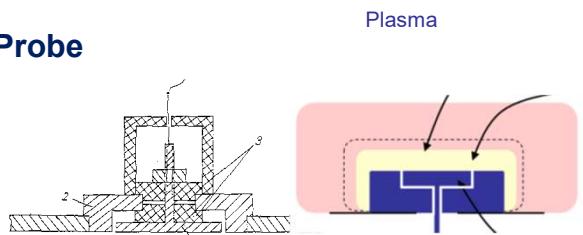
## Experimental Set-up for Flat Probe



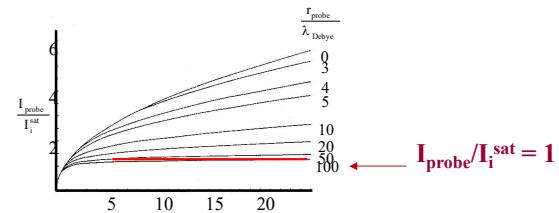
(a) Vacuum chamber with the magnetron assembly and the substrate holder



I. Petrov et al Contrib. Plasma Phys., 30 223 (1990).



(b) Electrostatic flat probe – embedded in the substrate holder at the same plane with minimal spacing ~ 1/4 mm



(c) Apply the same potential to the probe and the substrate holder

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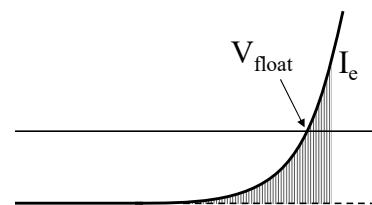
## Flat Probe, best to measure the ion saturation current

- Directly measure ion flux;  $I_{\text{probe}} = \frac{e J_{\text{ion}}^{\text{sat}}}{1 - \gamma}$

$\gamma$  : Secondary electron emission coefficient

$\gamma$  correction of the order ~ 10%

- Big probe
  - Electron saturation disturbs the plasma (**acts as an anode**).
  - Tangent method cannot be used.
  - Plasma potential and electron temperature can still be estimated

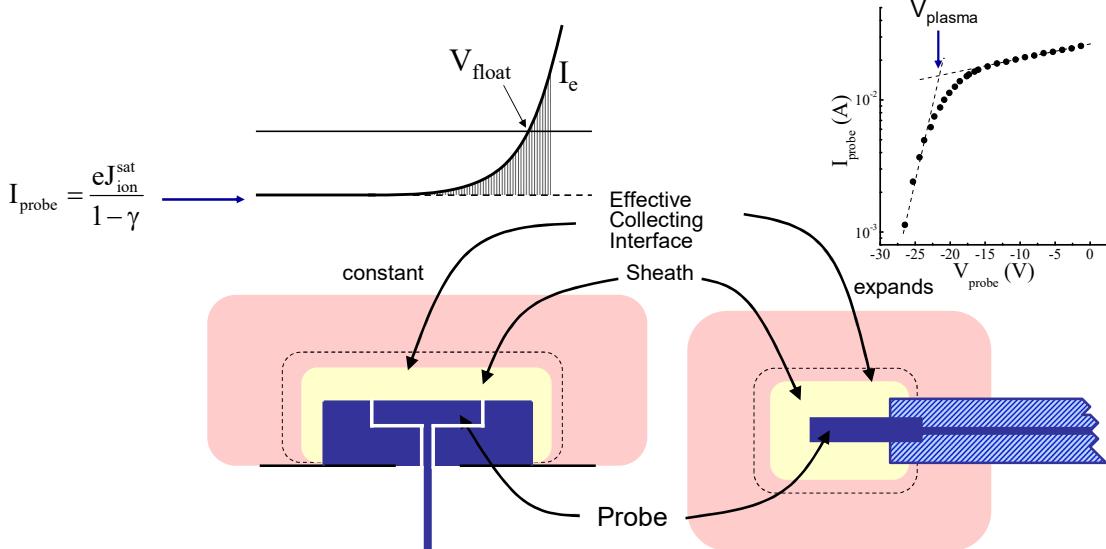


$T_e$  can be determined from the initial portion of the exponential rise of  $I_e$

$$V_{\text{plasma}} = V_{\text{float}} + \text{const. } T_e$$

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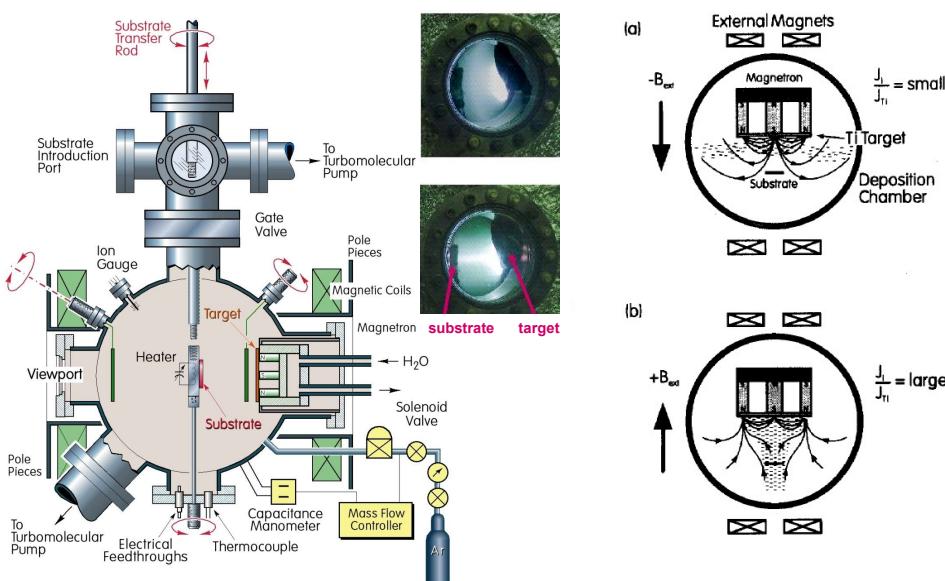
For film growth we need to know  
the ion flux  $J_i$  and ion energy  $E_i \approx e(V_{\text{substrate}} - V_{\text{plasma}})$



Best: a combination of a flat probe for  $J_i$  and a small probe for  $V_s$

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Example: plasma measurement in unbalanced magnetrons  
Ion current measured by flat probe, plasma potential by wire probe



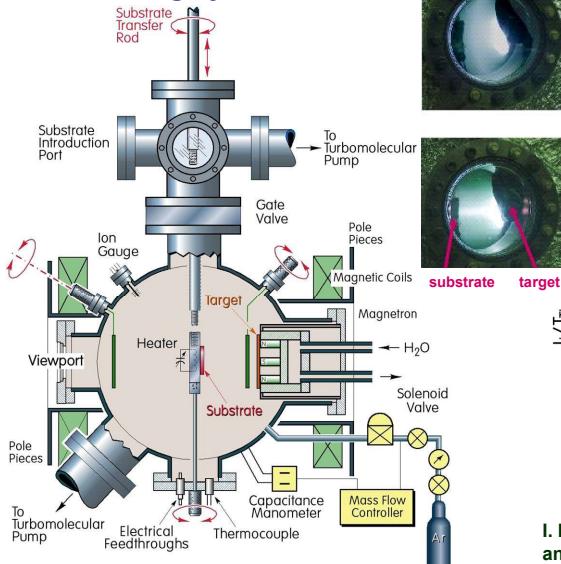
I. Petrov, F. Adibi, J.E. Greene, W.D. Sproul,  
and W.-D. Münz, JVST A10, 3283 (1992).

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**Example: plasma measurement in unbalanced magnetrons**  
Ion current measured by flat probe, plasma potential by wire probe

Plasma

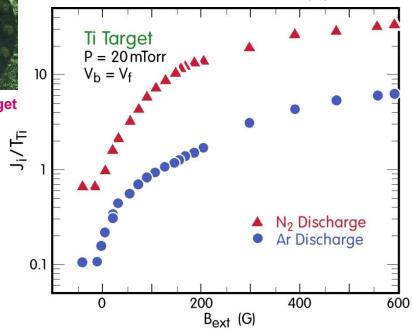
**Unbalancing by external coils**



$$E_i = e(V_{\text{plasma}} - V_{\text{bias}})$$

$$J_i = f(B_{\text{ext}})$$

$J_{Ti}$  remains approximately constant as a function of  $B_{\text{ext}}$ .



I. Petrov, F. Adibi, J.E. Greene, W.D. Sproul, and W.-D. Münz, JVSTA10, 3283 (1992).

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**Plasma potential and density in unbalanced magnetrons (type II)**  
depends on whether the substrate is grounded or not

Plasma

Floating or (-) bias

Grounded substrate

I. Petrov, F. Adibi, J.E. Greene, W.D. Sproul, and W.-D. Münz, JVSTA10, 3283 (1992).

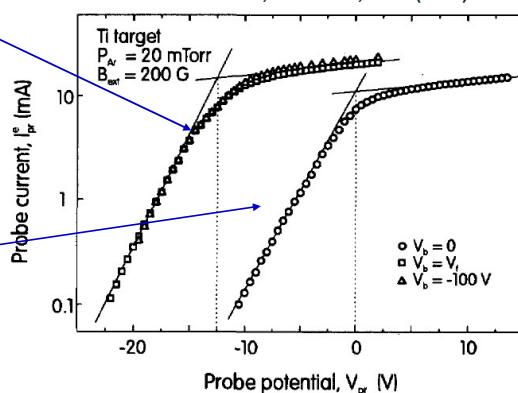


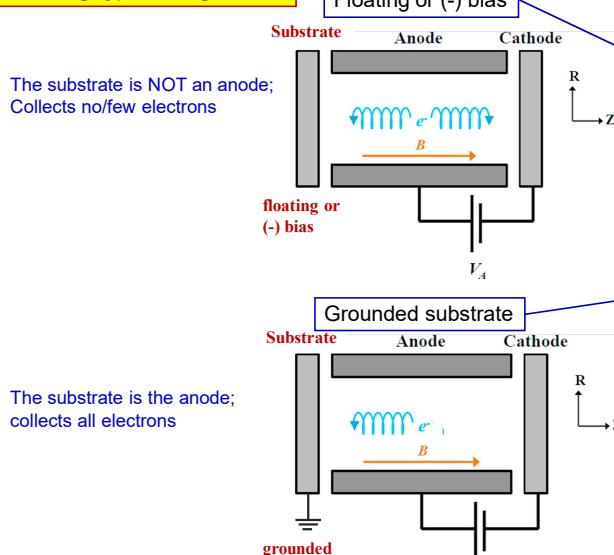
FIG. 7. Probe current  $I_{pr}^e$  due to electrons vs the applied probe potential  $V_{pr}$  during sputtering of Ti in a 20 mTorr Ar discharge with  $B_{\text{ext}} = 200$  G and the applied substrate bias  $V_b = 0$ ,  $V_f$ , and  $-100$  V. The plasma potential  $V_p$  (dotted lines) is 0 for  $V_b = 0$  and  $-12.5$  V for  $V_b = V_f$  and  $-100$  V.

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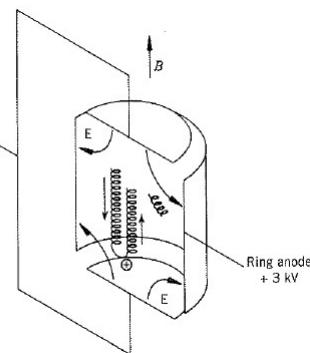
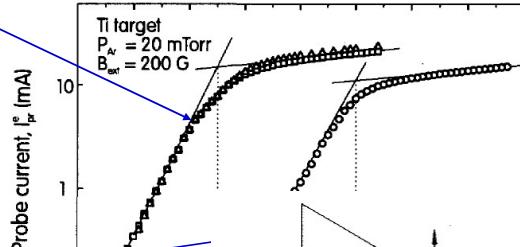
## Plasma potential and density in unbalanced magnetrons (type II) depends on whether the substrate is grounded or not

Plasma

### Penning-type configuration



I. Petrov, F. Adibi, J.E. Greene, W.D. Sproul, and W.-D. Münz, JVST A10, 3283 (1992).



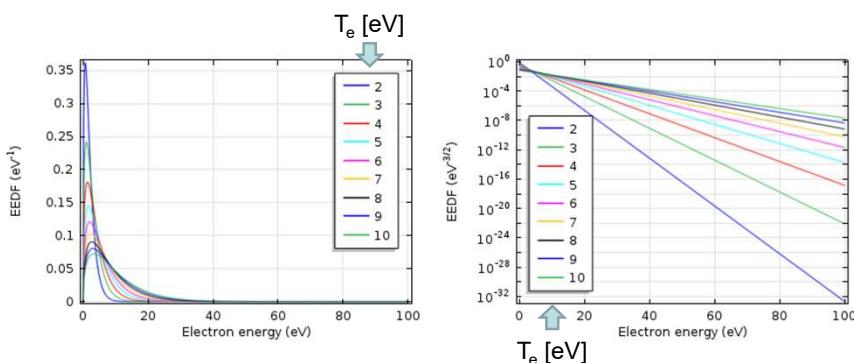
NB significant heating by electrons – measure substrate temperature rise

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## More on the Electron Energy Distribution Functions

Plasma

Maxwell electron energy distribution functions  
Elastic collision between electrons dominate



$$f(\epsilon) = \frac{2}{(kT)^{\frac{3}{2}}} \sqrt{\frac{\epsilon}{\pi}} \exp\left(-\frac{\epsilon}{kT}\right)$$

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## More on the Electron Energy Distribution Functions

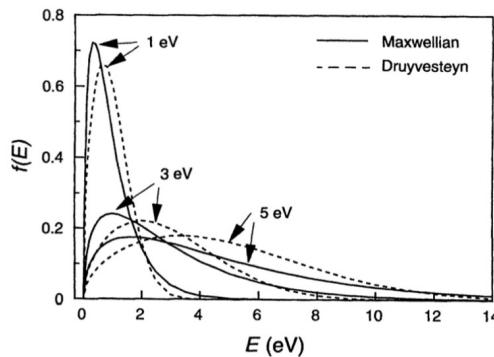
Plasma

**Druyvesteyn EEDF**  
Elastic collision between electrons and  
cold atoms included

$$f_D(\epsilon) = \frac{0.5648 n_e}{(kT)^{\frac{3}{2}}} \sqrt{\epsilon} \exp \left[ -0.243 \left( \frac{\epsilon}{kT} \right)^2 \right]$$

**Maxwell EEDF**  
Elastic collision between electrons dominate

$$f(\epsilon) = \frac{2}{(kT)^{\frac{3}{2}}} \sqrt{\frac{\epsilon}{\pi}} \exp \left( \frac{-\epsilon}{kT} \right)$$



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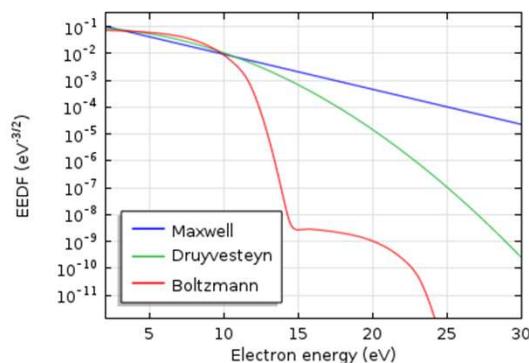
A. Grill, Cold Plasma Materials Fabrication: From Fundamentals to Applications. Wiley, 1994.

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## More on the Electron Energy Distribution Functions

Plasma

Boltzmann EEDF includes inelastic collisions



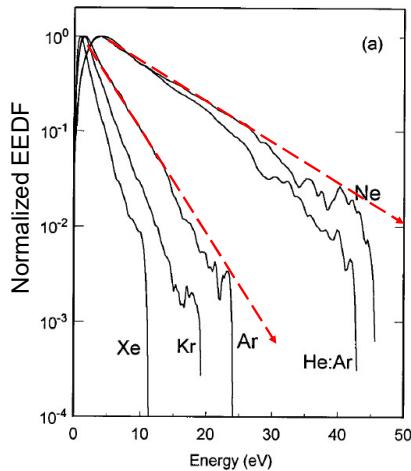
Computational example from:

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<https://www.comsol.com/>

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## Measured Electron Energy Distribution Functions

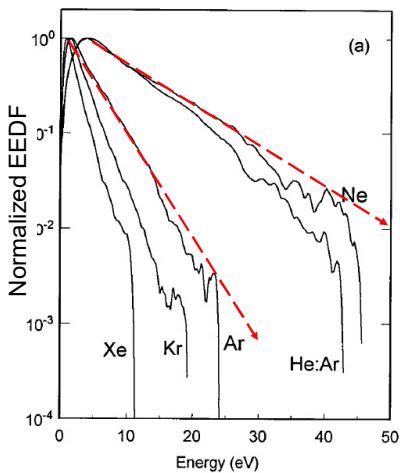


- The linear portion corresponds to Maxwell-like energy distribution
- Electron temperature  $T_e$  is the slope of the linear portion of the curve
- $T_e$  decreases as the ionization potential of the inert gas decreases
- In the area of inelastic collisions the high-energy tail is underpopulated
- extrapolation of the EEDF from the elastic energy range into the inelastic energy range may cause a significant error in the calculation of excitation and ionization rates
- Metal dominated plasmas in HIPIMS lack high energy electron needed to ionize the inert gas.**

37  
A. Schwabedissen et al Physical review E, 55 (1997) 3450

37

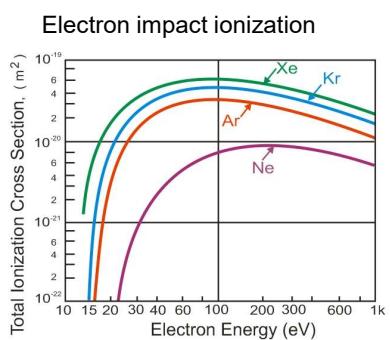
## Measured Electron Energy Distribution Functions



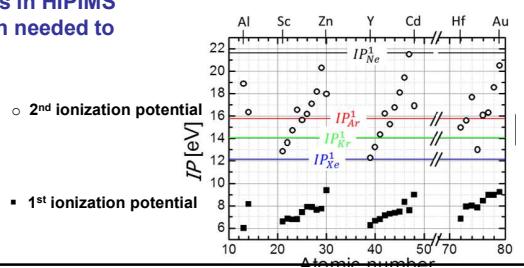
- The linear portion corresponds to Maxwell-like energy distribution
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- In the area of inelastic collisions the high-energy tail is underpopulated
- extrapolation of the EEDF from the elastic energy range into the inelastic energy range may cause a significant error in the calculation of excitation and ionization rates
- Metal dominated plasmas in HIPIMS lack high energy electron needed to ionize the inert gas.**

38

A. Schwabedissen et al Physical review E, 55 (1997) 3450



## Ionization potentials



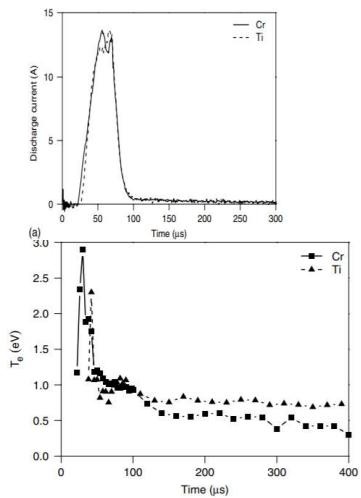
38

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## Cooling of the electrons in metal-rich phase of HIPIMS discharges

Plasma

Alena Vetuska and Arutun P Ehiasarjan  
J. Phys. D: Appl. Phys. 41 (2008) 015204



P Poolcharuansin and J W Bradley  
Plasma Sources Sci. Technol. 19 (2010) 025010

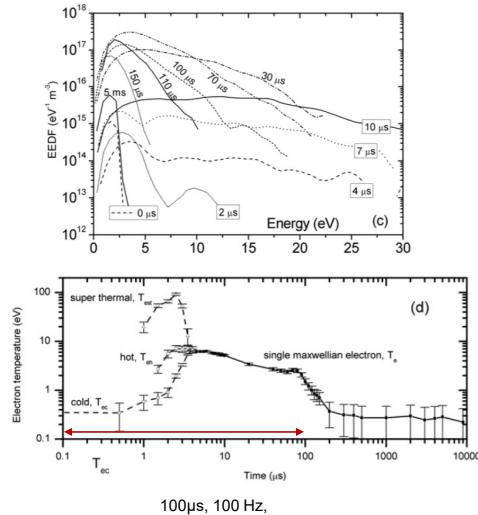


Figure 6. Effective electron temperature as a function of time for Cr and Ti targets at a pressure of 0.28 Pa.

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## Plasmas: practical example

Plasma

$$d^2[cm] = 8.64 \times 10^{-6} \frac{V^{3/2}[V]}{j \left[ \frac{mA}{cm^2} \right]}$$

$$\lambda_{CE} = \frac{kT}{p[Pa]\sigma[m^2]\sqrt{2}} \quad \sigma_{CE}^{Ar} = 4 \times 10^{-19} [m^2]$$

Cross-section for charge exchange collisions for Ar

Sputtering system		Voltage	Current density	Sheath width	$\lambda_{Ar}$
Diode $p_{Ar} = 70$ mTorr	target	3000 V	$1 \text{ mA cm}^{-2}$	12 mm	0.7 mm
	substrate	100 V	$0.1 \text{ mA cm}^{-2}$	3 mm	0.7 mm
magnetron $p_{Ar} = 3$ mTorr	target	500 V	$50 \text{ mA cm}^{-2}$	0.5 mm	16 mm
	substrate	100 V	$1 \text{ mA cm}^{-2}$	0.9 mm	16 mm

For magnetron sputtering  $\lambda_{Ar} >$  sheath width  $\rightarrow E_i \approx e(V_{\text{electrode}} - V_{\text{plasma}})$

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## Cold Cathode Discharge

### Ion surface interactions

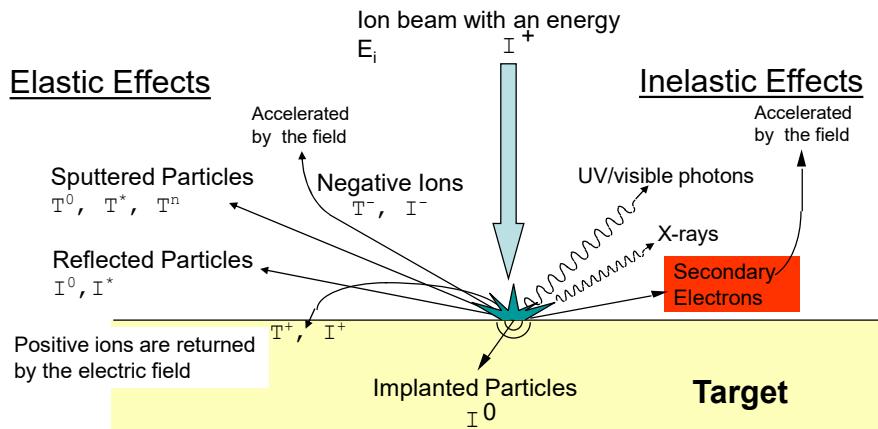


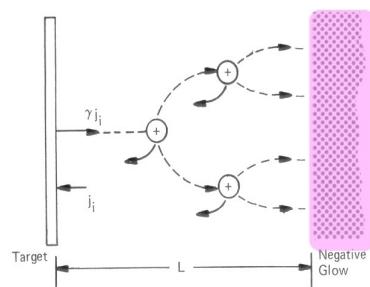
Figure after G.M. McCracken, Rep. Prog. Phys. **28**, 241 (1975).

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### Glow Discharge Voltage

Discharge



On the average, a secondary electron emitted from the cathode must acquire energy sufficient to produce a number of ions to release one further electron from the cathode.

$$\gamma_i \frac{V_T}{E_o} = 1$$

$$V_T = \frac{1}{E_o \gamma_i \epsilon_i \epsilon_e}$$

$E_o$  – the average energy to produce an ion (for Ar ~ 30 eV)

$\gamma_i$  – the secondary ion-electron yield (for Ar ~ 0.1)

$\epsilon_i$  – ion collection efficiency (fraction of created ions that strike the target)

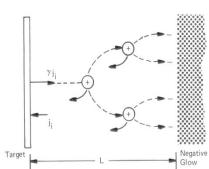
$\epsilon_e$  – fraction of the secondary electrons participating in ionization

$\epsilon_i \epsilon_e$  – characterizes the effectiveness of the ionization system; for magnetrons ~ 1

John A. Thornton and Alan S. Penfold, in *Thin Film Processes*, Ed. by John L. Vossen and Werner Kern (Academic Press, New York, 1978) p. 86.

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## Glow Discharge Maintenance



**Ionization potentials**  
 Ne - 21.56 eV  
 Ar - 15.76 eV  
 Kr - 14.00 eV  
 Xe - 12.13 eV

$$V_T = \frac{1}{E_0 \gamma_i \epsilon_i \epsilon_e}$$

### Electron impact ionization

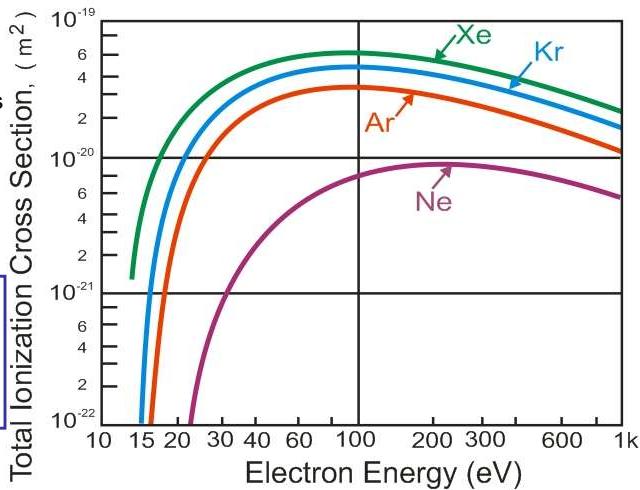
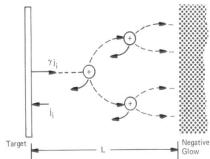


Figure after John A. Thornton and Alan S. Penfold, in *Thin Film Processes*, Ed. by John L. Vossen and Werner Kern (Academic Press, New York, 1978) p. 84.

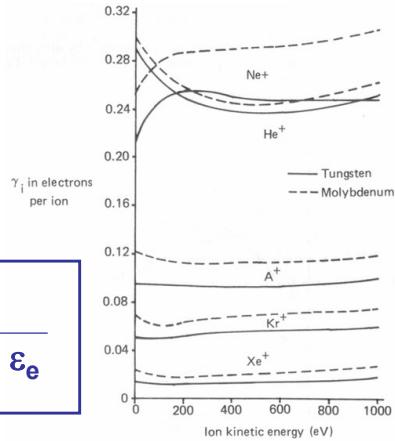
43

## Discharge

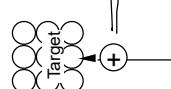
### Secondary ion-electron yield $\gamma_i$



$\gamma_i$  in electrons per ion

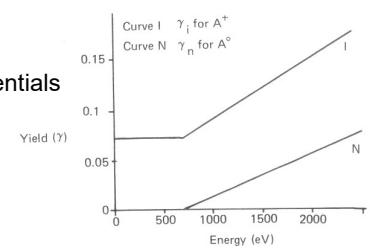


< 1 kV, electrons emitted from the conduction band of the target due to the potential energy of the ion



**Ionization potentials**

Ne - 21.56 eV  
 Ar - 15.76 eV  
 Kr - 14.00 eV  
 Xe - 12.13 eV



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R.A. BARAGIOLA, E.V. ALONSO, J. FERRON and A. OLIVA-FLORIO  
 Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, Instituto Balseiro,  
 Un

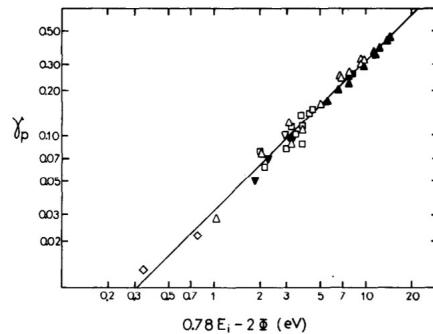
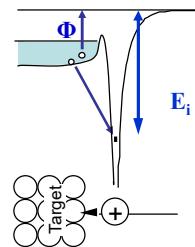


Fig. 1. PEE yields  $\gamma_p$  versus  $0.78E_i - 2\Phi$ ; ( $\diamond, \triangle$ ) Arifov [6] for  $\text{Ne}^+$  and  $\text{Ar}^+$  ions respectively; ( $\bullet, \nabla, \circ, \blacksquare$ ) Hagstrum [7] for  $\text{He}^+$ ,  $\text{Ne}^+$ ,  $\text{Ar}^+$ ,  $\text{Kr}^+$  and  $\text{Xe}^+$  ions respectively; ( $\square$ ) Oechsner [9] for  $\text{Ar}^+$  ions. The line is a least-square fit.



$$V_T = \frac{E_o}{\gamma_i \epsilon_i \epsilon_e}$$

Note on reactive sputtering

$$\gamma = 0.032(0.78E_i - 2\Phi) \longrightarrow \text{Note: potential electron emission possible for } E_i > 2.56 \Phi$$

$\gamma$  – secondary ion-electron emission coefficient  
 $E_i$  – ionization potential of the ion  
 $\Phi$  – workfunction of the material

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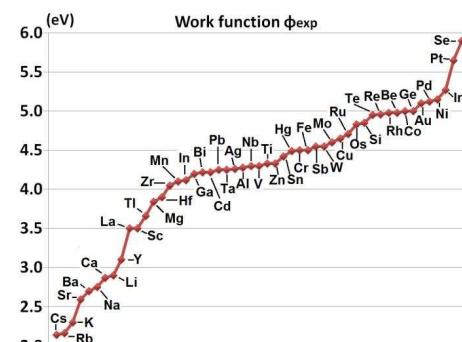
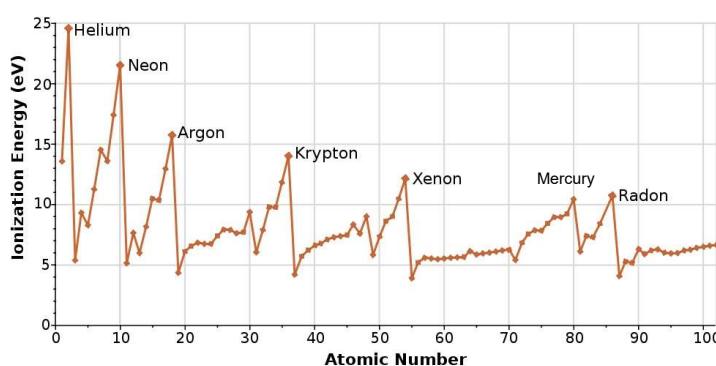
Note: potential electron emission possible for  $E_i > 2.56 \Phi$

### For most metal ions $E_i < 2.56 \Phi$

Sputtering discharges in pure metal plasmas (with singly charged ions) generally not possible

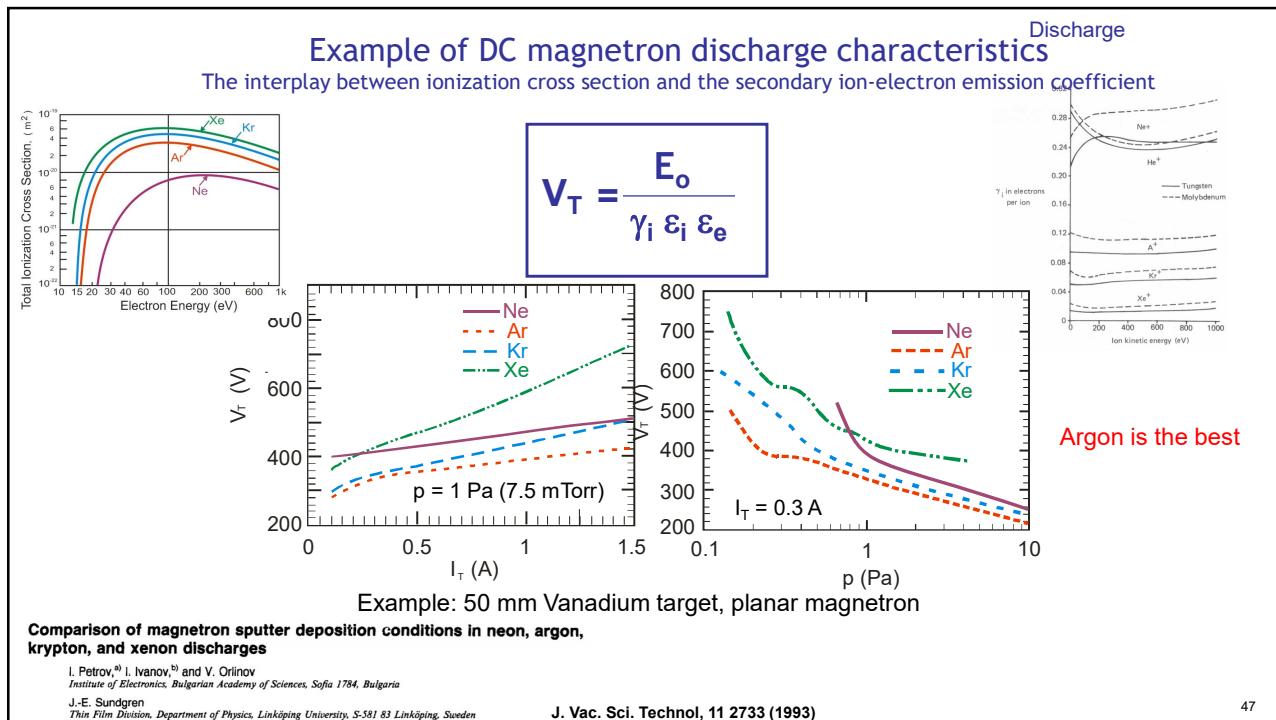
Reported for Cu under special conditions

Inter gas recycling in HiPIMS during the metal ion dominated phase



Eborg et al  
 DOI: 10.1109/HONET.2012.6421444

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## Ion surface interactions

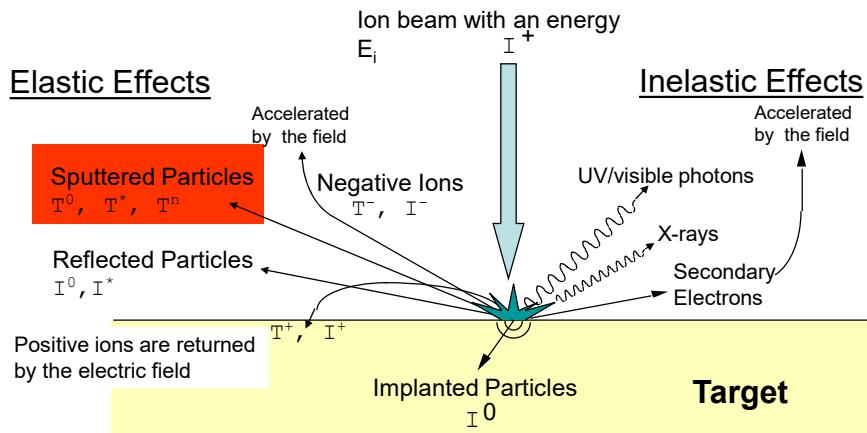
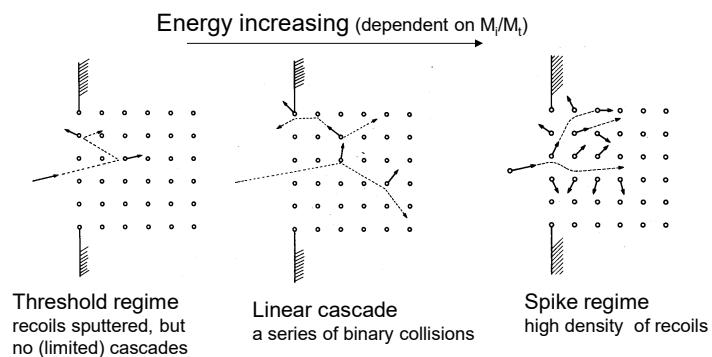


Figure after G.M. McCracken, Rep. Prog Phys. **28**, 241 (1975).

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## Collision Cascade



- Ions striking a surface interact with a number of atoms in a series collisions.
- recoiled target atoms in turn collide with atom at rest generating a collision cascade.
- The initial ion energy and momentum are distributed to among the target recoil atoms.
- When  $E_i > 1$  keV, the cascade is “linear”, i.e. approximated by a series of binary collisions in a stationary matrix.

P.Sigmund, “Sputtering by ion bombardment: theoretical concepts”, in *Sputtering by particle bombardment*, edited by R. Behrisch, Springer-Verlag, 1981

50

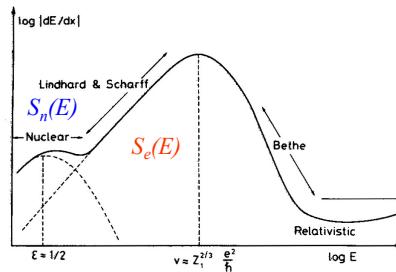
50

## Stopping cross section

$$\frac{dE}{dx} = -NS(E) = -N[S_n(E) + S_e(E)]$$

$S_n(E)$  - nuclear stopping  
 $S_e(E)$  - electronic stopping

$$Range = \int_0^E \frac{dE'}{NS(E')}$$



P.Sigmund, "Sputtering by ion bombardment: theoretical concepts", in *Sputtering by particle bombardment I*, edited by R. Behrisch, Springer-Verlag, 1981

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## Stopping cross section

$$\frac{dE}{dx} = -NS(E) = -N[S_n(E) + S_e(E)]$$

$$Range = \int_0^E \frac{dE'}{NS(E')}$$

**Sputter Deposition (keV)**  
nuclear stopping dominates

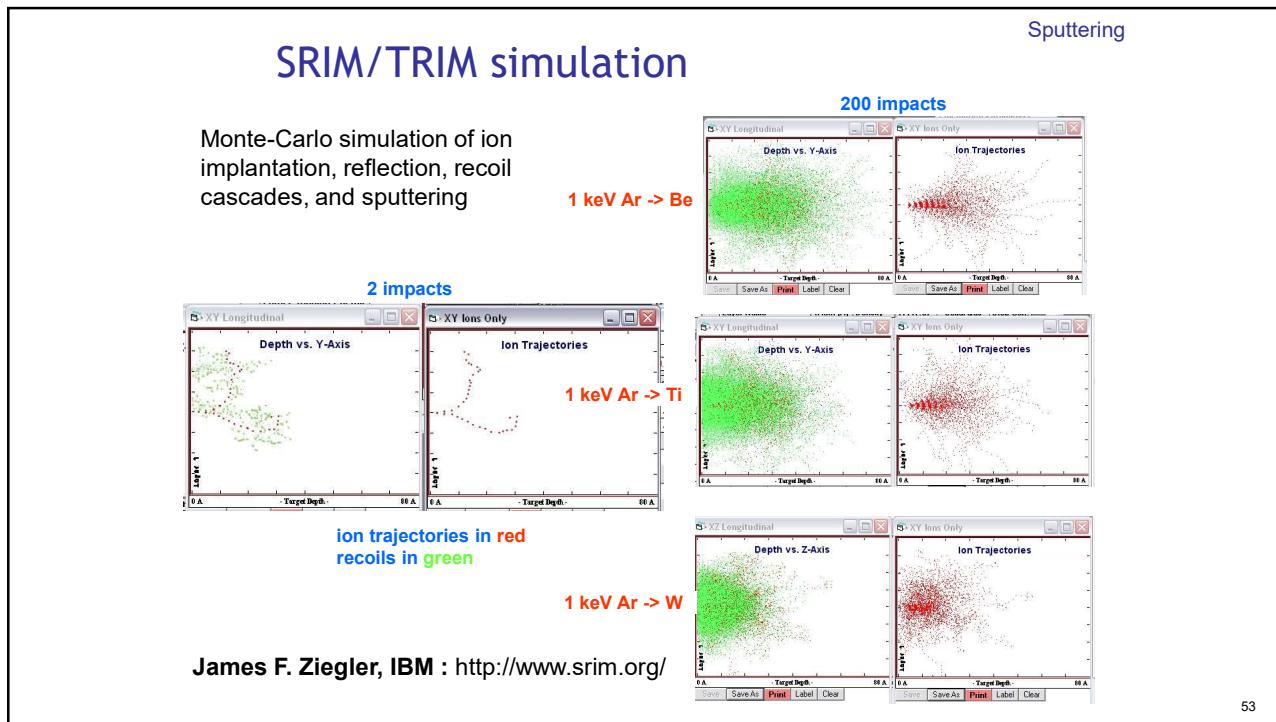
RBS,ERDA,NRA (MeV)  
electronic stopping dominates

**Ion Implantation (tens keV)**  
mixed

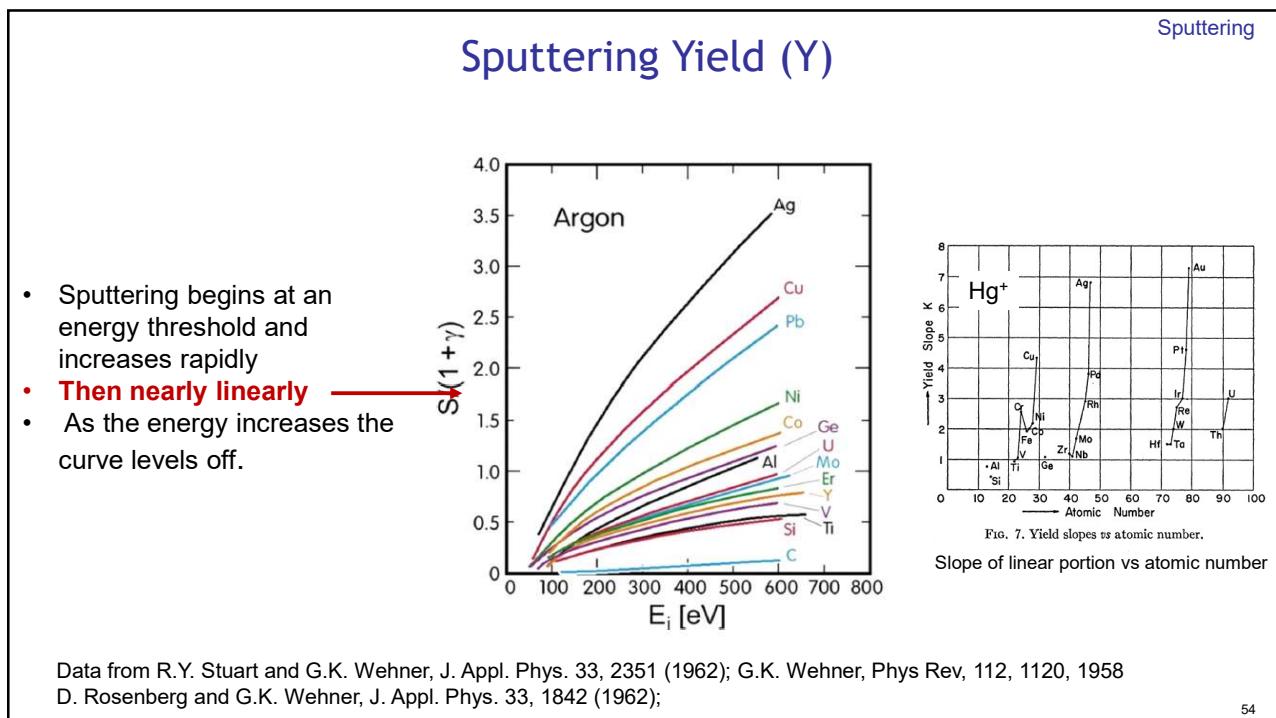
P.Sigmund, "Sputtering by ion bombardment: theoretical concepts", in *Sputtering by particle bombardment I*, edited by R. Behrisch, Springer-Verlag, 1981

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## Sputtering Yields at Very Low Bombarding Ion Energies\*



Gottfried Karl Wehner  
23 September 1910 (Dresden)  
13 June 1996 (Munich)

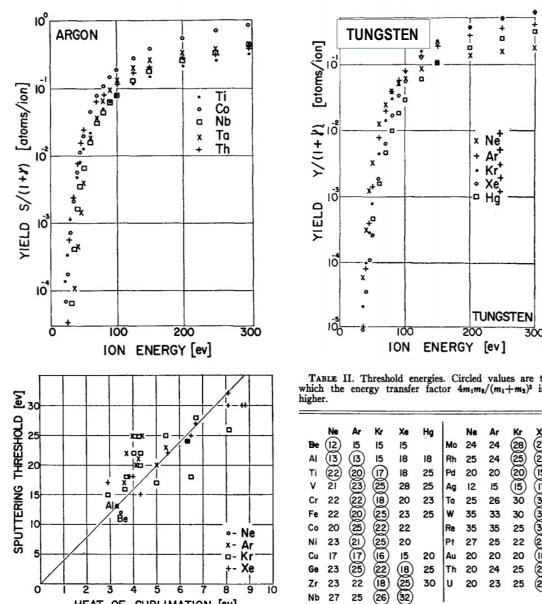


Fig. 13. Thresholds vs heats of sublimation.

TABLE II. Threshold energies. Circled values are those for which the energy transfer factor  $4m_1m_2/(m_1+m_2)^2$  is 0.9 or higher.

Ne	Ar	Kr	Xe	Hg	Ne	Ar	Kr	Xe	Hg
Be (12)	15	15	15	15	Mo 24	24	(27)	32	
Al (13)	15	18	18	18	Rh 25	24	(25)	(25)	
Ti (22)	20	(17)	18	18	Pd 20	20	(20)	(15)	20
V 21	(23)	(25)	28	25	Aq 12	15	(5)	(17)	
Cr 22	(22)	(18)	20	23	Tc 25	26	30	(30)	30
Fe 22	(20)	(25)	23	25	W 35	33	30	(30)	30
Co 20	(25)	(22)	22		Re 35	35	25	(30)	35
Ni 23	(21)	(25)	20		Pt 27	25	22	(22)	25
Cu 17	(17)	(6)	15	20	Au 20	20	20	(18)	
Ge 23	(25)	(22)	(18)	25	Th 20	24	25	(25)	
Zr 23	22	(18)	30		U 20	23	25	(22)	27
Nb 27	25	(26)	(32)						

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Sputtering Yields of Metals for Ar<sup>+</sup> and Ne<sup>+</sup> Ions with Energies from 50 to 600 ev\*†

To this day:  
the most comprehensive set of  
low-energy sputtering yields data

NILS LAEGREID AND G. K. WEHNER  
Mechanical Division of General Mills, Incorporated, Minneapolis, Minnesota  
(August 24, 1960)

Sputtering yields for polycrystalline metal and semiconductor targets under normally incident Ar<sup>+</sup> and Ne<sup>+</sup> ion bombardment were measured in the energy range from 50 to 600 ev. The yields (atoms/ion) were determined by measuring the weight loss of spherical targets immersed like large negative Langmuir probes. TABLE I. Sputtering yields for 28 elements under Ne<sup>+</sup> and Ar<sup>+</sup> ion bombardment.

Target	Neon				Argon					
	100 (ev)	200 (ev)	300 (ev)	600 (ev)	Yield at lowest ion energy Y	E (ev)	100 (ev)	200 (ev)		
Be	0.012	0.10	0.26	0.56	0.05	80	0.074	0.18	0.29	0.80
Al	0.031	0.24	0.43	0.83	0.11	100	0.11	0.35	0.65	1.24
Si	0.034	0.13	0.25	0.54	0.06	80	0.07	0.18	0.31	0.53
Ti	0.08	0.22	0.30	0.45	0.081	100	0.081	0.22	0.33	0.58
V	0.06	0.17	0.36	0.55	0.03	60	0.11	0.31	0.41	0.70
Cr	0.18	0.49	0.73	1.05	0.026	40	0.30	0.67	0.87	1.30
Fe	0.18	0.38	0.62	0.97	0.064	60	0.20	0.53	0.76	1.26
Co	0.084	0.41	0.64	0.99	0.048	60	0.15	0.57	0.81	1.36
Ni	0.22	0.46	0.65	1.34	0.067	60	0.28	0.66	0.95	1.52
Cu	0.26	0.84	1.20	2.00	0.10	60	0.48	1.10	1.59	2.30
Ge	0.12	0.32	0.48	0.82	0.017	30	0.22	0.50	0.74	1.22
Zr	0.054	0.17	0.27	0.42	0.027	60	0.12	0.28	0.41	0.75
Nb	0.051	0.16	0.23	0.42	0.017	60	0.068	0.25	0.40	0.65
Mo	0.10	0.24	0.34	0.54	0.027	60	0.13	0.40	0.58	0.93
Ru	0.078	0.26	0.38	0.67	0.012	60	0.14	0.41	0.68	1.30
Rh	0.081	0.36	0.52	0.77	0.19	100	0.19	0.55	0.86	1.46
Pd	0.14	0.59	0.82	1.32	0.033	50	0.42	1.00	1.41	2.39
Ag	0.27	1.00	1.30	1.98	0.22	60	0.63	1.58	2.20	3.40
Hf	0.057	0.15	0.22	0.39	0.004	40	0.16	0.35	0.48	0.83
Ta	0.056	0.13	0.18	0.30	0.01	60	0.10	0.28	0.41	0.62
W	0.038	0.13	0.18	0.32	0.008	60	0.068	0.29	0.40	0.62
Re	0.04	0.15	0.24	0.42	0.034	80	0.10	0.37	0.56	0.91
Os	0.032	0.16	0.24	0.41	0.057	100	0.057	0.36	0.56	0.95
Ir	0.069	0.21	0.30	0.46	0.019	60	0.12	0.43	0.70	1.17
Pt	0.12	0.31	0.44	0.70	0.032	60	0.20	0.63	0.95	1.56
Au	0.20	0.56	0.84	1.18	0.035	50	0.32	1.07	1.65	2.43 (500)
Th	0.028	0.11	0.17	0.36	0.017	60	0.097	0.27	0.42	0.66
U	0.063	0.20	0.30	0.52	0.14	100	0.14	0.35	0.59	0.97

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Sputtering

JOURNAL OF APPLIED PHYSICS      VOLUME 33, NUMBER 5      MAY, 1962

**Sputtering Yields for Low Energy He<sup>+</sup>-, Kr<sup>+</sup>-, and Xe<sup>+</sup>-Ion Bombardment\***

D. ROSENBERG AND G. K. WEINER  
The General Mills Electronics Group, Minneapolis, Minnesota  
(Received November 2, 1961)

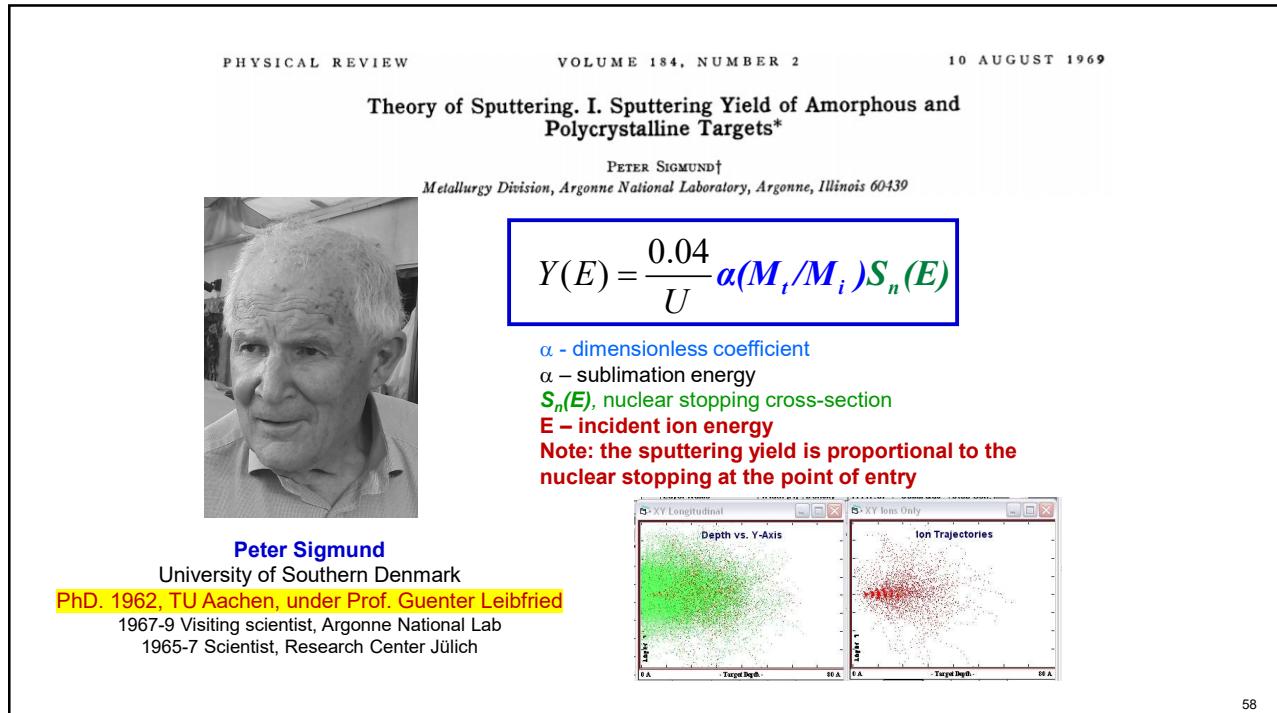
To this day:  
the most comprehensive set of  
low-energy sputtering yields data

TABLE I. Sputtering yields for 30 elements under He<sup>+</sup>-, Kr<sup>+</sup>-, and Xe<sup>+</sup>-ion bombardment. Numbers in brackets are doubtful due to surface layers.

Target	Helium			Krypton			Xenon					
	100 (ev)	200 (ev)	300 (ev)	600 (ev)	100 (ev)	200 (ev)	300 (ev)	600 (ev)	100 (ev)	200 (ev)	300 (ev)	600 (ev)
Be	(0.040)	(0.095)	(0.15)	(0.34)	0.03	0.17	0.24	0.61	...	0.12	0.24	0.42
C	0.008	0.020	0.035	0.085	0.005	0.045	0.090	0.18	...	0.04	0.08	0.21
Al	...	0.005	0.008	0.021	0.09	0.30	0.52	1.11	0.06	0.24	0.45	1.02
Si	0.015	0.045	0.075	0.15	0.05	0.12	0.23	0.64	...	0.08	0.21	0.51
Ti	0.010	0.038	0.05	0.08	0.03	0.16	0.29	0.53	...	0.13	0.24	0.50
V	(0.003)	(0.020)	(0.038)	(0.09)	0.06	0.21	0.35	0.69	0.05	0.20	0.39	0.72
Cr	0.030	0.070	0.105	0.20	0.21	0.56	0.88	1.55	0.13	0.44	0.85	1.90
Mn	...	...	...	...	0.11	0.40	0.69	1.80	0.08	0.34	0.60	1.07
Fe	0.030	0.065	0.09	0.17	0.12	0.38	0.64	1.23	0.06	0.29	0.54	1.20
Co	0.010	0.042	0.075	0.15	0.08	0.30	0.50	1.33	0.09	0.38	0.61	1.30
Ni	0.028	0.060	0.095	0.18	0.16	0.47	0.75	1.50	0.10	0.37	0.71	1.48
Cu	0.045	0.11	0.16	0.27	0.33	0.92	1.42	2.80	0.26	0.79	1.29	2.44
Ge	0.010	0.03	0.05	0.08	0.12	0.37	0.66	1.35	0.08	0.31	0.54	1.20
Zr	...	(0.004)	(0.013)	(0.025)	0.04	0.18	0.34	0.72	0.03	0.18	0.31	0.71
Nb	...	0.005	0.010	0.030	0.03	0.17	0.30	0.68	0.02	0.17	0.31	0.61
Mo	(0.001)	(0.005)	0.015	0.040	0.07	0.32	0.54	1.05	0.06	0.28	0.51	1.06
Ru	...	...	...	...	0.08	0.45	0.77	1.45	0.05	0.37	0.71	1.42
Rh	0.004	0.015	0.030	0.065	0.16	0.54	0.90	1.70	0.12	0.51	0.84	1.60
Pd	0.020	0.057	0.082	0.16	0.13	0.77	1.47	2.55	0.34	1.03	1.39	2.48
Ag	0.030	0.082	0.125	0.23	0.40	1.35	1.85	3.00	0.40	1.05	1.80	4.20
Hf	...	(0.002)	(0.010)	0.12	0.39	0.59	1.02	...	0.30	0.55	1.17	...
Ta	...	0.002	0.003	0.012	0.07	0.33	0.53	0.98	0.05	0.32	0.50	1.00
W	...	0.001	0.004	0.008	0.06	0.36	0.58	1.07	0.03	0.35	0.60	1.18
Re	...	...	...	...	0.08	0.42	0.74	1.43	0.02	0.31	0.80	1.40
Os	(0.0005)	(0.002)	(0.004)	(0.022)	0.05	0.39	0.73	1.45	0.03	0.39	0.74	1.53
Ir	...	(0.001)	(0.003)	(0.010)	0.10	0.42	0.66	1.58	0.05	0.52	0.86	1.79
Pt	...	0.004	0.010	0.035	0.15	0.67	1.15	2.11	0.19	0.72	1.25	2.23
Au	...	0.020	0.035	0.08	0.42	1.10	1.90	3.42	0.16	1.00	1.83	3.10
Th	...	(0.0005)	...	(0.002)	0.09	0.36	0.60	1.07	0.08	0.35	0.60	1.22
U	...	0.002	0.004	0.013	0.14	0.47	0.79	1.46	...	0.24	0.45	1.00

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## Sigmund's linear cascade formula for $Y(E)$

Sputtering

$$Y(E) = \frac{0.04}{U} \alpha(M_t/M_i) S_n(E)$$

$\alpha$  - dimensionless coefficient

$S_n(E)$ , collisional energy at the surface  
(nuclear energy loss function)

$U$  – sublimation energy

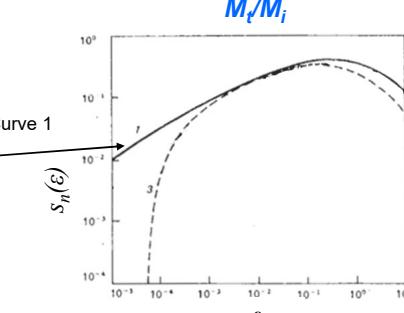
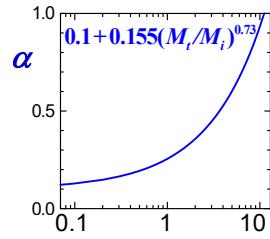
$$S_n(E) = 85 \frac{Z_i Z_t}{(Z_i^{2/3} + Z_t^{2/3})^{0.5}} \frac{M_i}{M_t + M_i} s_n(\varepsilon)$$

$s_n(\varepsilon)$  – function of the reduced energy which is the same for all ion-target combination

$$s_n(\varepsilon) = \frac{3.441\sqrt{\varepsilon} \ln(\varepsilon + 2.718)}{1 + 6.355\sqrt{\varepsilon} + \varepsilon(6.882\sqrt{\varepsilon} - 1.708)}$$

$\varepsilon$  – reduced energy

$$\varepsilon = \frac{0.03255}{Z_i Z_t (Z_i^{2/3} + Z_t^{2/3})^{0.5}} \frac{M_i}{M_t + M_i} E$$

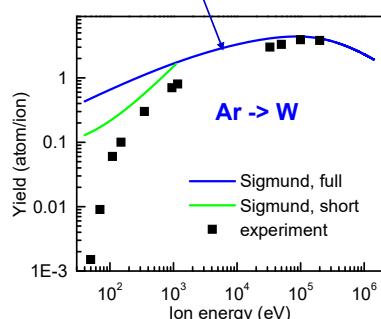
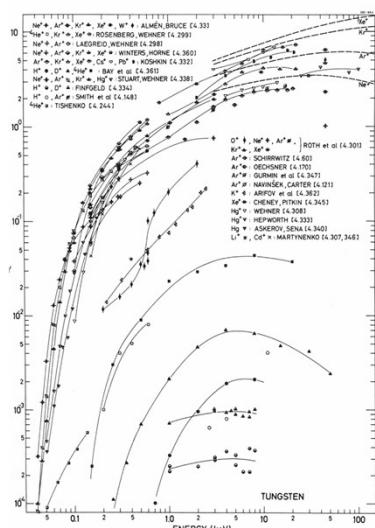


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## Sigmund formula: good agreement in the 10s keV, poor in the < 1 keV

Sputtering



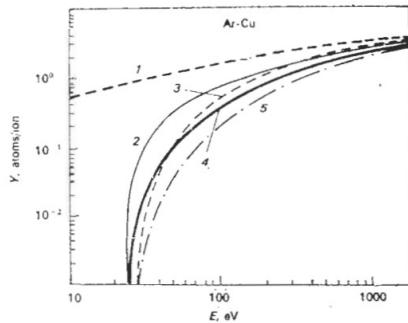
0.1 <  $E$  < 1kV, Sigmund derives a remarkably simple formula

$$Y(E) = \frac{3}{4\pi^2} \alpha(M_t/M_i) \frac{\gamma E}{U}$$

$$\gamma = \frac{4M_t M_i}{(M_t + M_i)^2}$$

## Formulas introducing Sputtering Threshold Energy, $E_{TH}$

Sputtering



$$Y(E) = Y_{\text{Sigmund}}(E) \cdot f(E),$$

$$f(E) = 0, E = E_{TH}$$

$$f(E) = 1, E >> E_{TH}$$

Each formula comes with its choice of  $E_{TH}$

Fig. 2. Energy dependence of the sputtering yield:  
curve 1 — Sigmund's expression, curve 2 —  
Matsunami I, curve 3 — Bohdansky, curve  
4 — Yamamura, curve 5 — Matsunami II

3. Matsunami, N., Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Shimizu. — Rad. Eff. Letters, 57, 1980, p. 15.
4. Yamamura, Y., N. Matsunami, N. Itoh. — Rad. Eff., 71, 1983, p. 65.
5. Bohdansky, J. — Nucl. Instr. Meth., B2, 1984, p. 587.
6. Matsunami, N., Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Shimizu, H. Tawara. — Atomic Data and Nucl. Data Tables, 31, 1984, p. 1.

Petrov, V. Orlinov, S. Grudeva, Comparison of the Low-Energy Sputtering Yield Formulas,  
Bulg. J. Phys., 19 102 (1991).

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## The best formula for low energy sputtering yield: Y. Yamamura et al formula

Sputtering

Sputtering begins at an energy threshold that depends on the efficiency of momentum transfer to the target. This depends on the mass match. It also depends on the surface binding energy of atoms in the target.

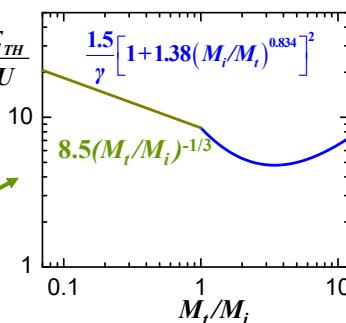
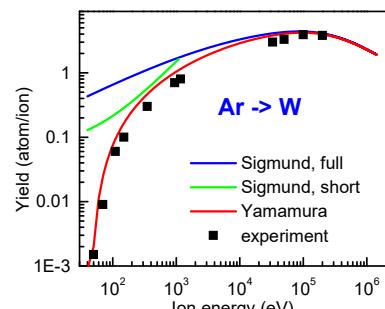
Petrov et al:

Y. Yamamura's correction for  $f(E)$ ,  $E_{TH}$  is best for  
Sputter-deposition combinations ion/target

$$Y(E) = \frac{0.04}{U} \alpha(M_t/M_i) Q S_n(E) \left(1 - \left(\frac{E_{TH}}{E}\right)^{0.5}\right)^2 \frac{E_{TH}}{U}$$

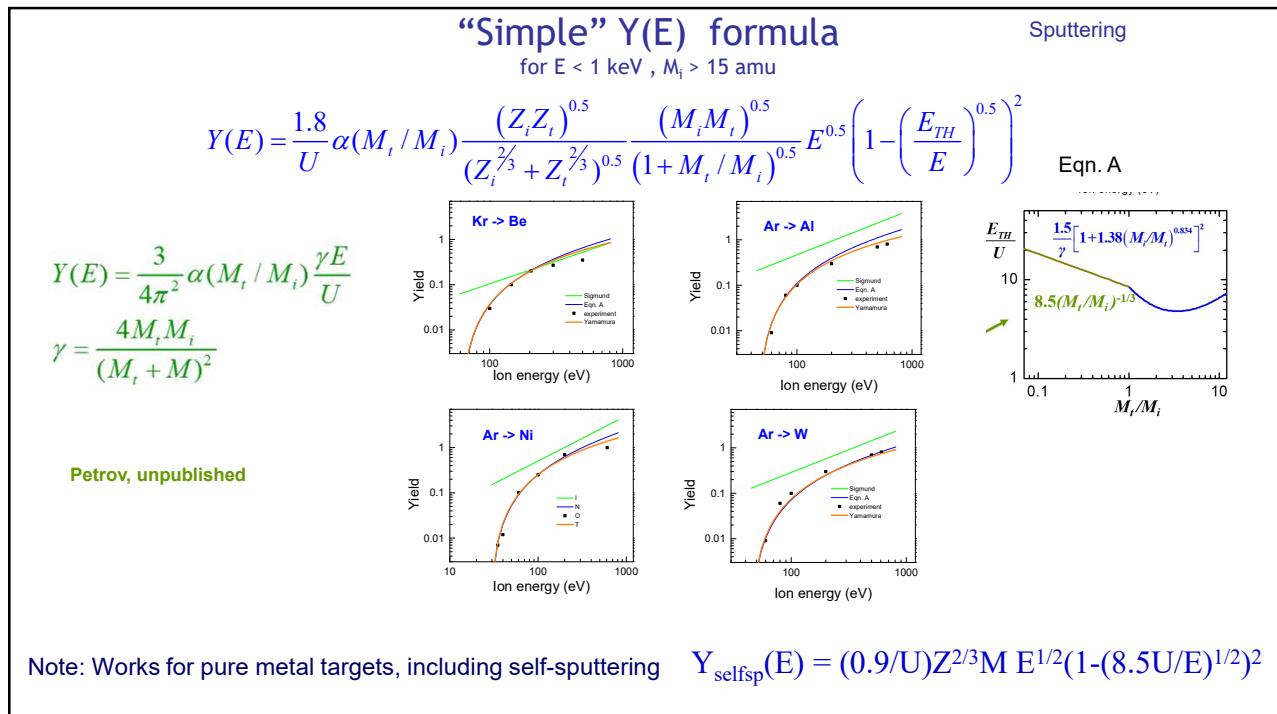
$$Q = \frac{q_T}{1 + s_e(\varepsilon)}$$

Y. Yamamura et al, Rad.Eff., 11 65 (1983)  
I. Petrov et al, Bulg.J.Phys., 18 203(1991)

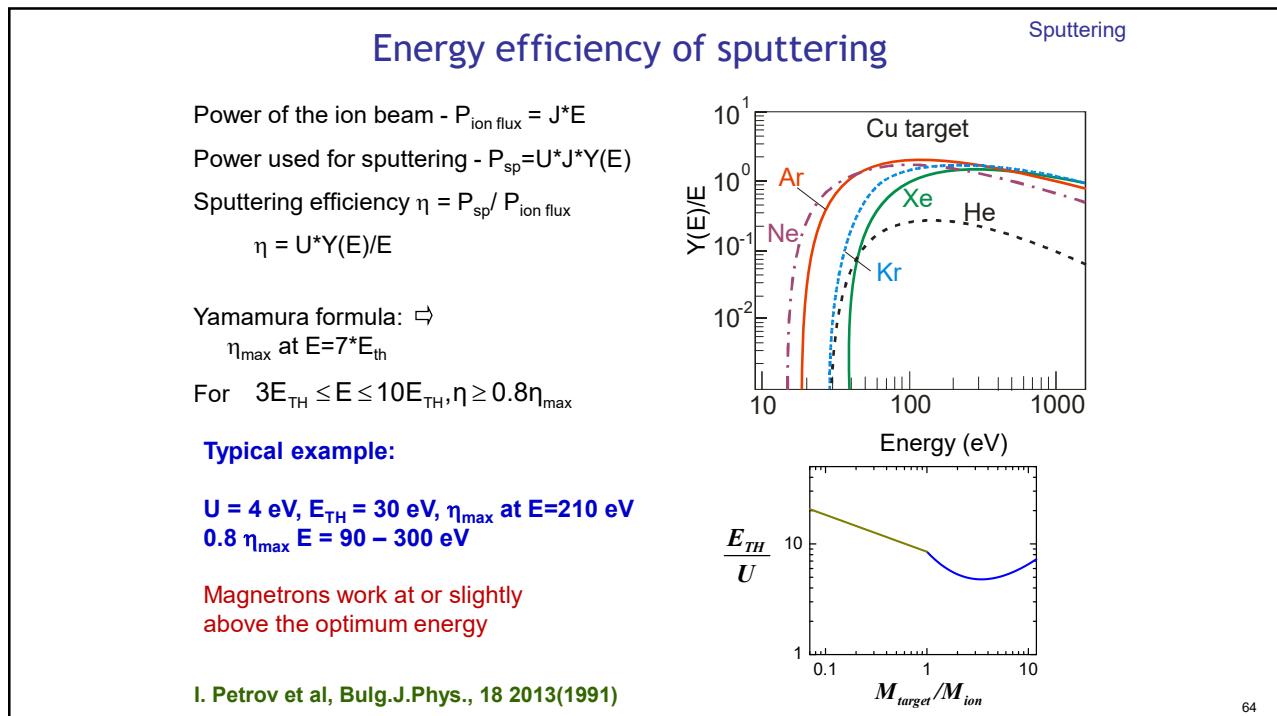


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## Energy efficiency of sputtering

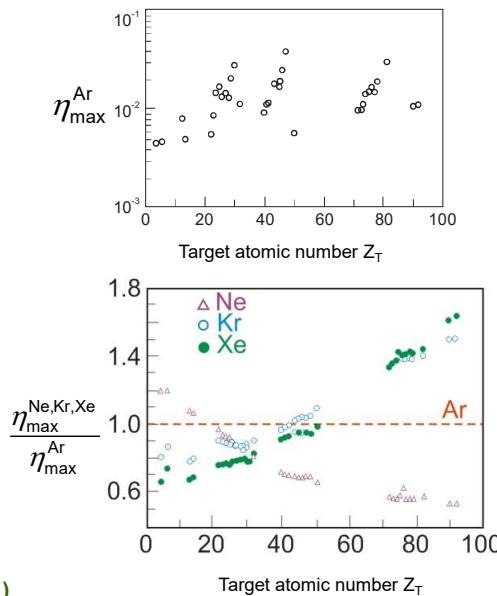
Sputtering

The maximum sputtering efficiency between 0.5 and 5 %

Ar provides high sputtering efficiency for a large number of metal targets (from Al to La)

Ne has ~ 20% advantage for Be and C

Kr ~ 40-60% advantage for targets heavier than Ta



I. Petrov et al, Bulg.J.Phys., 18 2013(1991)

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## Energy of Sputtered Particles

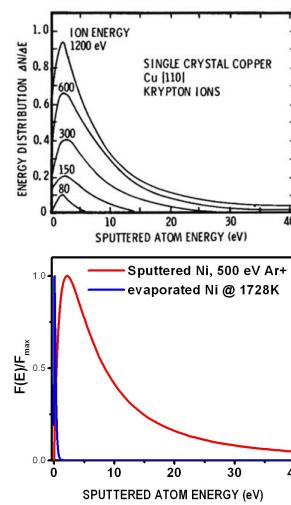
Sputtering

Sputtered atom energy has a maximum at  $\sim U/2$  (several eV) and tail extending to tens and hundreds of eV, depending on the ion energy.

Energy (Sigmund-Thompson) distribution:

$$F(E) \propto \frac{E}{(E+U)^3} \left( 1 - \left( \frac{E+U}{\gamma E_{ion}} \right)^{1/2} \right) \approx \frac{E}{(E+U)^3}$$

Has a maximum  $\sim U/2$



Comparison with thermal evaporation energies

66

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## Energetic particles in sputterdeposition Thermalization

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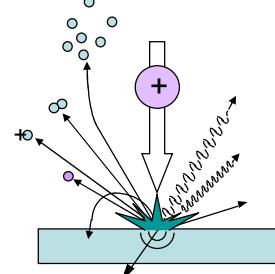
67

## Sputtering Yield: Other Species

Sputtering

Distribution of types of sputtered species:  
[Example for Ar sputtering of Cu]

Single atoms sputtered	100
Diatoms	1
Resputtered trapped gas	5
Single ions	0.1
Diatomical ions	0.001
Reflected incident species	3
Secondary electrons	10



Prof. Angus Rocket

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### Source of energetic particles bombardment

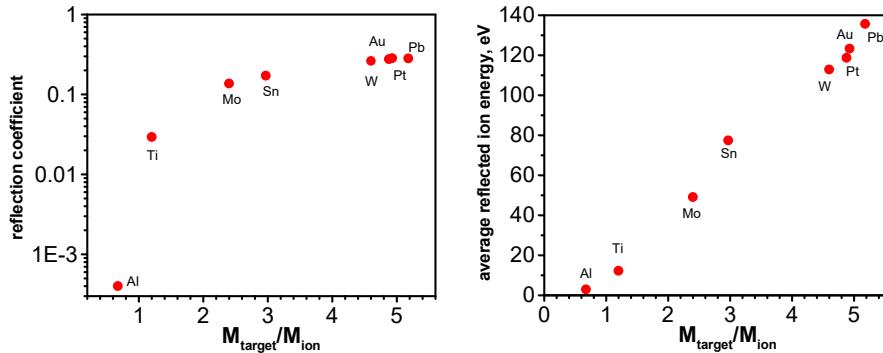
Energetic bombardment

## Reflection of Primary Ions

Incident ions may be reflected from the target surface.

Reflection coefficient = #reflected ions/#incident ions

Case study: TRIM simulation of 500 eV Ar ion scattering



Both reflection coefficient and the average energy of the reflected ions increase when the target atom is heavier than the ion

Petrov, unpublished

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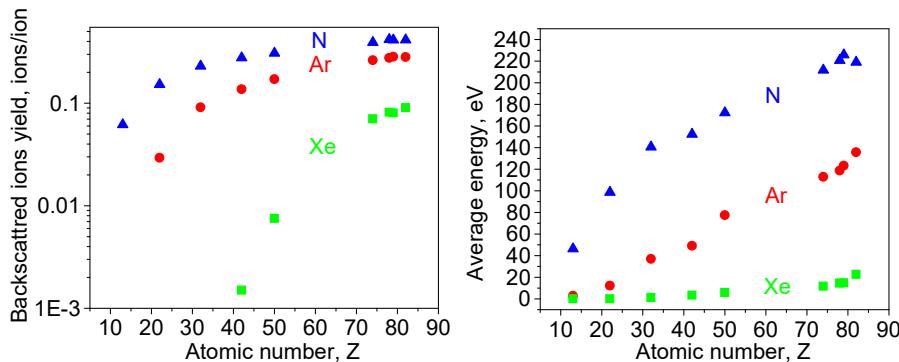
## Reflection of Primary Ions, cont.

Energetic bombardment

Incident ions may be reflected from the target surface.

Reflection coefficient = #reflected ion/#incident ion

Case study: TRIM simulation of 500 eV , Xe, Ar, and N ion scattering



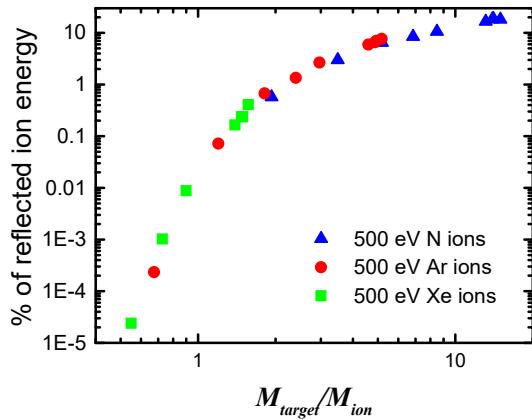
Both reflection coefficient and the average energy of the reflected ions for a given target decrease when heavier ions are used.

Petrov, unpublished

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## Reflection of Primary Ions, cont.

Case study: TRIM simulation of 500 eV , Xe, Ar, and N ion scattering



A significant fraction of the incident ion energy (> 10%) is reflected back when ions are much lighter than the target atoms

Petrov, unpublished

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## Another source of energetic particle bombardment

### The role of negative ions during sputter-deposition of oxides

Note: Oxygen has an electron affinity of 1.461 eV

Negative ion effects during magnetron and ion beam sputtering of  $\text{YBa}_2\text{Cu}_3\text{O}_x$

S. M. Rossnagel, and J. J. Cuomo

Citation: AIP Conference Proceedings **165**, 106 (1988); doi: 10.1063/1.37097

View online: <https://doi.org/10.1063/1.37097>

#### ABSTRACT

The sputtering of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  in both RF diode and magnetron systems has been plagued by negative ion effects. Negative ions are produced at the cathode surface during sputtering and are accelerated across the plasma sheath into the plasma. The dominant negative ion produced is  $\text{O}^-$ . The negative ion attains energy by crossing the sheath and may bombard the depositing film at a high rate. The attached electron is usually stripped in the plasma and the energetic, now neutral atom travels through the plasma and bombards the substrate location in front of the cathode. The effect of this bombardment is to reduce the net deposition rate and to alter the film composition. The negative ion yields

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## Another source of energetic particle bombardment

### The role of negative ions during sputter-deposition of oxides

JAPANESE JOURNAL OF APPLIED PHYSICS  
VOL. 20, NO. 3, MARCH, 1981 pp. 519-526

#### High-Energy Neutral Atoms in the Sputtering of ZnO

Kikuo TOMINAGA, Nozomu UESHIBA, Yoshihiro SHINTANI and Osamu TADA

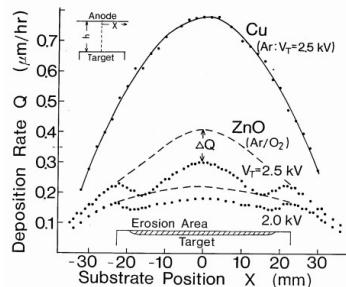


Fig. 1. Distributions of deposition rates at 0.05 Torr in DC diode sputtering, where  $V_T$  and  $\Delta Q$  represent discharge voltage and drop in deposition rate, respectively.

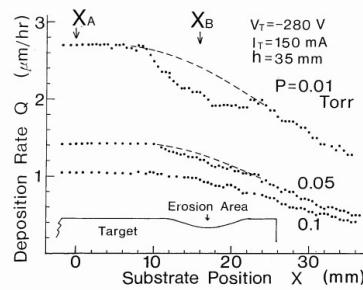
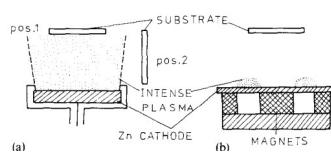


Fig. 2. Distributions of deposition rates at several gas pressures in planar magnetron sputtering.

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### The role of negative ions during sputter-deposition of oxides



Placing the substrates to the side of the target and increasing the deposition pressure eliminate the adverse effect of energetic oxygen bombardment

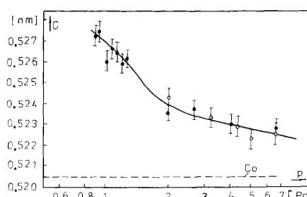


Fig. 6. Variation in the lattice parameter  $c$  of ZnO films magnetron sputtered at different total pressures and for constant  $Q = 80\%$ : ●,  $P = 55$  W; ○,  $P = 110$  W.

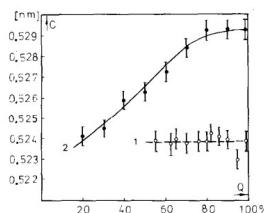


Fig. 7. Variation in the lattice parameter  $c$  of ZnO films with  $Q$  at two different total pressures and discharge powers: ●,  $p = 0.4$  Pa,  $P = 20$  W; ○,  $p = 6.6$  Pa,  $P = 110$  W.

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## Transport of sputtered species in the gas phase

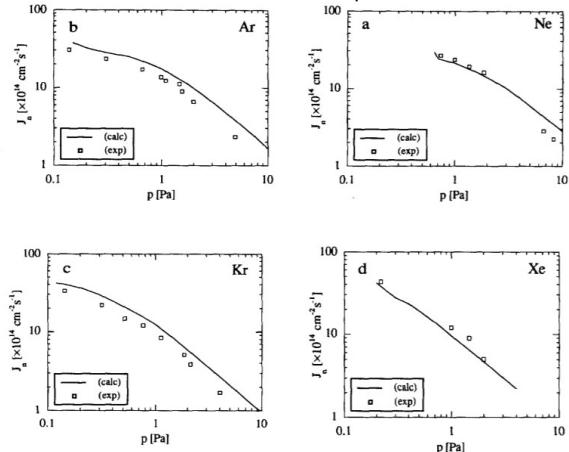
I. Petrov, I. Ivanov, V. Orlinov, and J.E. Sundgren, J. Vac. Sci. Technol., 11 2733 (1993)

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## Transport in the gas phase

Measured and calculated deposition fluxes



Calculated curves follow pressure dependence for all gases, only after accounting for diffusion

### Comparison of magnetron sputter deposition conditions in neon, argon, krypton, and xenon discharges

I. Petrov,<sup>a)</sup> I. Ivanov,<sup>b)</sup> and V. Orlinov  
Institute of Electronics, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria

J.-E. Sundgren  
Thin Film Division, Department of Physics, Linköping University, S-581 83 Linköping, Sweden

Vanadium target, 50 mm dia  
 $D_{\text{target-substrate}} = 10 \text{ cm}$

$I_T = 0.3 \text{ A}$

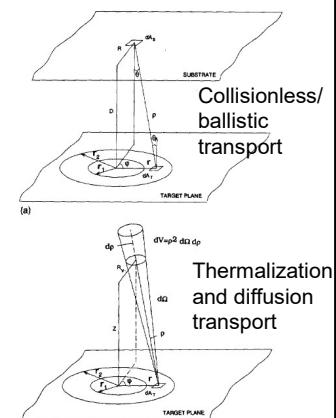
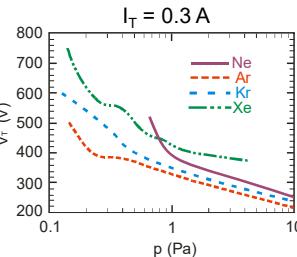


FIG. 1. Geometry used in the calculations for the ballistics transport (a), and thermalization in the gas phase (b).

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## Thermalization of sputtered species

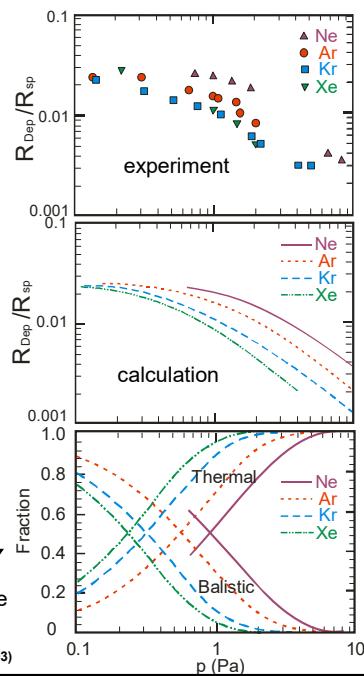
In typical pressure range for magnetron sputter deposition, both collisionless and diffusive transport are effective

Note: to get the relatively good agreement at low pressures several adjustments to the mean free path had to be made

To get agreement at high pressures diffusive transport had to be taken into account

I. Petrov, I. Ivanov, V. Orlinov, and J.E. Sundgren, J. Vac. Sci. Technol., 11 2733 (1993)

Transport the gas phase



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Transport the gas phase

<http://emaps.mrl.uiuc.edu/cassandra/> N!B! the site no longer works

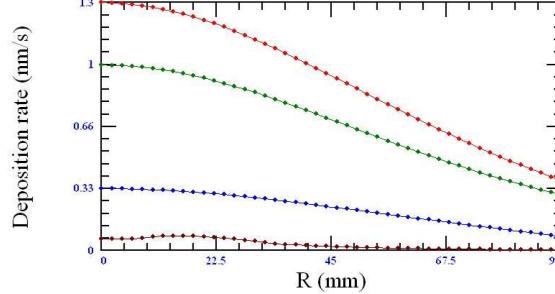


**Center for Microanalysis of Materials (CMM)**  
A User Facility for Electron Beam Microcharacterization  
Division of Materials Sciences/Basic Energy Sciences  
Department of Energy

### Sputter Calculator

Copyright ©2005 I. Petrov, J. C. Mabon, Center for Microanalysis of Materials, and the Board of Trustees of the University of Illinois. All Rights Reserved.

Magnetron sputtering of Al by Ar	Legend
Gas pressure: 0.5 Pa	Total deposition rate
Initial T: 300 K	Ballistic component
Corrected T: 330.714 K	Diffusive component
Discharge current: 0.5 A	Resputtered at target
Discharge voltage: 500 V	
Erosion disk inner radius: 10 mm	
Outer radius: 30 mm	
Distance to target: 100 mm	



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## Classic paper

Transport the gas phase

### Calculation of deposition rates in diode sputtering systems

W. D. Westwood Journal of Vacuum Science and Technology 15, 1 (1978); <https://doi.org/10.1116/1.569429>

#### Mean free path

$$\lambda^{-1} = 8.34 \times 10^{14} \rho \frac{(\sigma_s + \sigma_g)^2}{4} (1 + M_s/M_g)^{1/2},$$

$\rho$  – pressure [Pa],  $\sigma_s$ ,  $\sigma_g$  diameters [cm],

Author did not specify the temperature; it is 273 K

#### Number of collisions to thermalize the atom

An alternative approach is to use the concept of "persistence" introduced by Jeans.<sup>13</sup> This is the expectation that an atom of velocity  $v$  will have velocity  $v^1$  in the direction of  $v$  after the collision and is given by

$$\frac{v^1}{v} = \frac{1 - M}{1 + M} + \frac{2M}{1 + M} \left[ \frac{\ln[1 + M]^{1/2} + M^{1/2}}{4M^{3/2}(1 + M)^{1/2}} \right] + \frac{2M^4 + 5M^3 + 3M^2 - M - 1}{4M(1 + M)^3}. \quad (7)$$

The number of collisions required to reduce the initial velocity  $v_o$  to the thermal velocity  $v_g$  is

$$\eta^1 = \ln(v_g/v_o)/\ln(v^1/v). \quad (8)$$

<sup>13</sup>J. H. Jeans, in *The Dynamical Theory of Gases* (Dover New York, 1954).

#### Thermalization distance

$$D_3 = \eta^1 \lambda$$

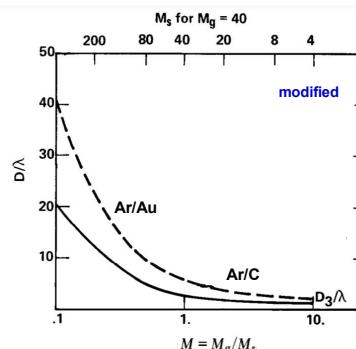


FIG. 4. The number of average collisions required to reduce a sputtered atom of mass  $M_s$  with initial energy of 5 (full lines) and 1000 eV (dashed lines) to thermal energies by collision with gas atoms, mass  $M_g$ .

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Transport the gas phase

### The thermalization of energetic atoms during the sputtering process

Cite as: Journal of Vacuum Science & Technology A 2, 1285 (1984); <https://doi.org/10.1116/1.572396>  
Submitted: 11 July 1983 . Accepted: 19 February 1984 . Published Online: 04 June 1998

R. E. Somekh

Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ England

(Received 11 July 1983; accepted 19 February 1984)

We consider the sputter deposition process and present a calculation of the rate of energy loss of sputtered atoms and reflected neutrals due to elastic collisions with the sputtering gas atoms. Compared to previous calculations we have explicitly taken into account the strong energy dependence of the scattering cross section recently reported by Robinson. The results suggest a much less efficient energy loss rate than previously envisaged using the classical thermal cross sections. Such thermal cross sections have been used in previous calculations to explain the high sputtering pressure required for preparing high critical transition temperature superconductors Nb<sub>3</sub>Ge and Nb<sub>3</sub>Sn.

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## The thermalization of energetic atoms during the sputtering process

Cite as: Journal of Vacuum Science & Technology A 2, 1285 (1984); <https://doi.org/10.1116/1.572396>  
Submitted: 11 July 1983 . Accepted: 19 February 1984 . Published Online: 04 June 1998  
R. E. Somekh

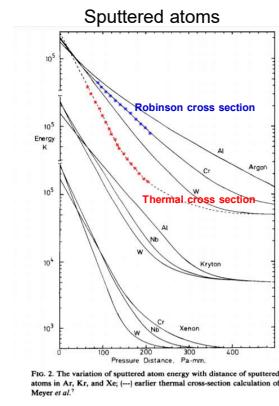


FIG. 2. The variation of sputtered atom energy with distance of sputtered atoms in Ar, Kr, and Xe. (—) earlier thermal cross-section calculation of Meyer *et al.*<sup>7</sup>

## Transport the gas phase

In order to estimate the collision cross section between sputtered metal atoms (atomic number  $Z_1$ ) and the inert sputtering gas atom (atomic number  $Z_2$ ) a simple interpolation scheme has been used. We interpolate linearly using the cross sections  $\sigma(E)$  based on Robinson's original calculations for Ar, Kr, and Xe ( $Z_2 = 18, 36, 54$ , respectively). Thus, the scattering cross section  $\sigma(E)$  is given by

$$\sigma(E) = \sigma_{Ar}(E) + [\sigma_{Kr}(E) - \sigma_{Ar}(E)] \frac{(Z_1 - Z_2)}{(Z_{Kr} - Z_{Ar})},$$

for the case with a mean atomic number  $[(Z_1 + Z_2)/2]$  lying between 18 and 36.<sup>1</sup>

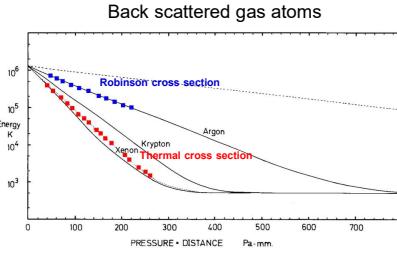


FIG. 3. The variation of energy with distance of reflected ions. Ar, Kr, and Xe for initial  $e = 110 \pm 55$  eV; (—) calculation of Gilbert *et al.*<sup>10</sup> (O-Ar); (—) calculation of Wu *et al.*<sup>11</sup> (Ar-Ar).

Thermal cross-sections severely underestimate thermalization distances

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## Energetic binary collisions in rare gas plasmas

## Transport the gas phase

Cite as: Journal of Vacuum Science and Technology 16, 185 (1979); <https://doi.org/10.1116/1.569903>  
Published Online: 04 June 1998

R. S. Robinson

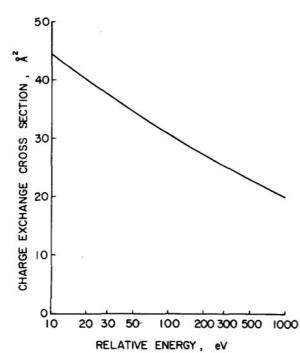


FIG. 1. Total resonance charge exchange cross section for argon as a function of relative energy.

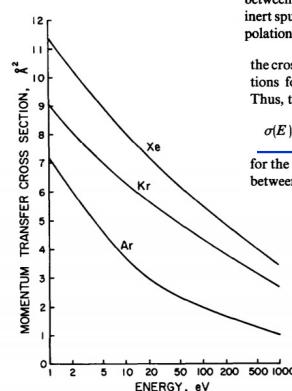


FIG. 4. Momentum transfer (diffusion) cross section for Ar, Kr, and Xe as a function of energy.

In order to estimate the collision cross section between sputtered metal atoms (atomic number  $Z_1$ ) and the inert sputtering gas atom (atomic number  $Z_2$ ) a simple interpolation scheme has been used. We interpolate linearly using the cross sections  $\sigma(E)$  based on Robinson's original calculations for Ar, Kr, and Xe ( $Z_2 = 18, 36, 54$ , respectively). Thus, the scattering cross section  $\sigma(E)$  is given by

$$\sigma(E) = \sigma_{Ar}(E) + [\sigma_{Kr}(E) - \sigma_{Ar}(E)] \frac{(Z_1 - Z_2)}{(Z_{Kr} - Z_{Ar})},$$

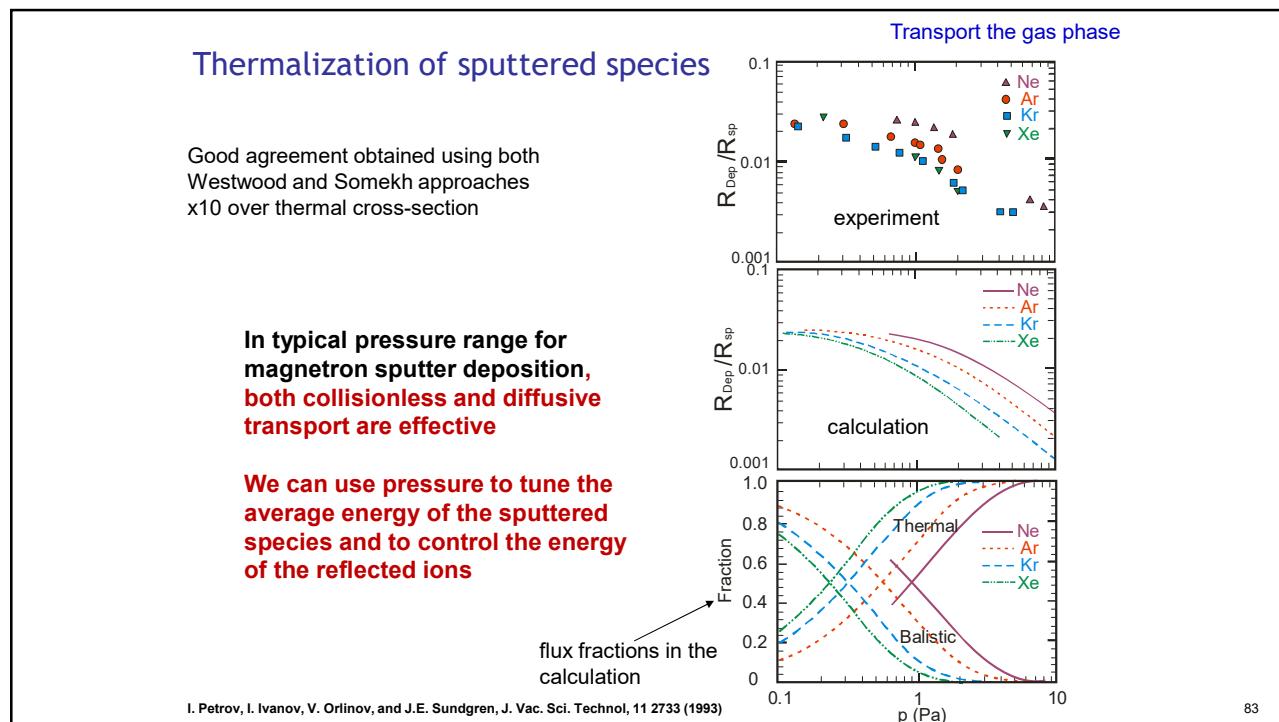
for the case with a mean atomic number  $[(Z_1 + Z_2)/2]$  lying between 18 and 36.<sup>1</sup>

For metal atom Somekh extrapolated between Robinson data for inert gases

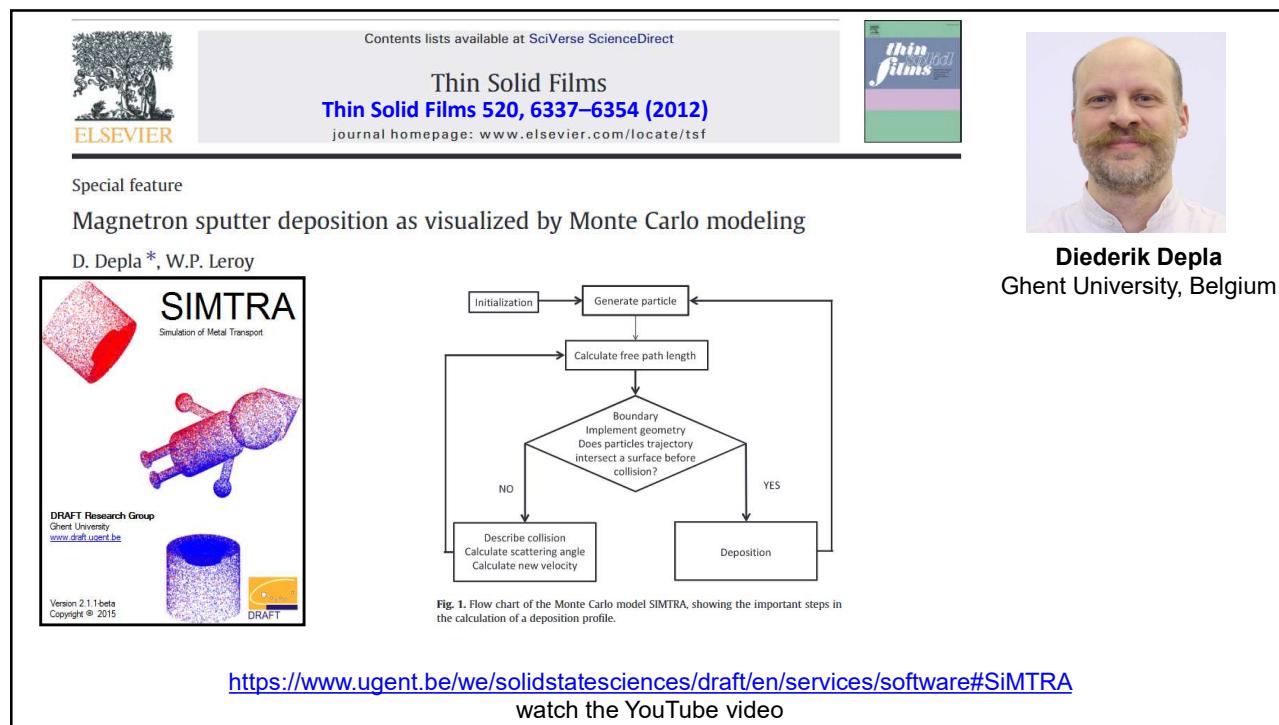
Faster atoms have smaller scattering cross-sections -> larger mean free path

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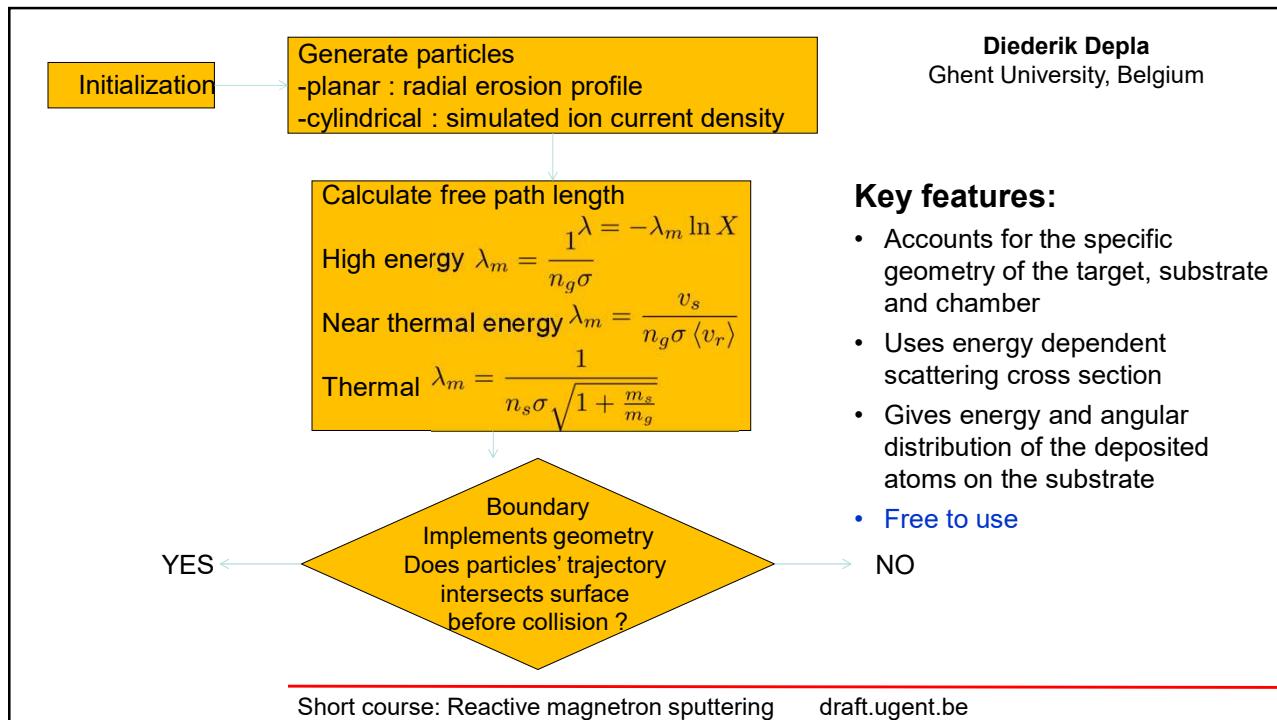
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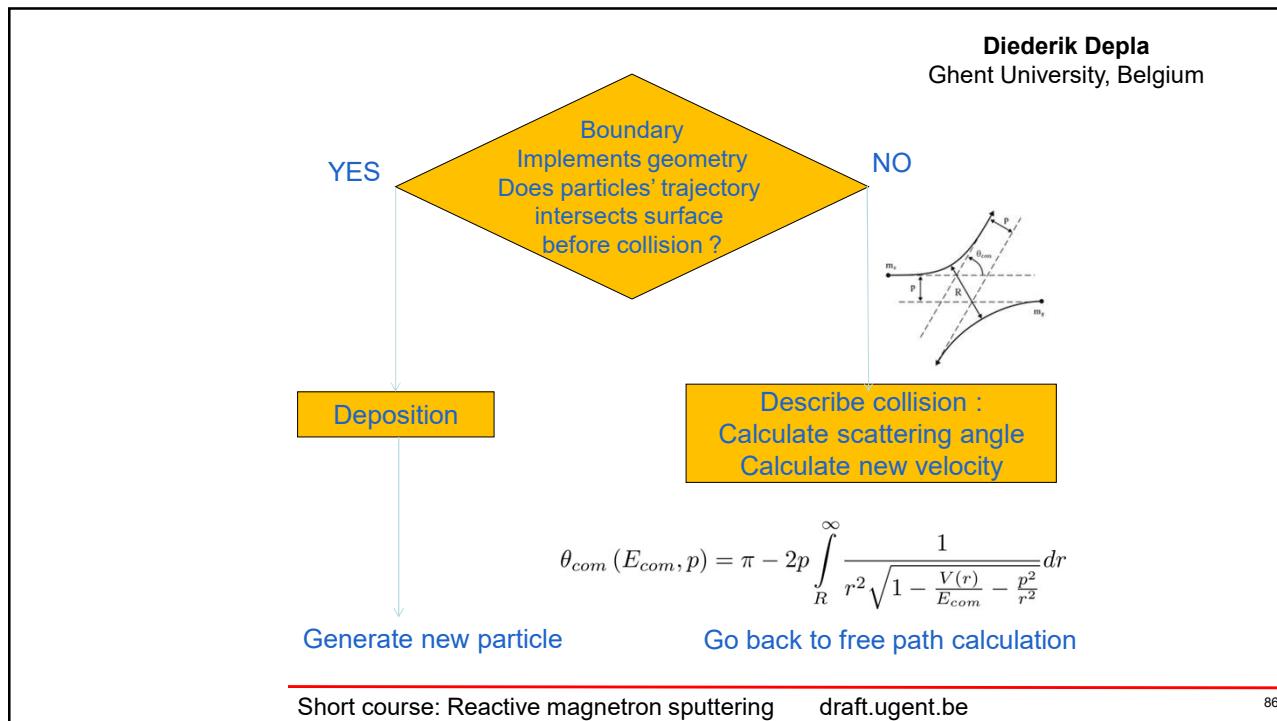
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## Influence of the sputtering gas on the deposition rate: SiMTRA comparison with literature data

unpublished

D. Depla

Department of Solid State Sciences, Ghent University, Krijgslaan 281 (S1), 9000 Gent, Belgium

(Dated: April 26, 2023)

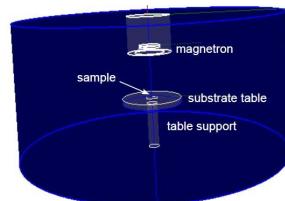
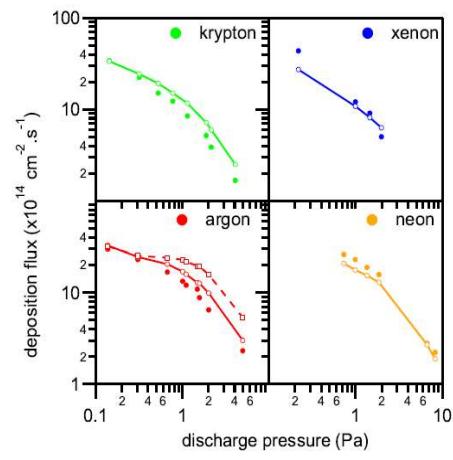
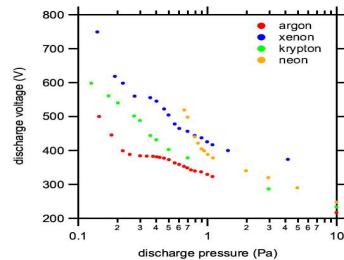
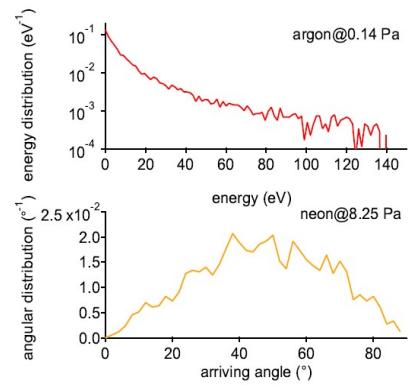


Figure 1. Used geometry. The vacuum chamber (blue) is a cylinder with a radius and a height of 0.25 m.



Exp. Data from: I. Petrov, I. Ivanov, V. Orlinov, and J.E. Sundgren, J. Vac. Sci. Technol., 11 2733 (1993)



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## Variations of sputtering systems

### Magnetron sputtering

### Unbalanced magnetrons

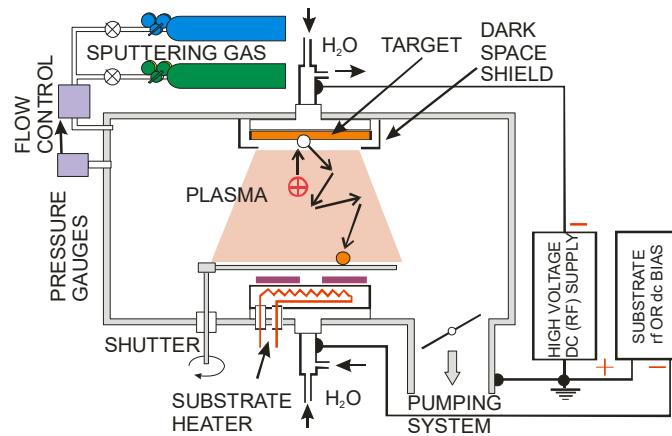
88

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## Diode sputter deposition system

Components and typical parameters

$V_T \sim 2-5 \text{ kV}$   
 $J_T \sim 1 \text{ mA/cm}^2$   
 $p \sim 50-80 \text{ mTorr}$   
 $\lambda \ll d_{TS}$



89

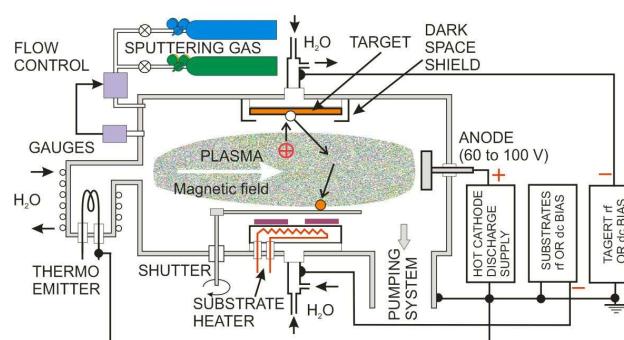
89

## Triode sputter deposition system

Components and typical parameters

$V_T \sim 1 \text{ kV}$   
 $J_T \sim 5 \text{ mA/cm}^2$   
 $p \sim 10-20 \text{ mTorr}$   
 $\lambda \sim d_{TS}$

Thermionic arc;  $V_{arc} \sim 10-30 \text{ V}$ ,  $I_{arc} \sim \text{several Amps}$   
Independent control of ion flux and energy  
The presence of a hot filament hampers reactive deposition



90

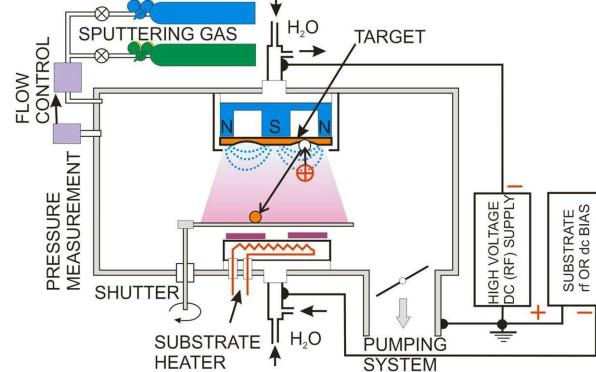
90

# Magnetron sputter deposition system

## Components and typical parameters

$V_T \sim 0.3\text{-}0.5 \text{ kV}$   
 $J_T \sim 10\text{-}100 \text{ mA/cm}^2$   
 $P_T \sim 3\text{-}50 \text{ W/cm}^2$   
 $p \sim 2\text{-}20 \text{ mTorr}$   
 $\lambda > d_{TS}, \lambda < d_{TS}$

ExB field near target enhances ionization efficiency, thus reducing both  $V_T$  and  $p$



91

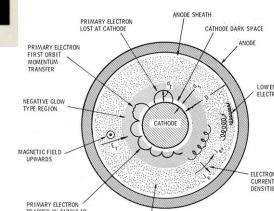
91

# Magnetron discharge characteristics

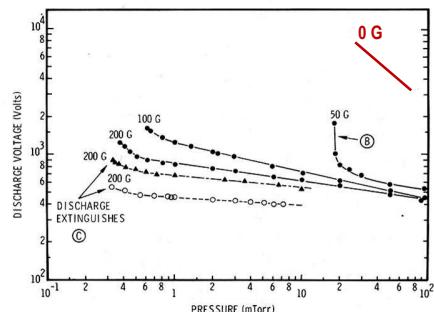
Thornton, cylindrical magnetrons



MATSE,  
University of Illinois



Conventional DC sputtering: kV, tens mTorr

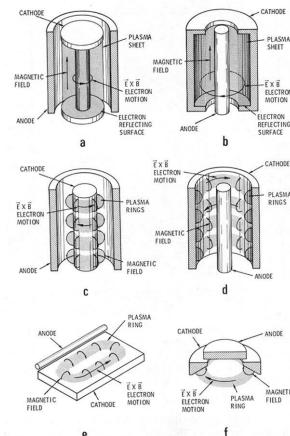
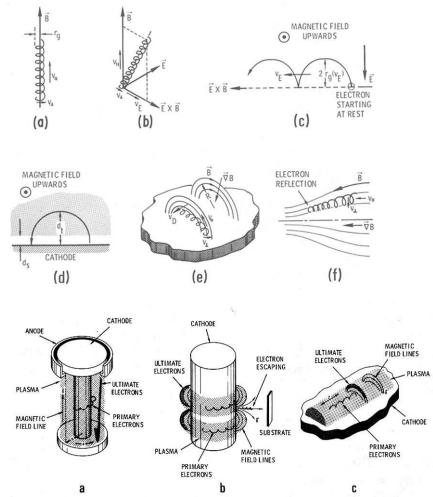


J.A. Thornton and A.S. Penfold, "Cylindrical Magnetron Sputtering," in *Thin Film Processes*, edited by J.L. Vossen and W. Kern, Academic Press, NY 1978.

92

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## ExB configurations



$$V_T = \frac{1}{E_o \gamma_i \epsilon_i \epsilon_e}$$

$$\epsilon_i \epsilon_e \approx 1$$

J.A. Thornton and A.S. Penfold, "Cylindrical Magnetron Sputtering," in *Thin Film Processes*, edited by J.L. Vossen and W. Kern, Academic Press, NY 1978.

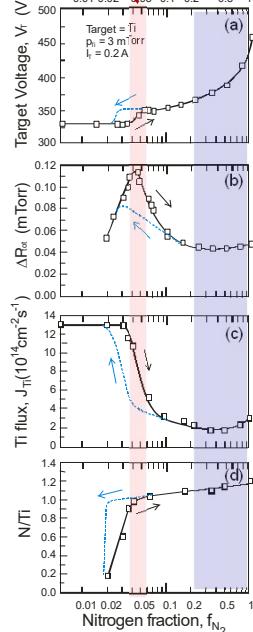
93

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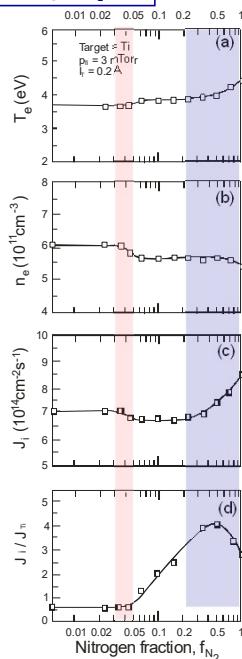
Target surface reaction, transition from Ar sputtering pure metal to nitride

### Sputtering of Ti target in Ar+N<sub>2</sub>

I. Petrov, A. Myers,  
J.E. Greene, and J.R.  
Abelson, JVST A 12,  
2846 (1994)



Transition from discharge in Ar to a discharge in N<sub>2</sub>



### Reactive sputtering

$$V_T = \frac{1}{E_o \gamma_i \epsilon_i \epsilon_e}$$

$$Y(E) = \frac{0.04}{U} \alpha(M_t/M_i) S_n(E)$$

94

94

### Reactive sputtering

## Magnetron sputter deposition: Linking discharge voltage with target properties

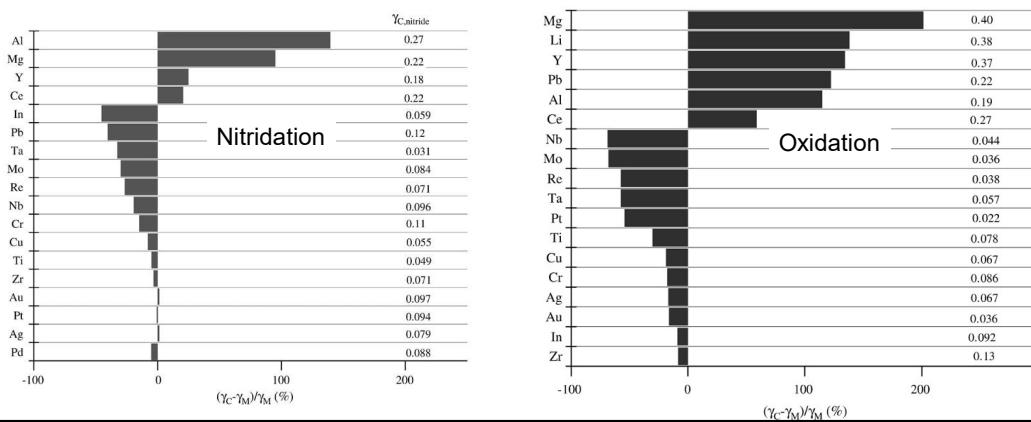
D. Depla <sup>\*</sup>, S. Mahieu, R. De Gryse

Thin Solid Films 517 (2009) 2825–2839

Department of Solid State Sciences, Ghent University, Krijgslaan 281(S1) 9000 Gent, Belgium

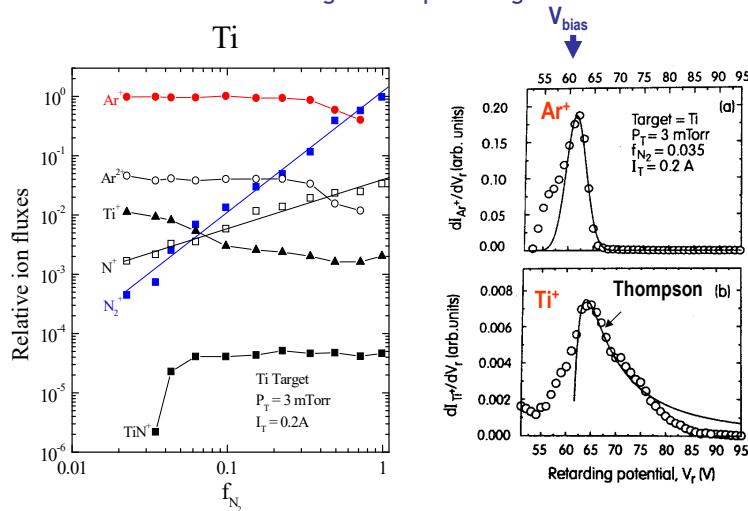
### Relative change of the effective secondary ion-electron emission coefficient upon target reaction “poisoning”

D. Depla et al. / Thin Solid Films 517 (2009) 2825–2839



95

### Ion distribution at the substrate DC magnetron sputtering



Gas ions dominate:  
 $Ar^+$  in most of the range,  $N_2^+$  in pure Nitrogen

Gas ions energy corresponds to the applied bias  
 $Ti^+$  extend to higher energies due to being sputter ejected

I. Petrov, A. Myers, J.E. Greene, and J.R. Abelson, JVST A 12, 2846 (1994)

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96

## Reactive sputtering, the big names

Modeling reactive magnetron sputtering: Opportunities and challenges

D. Depla\*, K. Strijckmans, A. Dulmaa, F. Cougnon, R. Dedoncker, R. Schelfhout, I. Schramm,  
F. Moens, R. De Gryse

Department of Solid State Sciences, Ghent University, Krijgslaan 281 (S1), 9000 Gent, Belgium

Thin Solid Films 688 (2019) 137326

Fundamental understanding and modeling of reactive  
sputtering processes

Thin Solid Films 476 (2005) 215–230

S. Berg\*, T. Nyberg

The Angstrom Laboratory, Uppsala University, Box 534, 751 21 Uppsala, Sweden

Control of reactive sputtering processes

Thin Solid Films 491 (2005) 1 – 17

W.D. Sproul<sup>a\*</sup>, D.J. Christie<sup>b</sup>, D.C. Carter<sup>b</sup>

<sup>a</sup>Reactive Sputtering Consulting, LLC, 3324 South Lemay Avenue, Fort Collins, CO 80525, USA  
<sup>b</sup>Advanced Energy Industries, Inc., 1625 Sharp Point Drive, Fort Collins, CO 80525, USA

**A parametric model for reactive high-power  
impulse magnetron sputtering of films**

J. Phys. D: Appl. Phys. 49 (2016) 055202 (18pp)

Tomáš Kozák<sup>1,2</sup> and Jaroslav Vlček<sup>1</sup>

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## Magnetron sputter deposition High Power Pulse Magnetron Sputtering (HPPMS) High Power Impulse MS (HiPIMS)

Main new features:

- Source of metal ions
- Time separation between the gas and the metal ions
- Higher energy ions
- Lower deposition rates

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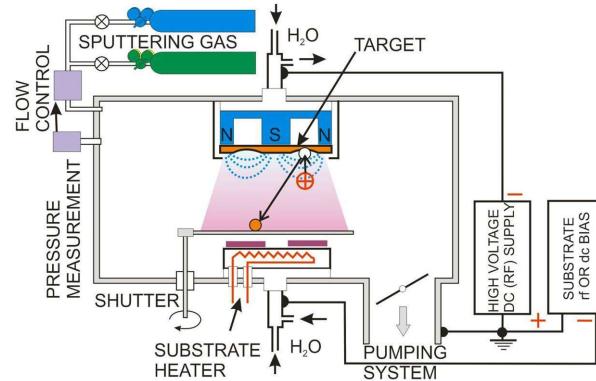
49

## Magnetron sputter deposition system High Power Pulse MS (HPPMS) High Power Impulse MS (HiPIMS)

**Frequency** ~ 50-500 Hz  
**Duty cycle** < 10%  
**peak values**  
 $V_T \sim 0.7\text{-}2 \text{ kV}$   
 $J_T \sim 100\text{-}1000 \text{ mA/cm}^2$   
 $P_T \sim 70\text{-}2000 \text{ W/cm}^2$   
 $p \sim 2\text{-}20 \text{ mTorr}$   
 $\lambda > d_{TS}, \lambda < d_{TS}$

**Main new features:**

- Source of metal ions
- Time separation between the gas and the metal ions
- Higher energy ions
- Lower deposition rates



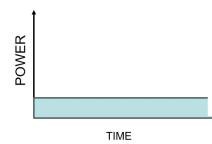
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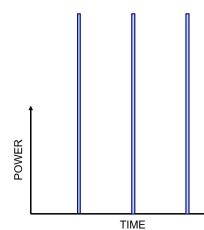
## DCMS      VS      HiPIMS

**Same average power**  
**Same hardware**

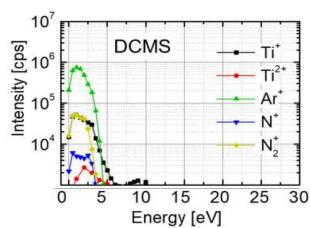
$V_T \sim 0.3\text{-}0.5 \text{ kV}$   
 $P_T \sim 10\text{-}50 \text{ W/cm}^2$   
 $p \sim 2\text{-}20 \text{ mTorr}$



**peak values**  
 $V_T \sim 0.7\text{-}2 \text{ kV}$   
 $P_T \sim 500\text{-}3000 \text{ W/cm}^2$   
 $p \sim 2\text{-}20 \text{ mTorr}$

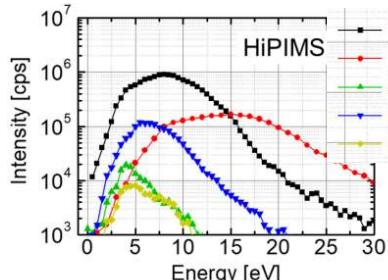


**Frequency** ~ 100-500 Hz  
**Duty cycle** < 1-4 %



1. Thermal gas ions
2. Neutral deposited atoms
3. High deposition rate

### Hybrid HiPIMS/DCMS



1. Energetic metal ions
2. Gas and metal ions separated in time
3. Lower deposition rates

100

100

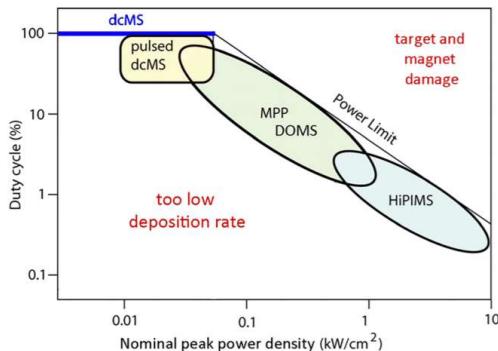


FIG. 36. Schematic showing various forms of magnetron sputtering in a duty-cycle—nominal peak power density diagram. Reprinted with permission from Gudmundsson *et al.*, J. Vac. Sci. Technol. A **30**, 030801 (2012). Copyright 2012 AIP Publishing LLC (Fig. 1 from Ref. 140).

Gudmundsson, Brenning, Lundin, Helmersson,  
J. Vac. Sci. Technol. A **30** (2012) 030801

Andre Anders, Tutorial: Reactive high power impulse magnetron sputtering (R-HiPIMS) JAP **121**, 171101 (2017)  
<https://doi.org/10.1063/1.4978350>

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## High Power Impulse Magnetron Sputtering



Surface and Coatings Technology 122 (1999) 290–293  
A novel pulsed magnetron sputter technique utilizing very high target power densities

Vladimir Kouznetsov <sup>a,\*</sup>, Karol Macák <sup>a</sup>, Jochen M. Schneider <sup>a</sup>, Ulf Helmersson <sup>a</sup>,  
Ivan Petrov <sup>b</sup>

Using a novel pulsed power supply in combination with a standard circular flat magnetron source, operated with a Cu target, a peak power density of  $2800 \text{ W cm}^{-2}$  was achieved. This results in a very intense plasma with peak ion current densities of up to  $3.4 \text{ A cm}^{-2}$  at the substrate situated 10 cm from the target. The ionized fraction of the deposited Cu flux was estimated to be approximately 70% from deposition rate measurements. The potential for high-aspect-ratio trench filling applications by high

**Source of metal ions**

Both May 1999

Vacuum 53 (1999) 133–136  
Impulse irradiation plasma technology for film deposition

I.K. Fetisov, A.A. Filippov, G.V. Khodachenko, D.V. Mozgrin, A.A. Pisarev\*

Department of Plasma Physics, Moscow State Engineering and Physics Institute, Kashirskoe shosse, 115409 Moscow, Russia

A new type of the sputtering discharge and its applications for film deposition are described in the paper. This is a pulse, quasi-stationary and high-current diffuse discharge in the magnetic field. The combination of its properties makes the discharge to be a promising instrument for film deposition. Complex films of high quality have been obtained by using this discharge. Features and

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# High Power Impulse Magnetron Sputtering

Surface and Coatings Technology 122 (1999) 290–293

A novel pulsed magnetron sputter technique utilizing very high target power densities

Vladimir Kouznetsov <sup>a,\*</sup>, Karol Macák <sup>a</sup>, Jochen M. Schneider <sup>a</sup>, Ulf Helmersson <sup>a</sup>,  
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Surface & Coatings Technology 293 (2016) 42–47

High-current impulse magnetron discharge with liquid target

Alexander V. Tumarkin \*, Andrey V. Kaziev, Maxim M. Kharkov, Dobrynya V. Kolodko,  
Igor V. Ilychev, Georgy V. Khodachenko<sup>1</sup>

Department of Plasma Physics, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoye Shosse, Moscow 115409, Russia

## 1. Introduction

The HiPIMS technology has been extensively developed over the recent two decades, and nowadays it is widely used for the deposition of superior thin films. The coatings prepared by HiPIMS find their applications in advanced areas of industry [1]. The HiPIMS technique emerged in 1999 [2] and quickly attracted major attention both among the industries and the academia. However, the pioneering studies in the field of the high power pulsed magnetron sputtering were carried out in the beginning of 1990s [3–5]. In particular, Mozgrin et al. [4] originally described the high-current impulse magnetron sputtering discharge (HCIMD), whose distinguishing feature is the behaviour of the voltage and current waveforms exhibiting the quasi-stationary stage duration up to tens ms (see Fig. 1). The pulsed discharge regimes are superior to di-

- [2] V. Kouznetsov, K. Macák, J.M. Schneider, U. Helmersson, I. Petrov, A novel pulsed magnetron sputter technique utilizing very high target power densities, Surf. Coat. Technol. 122 (1999) 290–293.
- [3] I.K. Fetisov, G.V. Khodachenko, D.V. Mozgrin, Quasi-stationary High Current Forms of Low Pressure Discharge in Magnetic Field, Proc. ICPG-XX, Pisa, Italy, 1991 476–478.
- [4] D.V. Mozgrin, I.K. Fetisov, G.V. Khodachenko, High-current low-pressure quasi-stationary discharge in a magnetic field: experimental research, Plasma Phys. Rep. 21 (1995) 422–433.
- [5] S.P. Bugaev, N.N. Koval, N.S. Sochugov, A.N. Zakharov, Investigation of a high-current pulsed magnetron discharge initiated in the low-pressure diffuse arc plasma, Proc. XVII Int. Symp. on Disch. and Electr. Insulation in Vac., Berkeley, USA 1996, pp. 1074–1076.

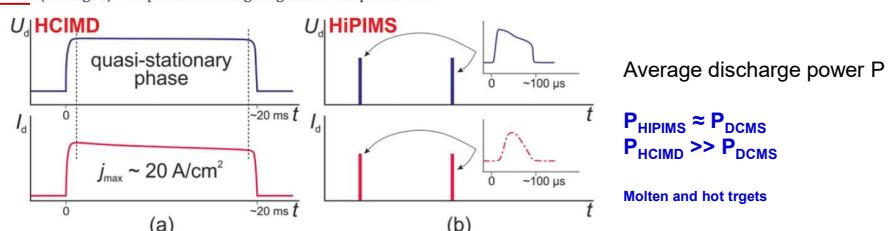
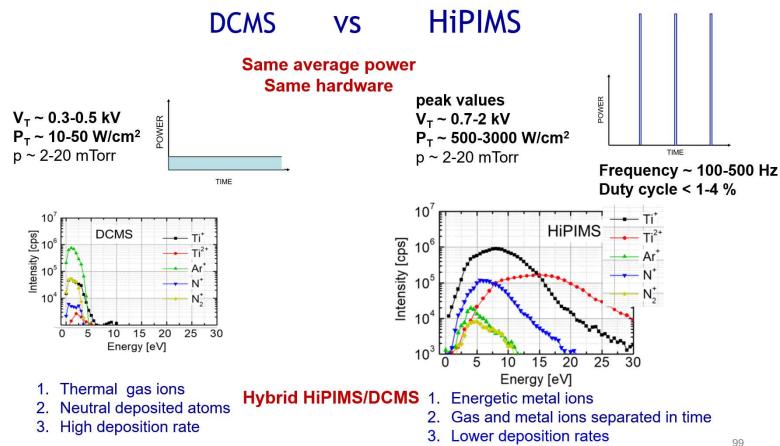


Fig. 1. Typical voltage and current traces of HCIMD (a) and HiPIMS (b).

[petrov@illinois.edu](mailto:petrov@illinois.edu)

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To properly exploit the advantages of HiPIMS it is necessary to know the energy and time evolution of the gas and metal ions



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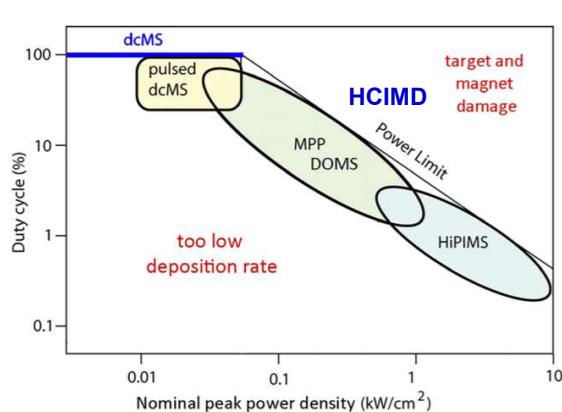


FIG. 36. Schematic showing various forms of magnetron sputtering in a duty-cycle—nominal peak power density diagram. Reprinted with permission from Gudmundsson *et al.*, J. Vac. Sci. Technol. A 30, 030801 (2012). Copyright 2012 AIP Publishing LLC (Fig. 1 from Ref. 140).

Gudmundsson, Brenning, Lundin, Helmersson,  
J. Vac. Sci. Technol. A 30 (2012) 030801

Andre Anders, Tutorial: Reactive high power impulse magnetron sputtering (R-HiPIMS) JAP 121, 171101 (2017)  
<https://doi.org/10.1063/1.4978350>

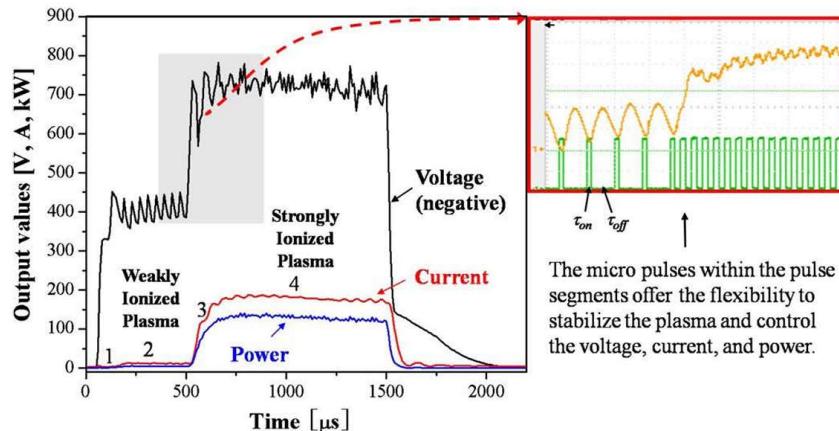
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## Modulated Pulse Power Magnetron Sputtering MPPMS

J. Lin et al. / Surface &amp; Coatings Technology 203 (2009) 3676–3685

3677

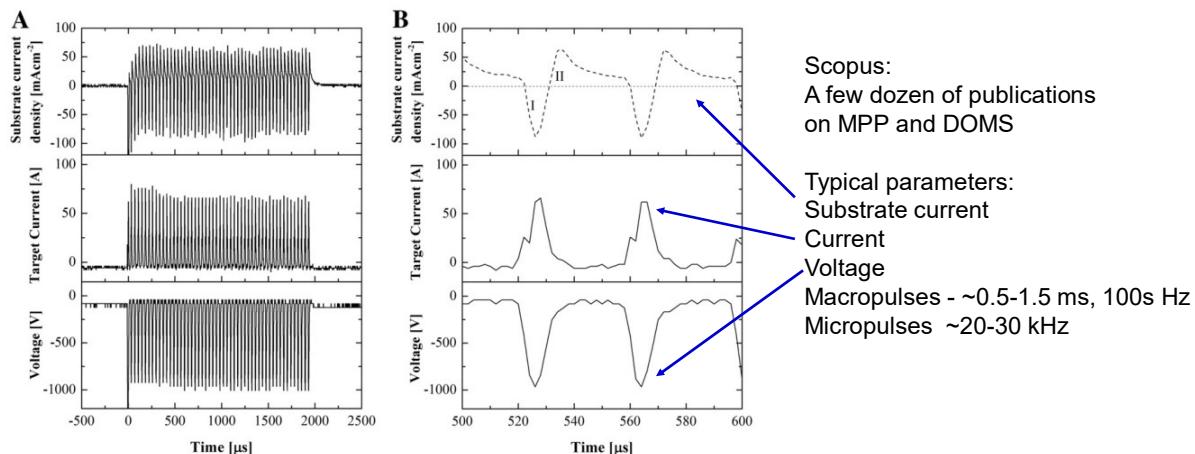


**Fig. 1.** Typical MPP pulse showing four steps of the target voltage, current and power evolutions during one modulated pulse (1500 μs overall pulse length in this example): 1) ignition of the weakly ionized plasma; 2) duration of the weakly ionized plasma; 3) transition stage from the weakly ionized plasma to the strongly ionized plasma; 4) duration of the strongly ionized plasma. The inserted figure on the right side shows the micro pulses within the pulse with adjustable voltage on ( $\tau_{on}$ ) and off ( $\tau_{off}$ ) times.

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## Deep Oscillation Magnetron Sputtering DOMS

Lin et al, Surface and Coatings Technology (2015) 276, pp. 70-76



"The DOMS technique offers virtually **arc-free conditions** for reactive sputtering of many **insulating films** e.g. AlN, Al<sub>2</sub>O<sub>3</sub>, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> etc."

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## Ionized sputter deposition using an extremely high plasma density pulsed magnetron discharge

Karol Macák, Vladimir Kouznetsov, Jochen Schneider, and Ulf Helmerson<sup>a)</sup>  
*Department of Physics, Linköping University, SE-581 83 Linköping, Sweden*

Ivan Petrov  
*Materials Science Department and Materials Research Laboratory, University of Illinois,  
 1533 J. Vac. Sci. Technol. A 18(4), Jul/Aug 2000*

### Transition from gas to metal vapor discharge/gas rarefaction; Time separation between the gas and the metal ions

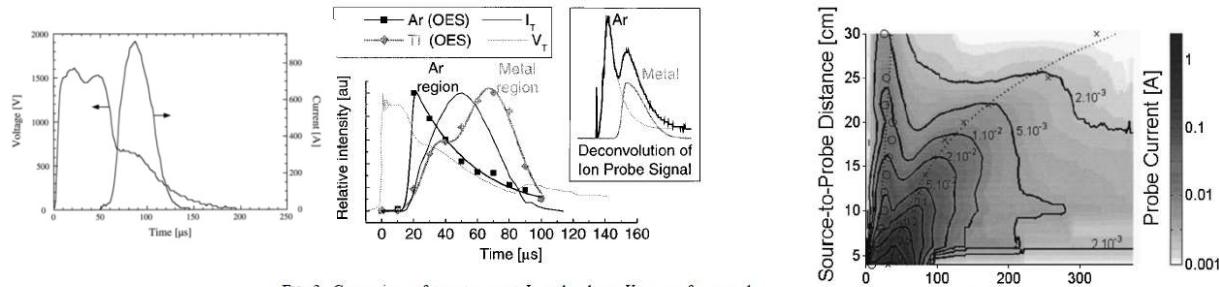


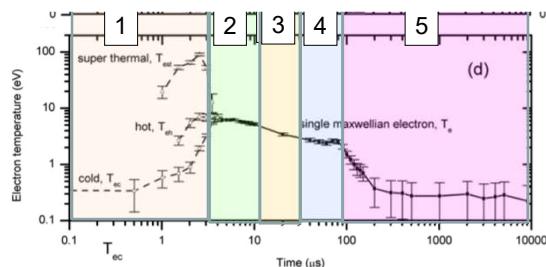
FIG. 3. Comparison of target current  $I_T$  and voltage  $V_T$  wave forms and

**The existence of time separation between the Ar and metal-ion dominated fluxes at the substrate opens the possibility for selection one of the components for ion-assisted by using a pulsed bias voltage with suitable synchronization**

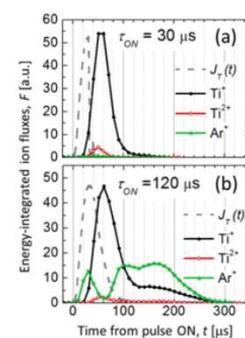
109

## Phases of the HIPIMS discharge

1. Ignition/discharge breakdown
2. Current rise
3. Gas depletion/rarefaction
4. Metal mode\*
5. Afterglow



P Poolcharuansin and J W Bradley  
*Plasma Sources Sci. Technol. 19 (2010) 025010*



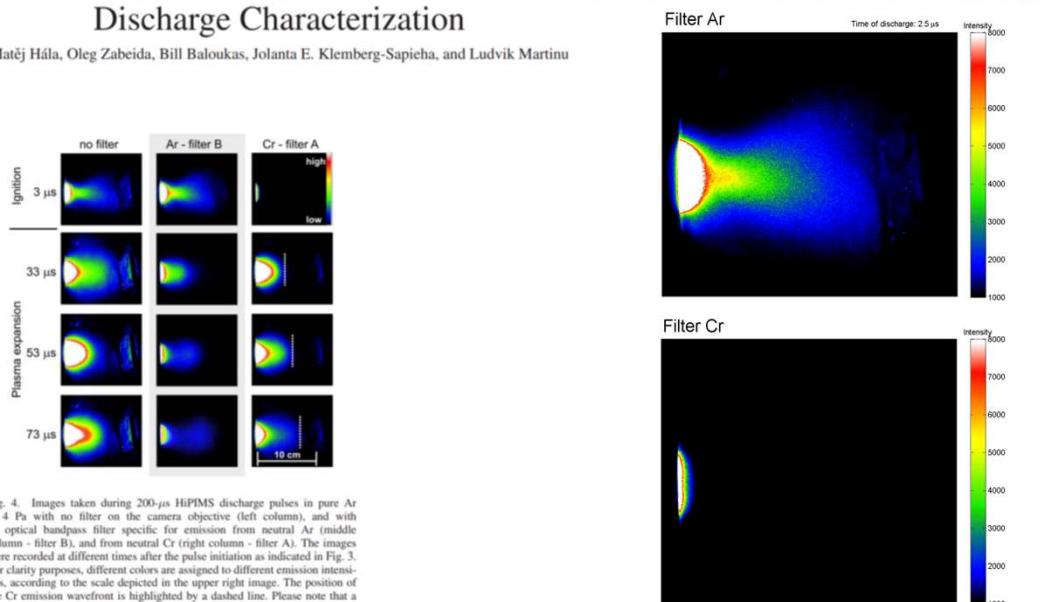
110

# Time- and Species-Resolved Plasma Imaging as a New Diagnostic Approach for HiPIMS Discharge Characterization

Matěj Hála, Oleg Zabeida, Bill Baloukas, Jolanta E. Klemba-Sapieha, and Ludvík Martinu

Page 3035

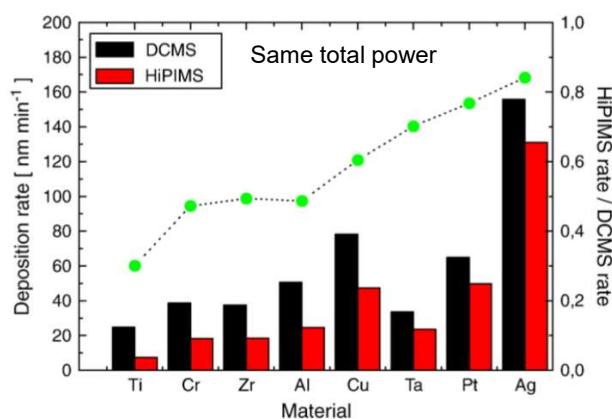
IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 38, NO. 11, NOVEMBER 2010



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## Lower deposition rates in HiPIMS due to back attraction of positive ions of the sputtered materials back to the target



Note: This is just typical example

The reduction of deposition rate may vary significantly for a given material depending on the experimental set-up and the HiPIMS characteristics, as discussed later

**Fig. 1.** The deposition rates for DCMS and HiPIMS discharges plotted as bars for the different target materials used (left axis). The deposition rate of HiPIMS over DCMS deposition rate is shown as a scatter plot (right axis).

M. Samuelsson, D. Lundin, J. Jensen, M. A. Raadu, J. T. Gudmundsson, and U. Helmersson, Surf. Coat. Technol. 202, 591 (2010).

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## Gas sputtering and recycling, metal self-sputtering

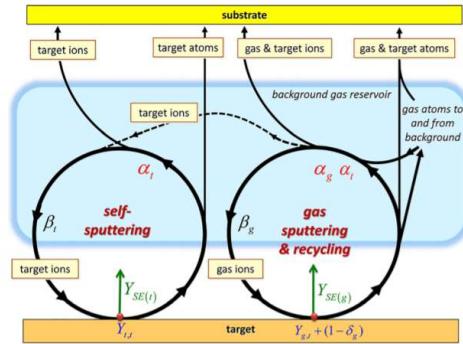
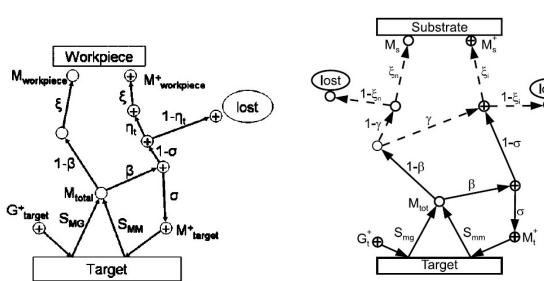


FIG. 19. Illustration of fluxes including self-sputtering, sputtering by gas, and repeated use ("recycling") of gas atoms. Figures like that illustrate a system of nonlinear rate equations. Reprinted with permission from Anders *et al.*, J. Phys. D: Appl. Phys. **45**, 012003 (2012). Copyright 2012 the IOP Publishing Ltd. (Fig. 1 from Ref. 84).

DJ Christie, JVST A 23,330, 2005  
J Vlcek K Burkalova  
Plasma Sources Sci Technol 19, 065010, 2010

A Anders, J Capek, M Hala and L Martinu  
J Phys D 45, 012003 (2012)

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## A unified treatment of self-sputtering, process gas recycling, and runaway for high power impulse sputtering magnetrons

N Brenning<sup>1,2,3</sup>, J T Gudmundsson<sup>1,2,4</sup> , M A Raadu<sup>1</sup>, T J Petty<sup>3</sup>,  
T Minea<sup>2</sup> and D Lundin<sup>2,5</sup>

Plasma Sources Sci. Technol. **26** (2017) 125003 (13pp)

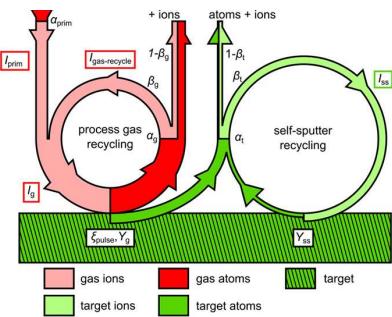


Figure 1. A schematic illustration, revised from Anders *et al.* [9], of the combined processes of process gas recycling and self-sputter recycling. The widths of the flow arrows are drawn to scale with a parameter combination  $\eta_{pump} = 1$ ,  $\zeta_{pump} = 1$ ,  $\alpha_2 = 0.7$ ,  $\beta_2 = 0.7$ ,  $Y_g = 0.4$ ,  $\alpha_3 = 0.8$ ,  $\beta_3 = 0.7$ , and  $Y_{SS} = 0.5$ . This combination is arbitrarily chosen as suitable to illustrate combined gas-recycling and SS-recycling.

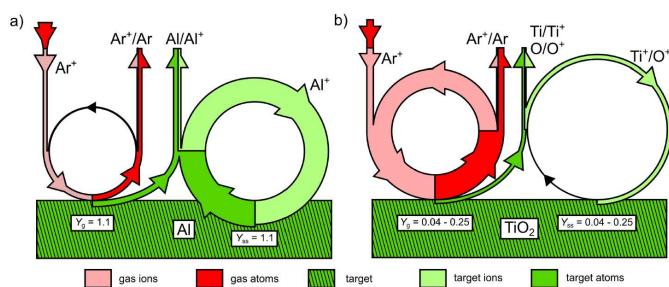


Figure 7. Recycling loops such as in figure 1, with the widths of the arrows drawn to scale for two cases from figure 6: one (a) showing the discharge with an Al target where SS-recycling dominates, and one (b) showing the discharge with a TiO<sub>2</sub> target where gas-recycling dominates.

Inert gas sputtering and self-sputtering yield important

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## Time evolution and the energy distribution of the gas and metal ion fluxes in HiPIMS by in-situ ion mass spectrometry measurements

- Time separation between the gas and the metal ions (gas rarefaction)  
important for HiPIMS with metal ions synchronized bias and bipolar HiPIMS
- Control of doubly charged ions in HIPIMS  
important for metastable films synthesis (examples tomorrow)
- High energy metal ions in HIPIMS

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Prof. Greg Greczynski

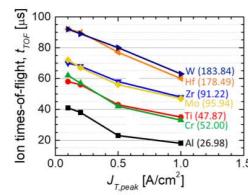
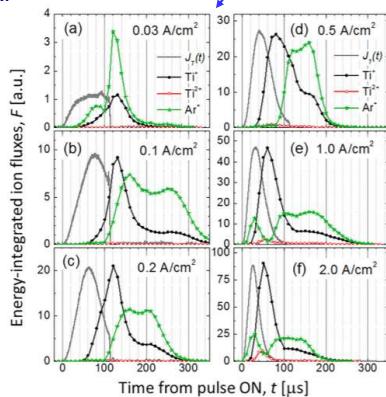
### Gas rarefaction effects during high power pulsed magnetron sputtering of groups IVb and Vb transition metals in Ar

JVST A, 35, 060601 (2017)

Grzegorz Greczynski, Igor Zhirkov, Ivan Petrov, J. E. Greene, and Johanna Rosen

#### Time separation between the gas and the metal ions

Depends on the peak current, on the material (next slide), and on the pulse length



Time of flight (average ion velocity) depends on the peak current and ion mass

The HiPIMS pulse length is 120 μs at a frequency of 300 Hz.

116

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## Gas rarefaction effects during high power pulsed magnetron sputtering of groups IVb and Vb transition metals in Ar

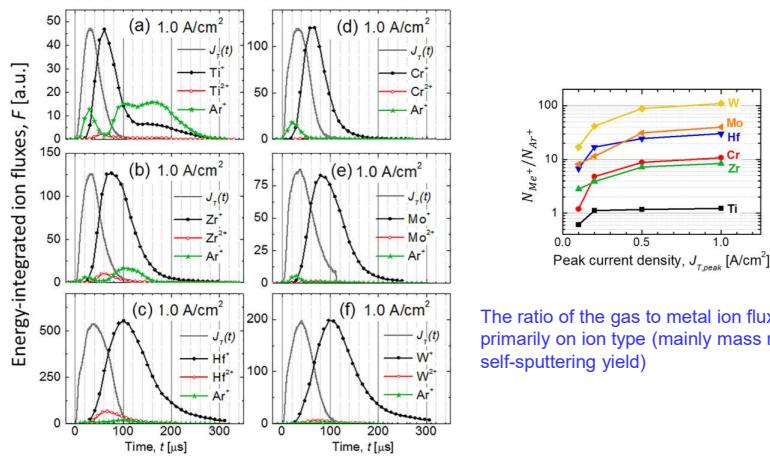
JVST A, 35, 060601 (2017)

Grzegorz Greczynski, Igor Zhirkov, Ivan Petrov, J. E. Greene, and Johanna Rosen

### Time separation between the gas and the metal ions

Depends on the peak current, on the material, on the pulse length (next slide)

IVB	Vb	VIb
22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996
40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95
72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.34



The ratio of the gas to metal ion fluxes depends primarily on ion type (mainly mass ratio and the self-sputtering yield)

117

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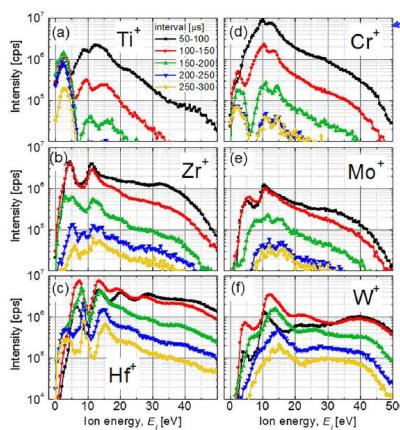
## Gas rarefaction effects during high power pulsed magnetron sputtering of groups IVb and Vb transition metals in Ar

JVST A, 35, 060601 (2017)

Grzegorz Greczynski, Igor Zhirkov, Ivan Petrov, J. E. Greene, and Johanna Rosen

### Time separation between the gas and the metal ions

Depends on the peak current, on the material, on the pulse length (next slide)



- The ions of lighter elements, Ti and Cr lose energy due to back filling with Ar
- The ions of the heavy elements Hf and W preserve the high energy tails **more pronounced rarefaction and more difficult to thermalize**

**The heavy metals promote gas rarefaction and high metal to gas ion ratio – an advantage in metal ion assisted film growth**

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FIG. 4. (Color online)  $Me^+$  ion energy distribution functions (IEDFs) recorded at the substrate position during HiPIMS sputtering of  $Me = Ti$  (a),  $Zr$  (b),  $Hf$  (c),  $Cr$  (d),  $Mo$  (e), and  $W$  (f) targets in Ar at 0.4 Pa (3 mTorr). The IEDFs are acquired during 50- $\mu$ s time intervals over the time period from 0 (pulse ignition) to 300  $\mu$ s. The pulse length is 120  $\mu$ s.

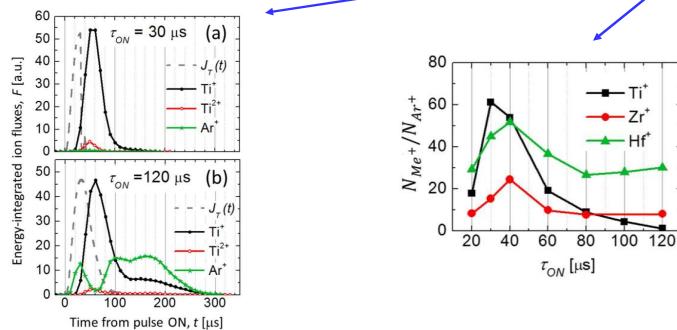
118

Control of the metal/gas ion ratio incident at the substrate plane during high-power impulse magnetron sputtering of transition metals in Ar

G. Greczynski<sup>a,\*</sup>, I. Zhirkov<sup>a</sup>, I. Petrov<sup>a,b</sup>, J.E. Greene<sup>a,b,c</sup>, J. Rosen<sup>a</sup>

*Thin Solid Films* 642 (2017) 36–40

**Time separation between the gas and the metal ions  
Depends on the peak current, on the material, on the pulse length )**



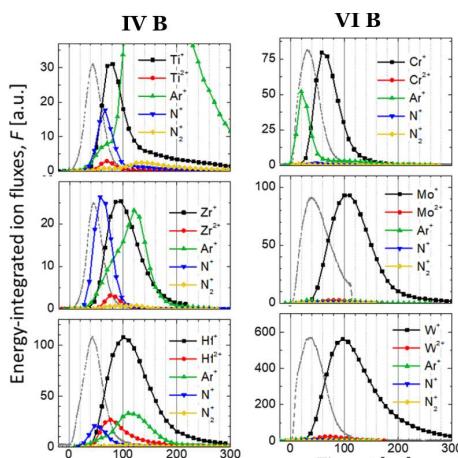
119

119

**Reactive sputtering: Ion mass spectrometry at substrate position  
to determine the metal ion dominated phase**

IV B	V B	VI B
22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996
40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95
72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84

$p = 3 \text{ mTorr}$ ;  $\text{N}_2/\text{Ar}$  flow ratio of 0.11  
Peak Current  $1 \text{ A/cm}^2$



$\text{Ar}^+$  overlaps with  $\text{Me}^+$      $\text{Ar}^+$  separated from  $\text{Me}^+$

Grzegorz Greczynski, Igor Zhirkov, Ivan Petrov, J. E. Greene, and Johanna Rosen, JVST A 36, 020602 (2018);

120

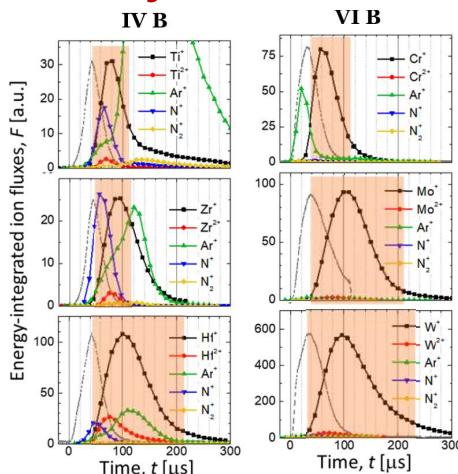
120

## Reactive sputtering: Ion mass spectrometry at substrate position to determine the metal ion dominated phase

### Metal ion synchronized bias

IV B    V B    VI B		
22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996
40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95
72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84

$p = 3 \text{ mTorr}$ ;  $\text{N}_2/\text{Ar}$  flow ratio of 0.11  
Peak Current 1 A/cm<sup>2</sup>



$\text{Ar}^+$  overlaps with  $\text{Me}^+$     $\text{Ar}^+$  separated from  $\text{Me}^+$

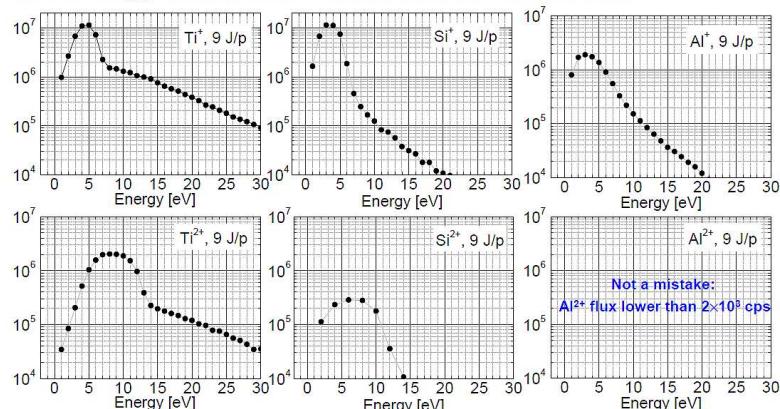
Grzegorz Greczynski, Igor Zhirkov, Ivan Petrov, J. E. Greene, and Johanna Rosen, JVST A 36, 020602 (2018);

121

121

## Changes in the $\text{Me}^{2+}$ component Important for metastable materials synthesis

### Ion energy distribution functions for metal ions



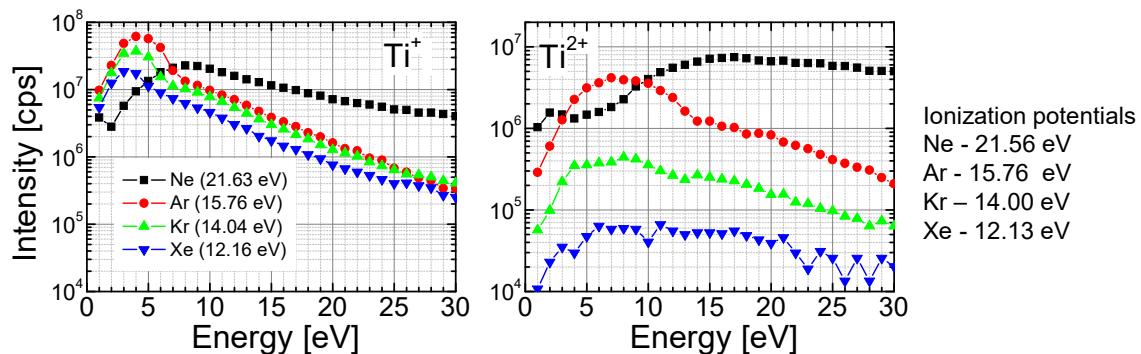
- Second ionization potential: Ti: 13.62 eV, Si: 16.35 eV, Al: 18.89 eV

↑  
Ar first ionization potential 15.76 eV

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## Control of doubly charged ions in HIPIMS

Model system: Ti sputtered in Ne, Ar, Kr, and Xe

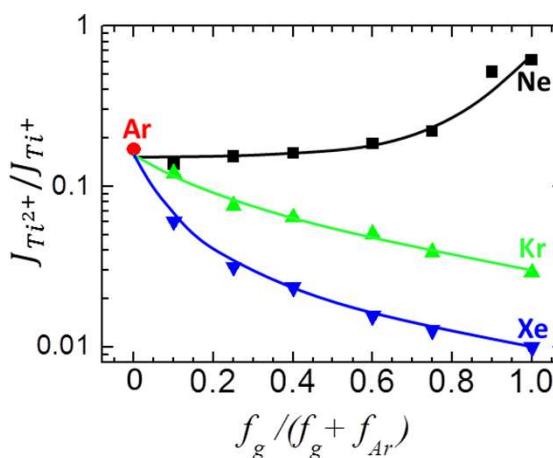


- $Ti^{2+}$  detrimental to TiAlN films grown by HIPIMS/DCMS
- Reason for high  $Ti^{2+}$  population while sputtering in Ar:  $IP_{Ti}^2 < IP_{Ar}^1$
- exchanging Ar for lower IP gases (Kr, Xe) decreases  $T_e$  and the relative amount of  $Ti^{2+}$ , while the opposite is valid for Ne which has highest IP

G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, Vacuum 116 (2015) 36

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## $J_{Ti^{2+}}/J_{Ti^{+}}$ : comparison for Ne, Ar, Kr and Xe

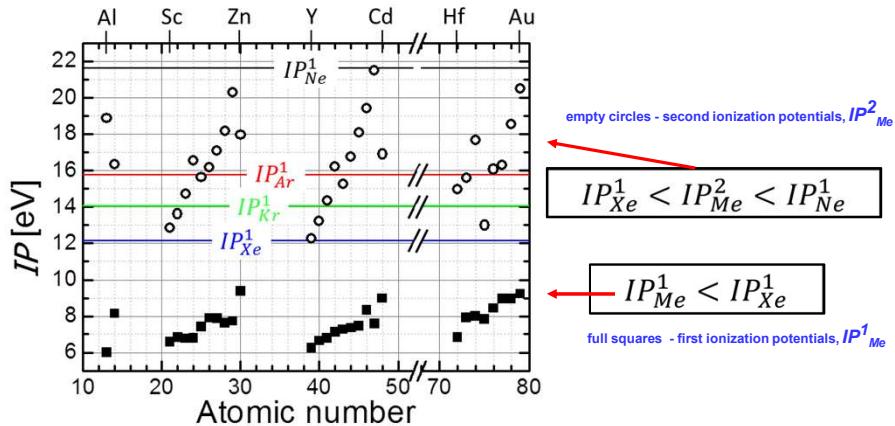


- by changing noble-gas mixtures,  $J_{Ti^{2+}}$  varies by more than two orders of magnitude with only a small change in  $J_{Ti^{+}}$ .
- This allows the ratio  $J_{Ti^{2+}}/J_{Ti^{+}}$  to be continuously tuned from 0.01 with Xe to 0.62 with Ne

G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, Vacuum 116 (2015) 36

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## Extension to other materials



G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, Vacuum 116 (2015) 36

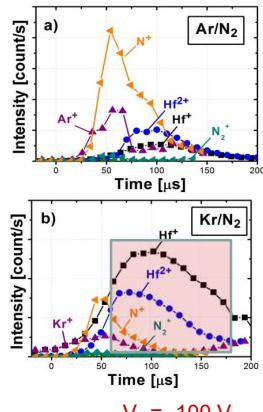
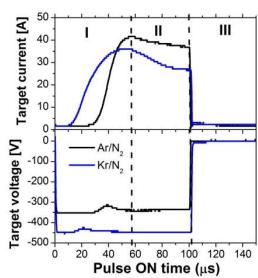
125

## An example of the importance of the choice of inert sputtering gas

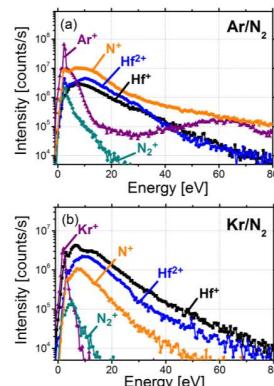
Low temperature epitaxial growth of HfN/MgO(100) via HiPIMS-synchronized pulsed substrate bias

HfN the highest melting point  
TM nitride:  $T_M \sim 3520$  K

$T_s < 70$  °C;  $T_s/T_M < 0.1$



$$\begin{aligned} IP_{Ar} &= 15.8 \text{ eV} \\ IP_{N} &= 14.5 \text{ eV} \\ IP_{N_2} &= 15.6 \text{ eV} \\ IP_{Kr} &= 14.0 \text{ eV} \end{aligned}$$



M.M.S. Villamayor, T. Shimizu, J. Keraudy, R.P.B. Viloan, R. Boyd, D. Lundin, J.E. Greene, Ivan Petrov, Ulf Helmersson J. Vac. Sci. Technol. A, Vol. 36 (2018) 06151

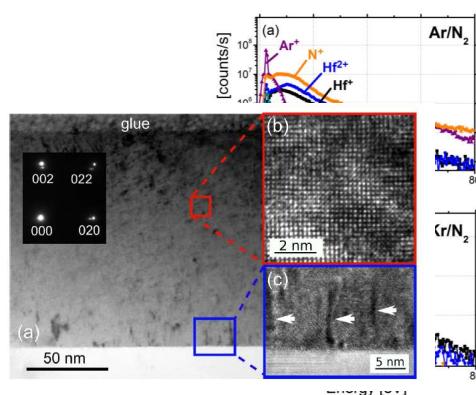
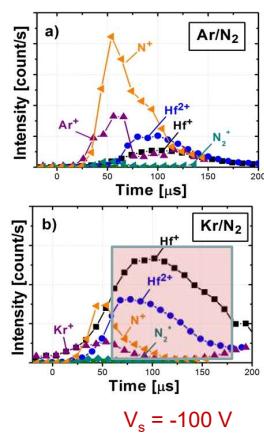
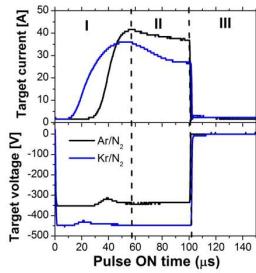
126

## An example of the importance of the choice of inert sputtering gas

Low temperature epitaxial growth of HfN/MgO(100) via HiPIMS-synchronized pulsed substrate bias

HfN the highest melting point  
TM nitride:  $T_M \sim 3520$  K

$T_S < 70$  °C;  $T_S/T_M < 0.1$



M.M.S. Villamayor, T. Shimizu, J. Keraudy, R.P.B. Viloan, R. Boyd, D. Lundin, J.E. Greene, Ivan Petrov, Ulf Helmersson J. Vac. Sci. Technol. A, Vol. 36 (2018) 06151

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## HiPIMS: source of energetic metal ions

J. Bohlmark, M. Lattemann, J.T. Gudmundsson, A.P. Eriasarian,  
Y. Aranda Gonzalvo, N. Brenning, U. Helmersson

The ion energy distributions and ion flux composition from a high-power impulse magnetron sputtering discharge  
Thin Solid Films 515 (2006) 1522-1526

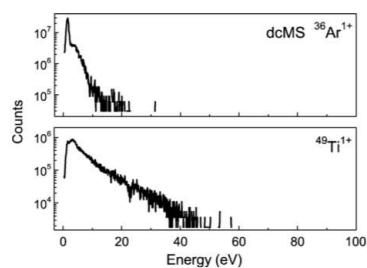


Fig. 2. The ion energy distributions taken from a conventional DC magnetron discharge. The Ar pressure was 0.4 Pa, the applied power 1 kW, and the target material was Ti. The recorded counts have been adjusted with the corresponding isotope abundance.

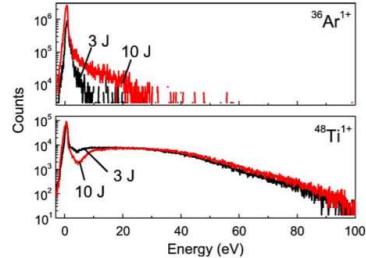
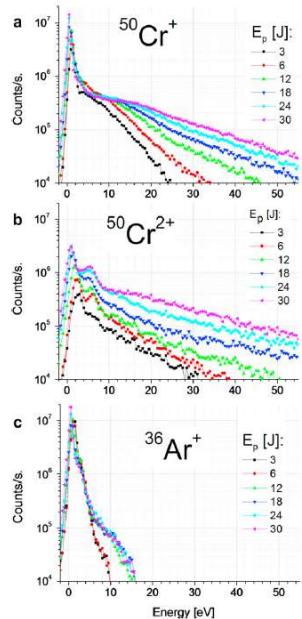


Fig. 3. The ion energy distributions for  $\text{Ar}^{1+}$  and  $\text{Ti}^{1+}$  ions measured from a HiPIMS discharge. The Ar pressure was 0.4 Pa, the pulse energy 3 and 10 J, and the target was made of Ti. The recorded counts have been adjusted with the corresponding isotope abundance.

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## Higher-energy metal ions



## Ion Energy Distribution Functions

high-energy tails due to

- gas rarefaction
- potential humps of associated with traveling ionization zones – next slide

G. Greczynski, L. Hultman, Vacuum 84 (2010) 1159

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## Higher-energy metal ions

APPLIED PHYSICS LETTERS 103, 144103 (2013)

### Drifting potential humps in ionization zones: The “propeller blades” of high power impulse magnetron sputtering

André Anders,<sup>1,a)</sup> Matjaž Panjan,<sup>1,2</sup> Robert Franz,<sup>1,3</sup> Joakim Andersson,<sup>1,4</sup> and Pavel Ni<sup>1</sup>

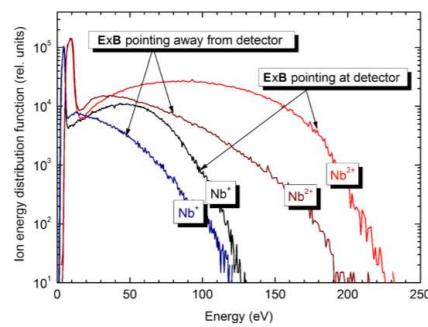
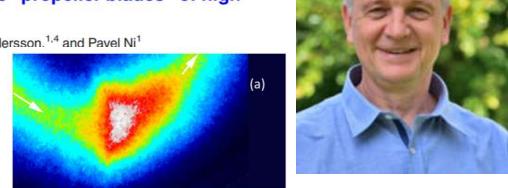


FIG. 2. Ion energy distribution function measured with a Hiden EQP300 energy analyzer at 140 mm distance from the target, recording niobium ions emitted near the target plane tangentially from the racetrack; discharge voltage 350 V, 200  $\mu$ s pulse length, 100 pulses per second, 275 A peak, in 0.53 Pa of Ar.



Andre Anders

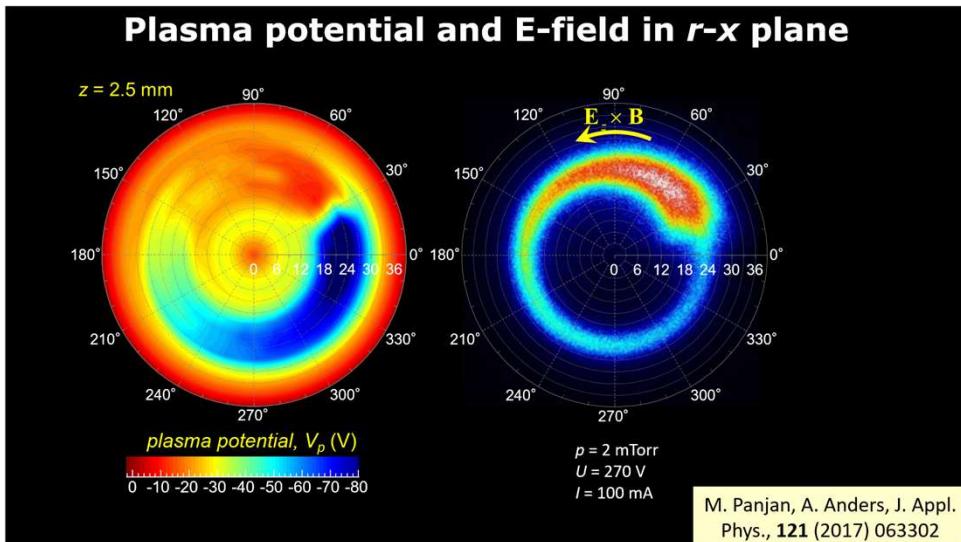
$$E_i = E_0 + \frac{m_i}{2} v_{IZ}^2 + e Q V_{hump}, \quad (8)$$

where  $E_0$  represents the energy from the sputtering and collisional processes,  $v_{IZ}$  is the drift velocity of the ionization zone,  $Q$  is the ion charge state number, and  $V_{hump}$  is the height of the potential hump. Ions moving in the opposite

## Potential humps – double layer

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### Further reading on spokes and high energy metal ions in HiPIMS

IOP Publishing

J. Phys. D: Appl. Phys. **47** (2014) 224002 (13pp)

Journal of Physics D: Applied Physics

doi:10.1088/0022-3727/47/22/224002

### Origin of the energetic ions at the substrate generated during high power pulsed magnetron sputtering of titanium

C Maszl, W Breilmann, J Benedikt and A von Keudell

Research Department Plasmas with Complex Interactions, Ruhr-Universität Bochum, Institute for Experimental Physics II, D-44780 Bochum, Germany

The IEDF of metal species arriving at the substrate defines the energy input during film growth, which is of paramount importance for all film properties. Since the DL around the spokes provides a mechanism to overcome the return effect in HiPIMS and to provide energetic  $\text{Ti}^+$  species, one may conclude that the spoke phenomenon is not a nuisance or peculiarity of the HiPIMS process, but rather the *essence* of HiPIMS plasmas explaining their good performance for material synthesis applications.

Plasma Chemistry and Plasma Processing (2020) 40:643–660  
<https://doi.org/10.1007/s11090-019-10052-3>

ORIGINAL PAPER

### Pattern Formation in High Power Impulse Magnetron Sputtering (HiPIMS) Plasmas

Julian Held<sup>1</sup> · Achim von Keudell<sup>1</sup>

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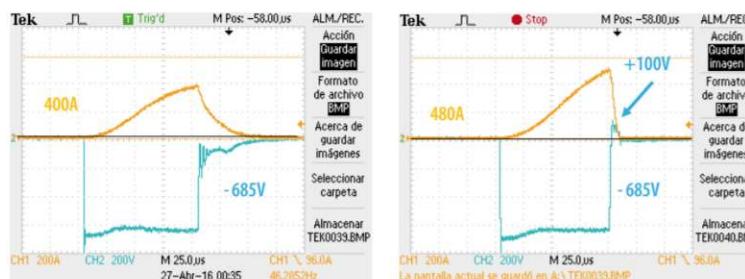
132

## Bipolar pulsed high-power impulse magnetron sputtering

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## Bipolar pulsed high-power impulse magnetron sputtering

G.Eichenhofer, I Fernandez, A Wennberg  
Vakuum in Forschung und Praxis · April 2017



Ivan Fernandez: Nano4Energy

- Novel HIPIMS power supply the hiPV, hiPlus option
- positive voltage reversal for **positive ion assisted deposition on insulating substrates with reducing the tendency to arcing.**

**nano4ENERGY**

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## Bipolar pulsed high-power impulse magnetron sputtering

**Increased deposition rate**

Wu, Haehlein, Shchelkanov, McLain, Patel, Uhlig, Jurczyk, Leng, Ruzic, *Vacuum*, 150, 216 (2018)

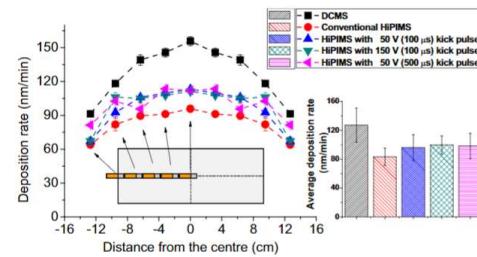
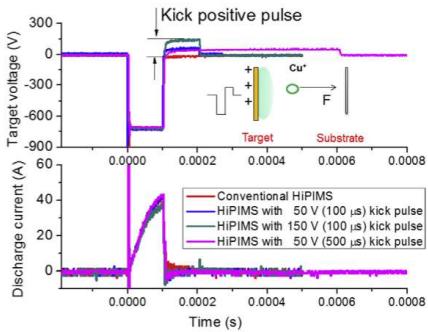


Fig. 3. Deposition rate of Cu films across the center-line length of Cu target. Average deposition rate is the average value of deposition rate of all the samples at different position.



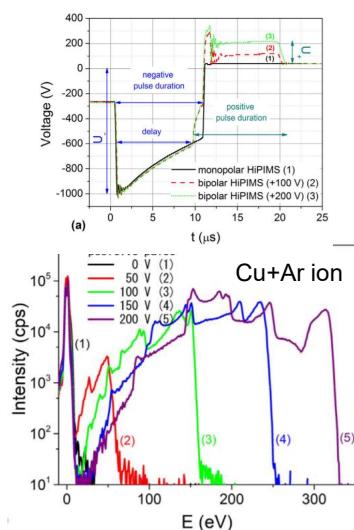
135

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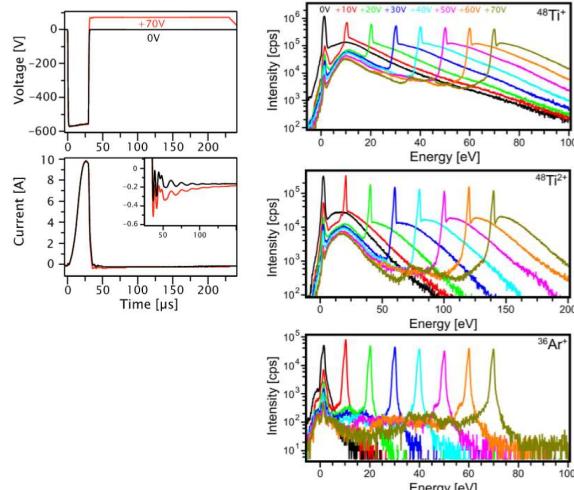
## Bipolar pulsed high-power impulse magnetron sputtering

**Precise control of ion energy**

Velicu, Ianoş, Porosnicu, Mihăilă, Burducea, Velea, Cristea, Munteanu, Tiron, *SCT* 359, (2019), 97-107



Keraudy, Viloan, Raadu, Brenning, Lundin, Helmersson, *SCT* 359, (2019), 433



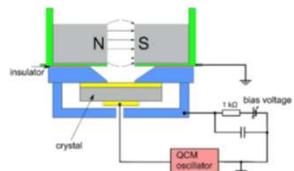
136

68

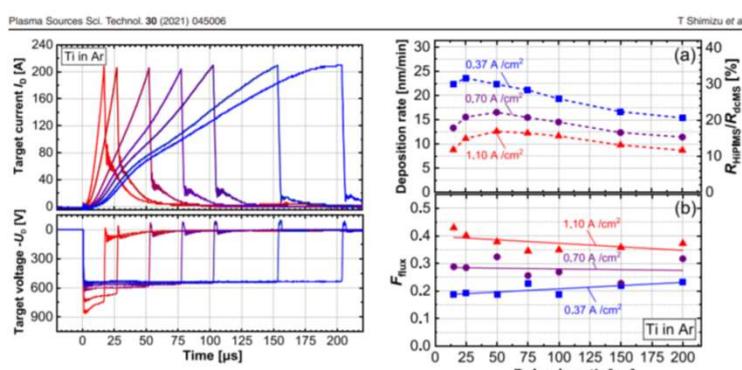
## Experimental verification of deposition rate increase, with maintained high ionized flux fraction, by shortening the HiPIMS pulse

Plasma Sources Sci. Technol. **30** (2021) 045006 (8pp)

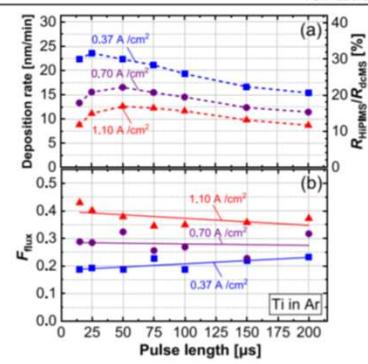
T Shimizu<sup>1,2</sup>, M Zanáška<sup>1</sup>, R P Viljoen<sup>1</sup>, N Brenning<sup>1,3</sup>,  
U Helmersson<sup>1</sup> and Daniel Lundin<sup>1,4,\*</sup>



**Figure 5.** Schematic of the gridless ion meter. Impinging electrons are repelled by a local magnetic field, which prevents the electrons from reaching the biased top QCM electrode.



**Figure 1.** The applied discharge voltage  $U_D$  (lower panel) and the resulting discharge current ( $I_D$ ) (upper panel) waveforms of the Ti/Ar discharge when varying the pulse length in the range 15–200  $\mu\text{s}$ . The discharge voltage was adjusted to maintain a peak current of 200 A ( $J_{D,\text{peak}} = 1.10 \text{ A cm}^{-2}$ ). The pulse repetition frequency was adjusted to maintain a constant time-averaged power of 1 kW.



**Figure 2.** (a) Deposition rate (left axis) with corresponding normalized HiPIMS deposition rate to the dcMS deposition rate,  $R_{\text{HiPIMS}}/R_{\text{dcMS}}$  (right axis), and (b) ionized flux fraction  $F_{\text{flux}}$  as a function of pulse length for three different  $J_{D,\text{peak}}$  of 0.37, 0.70 and 1.10  $\text{A cm}^{-2}$ . An averaged power of 1 kW is maintained constant independent of pulse length and  $J_{D,\text{peak}}$ .

## Tutorial: Reactive high power impulse magnetron sputtering (R-HiPIMS)

Cite as: J. Appl. Phys. **121**, 171101 (2017); <https://doi.org/10.1063/1.4978350>

Submitted: 17 November 2016 . Accepted: 18 February 2017 . Published Online: 21 March 2017

André Anders

JOURNAL OF APPLIED PHYSICS **121**, 080901 (2017)



### Perspective: Is there a hysteresis during reactive High Power Impulse Magnetron Sputtering (R-HiPIMS)?

K. Strijckmans, F. Moens, and D. Depla

Department of Solid State Sciences, Ghent University, Krijgslaan 281(S1), 9000 Gent, Belgium

## Smooth composition control of oxynitrides - TaON (HIPIMS with feedback pulsed reactive gas flow control (RGFC))

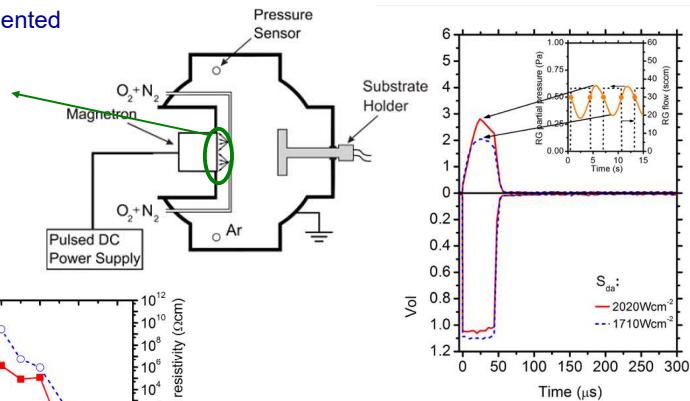
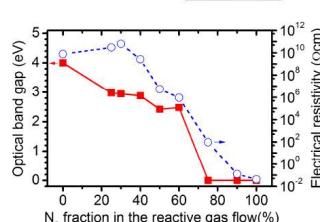
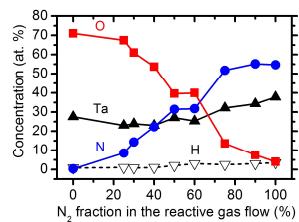
J. Rezek, J. Vlcek, J. Houska, R. Cerstvy, Thin Solid Films 566, 70 (2014)

Reactive gas inlets in front of the target and oriented towards the target + dense HIPIMS plasma

$\Downarrow$   
dissociation of  $O_2$  and  $N_2$

~~different reactivities of  $O_2$  and  $N_2$~~

comparable reactivities of O and N



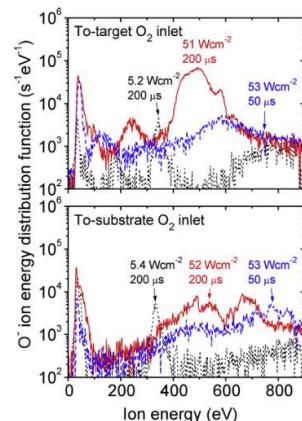
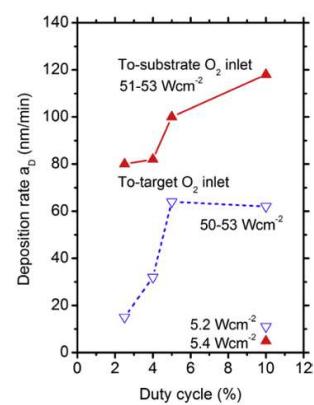
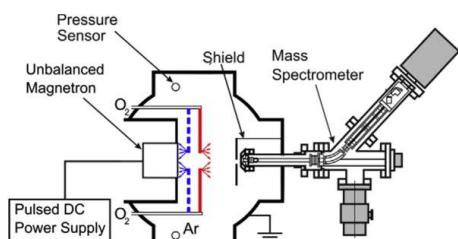
139

## Benefits of the controlled reactive high-power impulse magnetron sputtering of stoichiometric $ZrO_2$ films

J. Vlček\*, J. Rezek, J. Houška, T. Kozák, J. Kohout Vacuum 114 (2015) 131–141

*Department of Physics and NTIS, European Centre of Excellence, University of West Bohemia, Univerzitní 8, 30614 Plzeň, Czech Republic*

Major advance: HIPIMS with feedback pulsed reactive gas flow control (RGFC)



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## Bibliography (vacuum, plasmas)

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## Bibliography (sputtering, sputter deposition)

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## Part 1. Fundamentals of Sputter Deposition

### 1.1 Elements of kinetic theory of gases

- Gas laws
- mean free path
- gas impingement rate

### 1.2 Elements of plasma physics

- Plasma probes
- Sheath width
- Penning ionization
- Electron energy distribution functions

### 1.3 Glow discharge maintenance

- Secondary ion-electron emission
- Electron ionization cross-sections

### 1.4 Sputtering yield

- Linear cascade model
- Correction for threshold effects
- Sputtering efficiency
- Energy of sputtered atoms
- Other energetic particles: backscattered ions and negative oxygen ions

### 1.5 Transport in the gas phase

- Thermalization
- Deposition rate calculation

### 1.6 Sputtering systems

- Magnetron sputtering
- Reactive sputtering

### 1.7 HIPIMS

- Source of metal ions
- Time separation between gas and metal ions
- High energy ions
- Lower deposition rates
- Bipolar HIPIMS
- Control of doubly charged ions

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