

Přehled magnetronové depozice

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Oddělení nízkoteplotního plazmatu
Sekce optika
Fyzikální ústav AV ČR, v.v.i.
Na Slovance 2
182 21 Praha 8

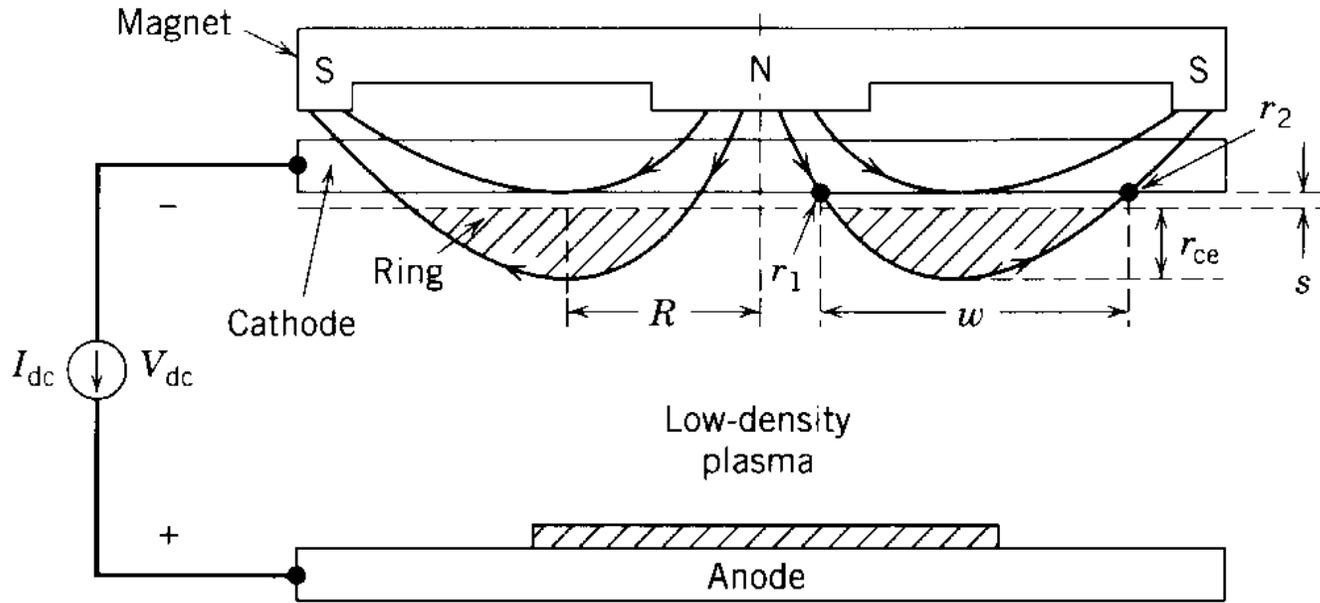
Podpořeno z projektu OP VVV „Partnerská síť v oblasti výzkumu a vývoje zobrazovací a osvětlovací techniky a optoelektroniky pro optický a automobilový průmysl“, registrační číslo: CZ.02.1.01/0.0/0.0/17_049/0008422.



EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání



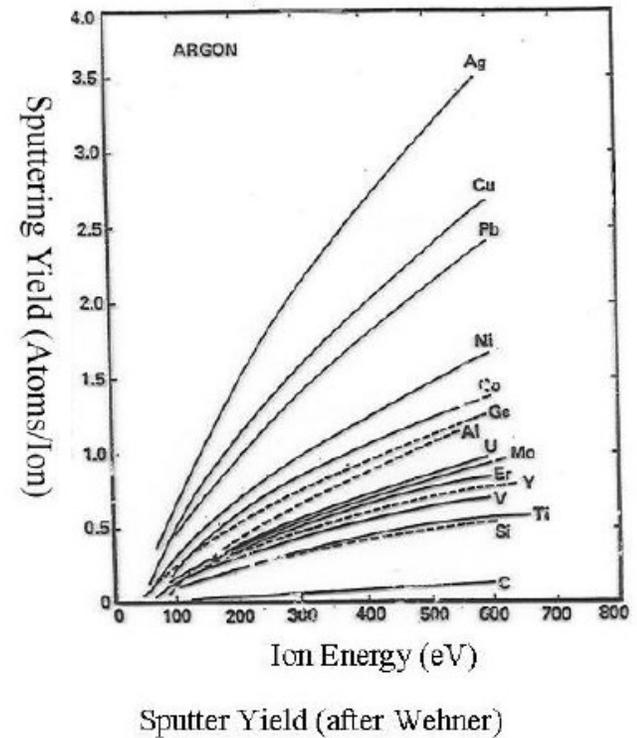
Magnetronové naprašování tenkých vrstev



DC magnetron

výhody magnetronového naprašování

- vysoká hustota a adheze deponované vrstvy
- depozice při nižších teplotách
- reaktivní naprašování
- uspokojivá rychlost depozice
- parametry tenkých vrstev

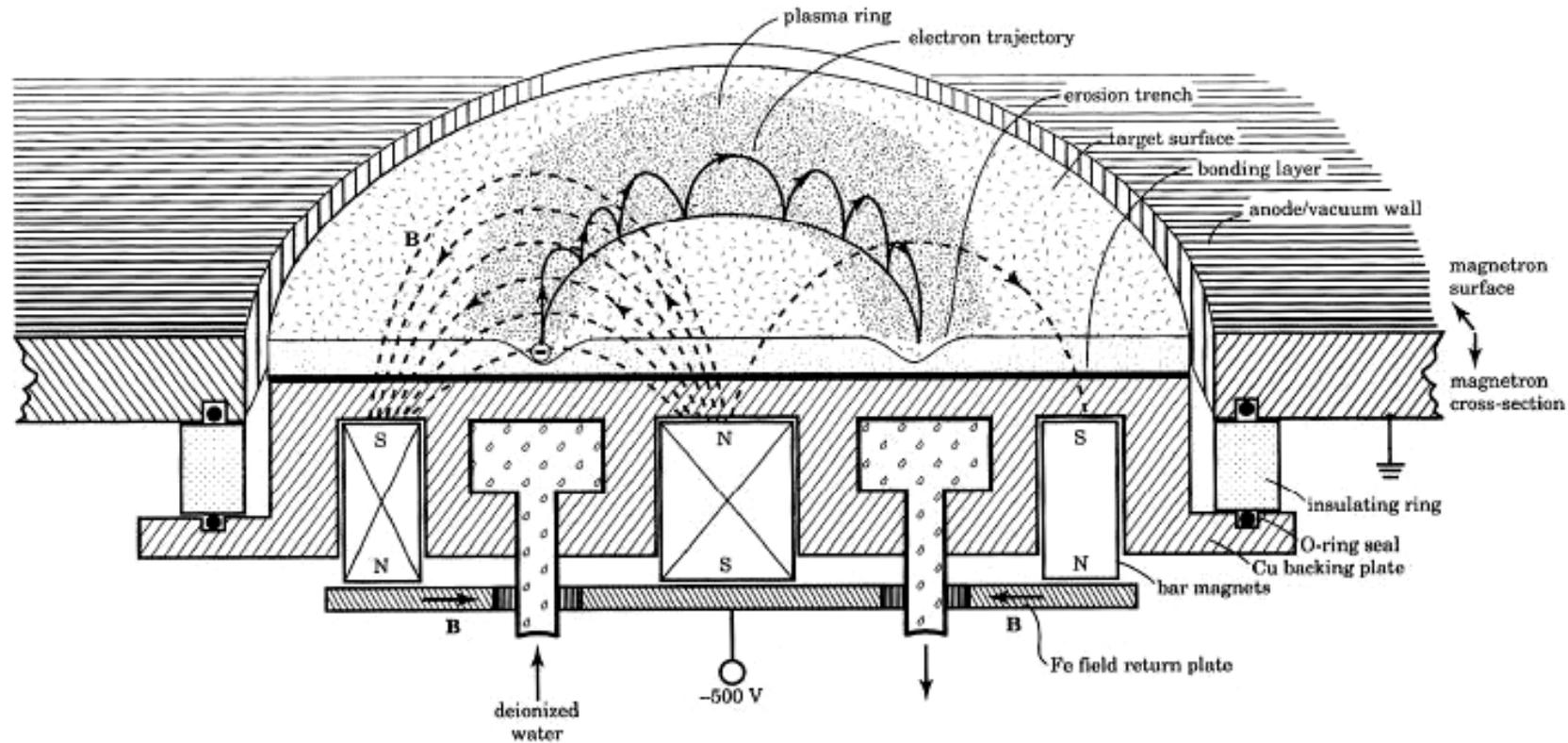


Příklady produktů, kde bylo využito magnetronové naprašování



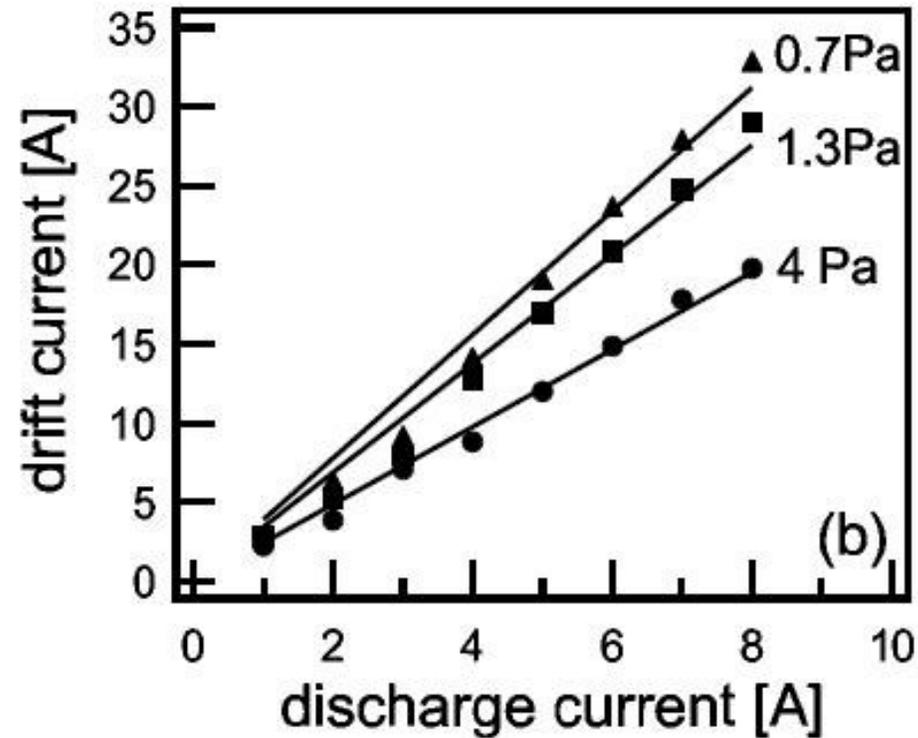
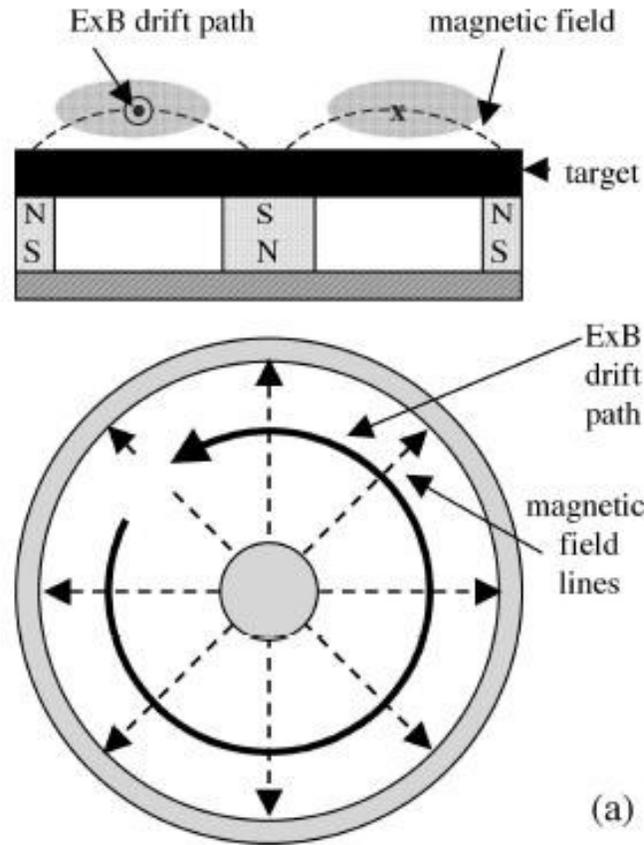
Fyzikální princip magnetronového naprašování

Principle of a Magnetron Discharge



Scheme of a circular planar magnetron according to Smith. The magnetic field is depicted as dashed lines, while the cycloid electron path is shown in larger size for clarity.

Fyzikální princip magnetronového naprašování



(a) Top and side view of a planar circular magnetron, the schematic magnetic and electric field and the resulting $\vec{E} \times \vec{B}$ drift path (after Rossnagel and Kaufman [50]). (b) Measured total drift currents as a function of the discharge current at different working pressures in an argon discharge with a copper target [49].

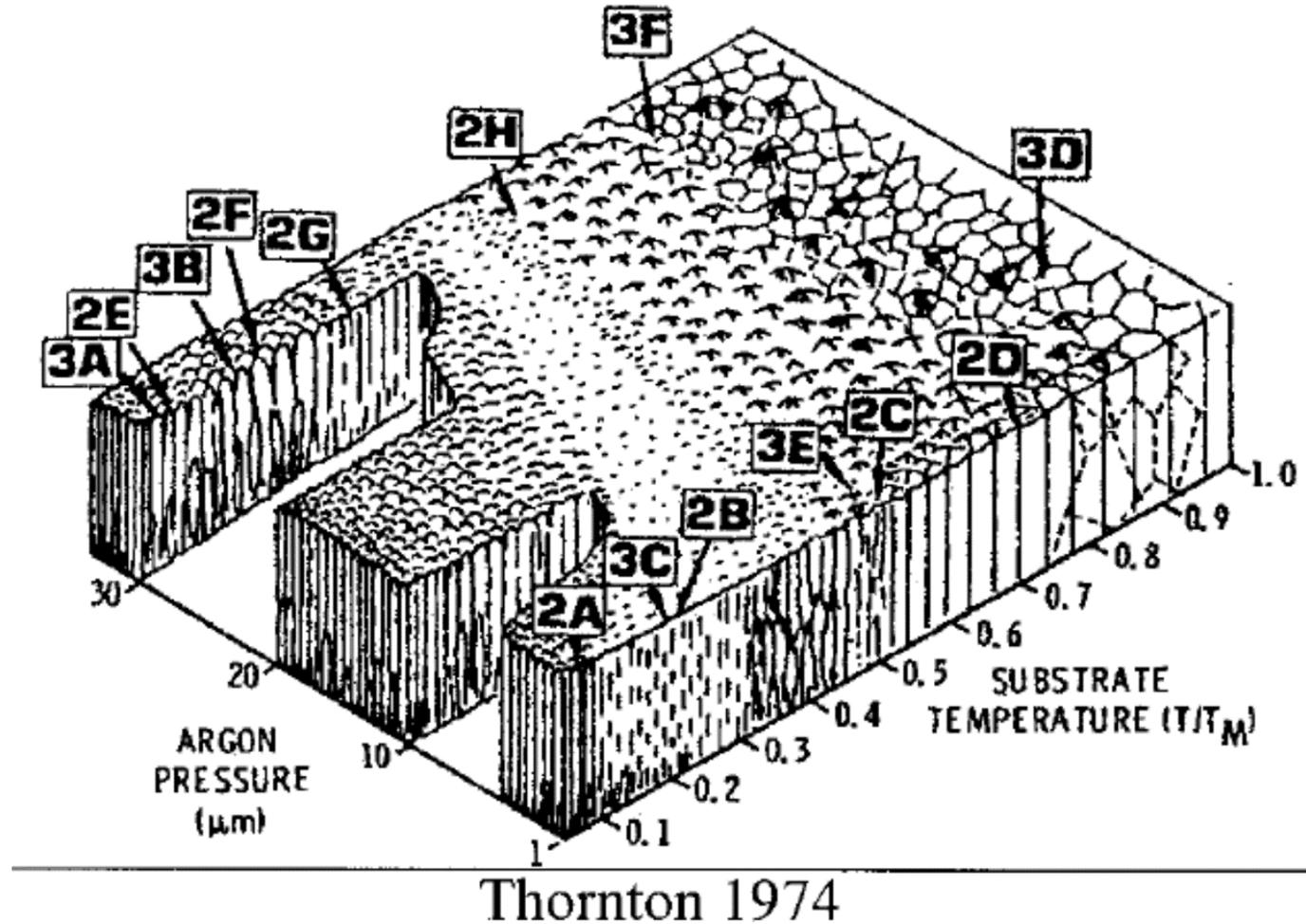
Typické podmínky v DC magnetronovém naprašovacím výboji

- $B_0 \sim 200 \text{ G}$
- $p \sim 2\text{--}5 \text{ mTorr argon}$
- $\bar{J}_i \sim 20 \text{ mA/cm}^2$
- $V_{dc} \sim 600 \text{ V}$
- Deposition rate $\sim 2000 \text{ \AA/min}$

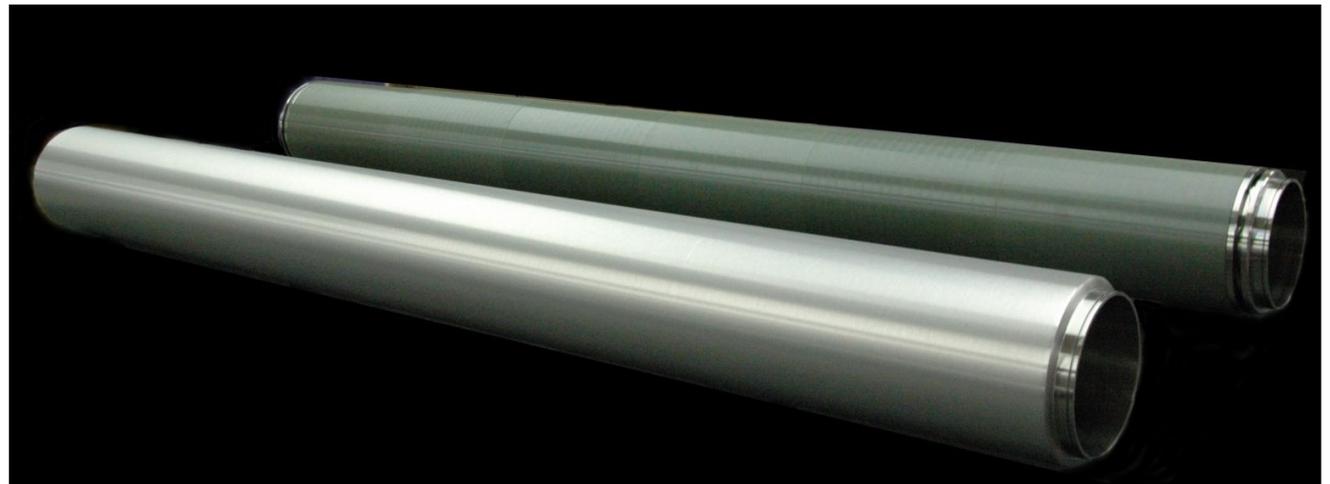
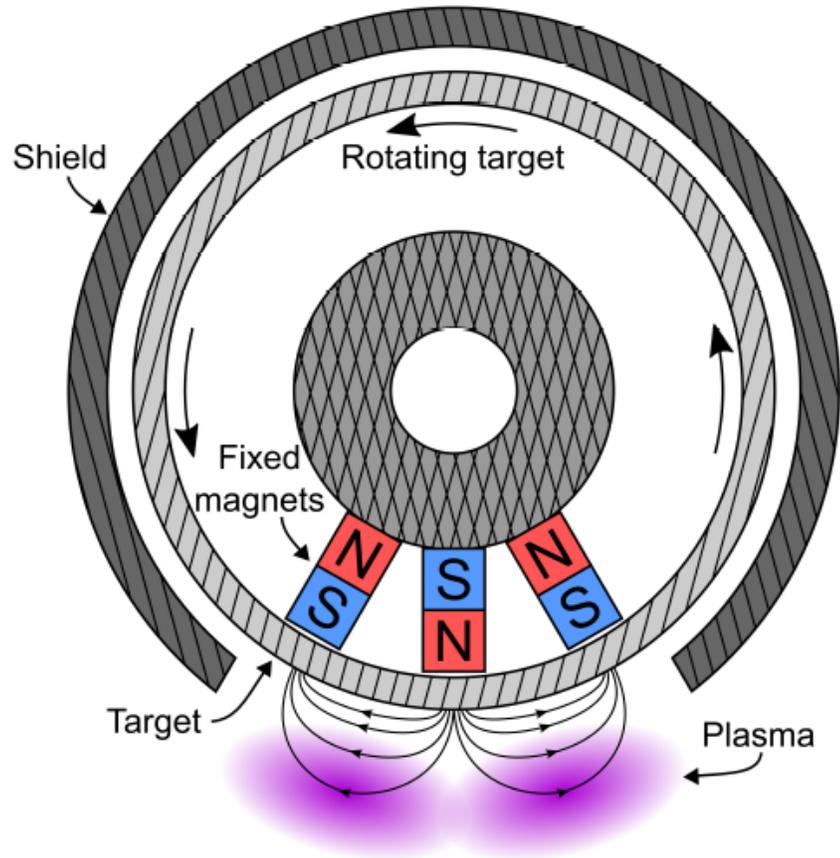
Here B_0 is the magnetic field strength at the radius R where the magnetic field line is tangential to the cathode surface, and \bar{J}_i is the average ion current density over the ring area.

Depozice kovových vrstev magnetronovým naprašováním

- původní aplikace magnetronového naprašování (MS): metalizace Si integrovaných obvodů Al
- byly deponovány další kovové vrstvy pomocí MS
- pro vyšší teploty substrátu a nižší tlak plynu jsou vrstvy více kompaktní bez mezer s větším krystalovým zrnem
- nižší tlak plynu znamená větší energii částic iontů a rozprášených částic bombardující substrát což zvyšuje povrchovou difúzi při nukleaci, ale taky mechanické napětí ve vrstvě

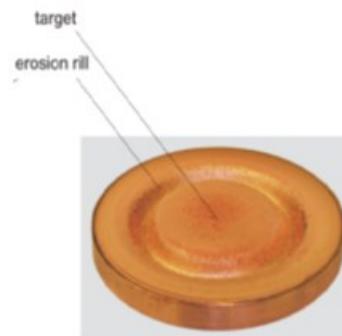
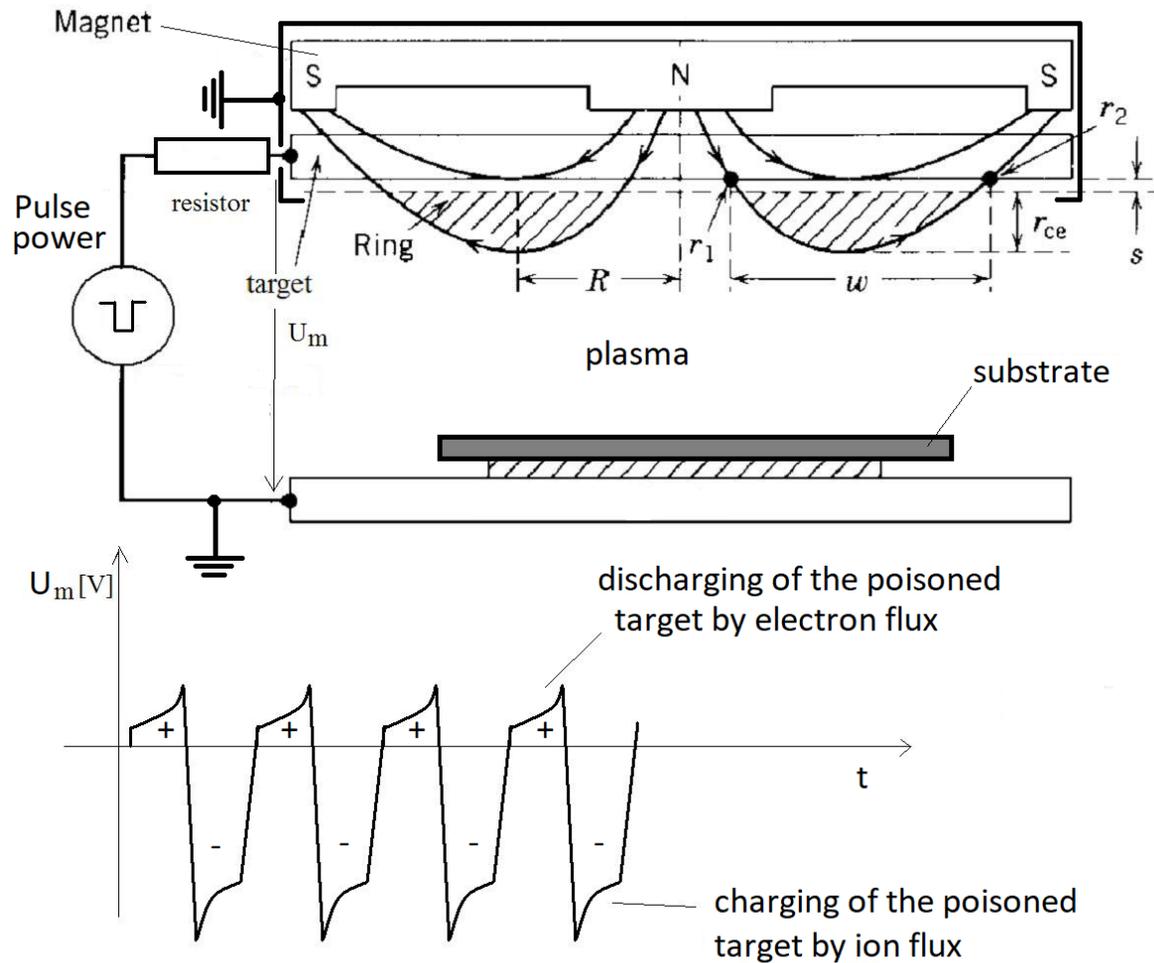


Průmyslové magnetronové naprašovací systémy (povlakování velkých ploch) TiO_2 , Al_2O_3 , ITO, $\text{ZnO}:\text{Al}$

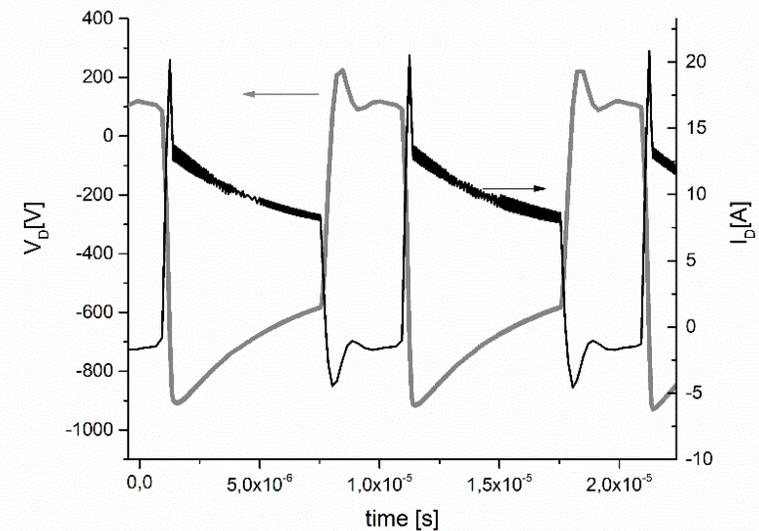
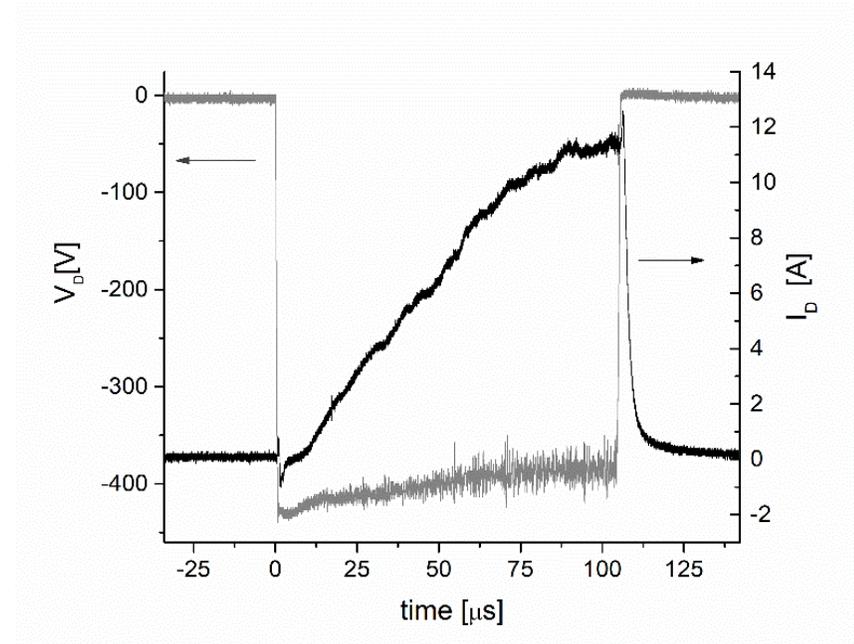
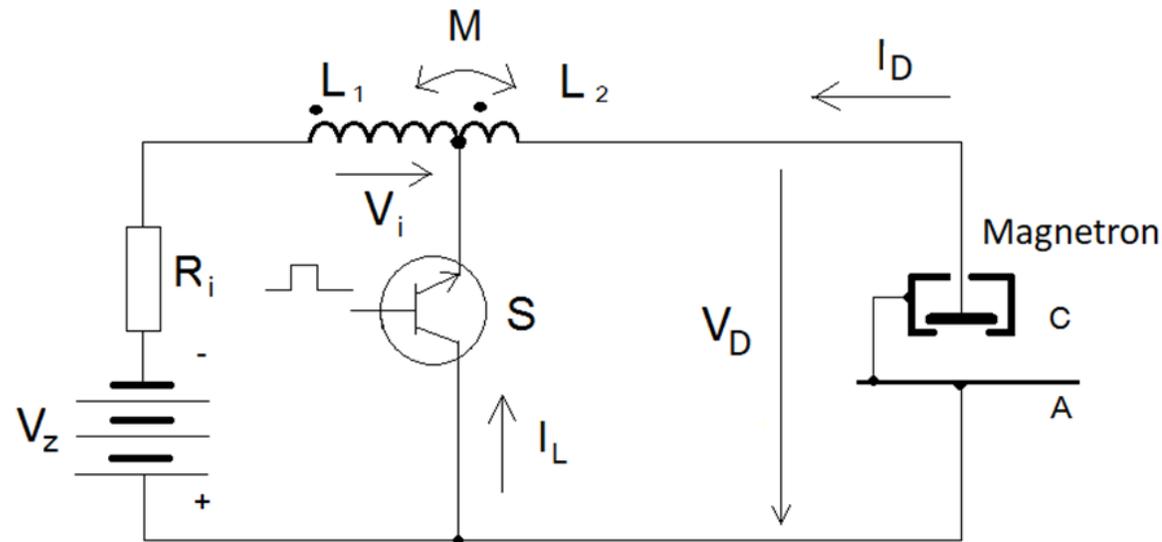
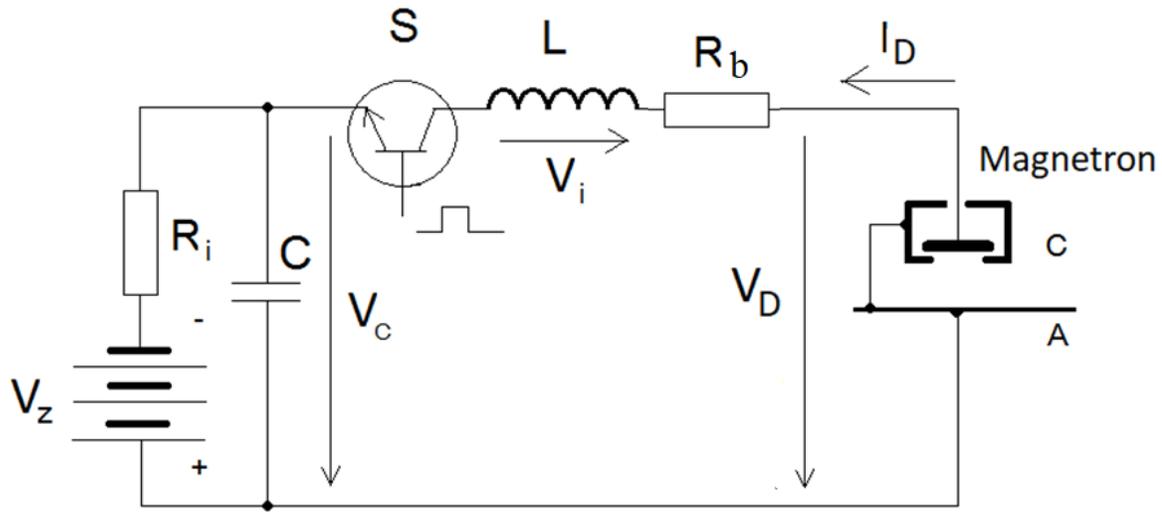


Pulzní reaktivní naprašování tenkých optických vrstev

Ar + O₂ gas mixture



Basic concept of pulsed reactive magnetron sputtering



Pulsing concept with capacitor storage

Energy for pulse is stored in capacitor C:

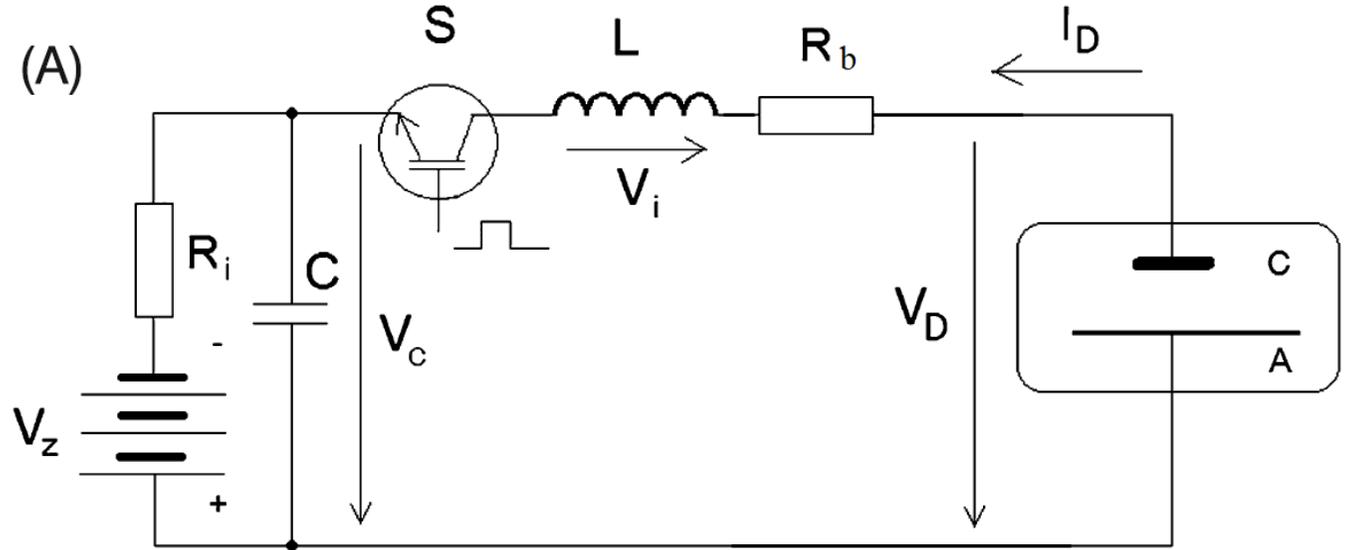
$$\mathcal{E}_C = \frac{1}{2} C V_C^2$$

Current can be accumulated in the pulse.

The inductor L controls (slows down) the rate of current increase and protects the transistor switch from large current surges.

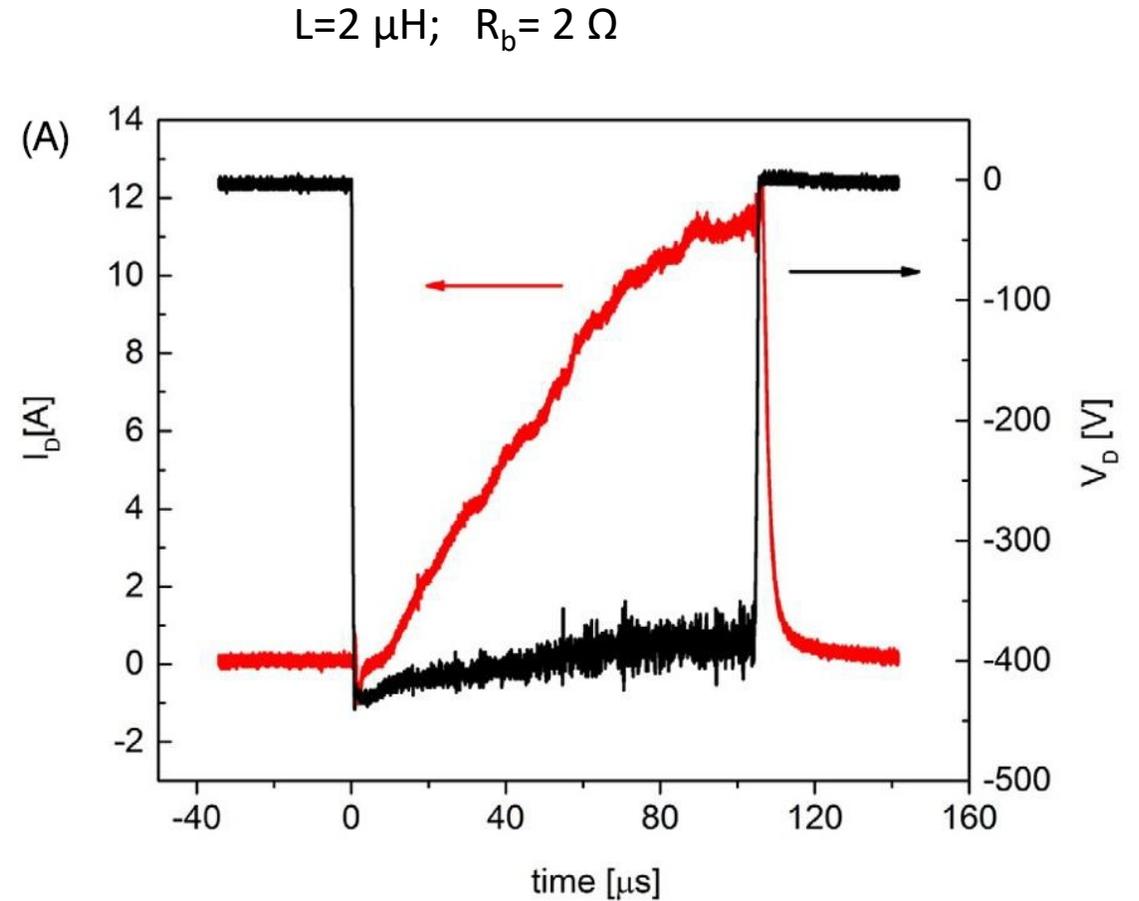
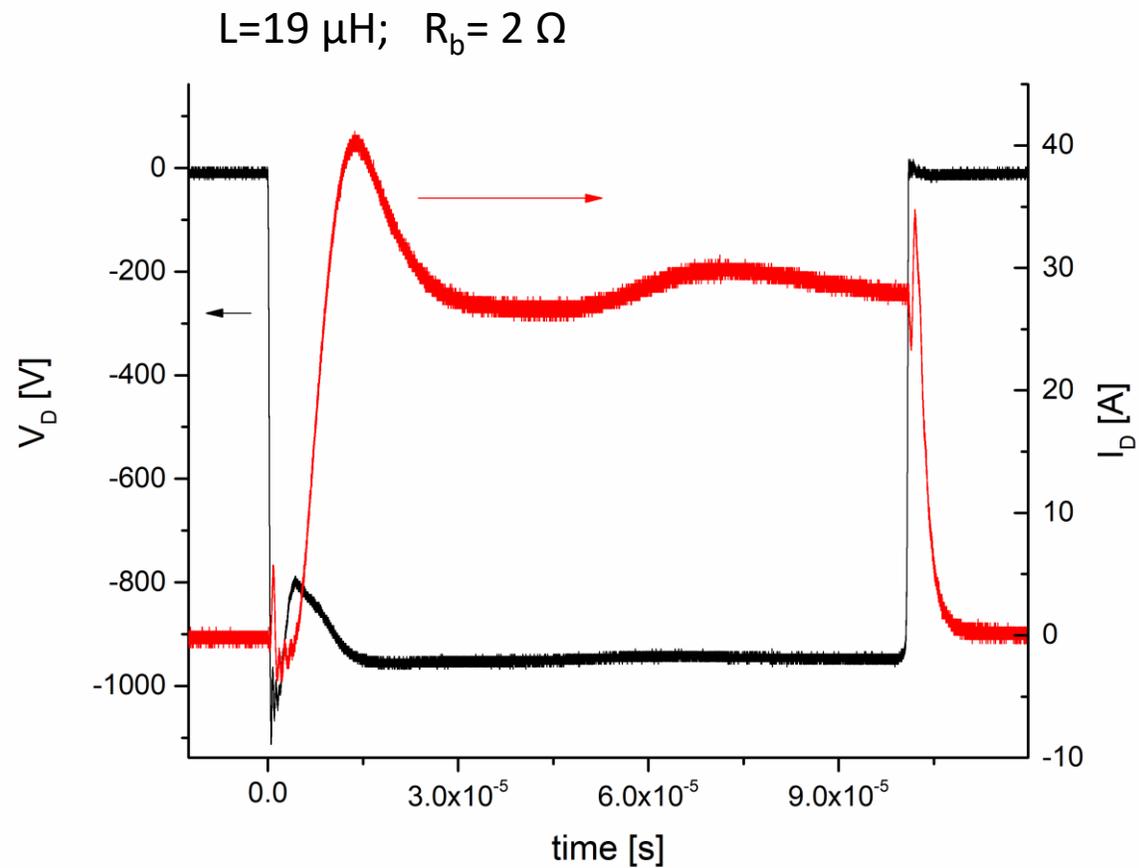
When current I_D grows, the inductance L induces a voltage V_i , which is oriented against the current change:

$$V_i = -\frac{dI_D}{dt} L$$



Pulsing concept with capacitor storage

Typical current and voltage waveforms with capacitor storage pulsing circuit



Pulsing concept with inductor storage

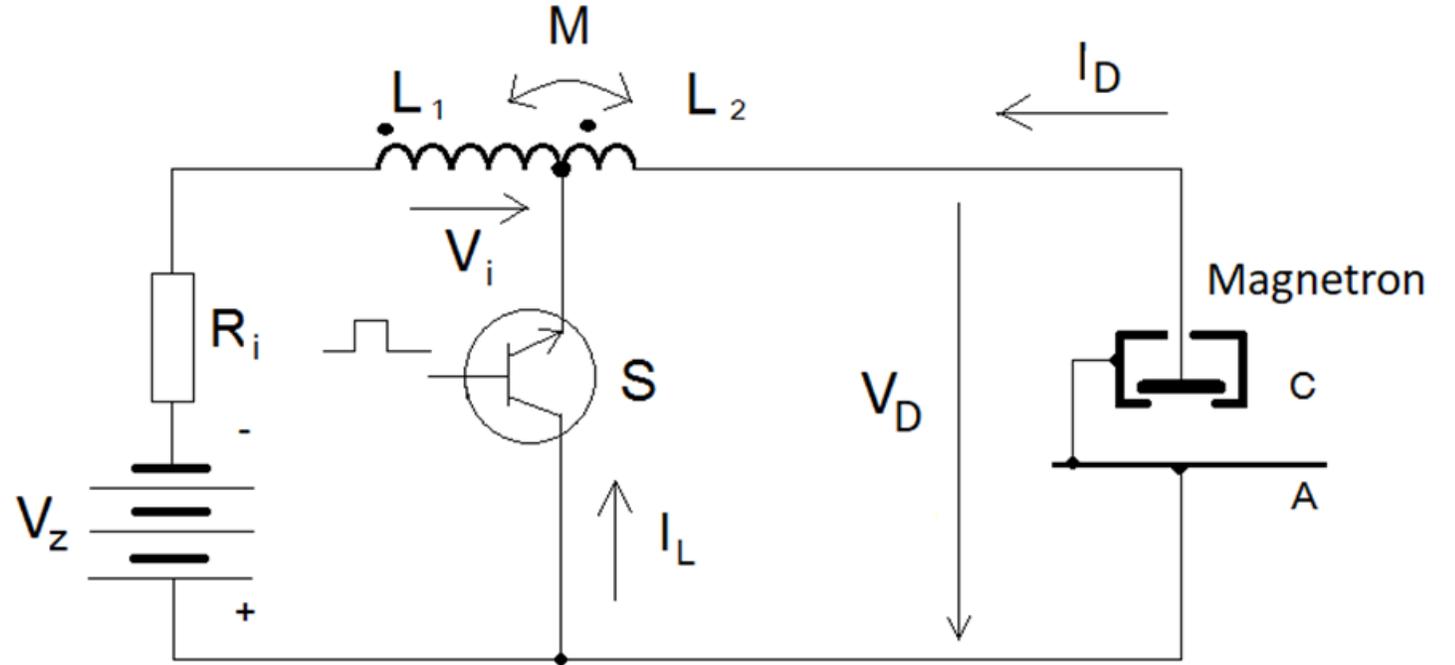
A large tapped inductance L_1-L_2 ($L_1 > L_2$) with a mutual inductance M is used as an accumulating element.

A significant energy is accumulated by the inductor L_1 when switch S is ON:

$$\mathcal{E}_L = \frac{1}{2} L_1 I_L^2$$

Once S is switched off, the inductor L_1 will generate a high voltage V_i across L_1 with the same orientation as V_z in order to maintain the current flow through L_1 (the current I_{L1} through L_1 now decreases):

$$V_i = -\frac{dI_{L1}}{dt} L_1$$



Drummond, G.N., 1996. Enhanced thin film DC plasma power supply. U.S. Patent no. 5,576,939 A (November 19, 1996).

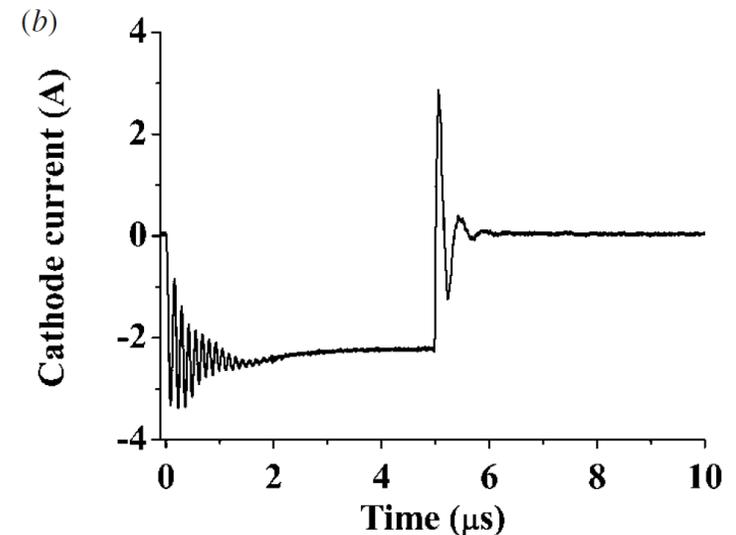
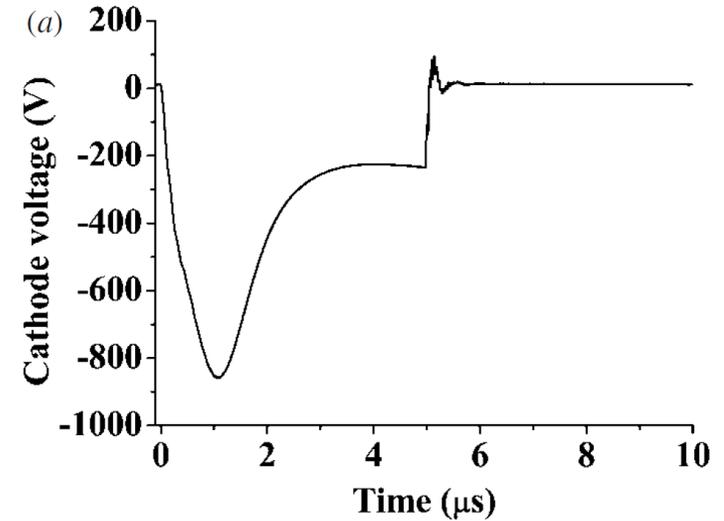
Pulsing concept with inductor storage

Current and voltage waveforms on magnetron discharge
(positive overshoot after discharge is switched off)

When the S is switched on at the end of the active pulse, the current I_{L1} starts to increase through L_1 , and, due to the mutual inductance M between L_1 and L_2 , a temporary positive voltage V_D is generated on the magnetron cathode (i.e. the magnetron cathode potential is positive relative to the anode), which is expressed by:

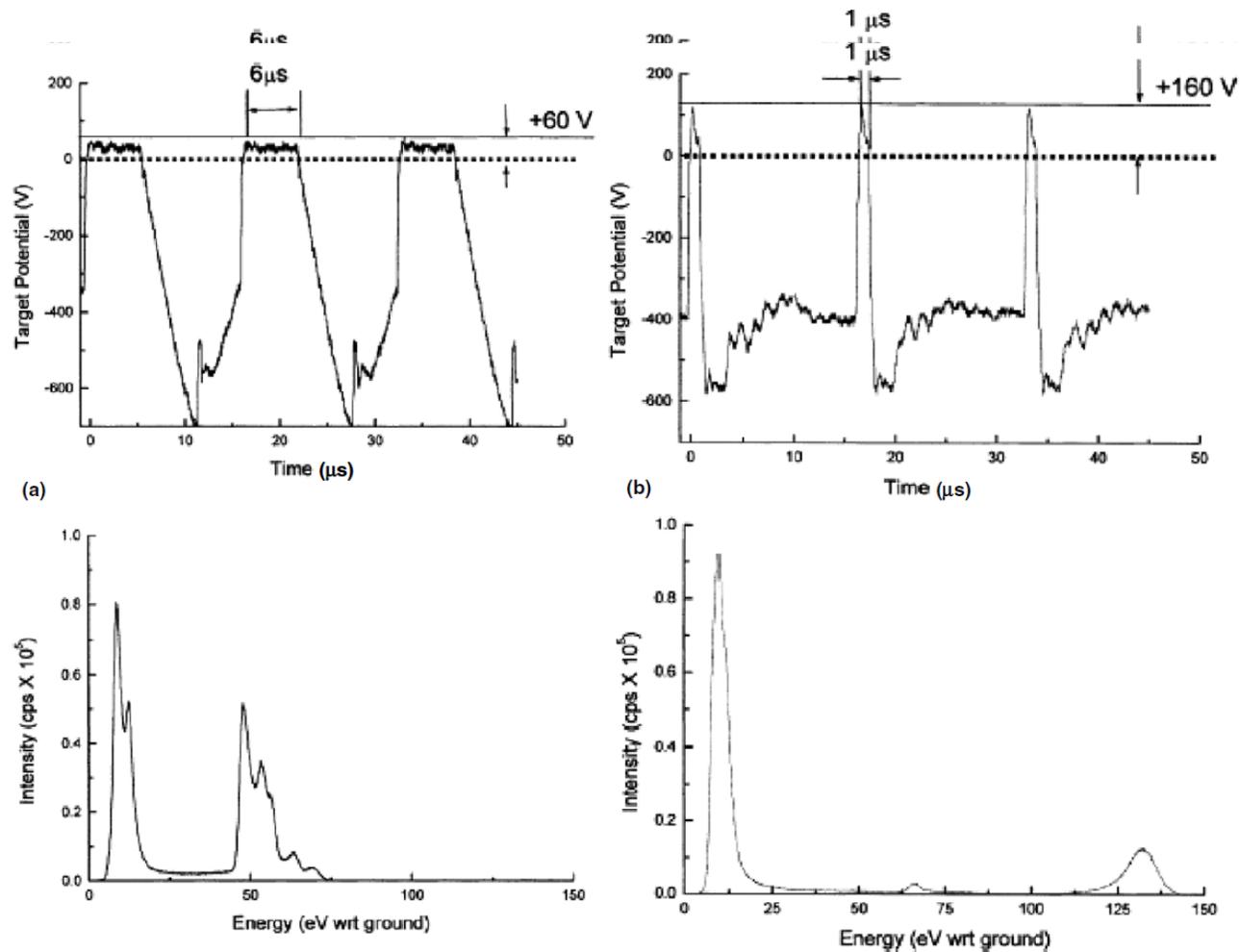
$$V_D = \frac{dI_{L1}}{dt} M$$

This temporal positive voltage V_D is valuable in reactive pulsed magnetron sputtering, since it will generate a high electron flux onto a poisoned magnetron target.

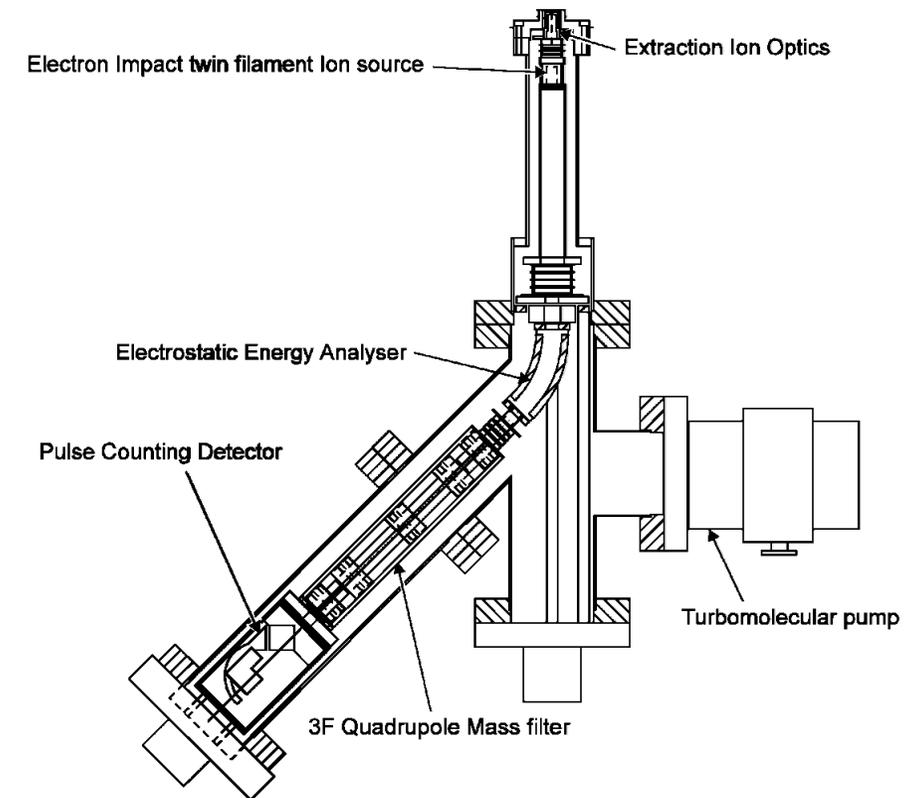


S. A. Voronin, G. C. B. Clarke, M. Čada, P. J. Kelly and J. W. Bradley, Meas. Sci. Technol. 18 (2007) 1872–1876.

IEDF in pulsed magnetron sputtering with positive overshoot

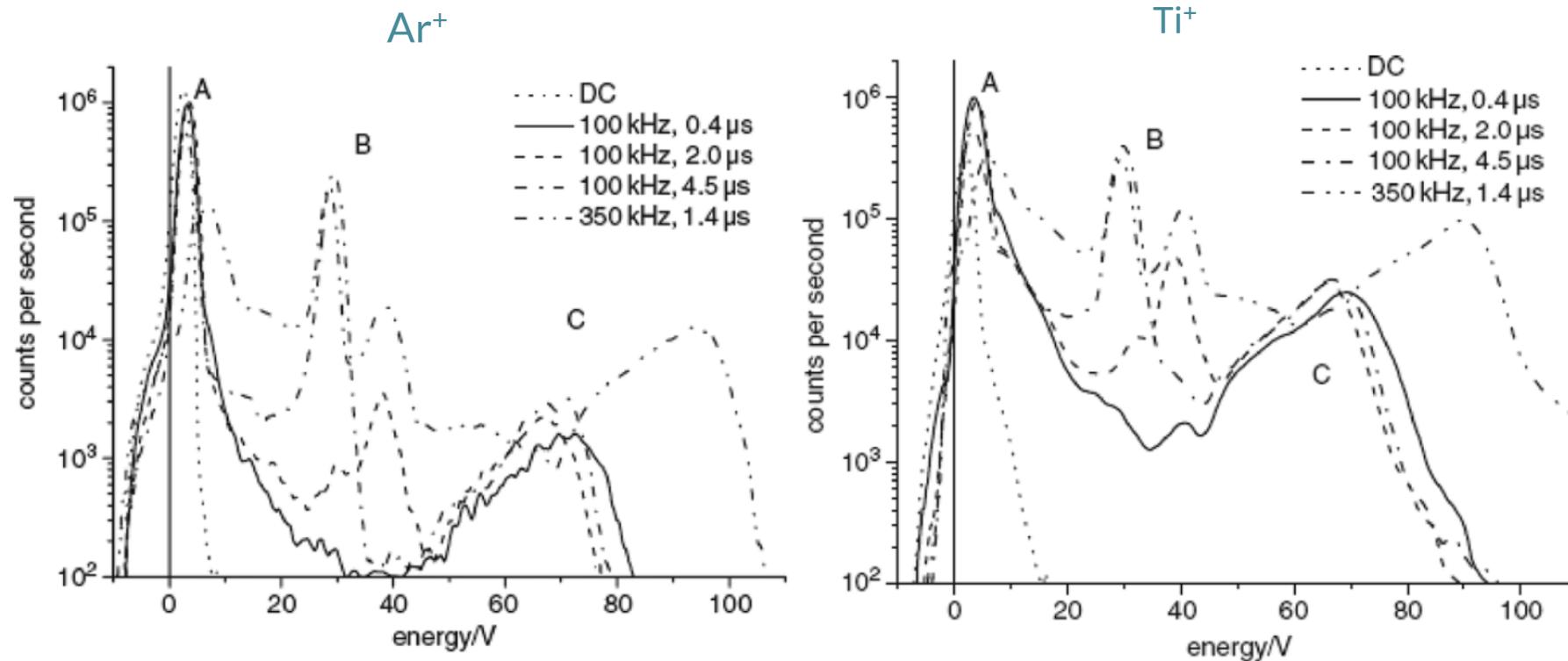


Target voltage waveforms and Ar⁺ IEDFs are shown for the (a) 60 kHz pulsed discharge with 6 μs reverse time and (b) 60 kHz pulsed discharge with 1 μs reverse time.



Time average Ar^+ and Ti^+ energy spectra (IEDF) for 100 kHz and 350 kHz

different pulsing frequencies and reverse time

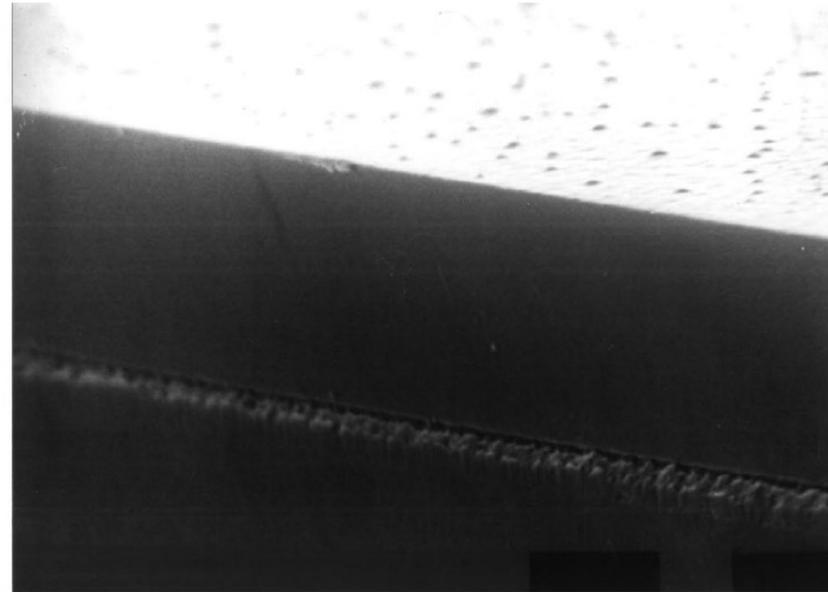
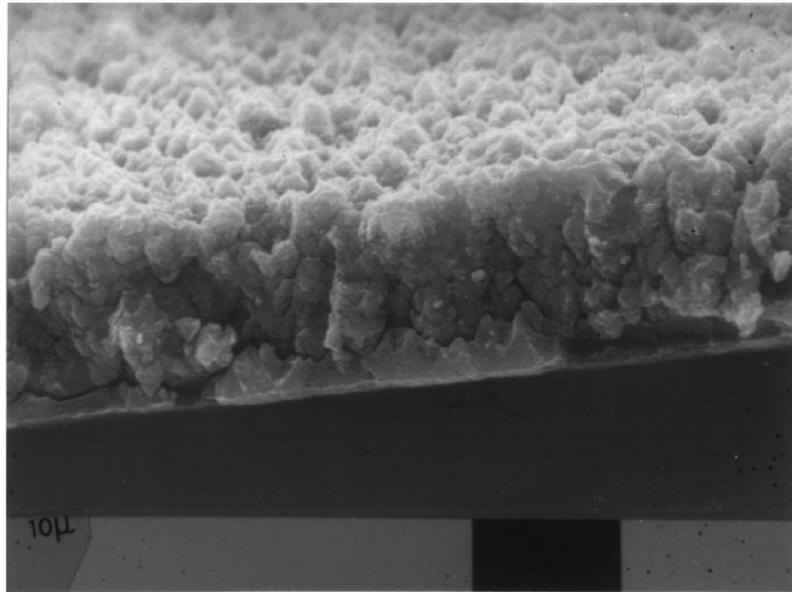


Bradley J W, Backer H, Aranda-Gonzalvo Y, Kelly P J and Arnell R D The distribution of ion energies at the substrate in a bi-polar pulsed dc magnetron discharge Plasma Sources Sci. Technol. 11 (2002) 165.

Typical results of reactive sputtering of Al_2O_3 films

Advantage of pulsed reactive sputtering:

- | reduced arcing
- | deposition of dense high quality films due to higher ion and energy flux to the substrate

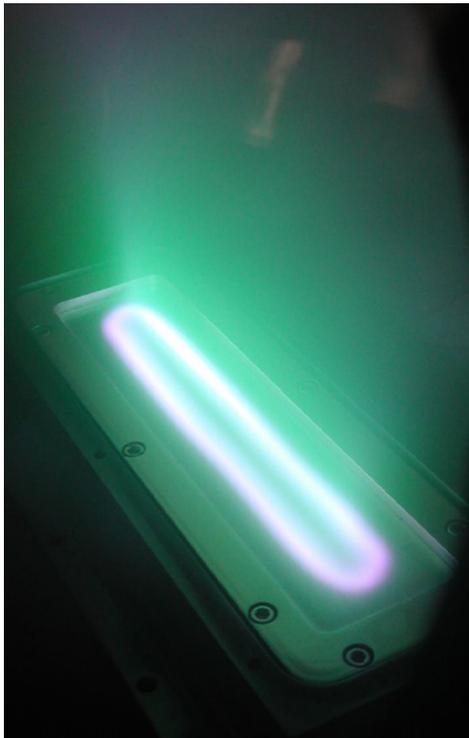


SEM micrographs of fracture sections of aluminium oxide coatings deposited by (a) DC reactive sputtering, and (b) pulsed reactive sputtering.

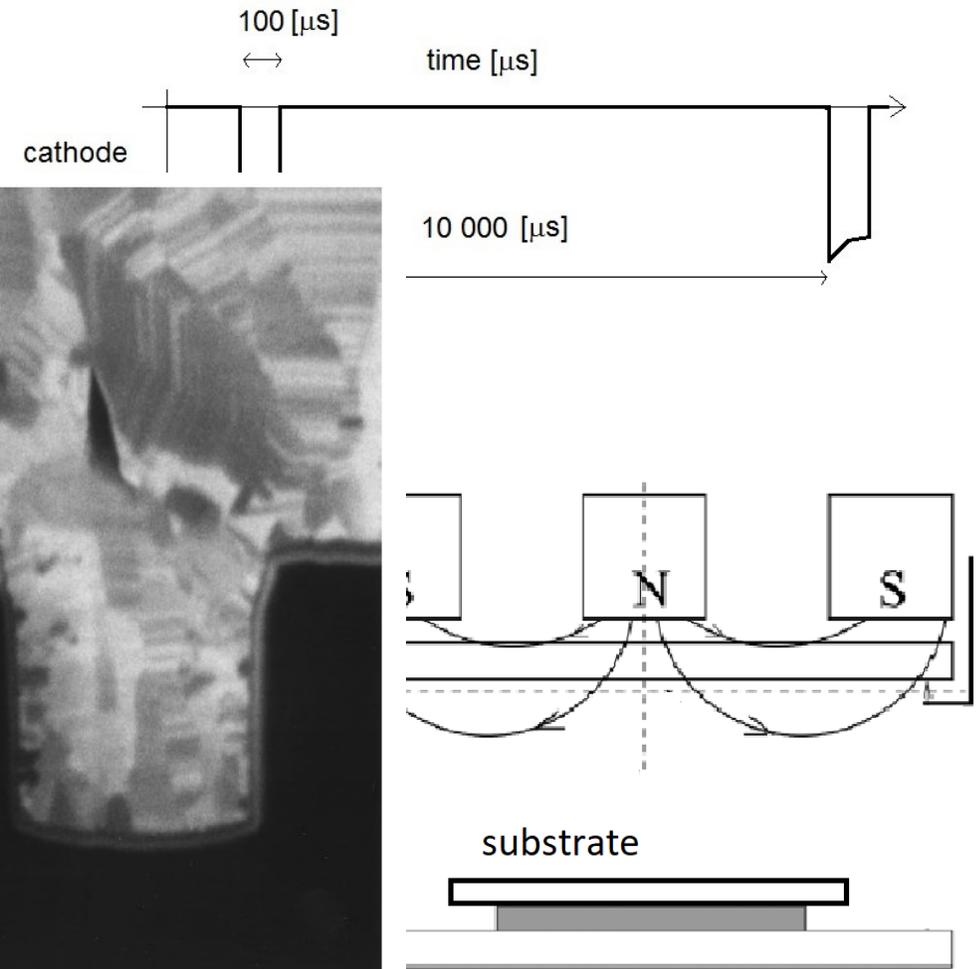
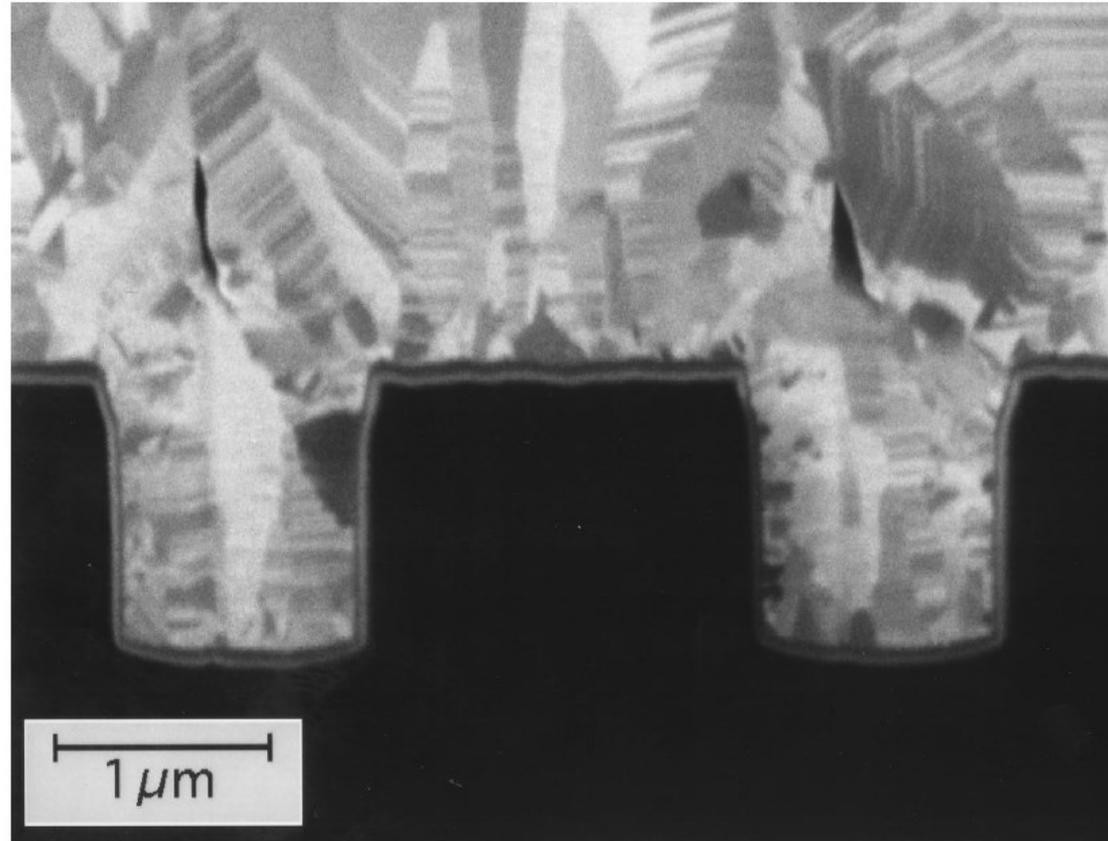
R.D. Arnell, P.J. Kelly / Surface and Coatings Technology 112 (1999) 170-176

HiPIMS High power impulse magnetron sputtering

- | high power in pulse and low mean power $n_{e,i} \approx 10^{19} \text{ m}^{-3}$
- | major fraction of sputtered atoms are ionized (IPVD)
- | lower porosity and higher density of deposited films
- | low heating flux to the substrate
- | HiPIMS, high ion flux



Angstromsciences

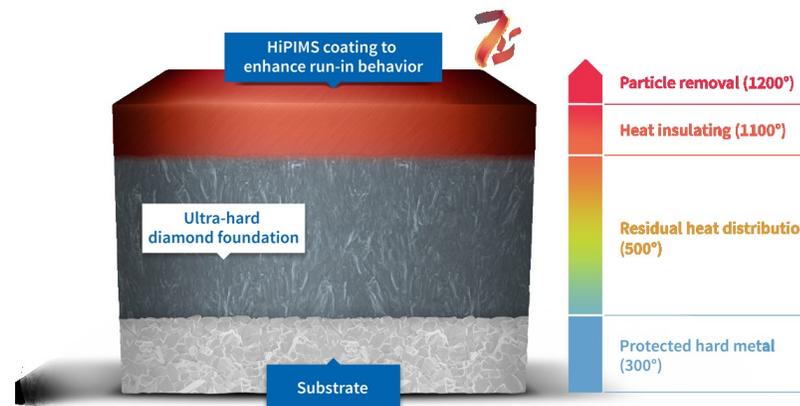


MAGNETRON – HiPIMS industrial technology for coatings



Source: Kurt J. Lesker Inc.

- | HiPIMS power source are commercially available.
- | Commercial thin films demonstrate improved properties.



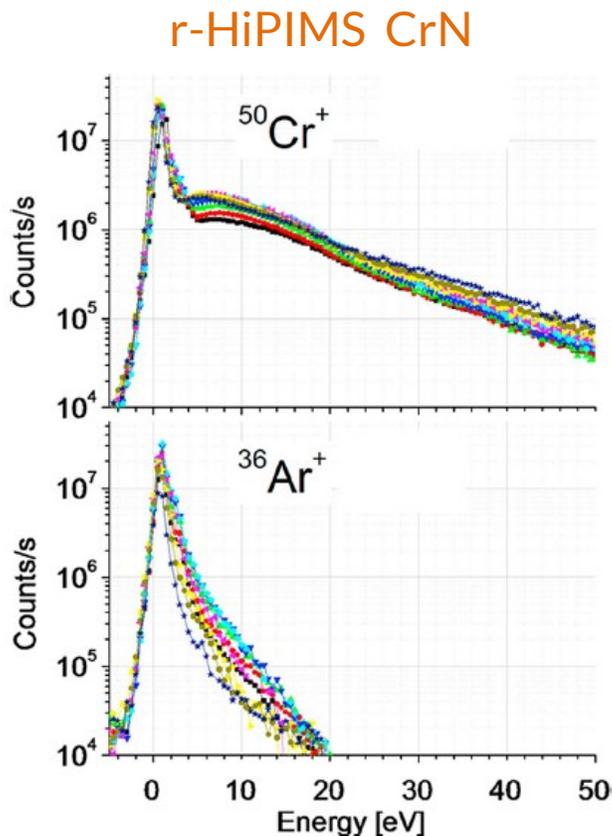
Source: CemeCon



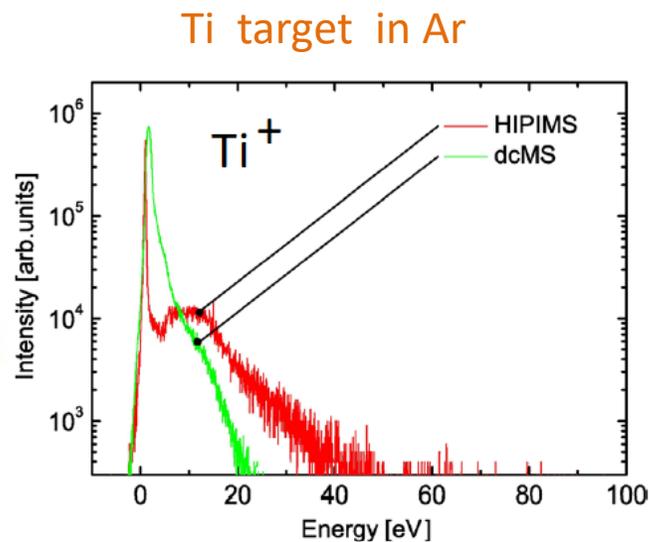
Source: CemeCon

HiPIMS - High power impulse magnetron sputtering

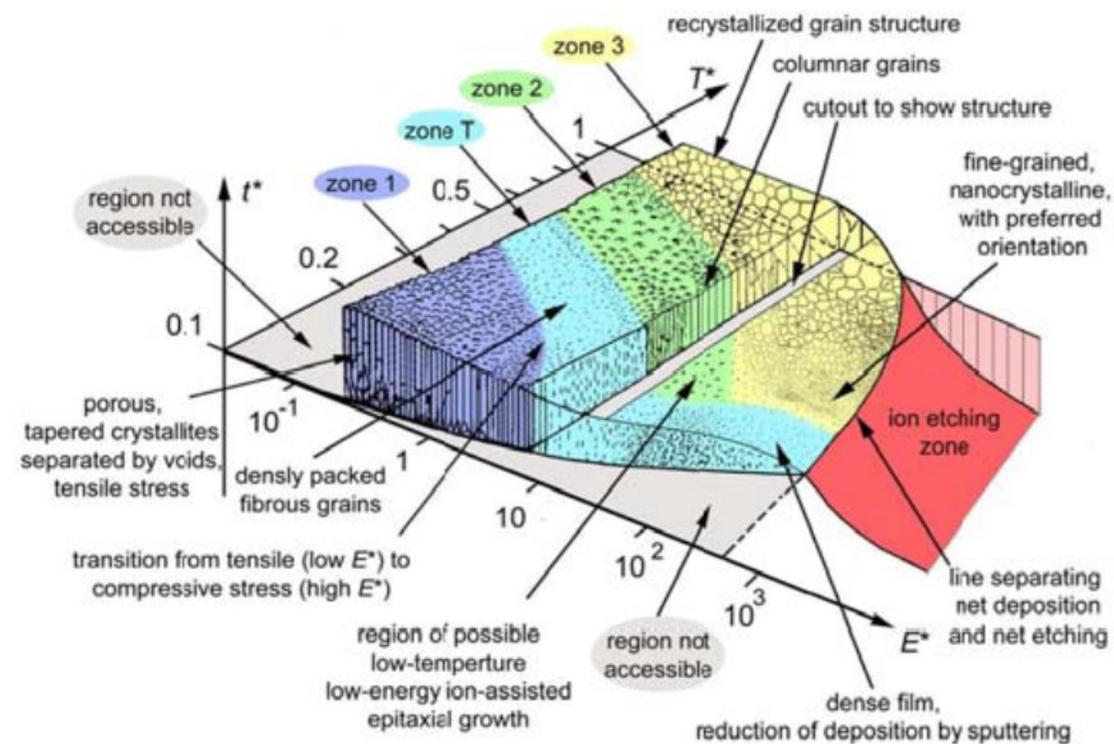
- | ion energy distribution function at the substrate
- | energetic ion bombardment of growing film by sputtered particles



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



D. Lundin, et. Al. Plasma Sources Sci. Technol. 17, 035021 (2008).



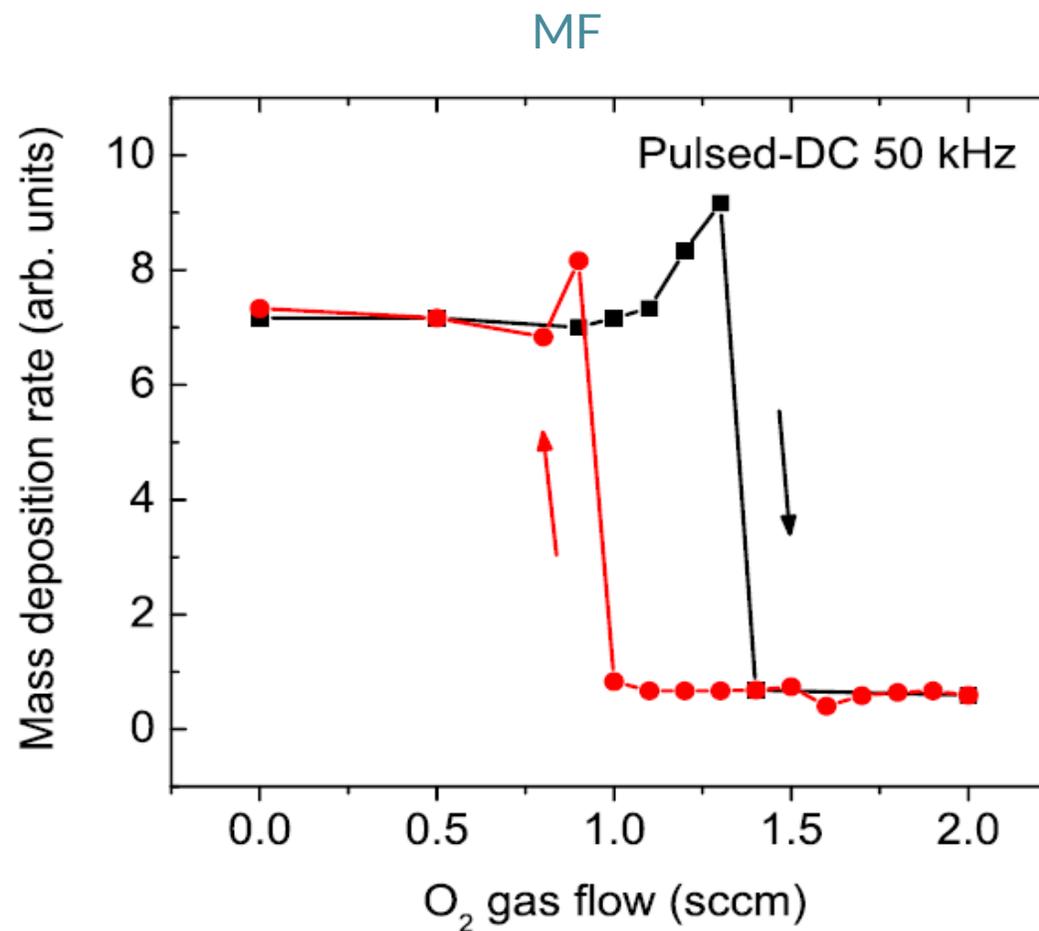
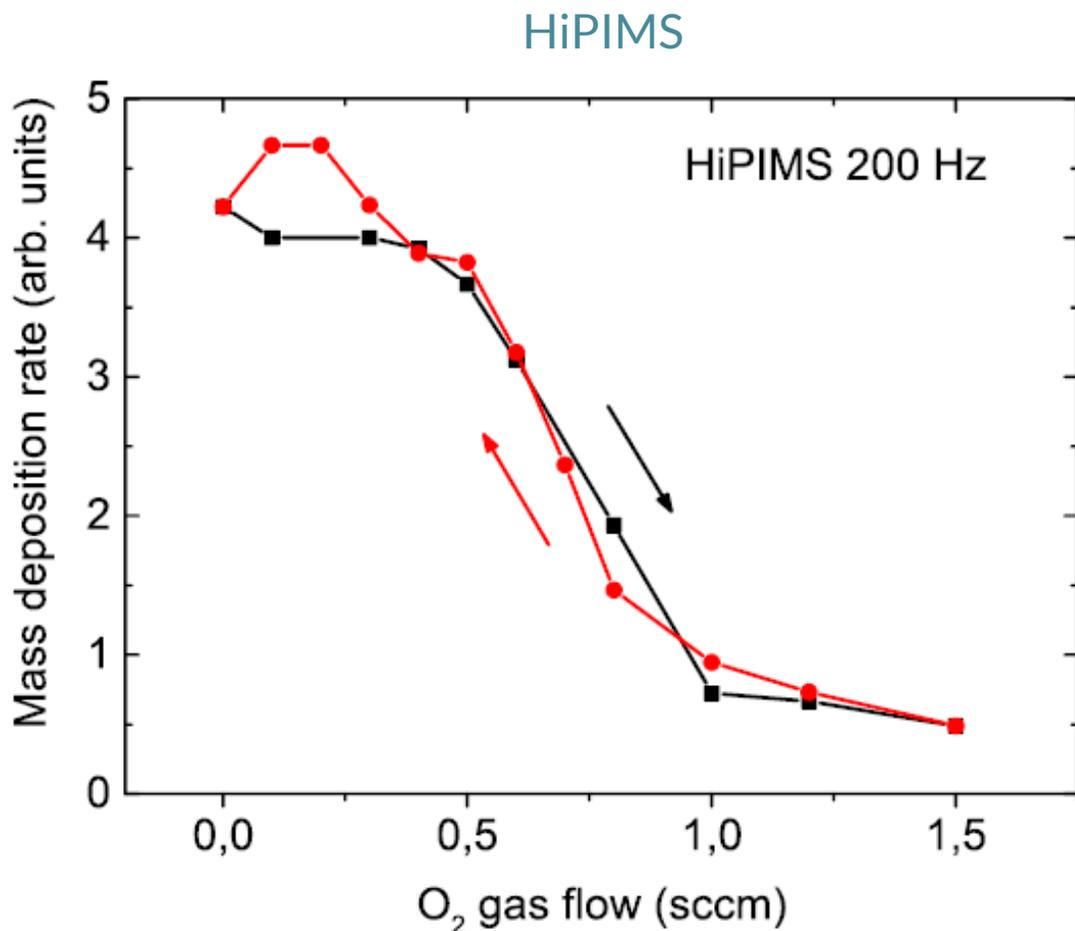
Anders, TSF 518 (2010) 4087

modified structure zone diagram for PVD

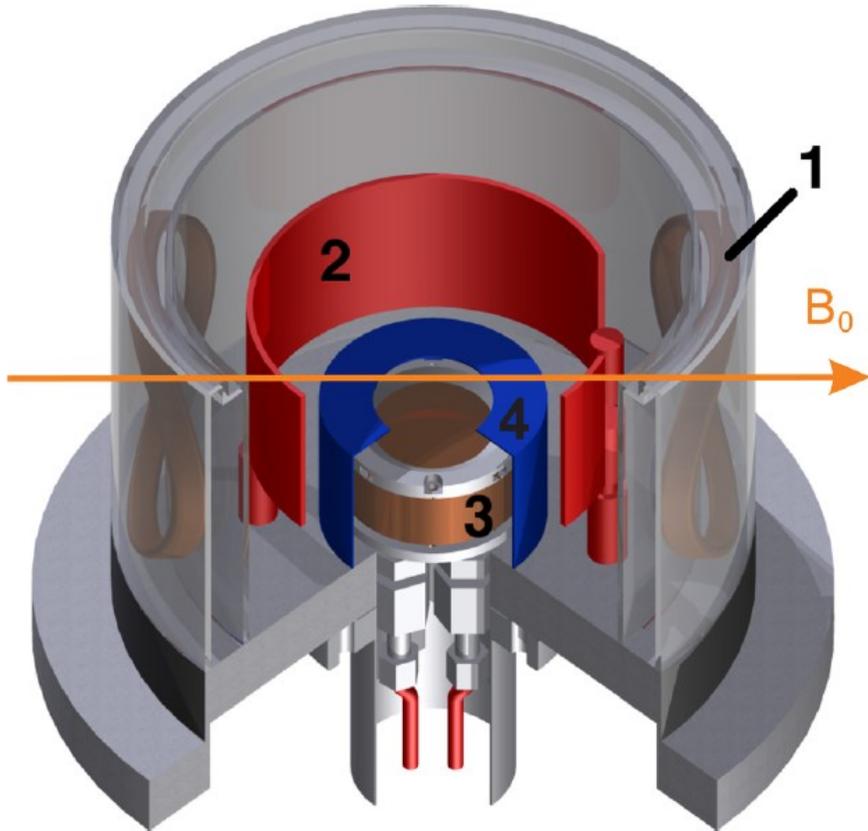
Reactive sputtering of (oxide) thin films by HiPIMS

| reduced hysteresis by transition from metallic to compound mode

Examples of hysteresis effect for TiO_2 thin deposition by HiPIMS and MF (small target 50 mm diameter)

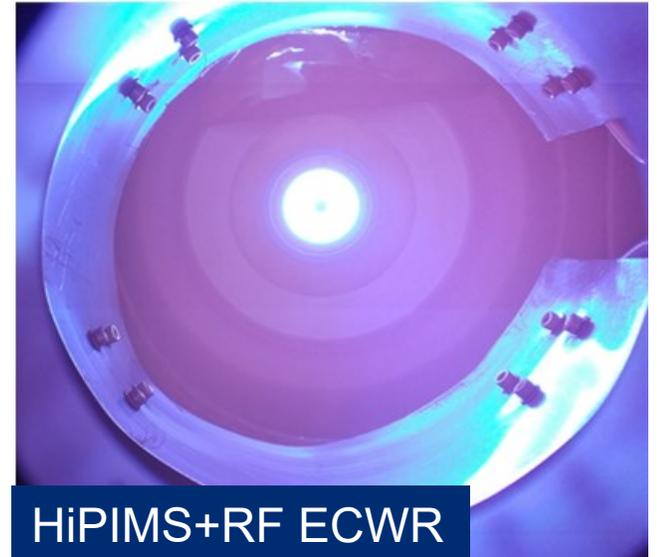


RF (13.56 MHz) ECWR plasma with HiPIMS magnetron



Schema of a sputtering magnetron gun implemented into the axis of an ECWR facility.

- 1 | pair of Helmholtz coils
- 2 | single turned RF electrode
- 3 | magnetron
- 4 | shielding of magnetron/anode
- B_0 | static magnetic field



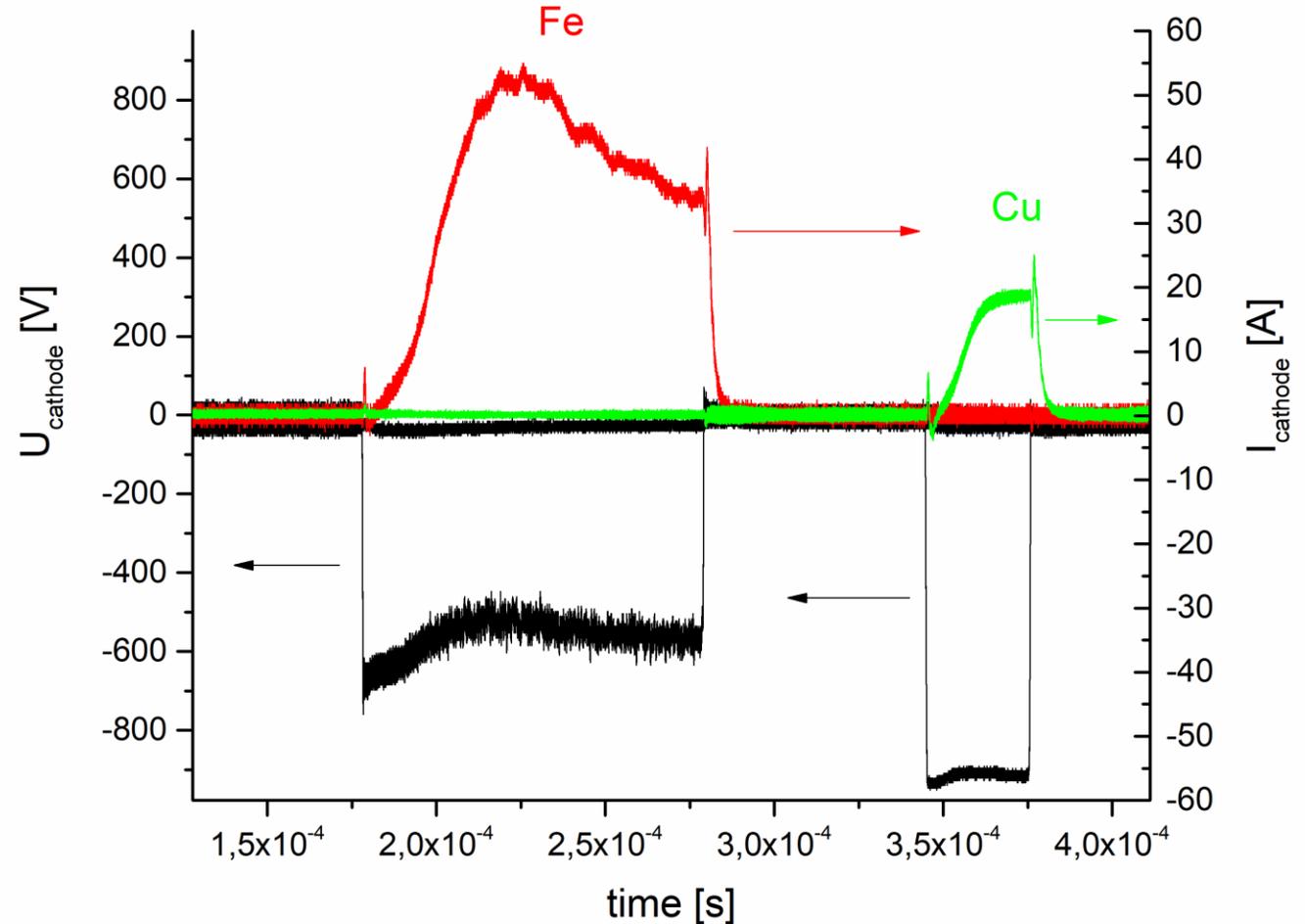
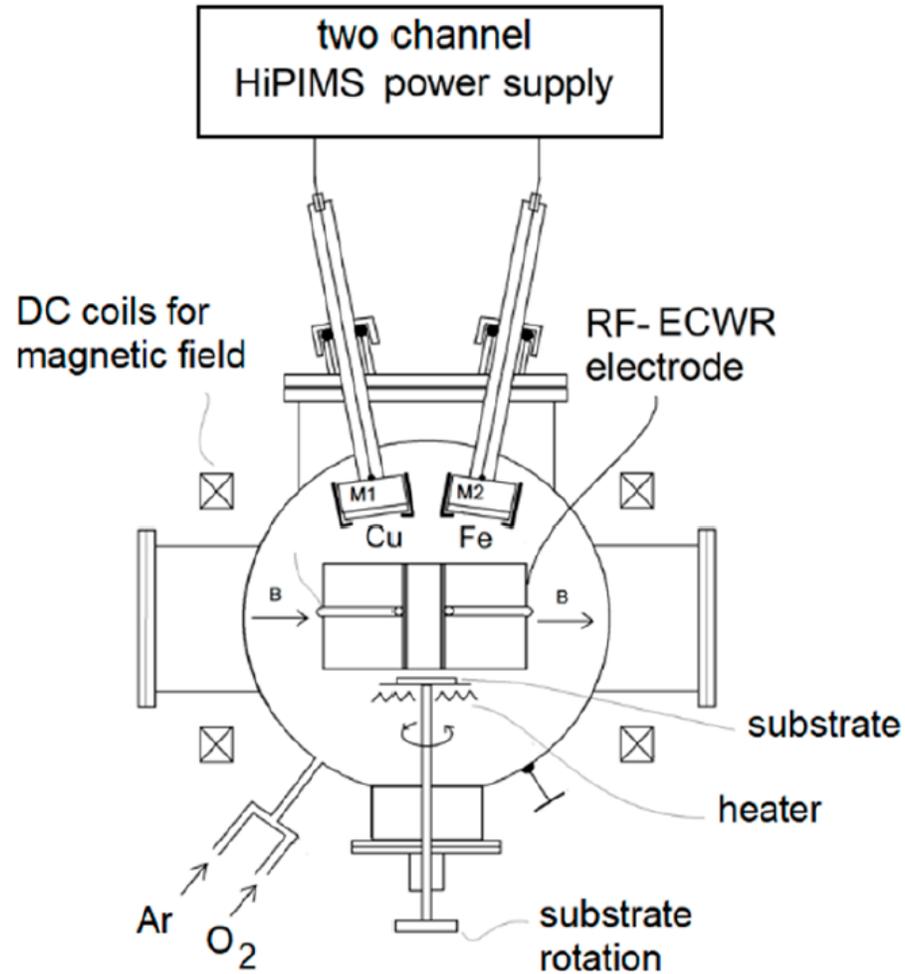
HiPIMS+RF ECWR



RF ECWR

HiPIMS or HiPIMS+ECWR with dual magnetron for alloy and multicomponent thin films $\text{Cu}_{1+y}\text{FeO}_x$

(semiconducting films: $\text{Cu}_{1+y}\text{FeO}_x$)

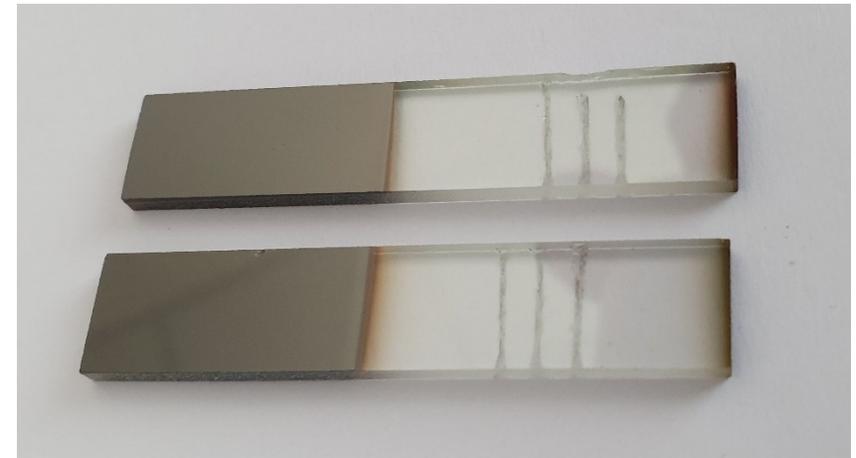
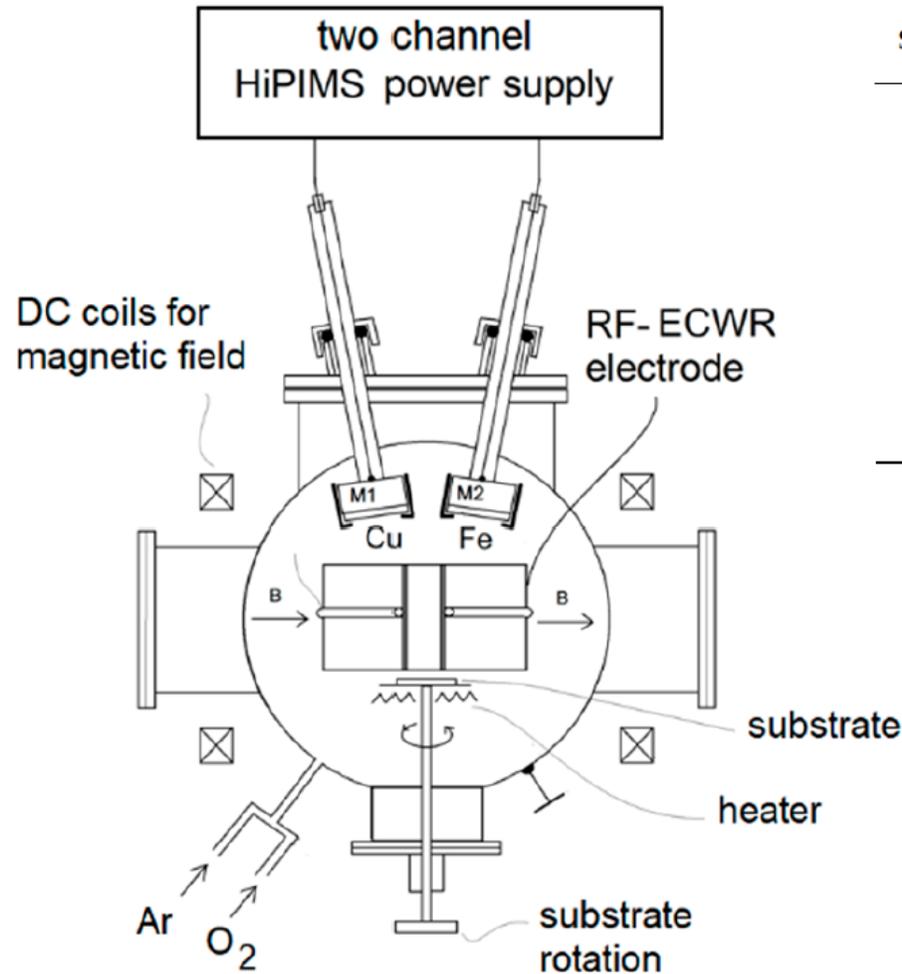


HiPIMS or HiPIMS+ECWR with dual magnetron for alloy and multicomponent thin films $\text{Cu}_{1+y}\text{FeO}_x$

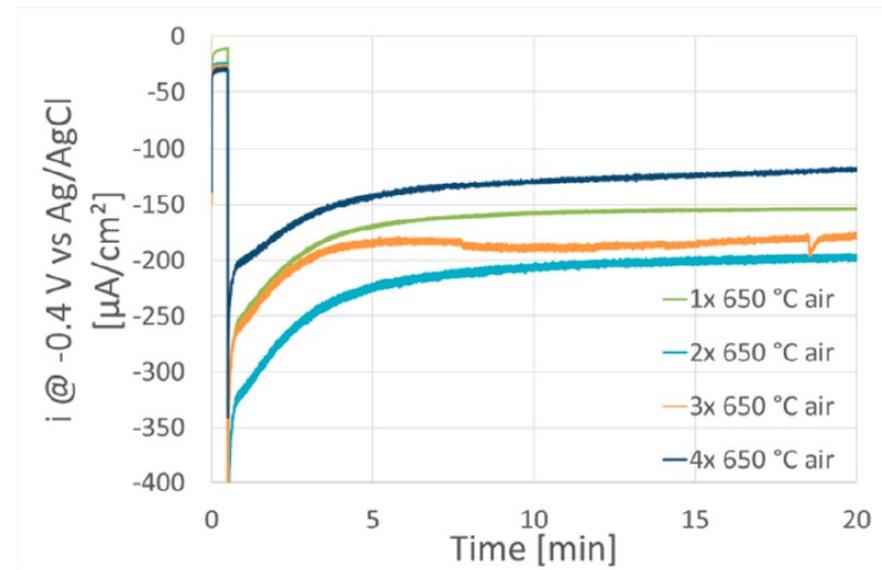
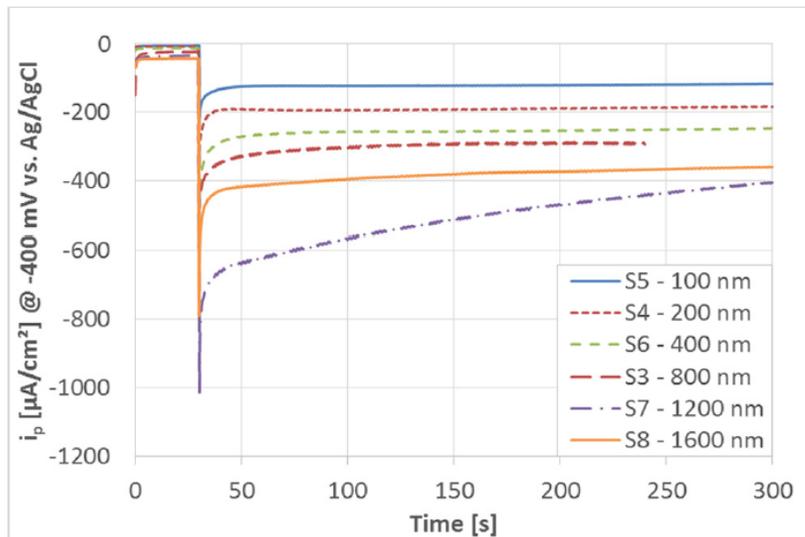
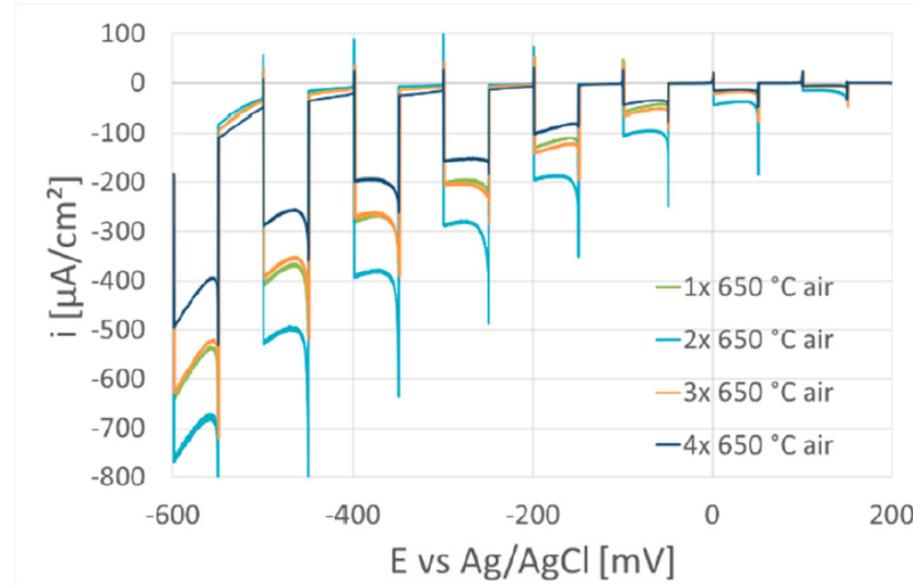
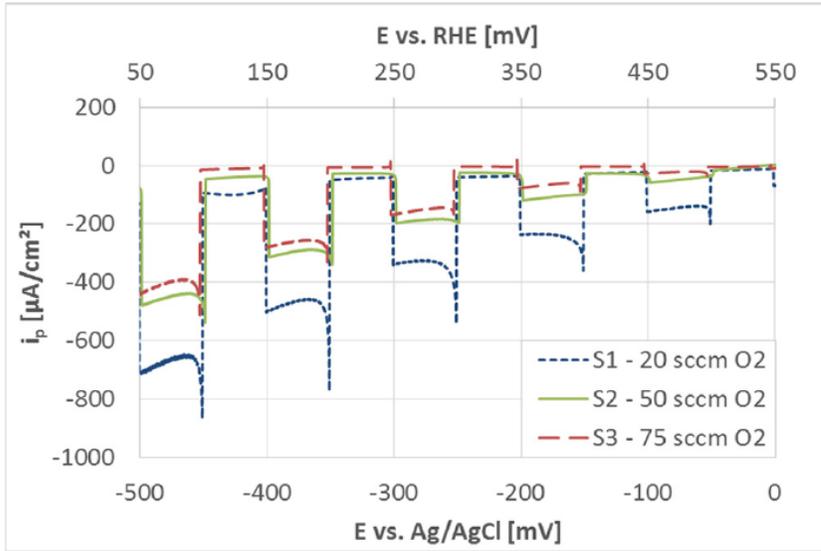
(semiconducting films: $\text{Cu}_{1+y}\text{FeO}_x$)

Table 1. List of films with significant deposition parameters.

Sample	I_{Feav} [mA]	U_{Fe} [V]	I_{Cuav} [mA]	U_{Cu} [V]	Q_{O_2} [sccm]	$t_{dep.}$ [°C]	Thickness [nm]	mol. Ratio Cu/Fe	P_{ECWR} [W]
1x	500	720	84	975	10	250	900	4.77	180
2x	500	720	176	1000	10	250	2200	12.35	180
3x	600	720	56	1000	10	250	580	4.27	180
4x	500	720	50	895	5	250	535	1.79	180
5x	550	600	40	841	5	250	250	1.33	180
6x	440	700	42	834	2	500	350	0.82	0
7x	400	700	47	816	1.3	500	600	0.82	0
8x	500	700	44	842	3.2	500	300	0.79	0
9x	500	700	40	804	2	500	400	0.94	0
10x	500	700	30	789	2	500	240	0.86	0



HiPIMS or HiPIMS+ECWR with dual magnetron for alloy and multicomponent thin films $\text{Cu}_2\text{O}/\text{CuO}$ and $\text{Cu}_{1+y}\text{FeO}_x$



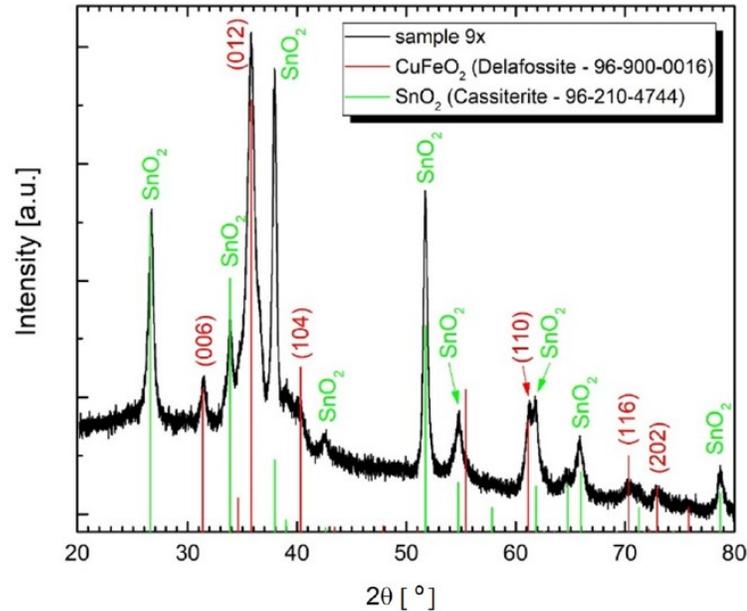
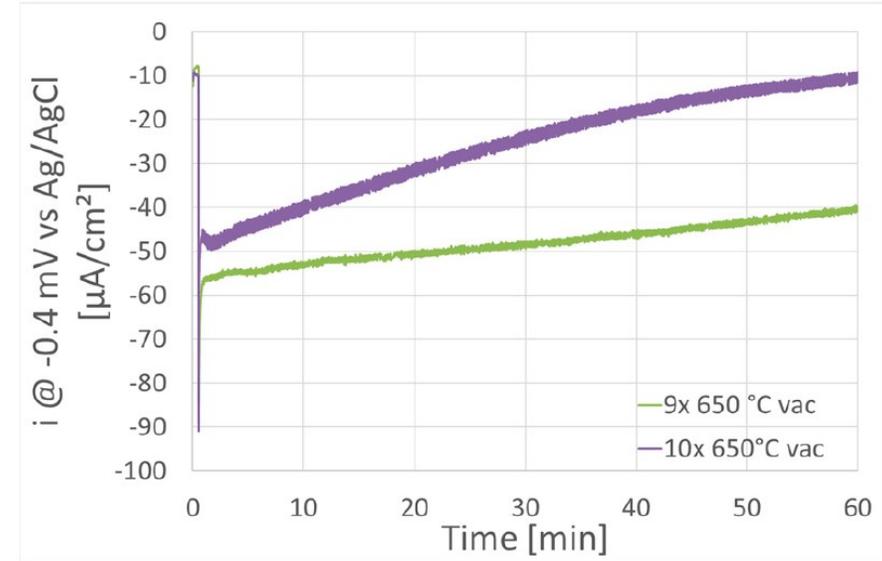
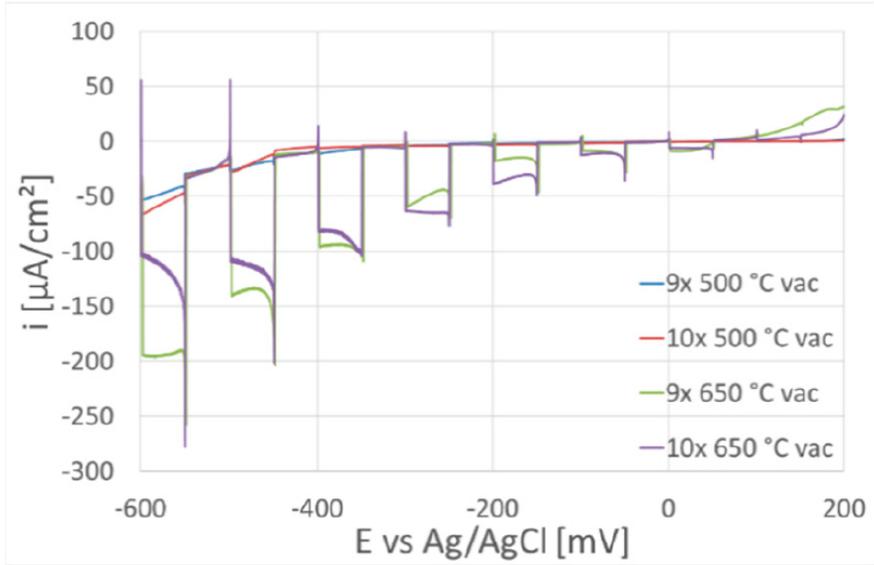
**$\text{Cu}_2\text{O}/\text{CuO}$
r-HiPIMS**

**$\text{Cu}_{1+y}\text{FeO}_x$
r-HiPIMS+
ECWR**

Z. Hubička, M. Zlámá, M. Čada, Š. Kment, J. Krýsa, *Catal. Today* 2019, 328, 29–34.

Z. Hubička, M. Zlámá, J. Olejníček, D. Tvarog, M. Čada, J. Krýsa, *Coatings* 10 (2020) 232.

HiPIMS or HiPIMS+ECWR with dual magnetron for alloy and multicomponent thin films CuFeO_2 with delafossite phase



Phase	Semiquantitative Phase Composition/%			
	9x 650 °C vac NM	9x 650 °C vac ME	10x 650 °C vac NM	10x 650 °C vac ME
CuFeO_2	67	29	80	100
Cu_2O	33	43	20	-
Fe_3O_4	-	28	-	-

Závěr

- magnetronové (reaktivní) naprašování je dnes součástí průmyslové výroby mnoha produktů
- pulzní reaktivní magnetronové naprašování + r-HiPIMS jsou nové směry pro přípravu nových materiálů v průmyslu
- hybridní systémy HiPIMS+ECWR byly studovány pro přípravu polovodivých vrstev s vodivostí typu P

Podpořeno z projektu OP VVV „Partnerská síť v oblasti výzkumu a vývoje zobrazovací a osvětlovací techniky a optoelektroniky pro optický a automobilový průmysl“, registrační číslo: CZ.02.1.01/0.0/0.0/17_049/0008422.



EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání



MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY