Thin Films Technology

Lecture 4:
Physical Vapor Deposition PVD

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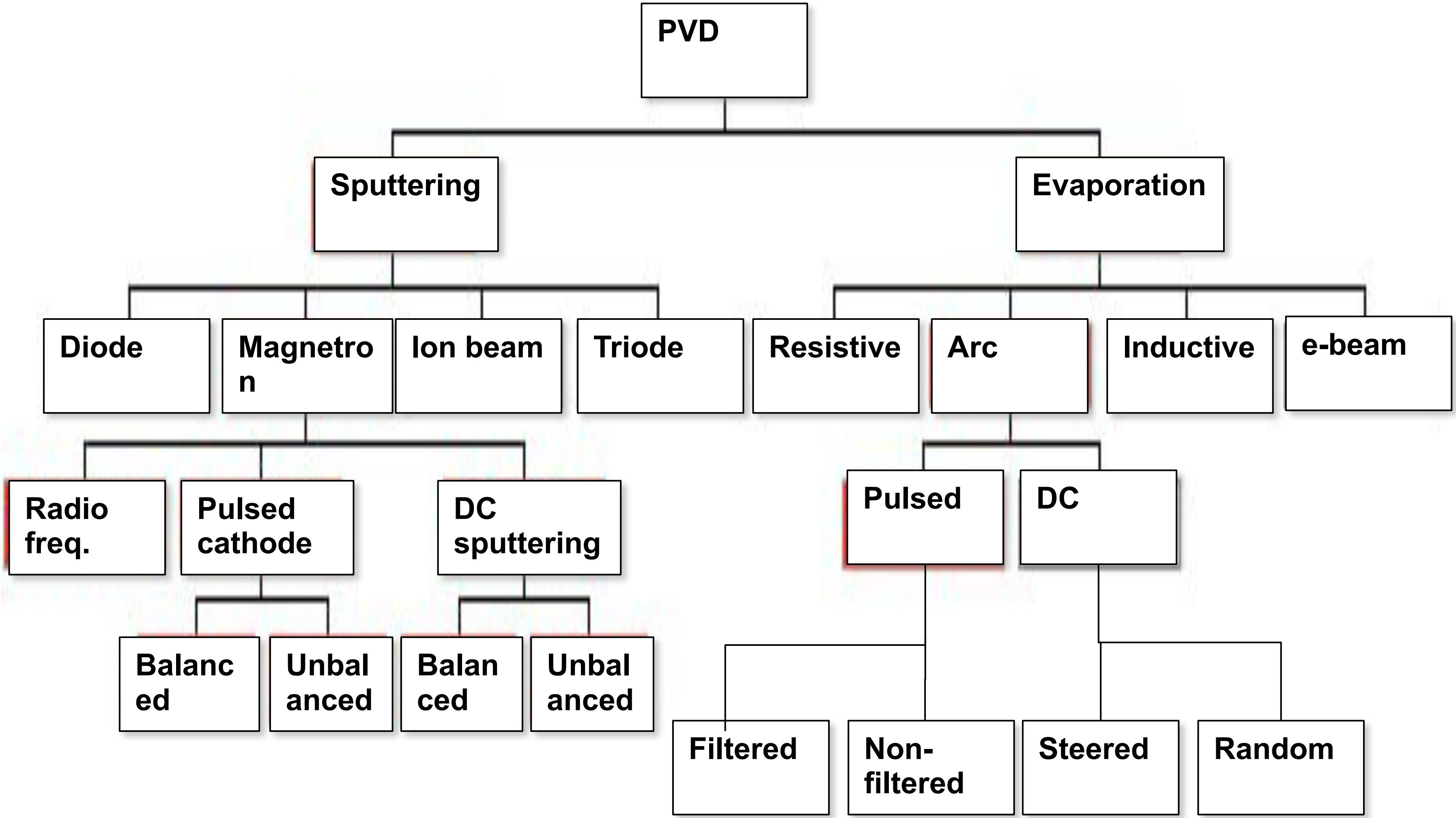
Contents

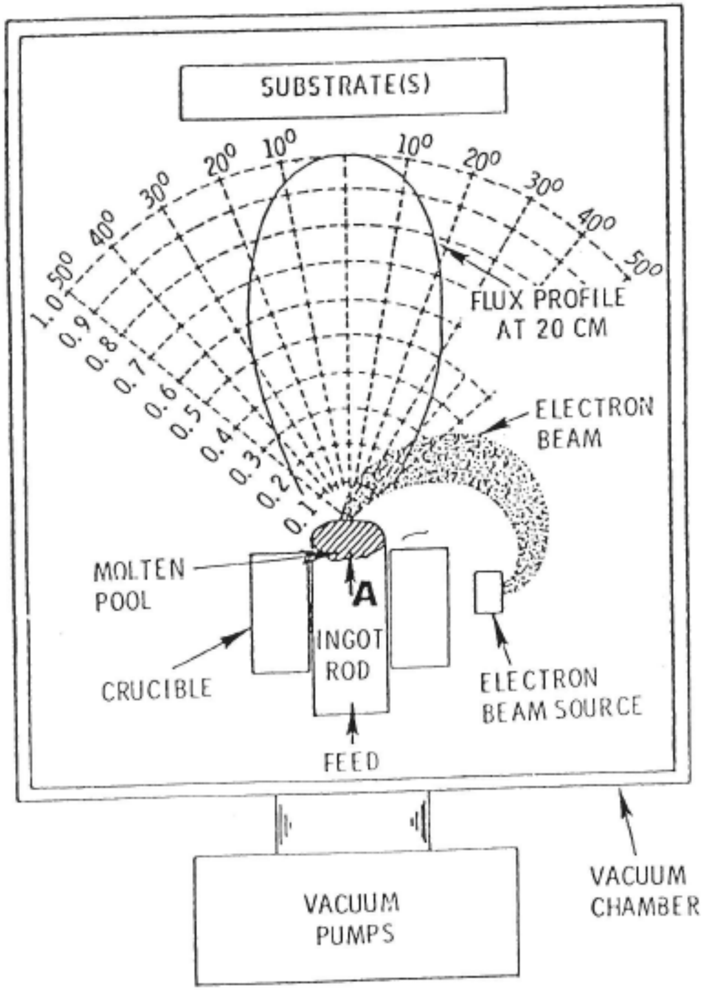
- Plasma
- Ion surface interactions
- Film growth mechanisms
- **Different PVD methods**
- Commercial PVD coatings
- Scale up

PVD methods

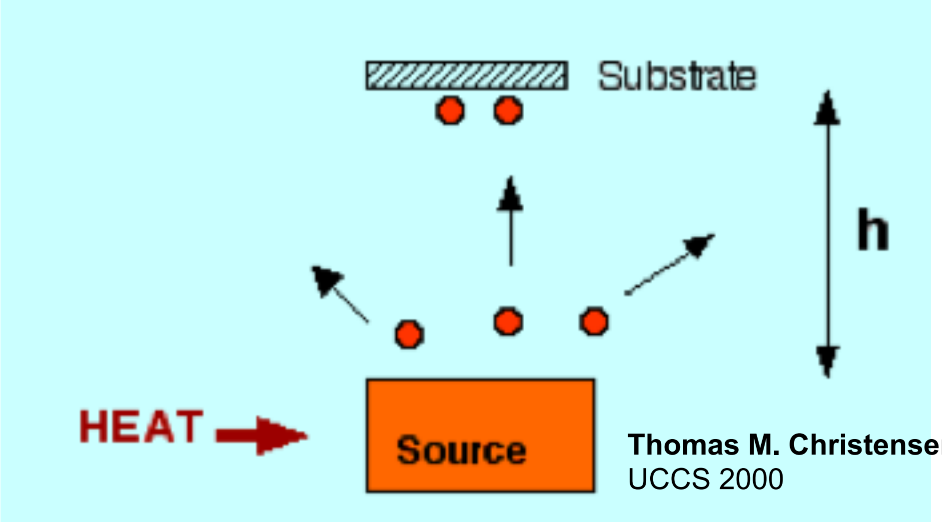


- PVD
  - Sputtering
    - Diode
    - Magnetron
      - Radio freq.
      - Pulsed cathode
        - Balanced
        - Unbalanced
      - DC sputtering
        - Balanced
        - Unbalanced
    - Ion beam
    - Triode
  - Evaporation
    - Resistive
    - Arc
      - Pulsed
        - Filtered
        - Non-filtered
      - DC
        - Steered
        - Random
    - Inductive
    - e-beam

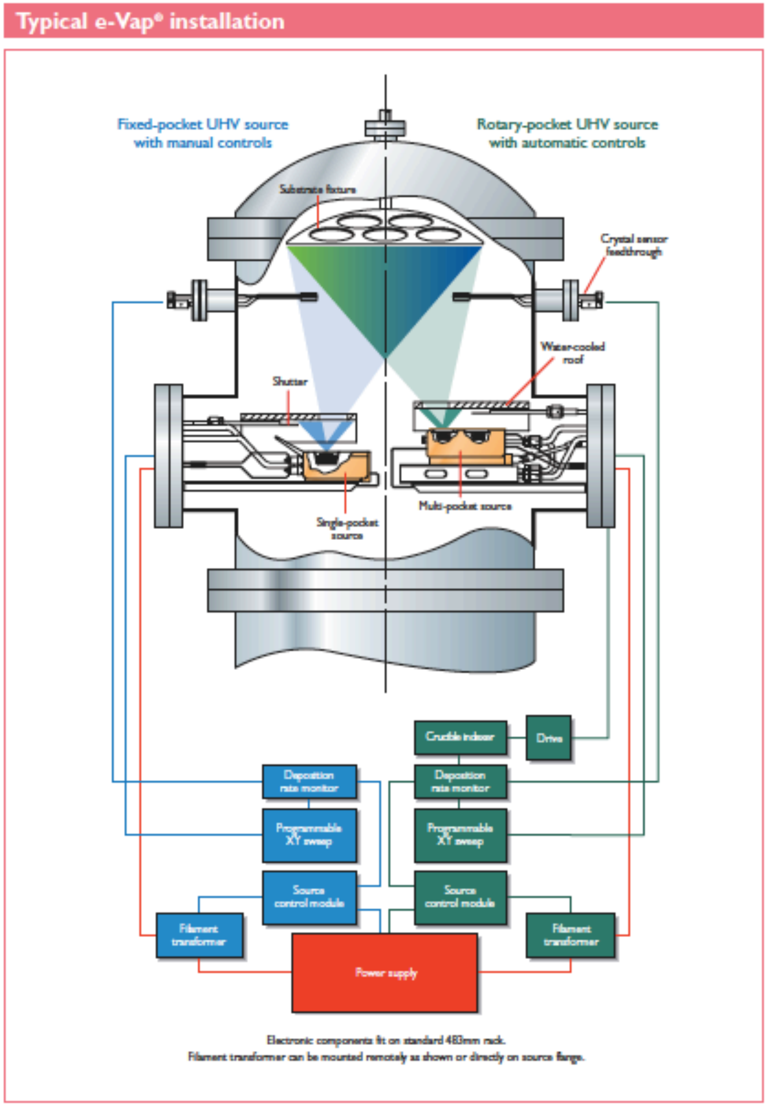
Electron beam evaporation



Evaporation



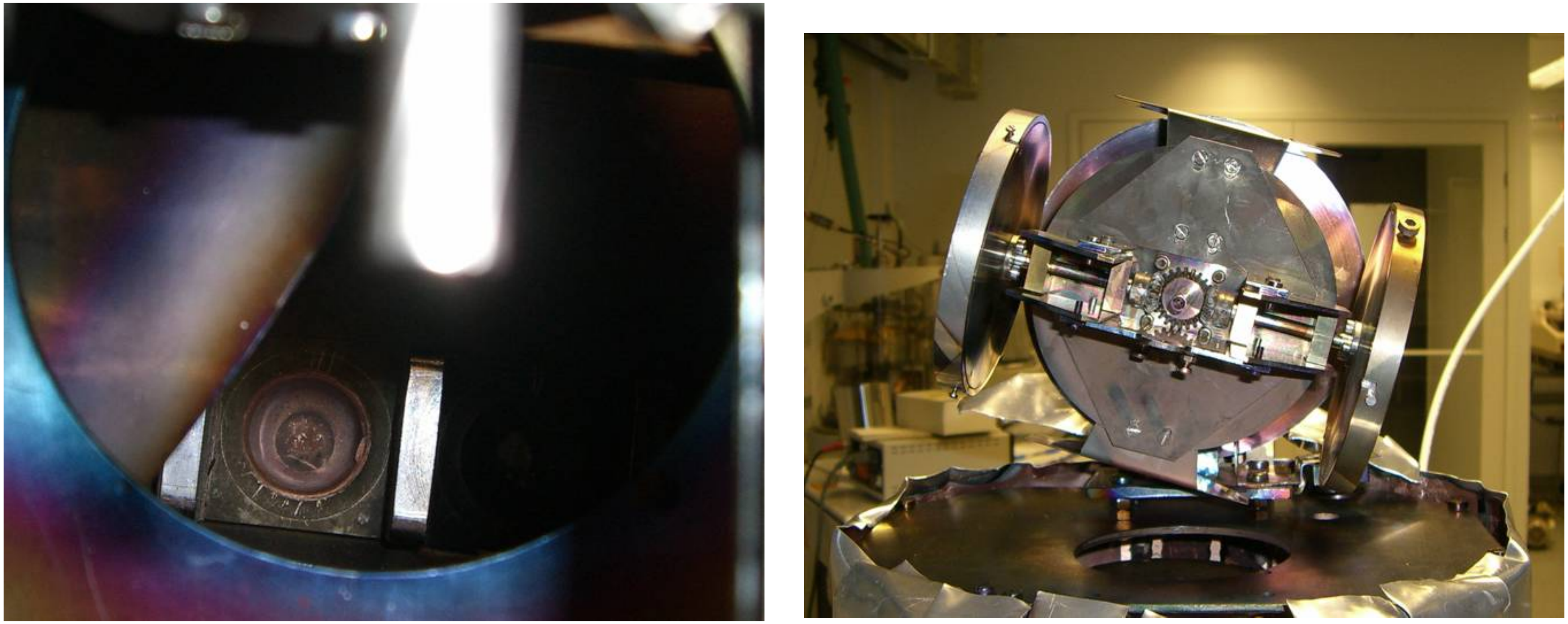
Thomas M. Christensen
UCCS 2000


Typical e-Vap® installation

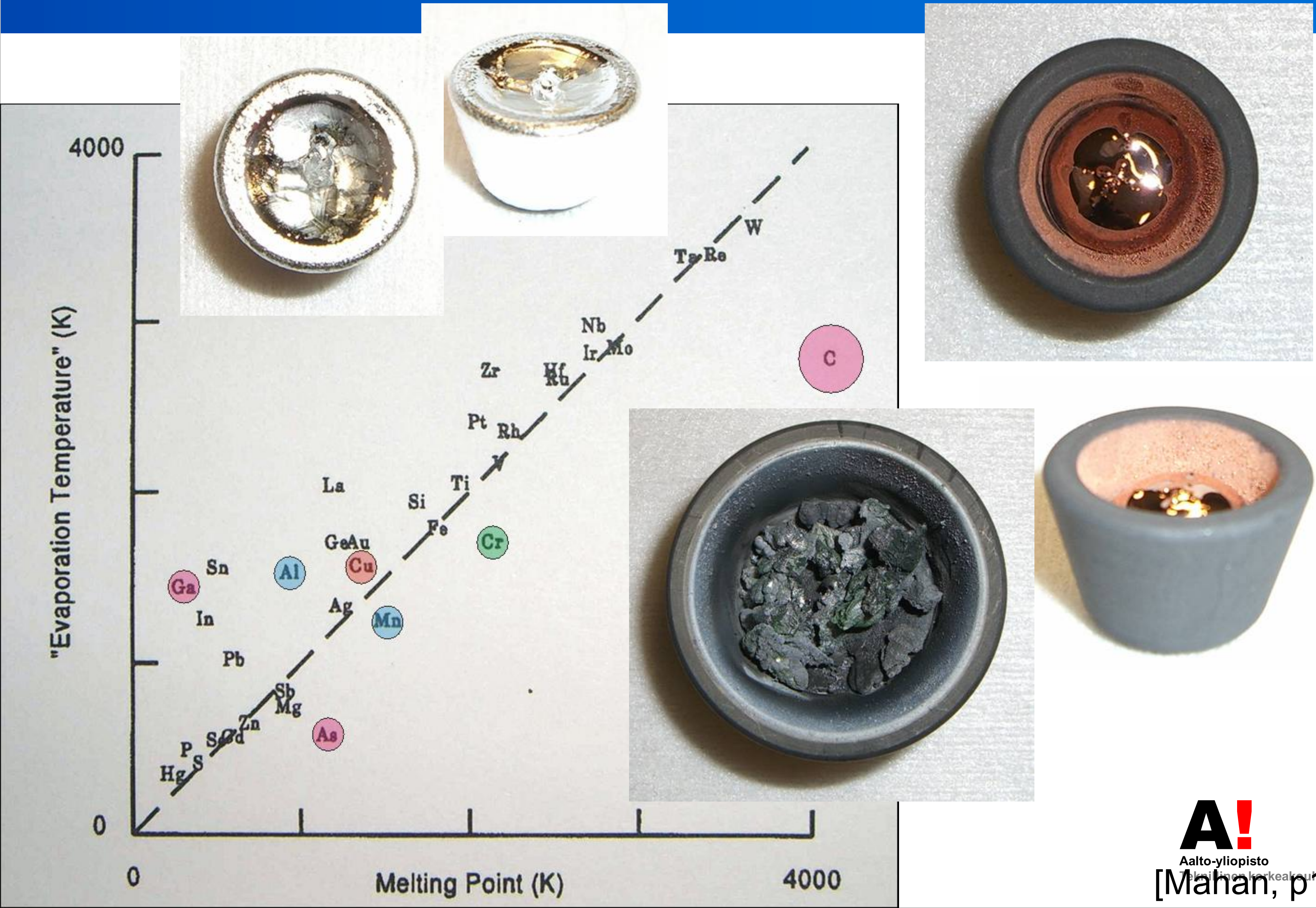
Electronic components fit on standard 483mm rack.
Filament transformer can be mounted remotely as shown or directly on source flange.

electron beam evaporator

view of sample with beam shutter



Evaporation temperature for p = 10^{-2} torr = $1.33 \cdot 10^{-2}$ mbar



Aalto-yliopisto
Teknillinen korkeakoulu

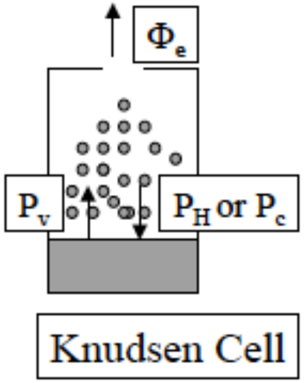
[Mahan, p149]

Vaporization

- **Evaporation or sublimation of atoms from surface due to thermal energy**
- **If the surface of source is in equilibrium with the vapor, the rate of molecules flowing from the source is:**

Coefficient of Evaporation Between 0 and 1

$$\Phi_e = \frac{\alpha_e N_a (P_v - P_h)}{\sqrt{2\pi MRT}}$$



Prof. S. Gleixner, San Jose State University: MatE 270

Vapor pressure

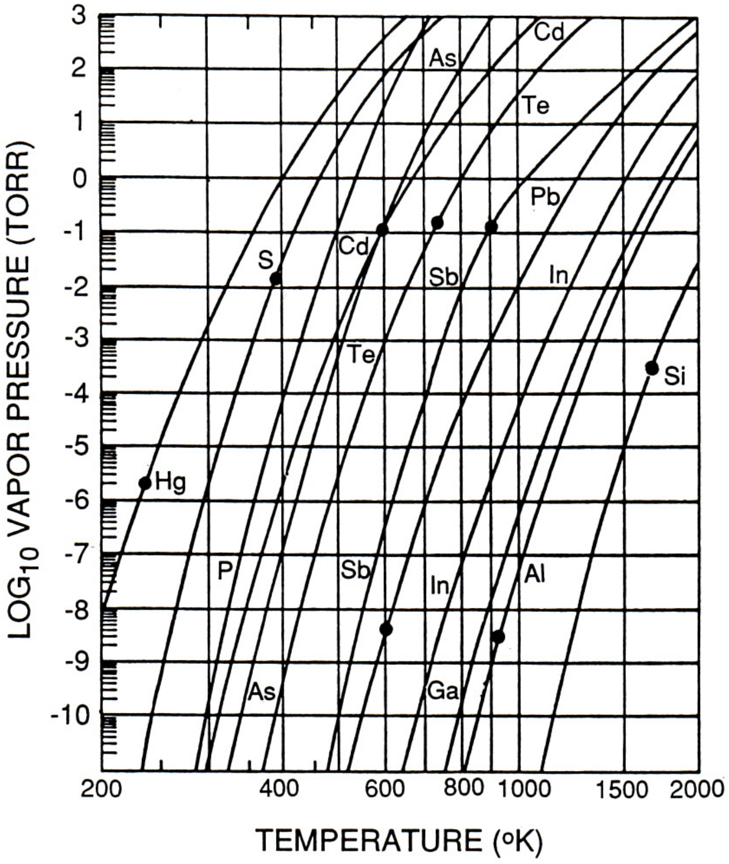


Figure 3-2. Vapor pressures of elements employed in semiconductor materials. Dots correspond to melting points. (Adapted from Ref. 8).

Aalto-yliopisto
Teknillinen korkeakoulu

Vapor pressure

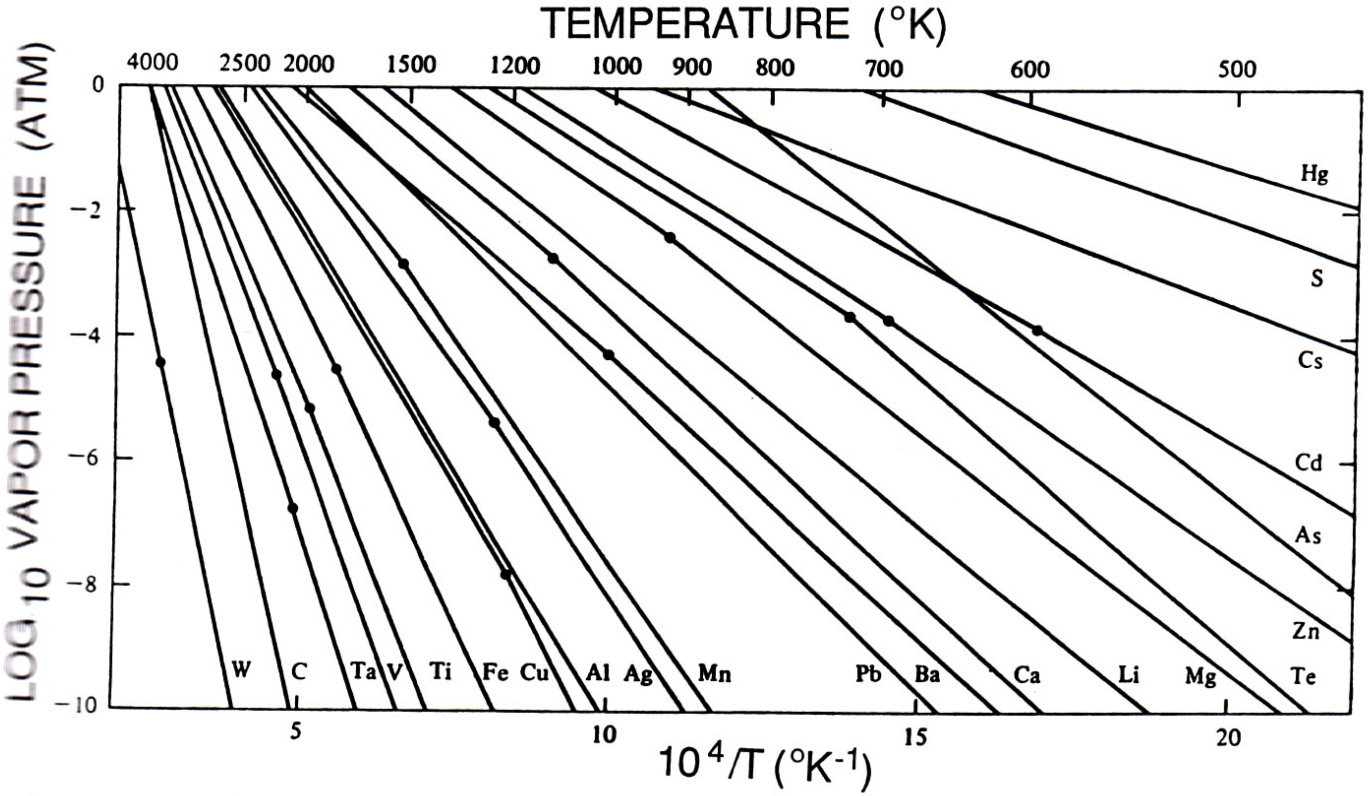


Figure 3-1. Vapor pressures of selected elements. Dots correspond to melting points. (From Ref. 7).

Vapor pressure from tabulations

$$\log(p/atm) = A + B/T + C*\log(T) + D/T^3$$

element	State	A	B	C	D	T(melt) K
'Li'	'solid'	5.667	-8310	0	0	453
'Li'	'liquid'	5.055	-8023	0	0	0
'Na'	'solid'	5.298	-5603	0	0	371
'Na'	'liquid'	4.704	-5377	0	0	0
'K'	'solid'	4.961	-4646	0	0	336
'K'	'liquid'	4.402	-4453	0	0	0
'Rb'	'solid'	4.5857	-4215	0	0	313
'Rb'	'liquid'	4.312	-4040	0	0	0
'Cs'	'solid'	4.711	-3999	0	0	301.6
'Cs'	'liquid'	4.165	-3830	0	0	0
'Be'	'solid'	8.042	-17020	-0.444	0	1560
'Be'	'liquid'	5.786	-15731	0	0	0
'Mg'	'solid'	8.489	-7813	-0.8253	0	923
'Mg'	'liquid'	0	0	0	0	0
'Ca'	'solid'	10.127	-9517	-1.403	0	1112
'Ca'	'liquid'	0	0	0	0	0
'Sr'	'solid'	9.226	-8572	-1.1926	0	1042
'Sr'	'liquid'	0	0	0	0	0

Reference: Alcock, CB< Itkin, VP, and Horrigan MK Canadian Metallurgical Quartely, 23, 309, 1984.

Vapor pressure of alloys

The complication arises because the different elements do not necessarily have the same vaporization rate (leading to different p_v and Q_e).

$$\frac{\Phi_B}{\Phi_C} = \frac{\gamma_A X_A}{\gamma_B X_B}\frac{P_A(0)}{P_B(0)}\sqrt{\frac{M_B}{M_A}}$$

Prof. S. Gleixner, San Jose State University: MatE 270

Vapor pressure of alloys

Textbook Example

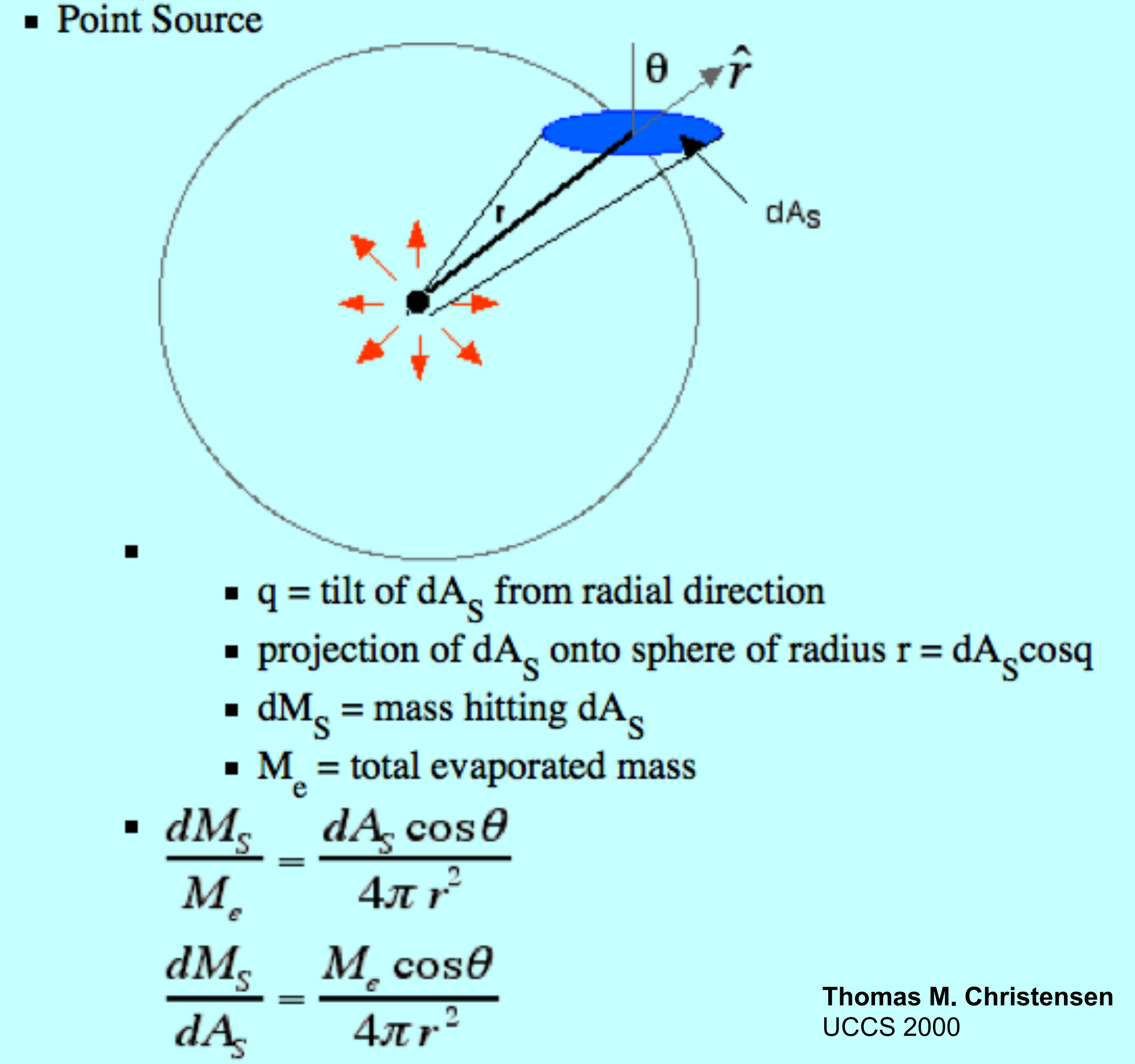
- Want to deposit an Al-2 wt% Cu film from a crucible heated to 1350K
- Therefore want: $\frac{\Phi_{Al}}{\Phi_{Cu}} = \frac{98M_{Cu}}{2M_{Al}}$
- Assuming $\gamma_{Cu}=\gamma_{Al}$
- From Fig 3-1

$$\frac{P_{Al}(0)}{P_{Cu}(0)} = \frac{10^{-3}}{2\times10^{-4}}$$

- So

$$\frac{X_{Al}}{X_{Cu}} = \frac{98(2\times10^{-4})\sqrt{63.7}}{2(10^{-3})\sqrt{27}} = 15$$

- Need a 15:1 molar ratio of Al to Cu



- Point Source

-
  - q = tilt of dA_S from radial direction
  - projection of dA_S onto sphere of radius r = dA_Scosq
  - dM_S = mass hitting dA_S
  - M_e = total evaporated mass
- $$\frac{dM_S}{M_e} = \frac{dA_S\cos\theta}{4\pi r^2}$$

$$\frac{dM_S}{dA_S} = \frac{M_e\cos\theta}{4\pi r^2}$$

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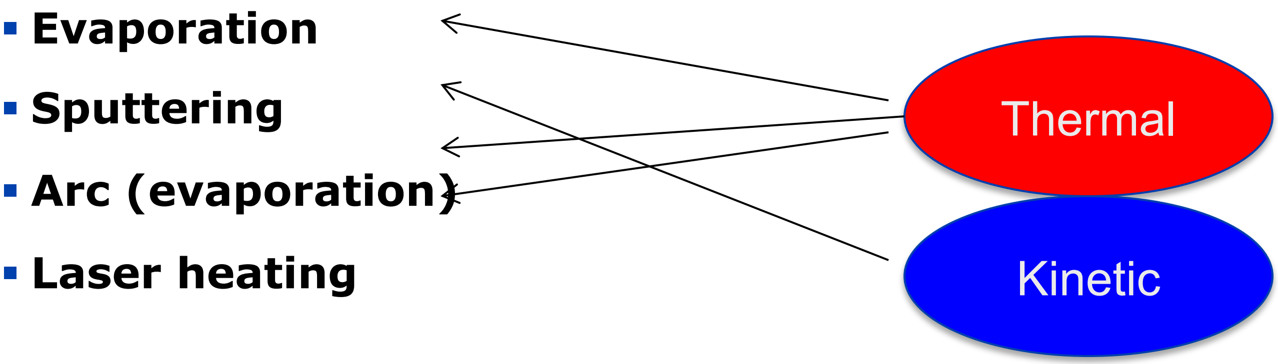
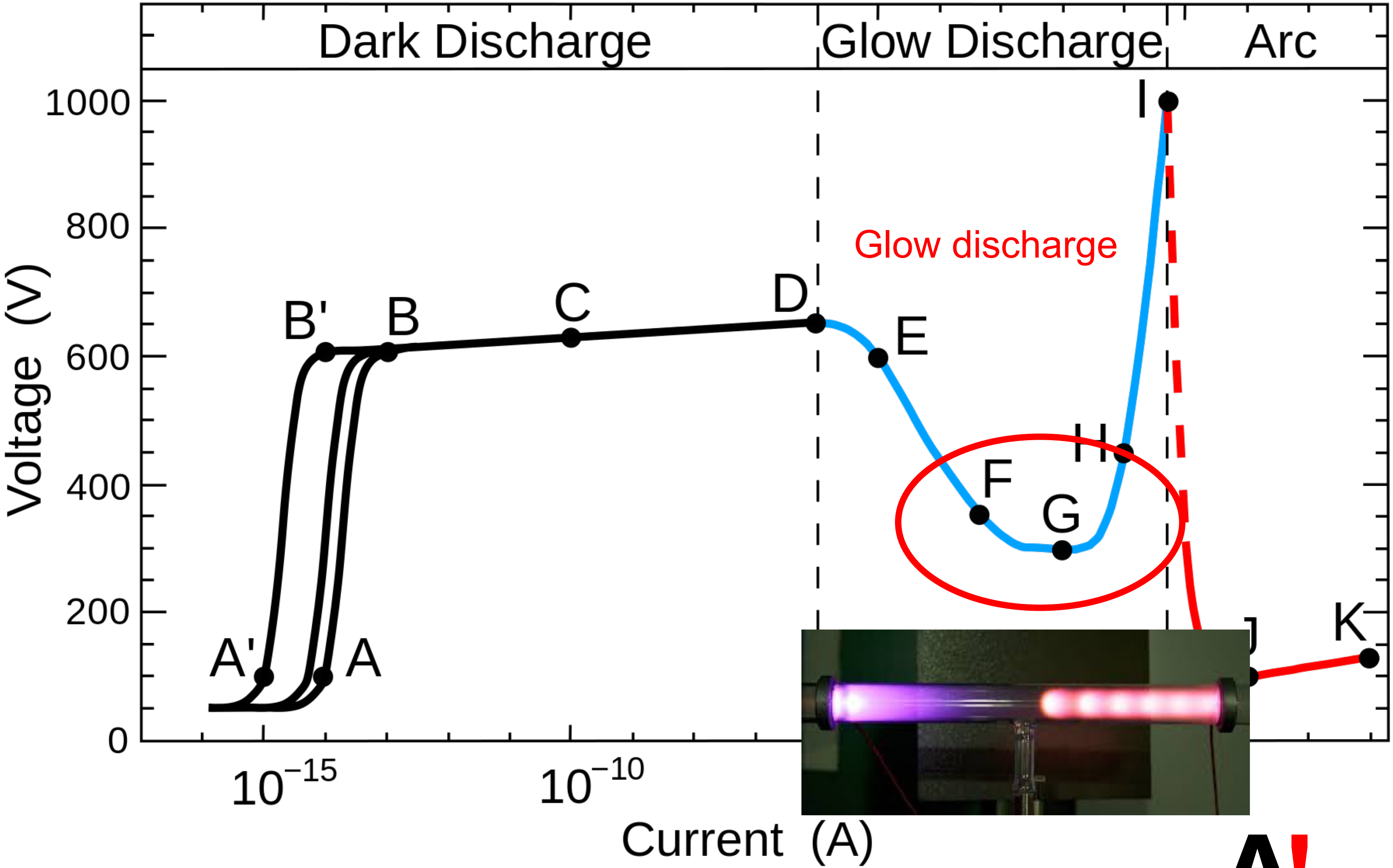
UCCS 2000

Extraction of materials from solid

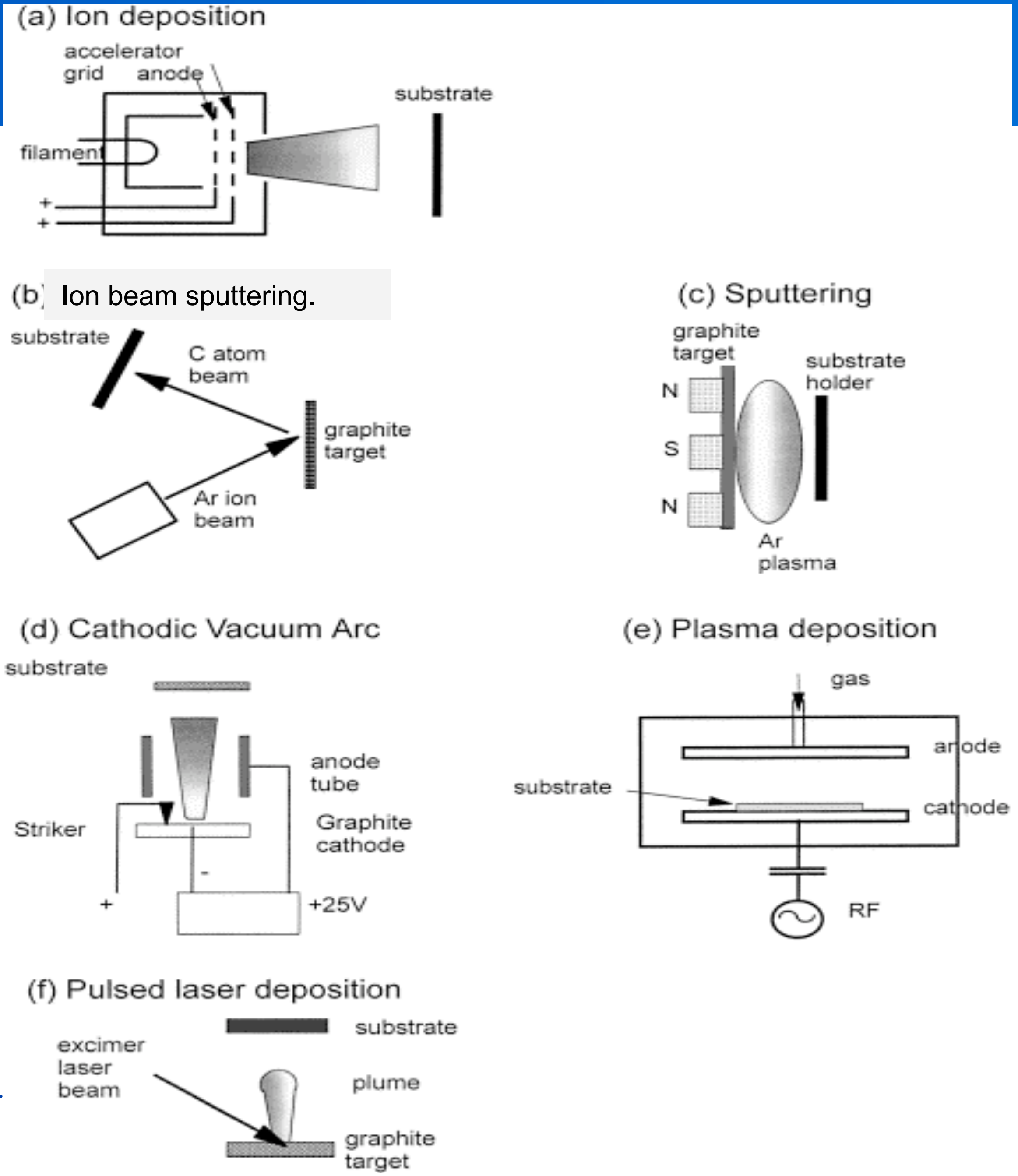


- **Evaporation**
- **Sputtering**
- **Arc (evaporation)**
- **Laser heating**

DC Plasma glow discharge and arc



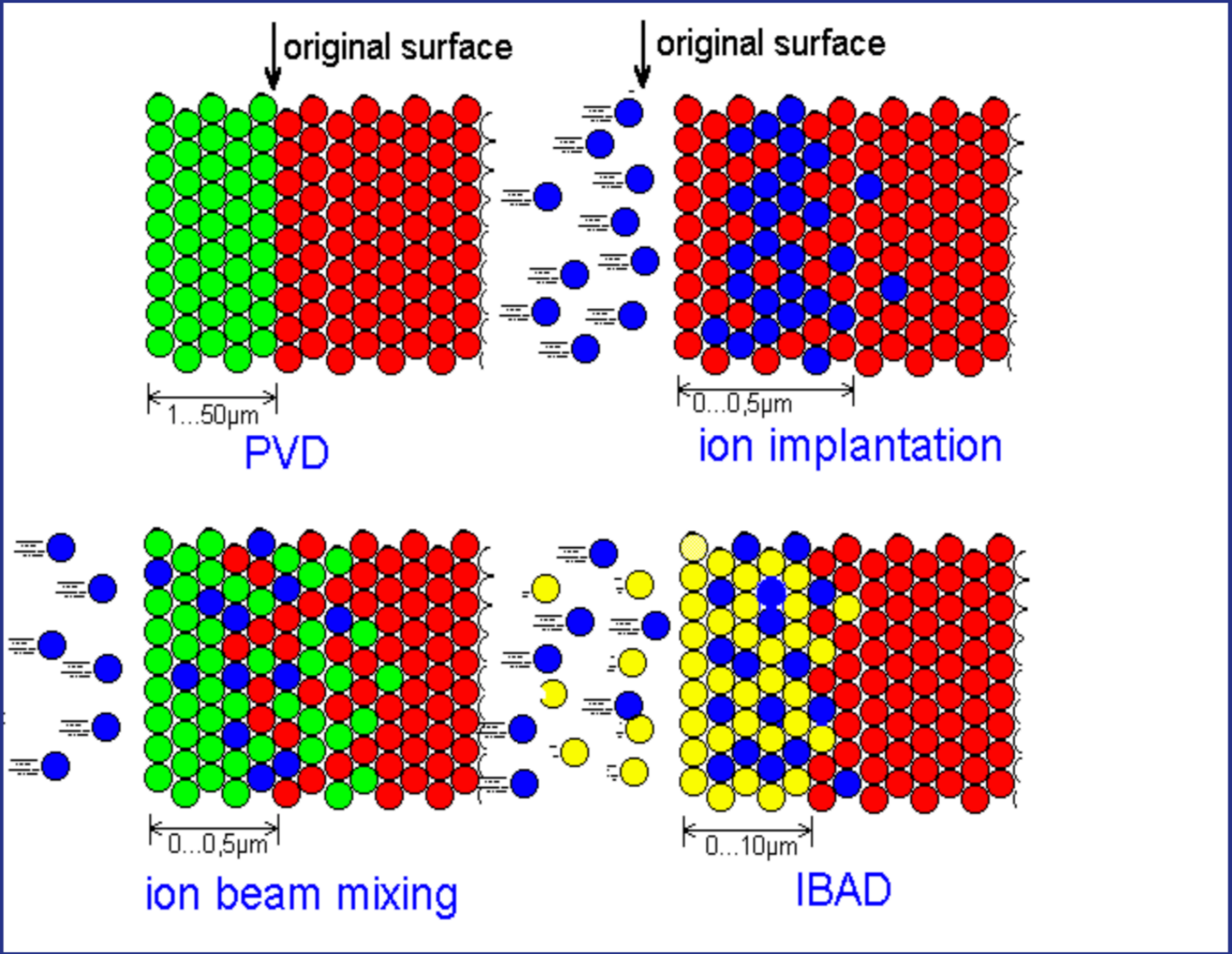
PVD methods



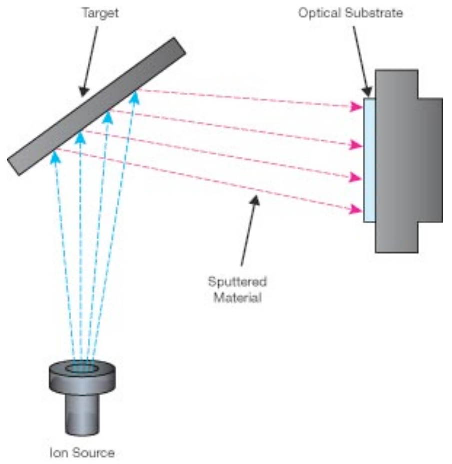
Ion beam sputtering.

PVD and Ion Assisted Processes

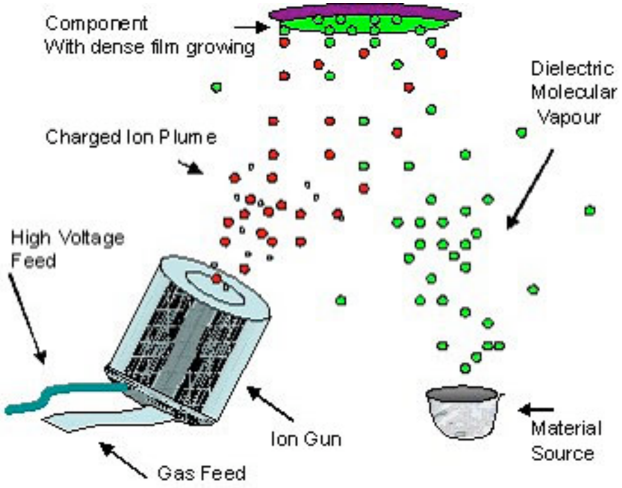
Which role can energetic ions play

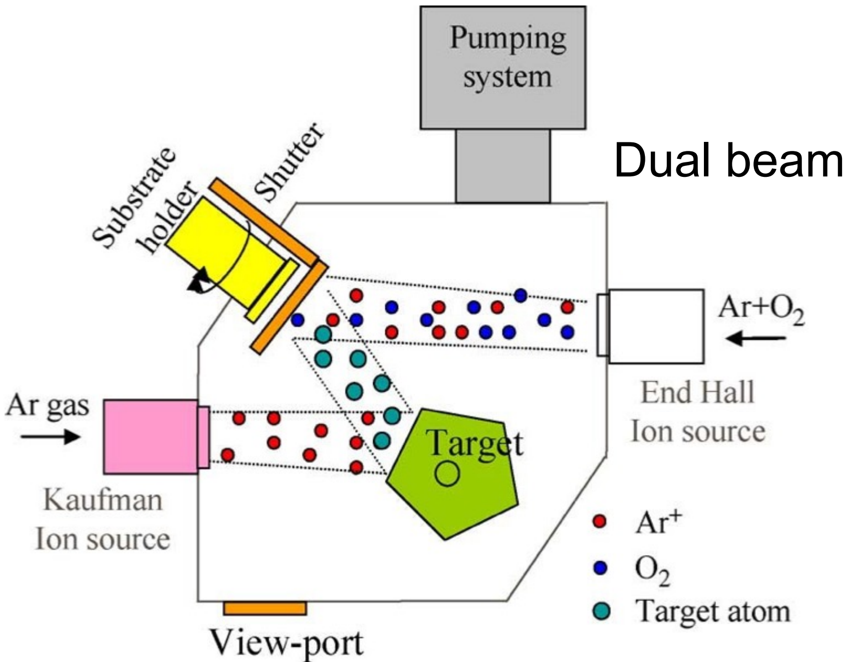


Ion beam sputtering

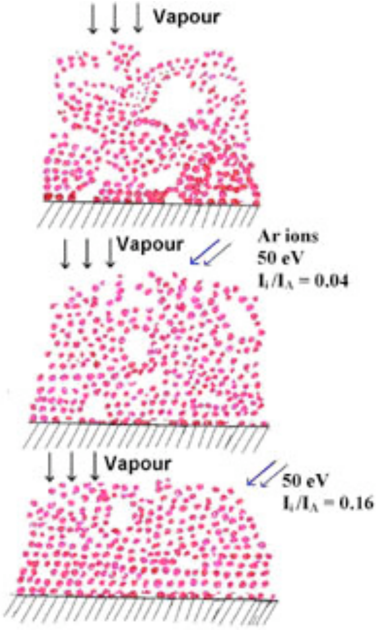


Kaufman
http://www.youtube.com/watch?v=lbcr-B258J8&NR=1

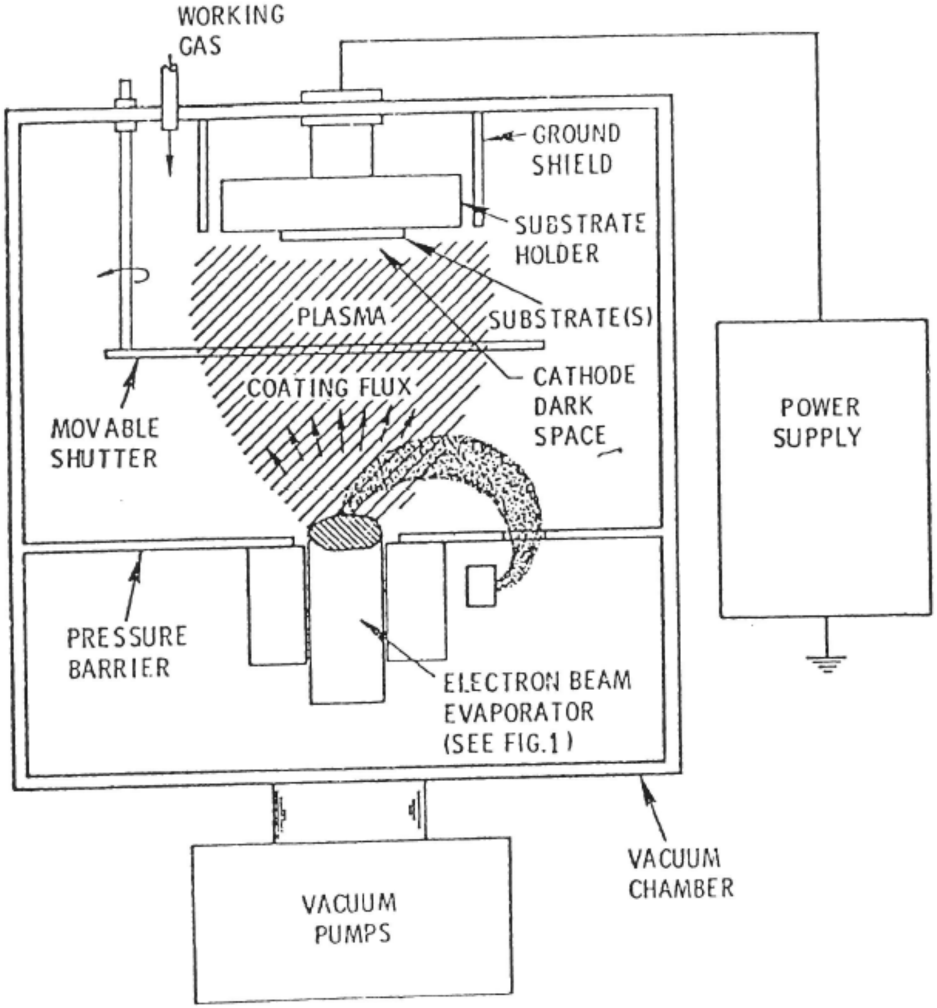




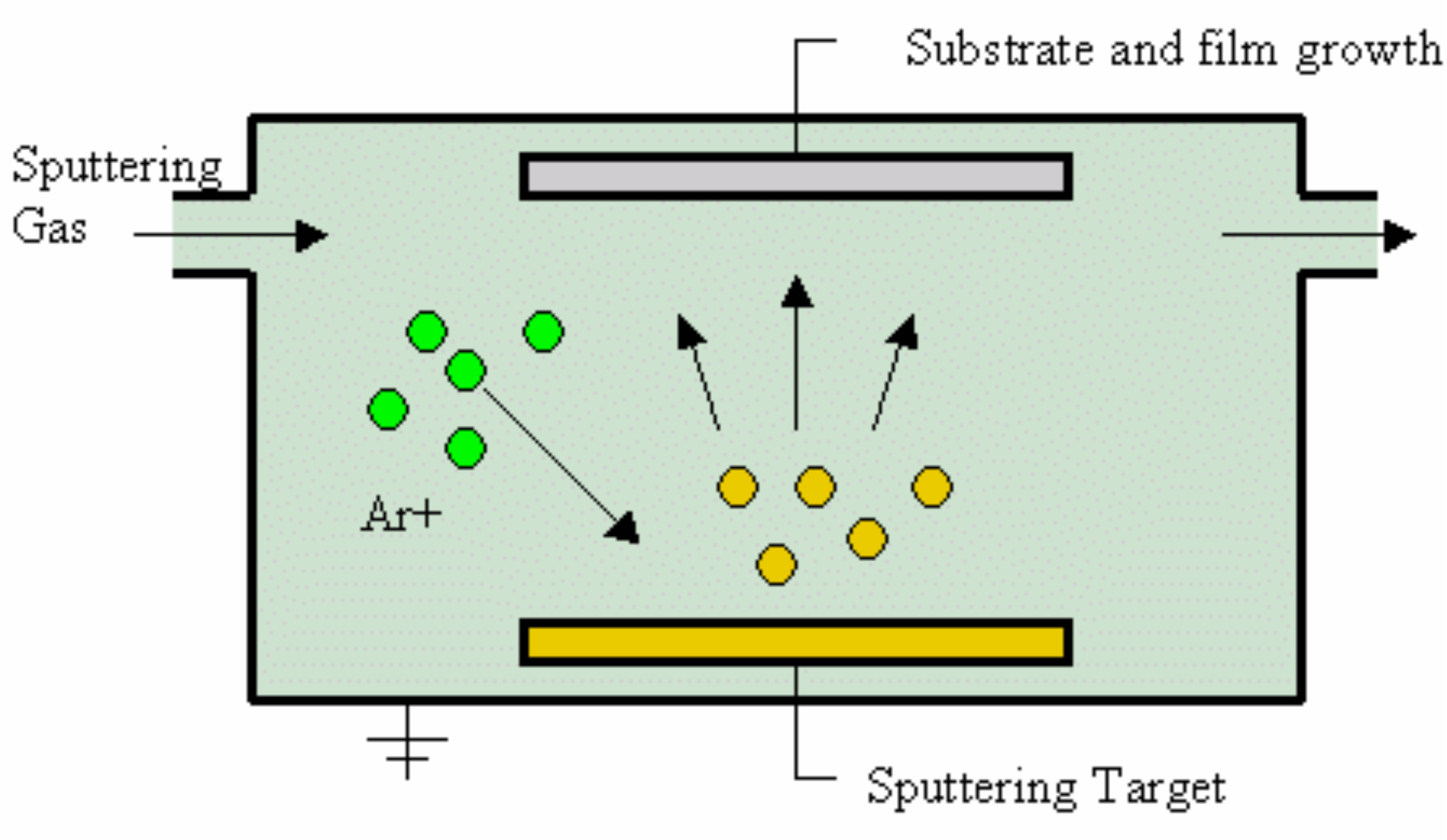
Dual beam sputtering



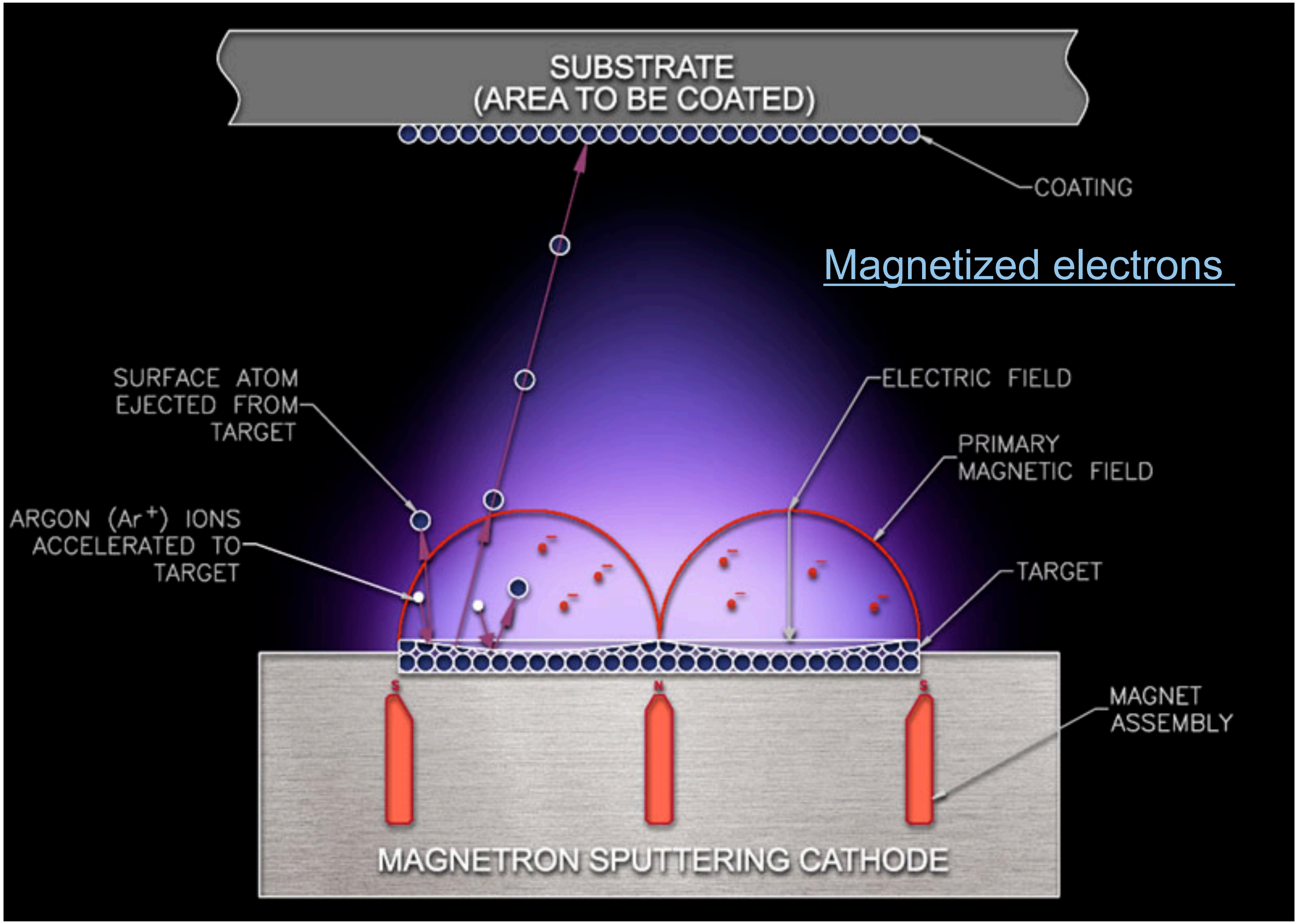
Ion plating


WORKING GAS
GROUND SHIELD
SUBSTRATE HOLDER
PLASMA
SUBSTRATE(S)
CATHODE DARK SPACE
COATING FLUX
MOVABLE SHUTTER
POWER SUPPLY
PRESSURE BARRIER
ELECTRON BEAM EVAPORATOR (SEE FIG.1)
VACUUM PUMPS
VACUUM CHAMBER

Sputtering


Substrate and film growth
Sputtering Gas
Ar+
Sputtering Target

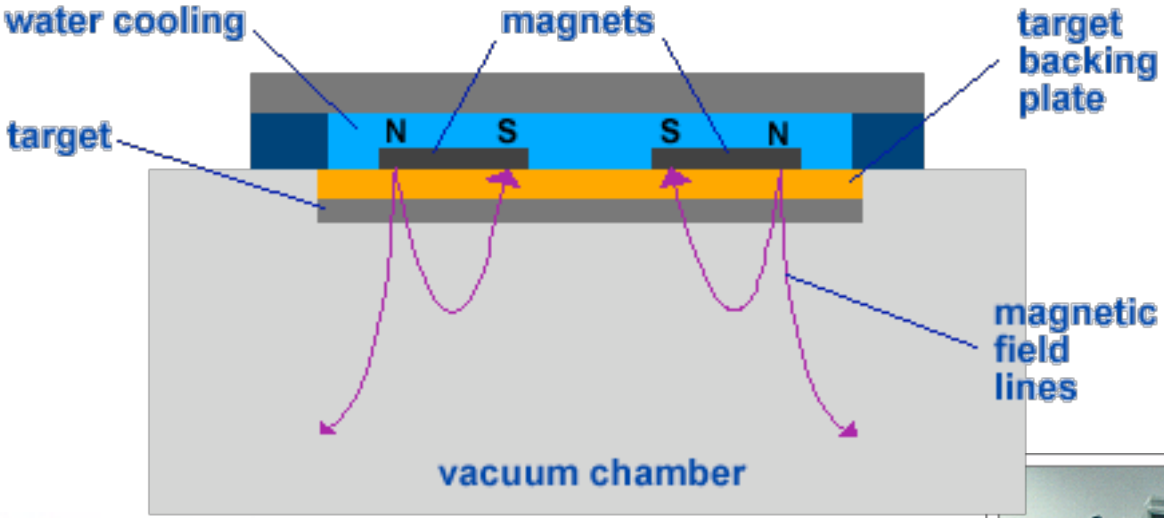
Magnetron-sputtering



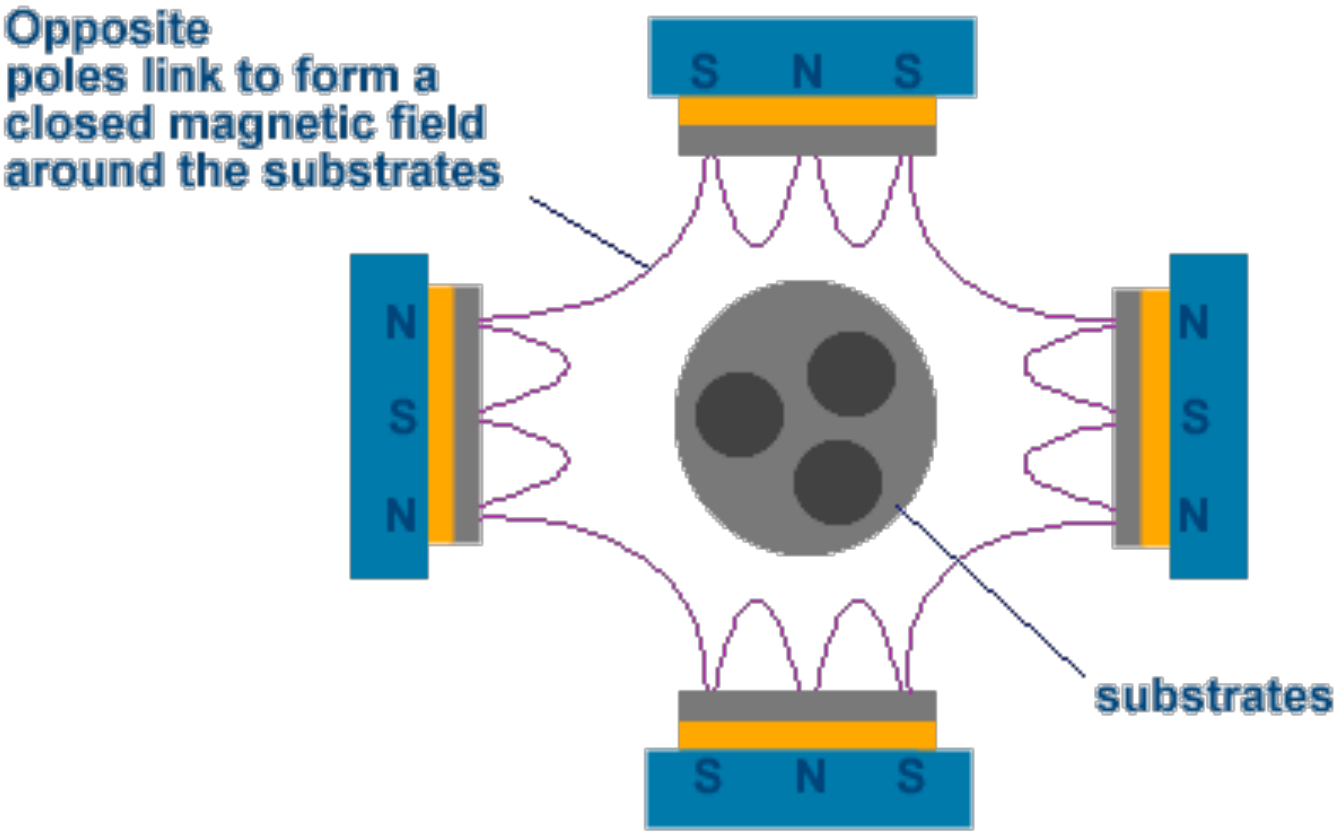
Magnetized electrons

Lähde: Angstrom Sciences, Inc.

Unbalanced magnetron sputtering



Closed field magnetron sputtering



Opposite poles link to form a closed magnetic field around the substrates

substrates


TEER
COATINGS
LIMITED

Magnetron Sputtering video

Surface coating methods – more details

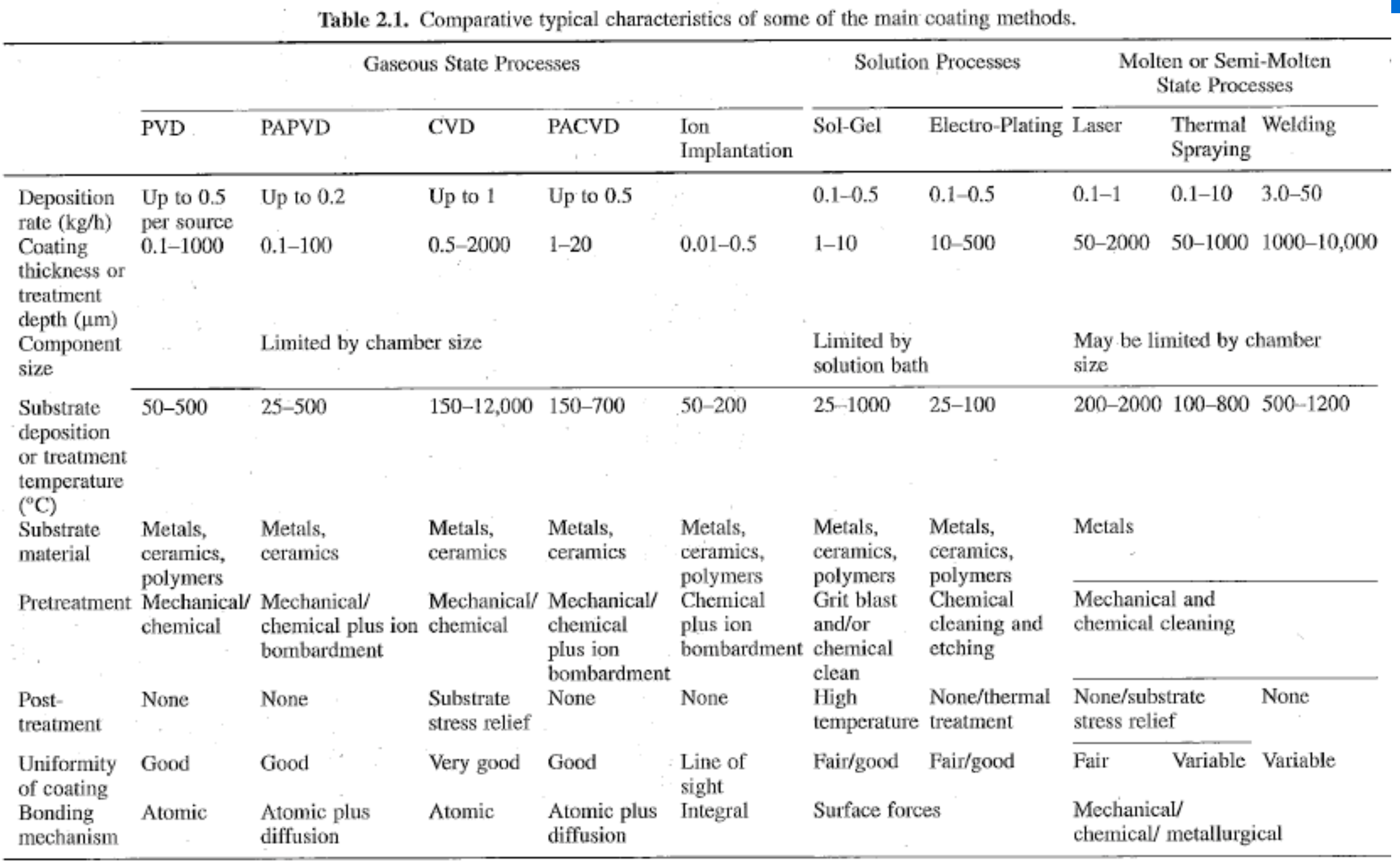


Table 2.1. Comparative typical characteristics of some of the main coating methods.

	Gaseous State Processes					Solution Processes		Molten or Semi-Molten State Processes		
	PVD	PAPVD	CVD	PACVD	Ion Implantation	Sol-Gel	Electro-Plating	Laser	Thermal Spraying	Welding
Deposition rate (kg/h)	Up to 0.5 per source	Up to 0.2	Up to 1	Up to 0.5		0.1–0.5	0.1–0.5	0.1–1	0.1–10	3.0–50
Coating thickness or treatment depth (µm)	0.1–1000	0.1–100	0.5–2000	1–20	0.01–0.5	1–10	10–500	50–2000	50–1000	1000–10,000
Component size		Limited by chamber size				Limited by solution bath		May be limited by chamber size		
Substrate deposition or treatment temperature (°C)	50–500	25–500	150–12,000	150–700	50–200	25–1000	25–100	200–2000	100–800	500–1200
Substrate material	Metals, ceramics, polymers	Metals, ceramics	Metals, ceramics	Metals, ceramics	Metals, ceramics, polymers	Metals, ceramics, polymers	Metals, ceramics, polymers	Metals		
Pretreatment	Mechanical/ chemical	Mechanical/ chemical plus ion bombardment	Mechanical/ chemical	Mechanical/ chemical plus ion bombardment	Chemical plus ion bombardment	Grit blast and/or chemical clean	Chemical cleaning and etching	Mechanical and chemical cleaning		
Post-treatment	None	None	Substrate stress relief	None	None	High temperature	None/thermal treatment	None/substrate stress relief		None
Uniformity of coating	Good	Good	Very good	Good	Line of sight	Fair/good	Fair/good	Fair	Variable	Variable
Bonding mechanism	Atomic	Atomic plus diffusion	Atomic	Atomic plus diffusion	Integral	Surface forces		Mechanical/ chemical/ metallurgical		

High power pulsed Magnetron Sputtering

High Power Pulsed Magnetron Sputtering (HPPMS)

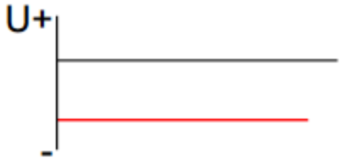
- Introduced by Kouznetsov et al.*
  - Also known as HIPIMS – High Power Impulse Magnetron Sputtering
- High power pulses of short duration
  - Peak value typically 100 times greater than conventional magnetron sputtering
    - Peak power densities of 1-3 kW/cm²
  - Pulse width of 100 - 150 µsec
  - Discharge voltages of 500-1000 V

*V. Kouznetsov, K. Macák, J. M. Schneider, U. Helmersson, and I. Petrov, "A Novel Pulsed Magnetron Sputter Technique Utilizing Very High Target Power Densities," Surf. Coat. Technol. 122 (1999) 290.

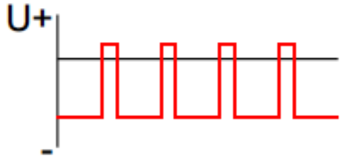
PULSED SPUTTERING

Definitions

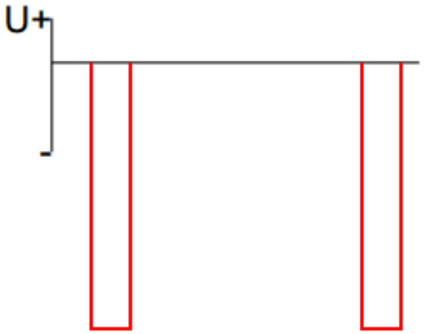
- DC-sputtering



- Pulsed DC



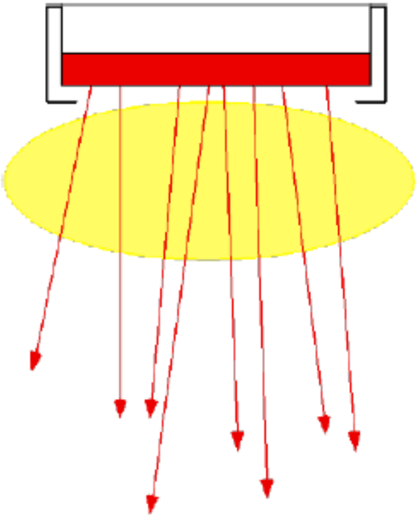
- HiPIMS



III. High power pulsing

- High Power Impulse Magnetron Sputtering – HiPIMS
- High Power Pulsed Magnetron Sputtering – HPPMS
- Modulated Pulsed Power - MPP

What is HiPIMS?



High peak powers (500-2000 W/cm^2)
Reasonable average powers
Low duty factors (0.5 – 5 %)

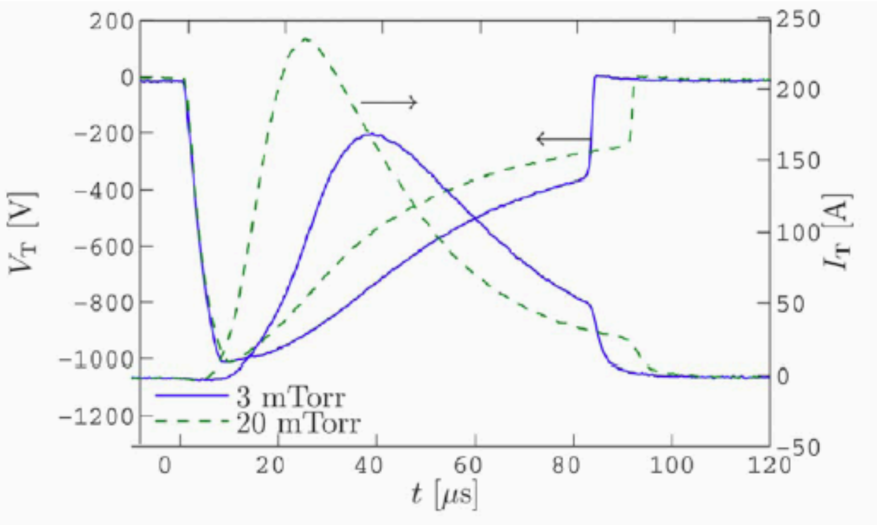
Plasma densities in the range of 10^{19} m^{-3}
(Normal magnetron sputtering 10^{16} m^{-3})

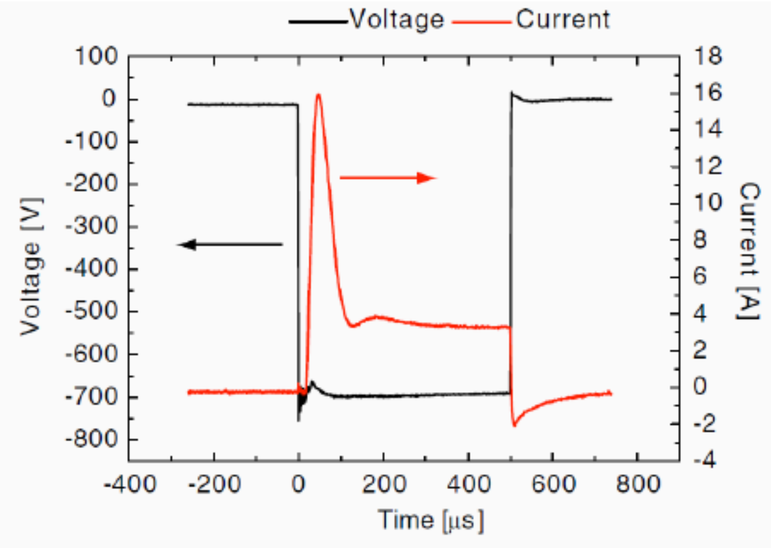
D.V. Mozgrin, I.K. Fetisov, and G.V. Khodachenko, Plasma Phys. Rep. **21,** 400 (1995)

S.P. Bugaev, N.N. Koval, N.S. Sochugov, and A.N. Zakharov, Proceedings of the XVIIth International Symposium on Discharges and Electrical Insulation in Vacuum, July 21-26, 1996, Berkeley, CA, USA, vol., p.1074

V. Kouznetsov, K. Macák, J.M. Schneider, U. Helmersson, and I. Petrov, Surf. Coat. Technol. **122**, 290 (1999)

Typical HiPIMS pulses



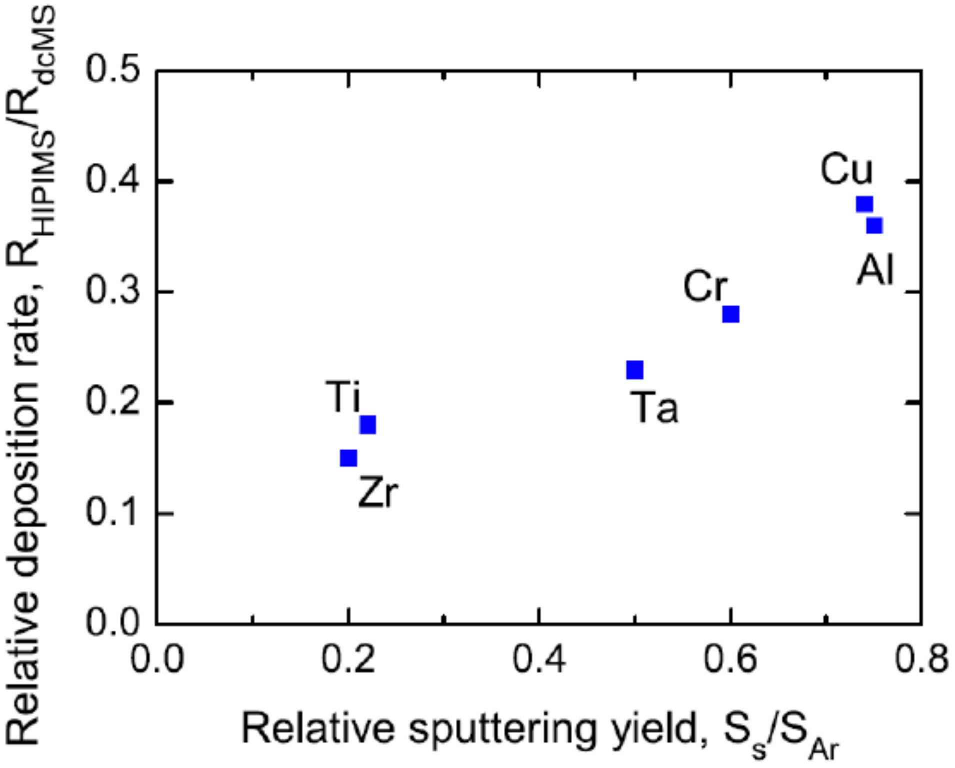


J.T. Gudmundsson, P. Sigurjonsson, P. Larsson, D. Lundin, U. Helmersson, J. Appl. Phys. **105**, 123302 (2009)

D. Lundin, N. Brenning, D. Jädernäs, P. Larsson, E. Wallin, M. Lattemann, M.A. Raadu and U. Helmersson, Plasma Sources Sci. Technol. **18**, 045008 (2009).

Deposition rate

The deposition rate in HiPIMS is in general lower compared to DC sputtering at the same average power



U. Helmersson, M. Lattemann, J. Bohlmark, A.P. Ehiasarian, and J.T. Gudmundsson, Thin Solid Films **513**, 1 (2006)

HIPIMS denser films

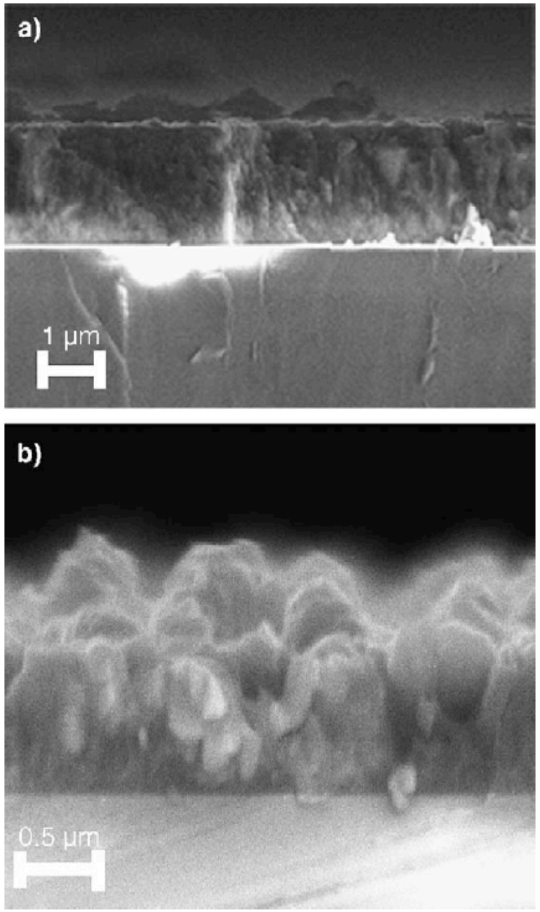
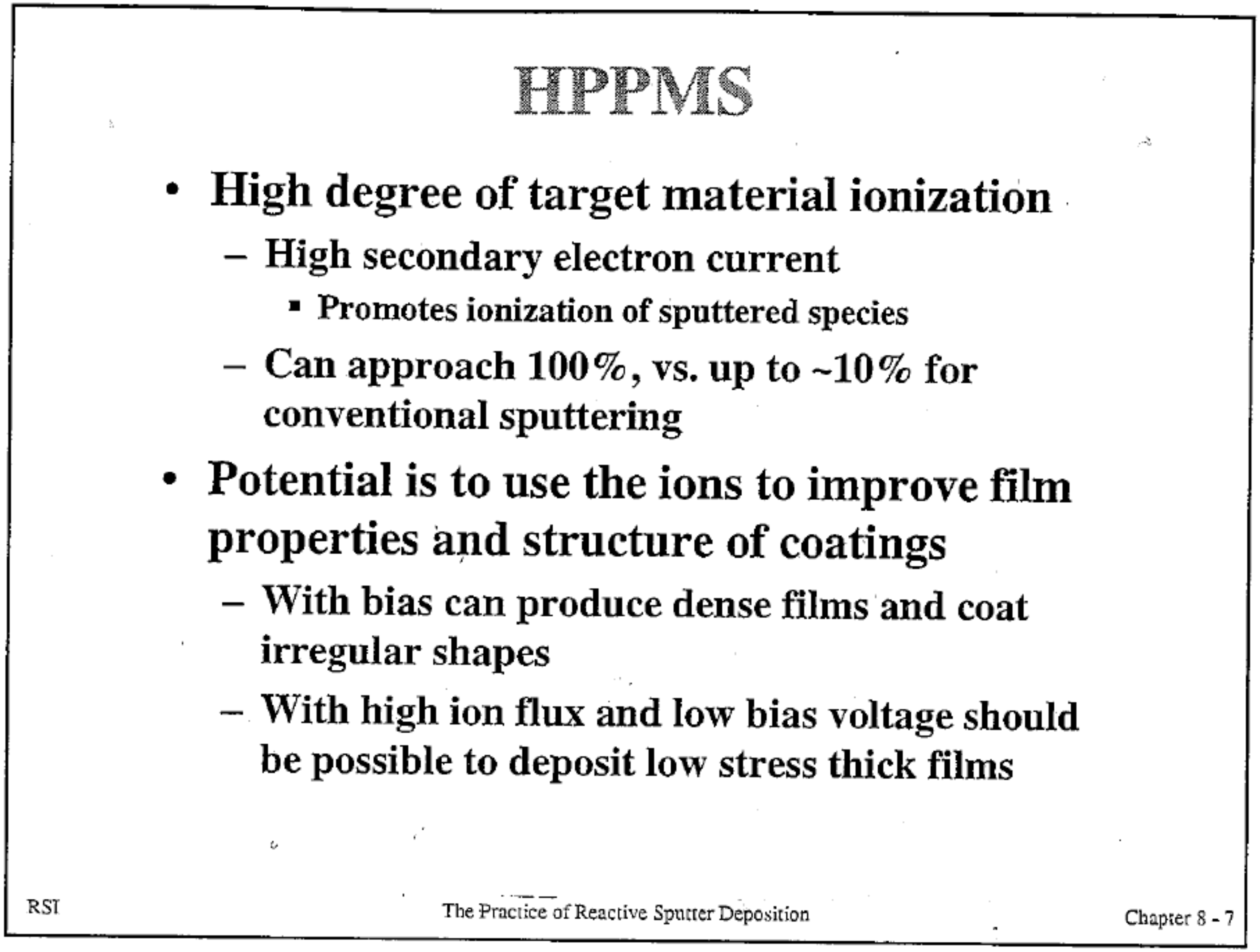
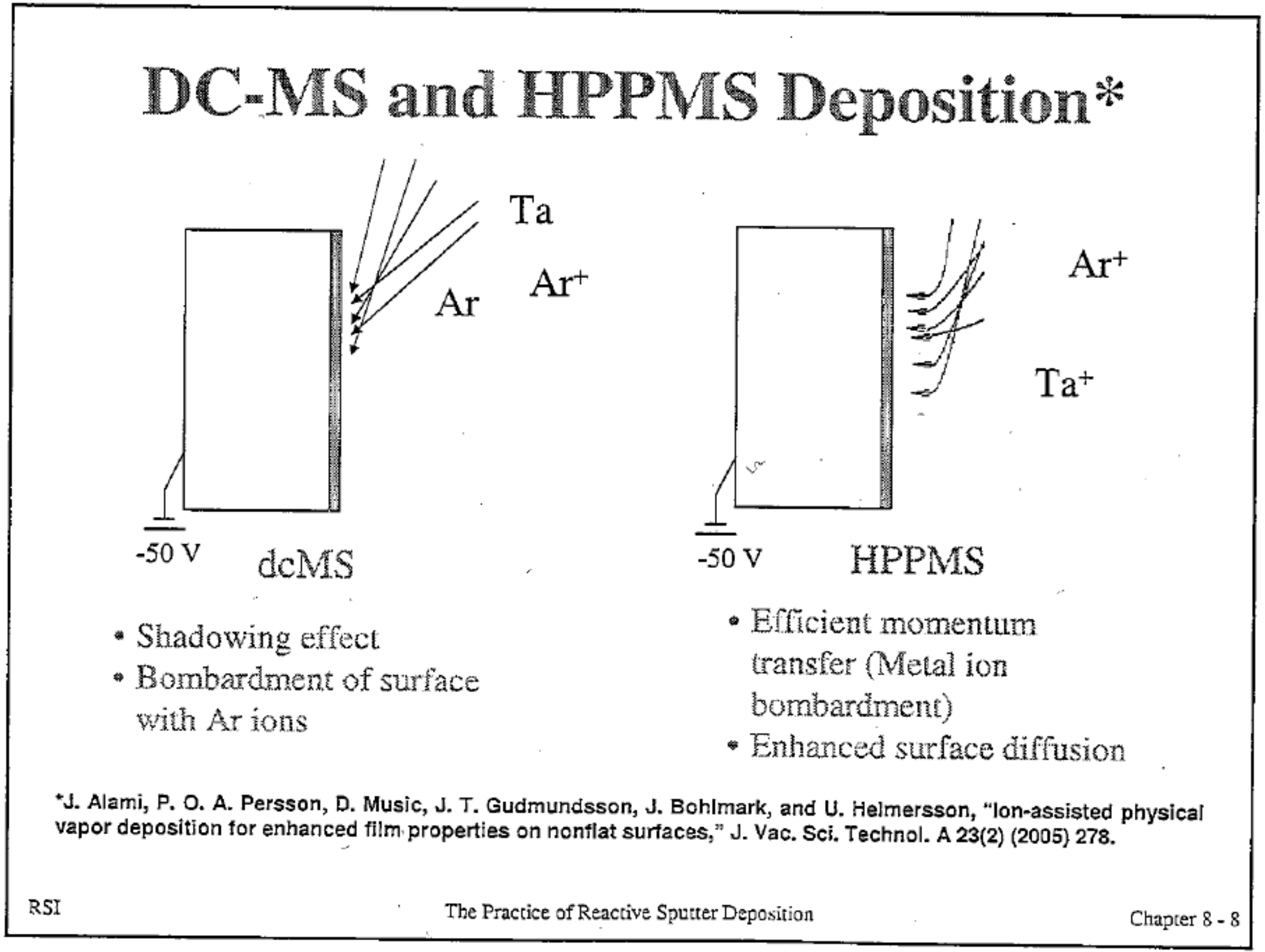


Fig. 2. SEM micrographs from Ti–Si–C films grown facing the target surface by HIPIMS (a) and dcMS (b), using 20 mTorr Ar, a sputtering gas and a substrate bias of −20 V.



HPPMS

- High degree of target material ionization
  - High secondary electron current
    - Promotes ionization of sputtered species
  - Can approach 100%, vs. up to ~10% for conventional sputtering
- Potential is to use the ions to improve film properties and structure of coatings
  - With bias can produce dense films and coat irregular shapes
  - With high ion flux and low bias voltage should be possible to deposit low stress thick films



DC-MS and HPPMS Deposition*

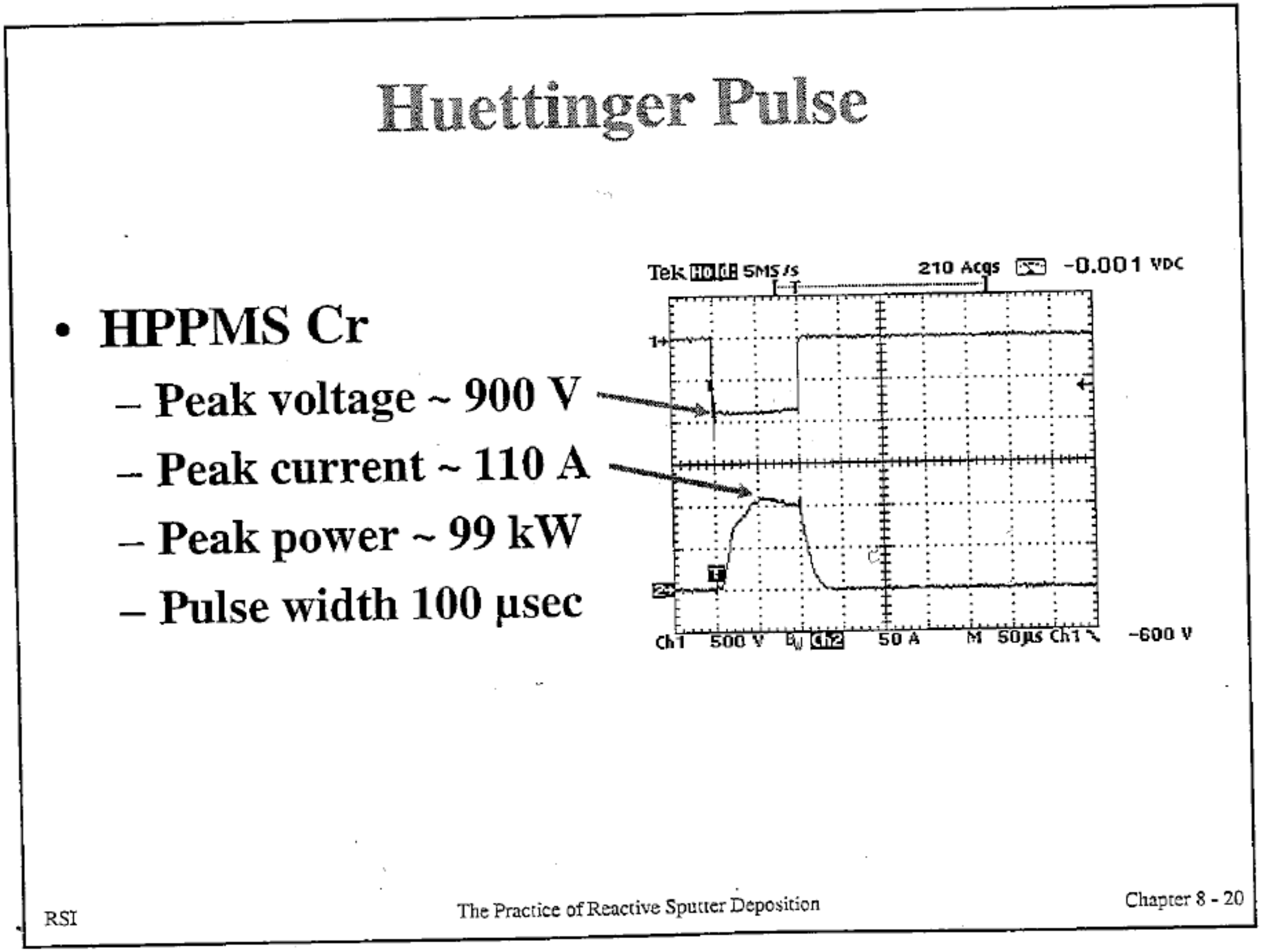
dcMS

- Shadowing effect
- Bombardment of surface with Ar ions

HPPMS

- Efficient momentum transfer (Metal ion bombardment)
- Enhanced surface diffusion

*J. Alami, P. O. A. Persson, D. Music, J. T. Gudmundsson, J. Bohlmark, and U. Helmersson, "Ion-assisted physical vapor deposition for enhanced film properties on nonflat surfaces," J. Vac. Sci. Technol. A 23(2) (2005) 278.



Huettinger Pulse

- **HPPMS Cr**
  - Peak voltage ~ 900 V
  - Peak current ~ 110 A
  - Peak power ~ 99 kW
  - Pulse width 100 µsec

RSI

The Practice of Reactive Sputter Deposition

Chapter 8 - 20

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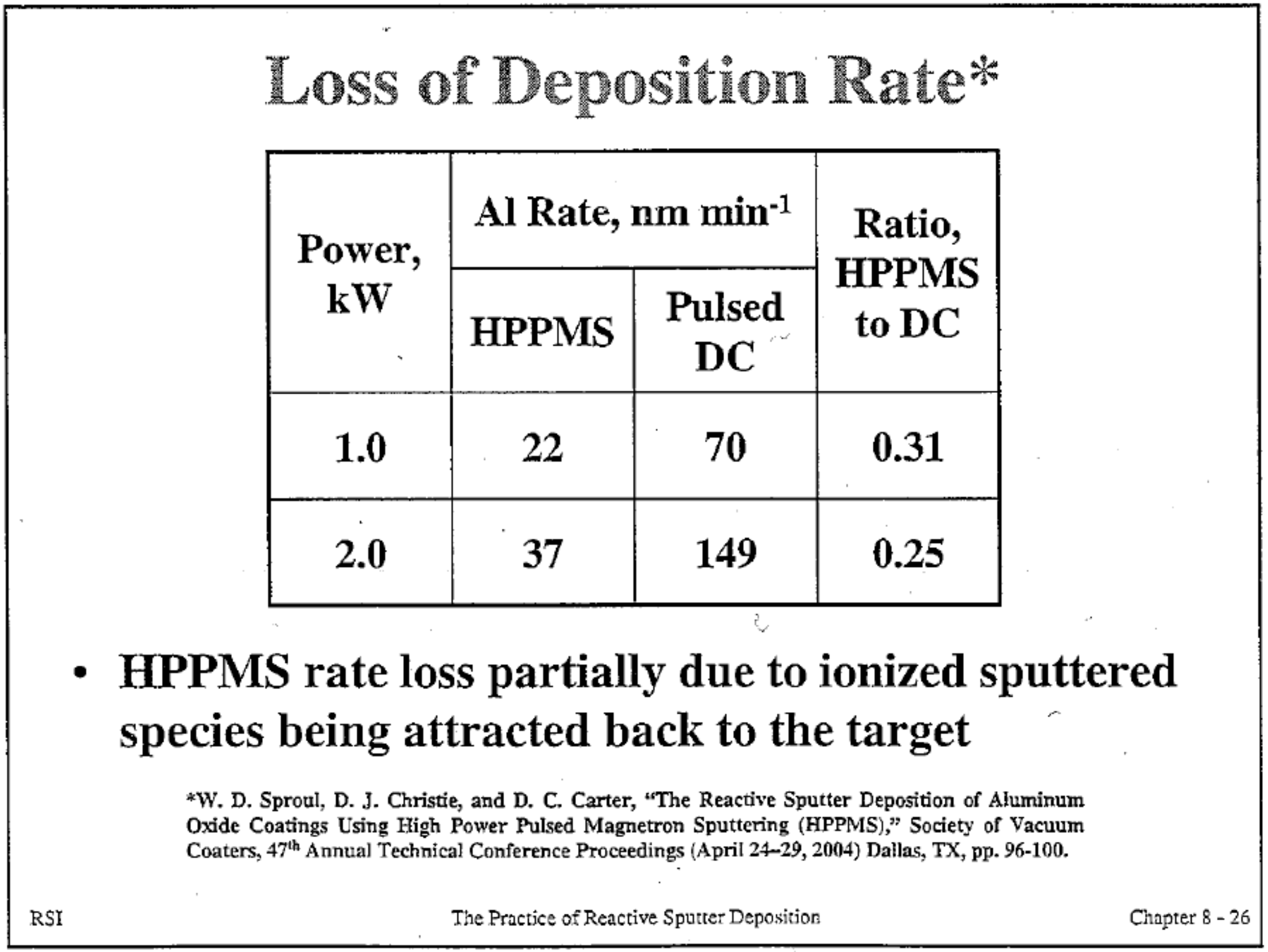


Loss of Deposition Rate*

Power, kW	Al Rate, nm min^{-1}		Ratio, HPPMS to DC
	HPPMS	Pulsed DC	
1.0	22	70	0.31
2.0	37	149	0.25

- HPPMS rate loss partially due to ionized sputtered species being attracted back to the target

*W. D. Sproul, D. J. Christie, and D. C. Carter, "The Reactive Sputter Deposition of Aluminum Oxide Coatings Using High Power Pulsed Magnetron Sputtering (HPPMS)," Society of Vacuum Coaters, 47th Annual Technical Conference Proceedings (April 24–29, 2004) Dallas, TX, pp. 96-100.

RSI The Practice of Reactive Sputter Deposition Chapter 8 - 26

HPPMS denser films

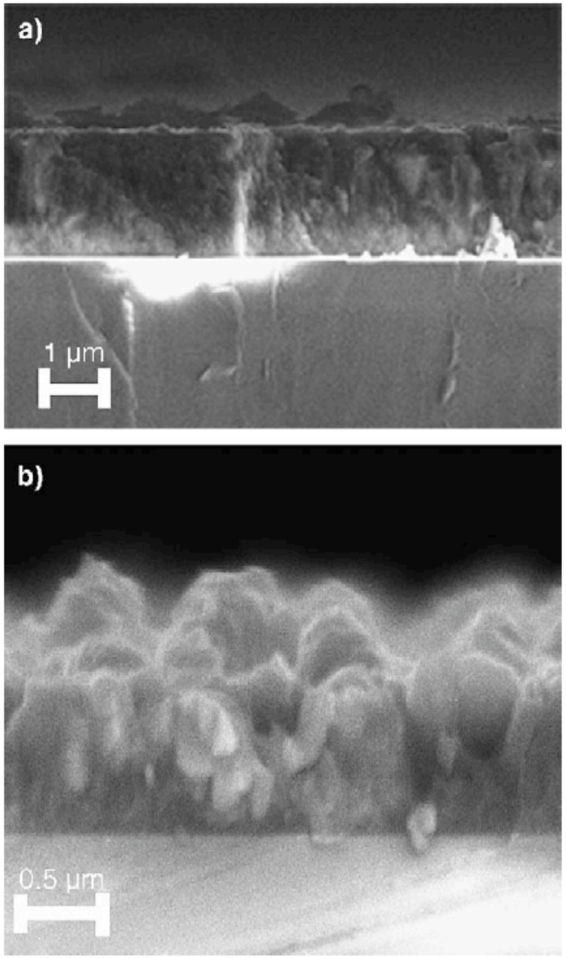
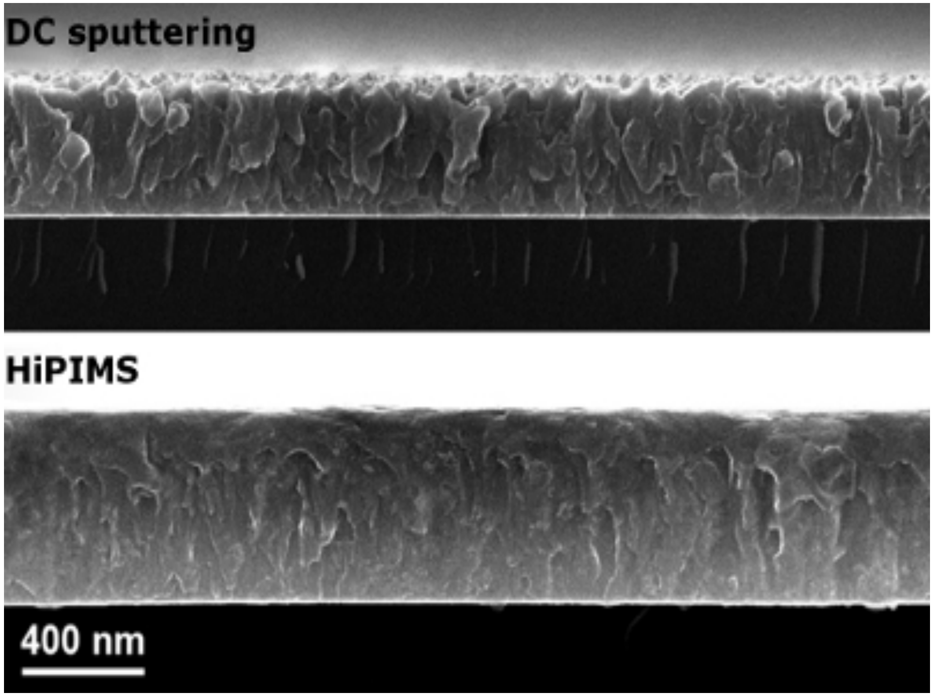
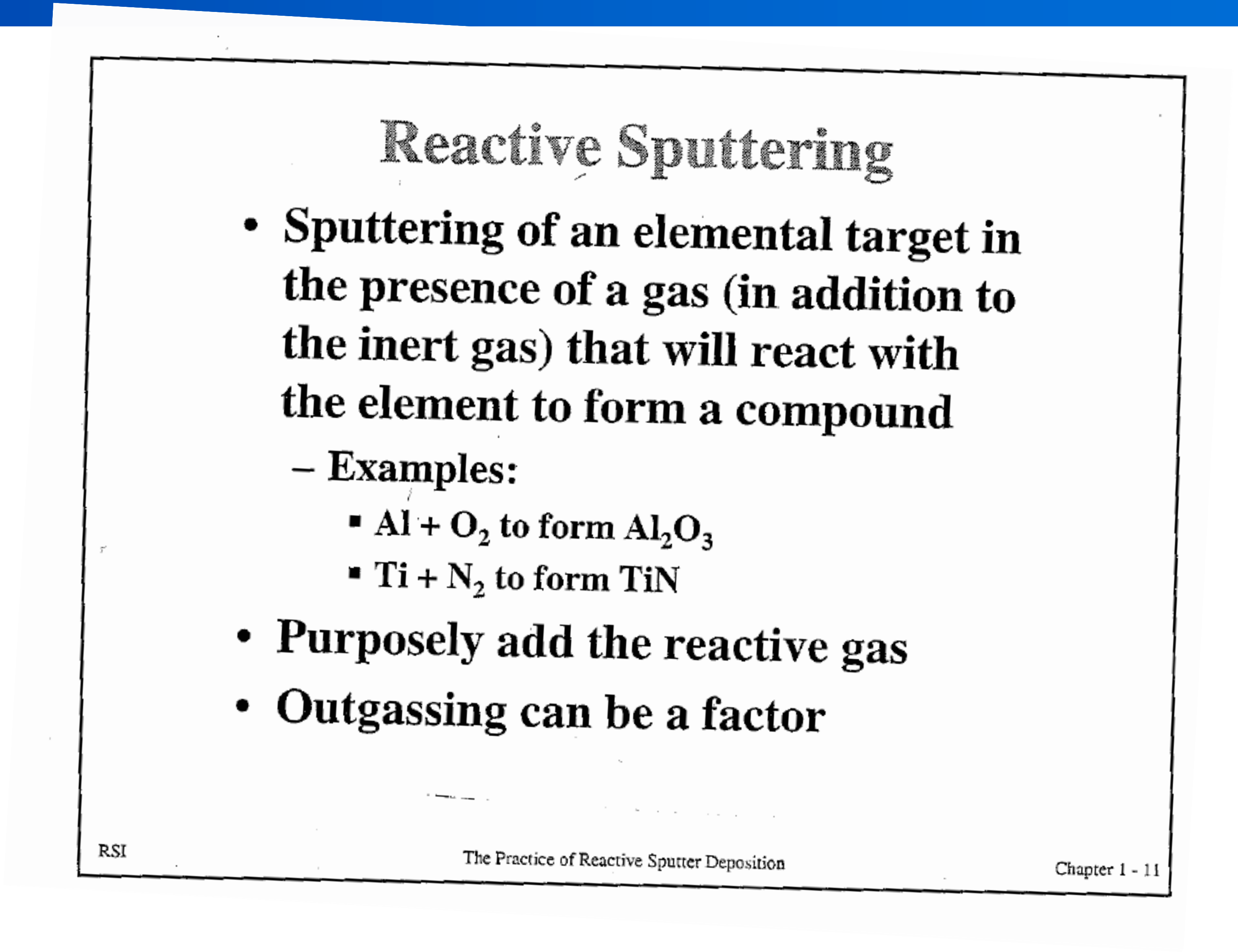


Fig. 2. SEM micrographs from Ti–Si–C films grown facing the target surface by HIPIMS (a) and dcMS (b), using 20 mTorr Ar, a sputtering gas and a substrate bias of −20 V.



Ti sputtered by DC magnetron and HPPMS. Note the difference in film density and smooth top surface of HPPMS film

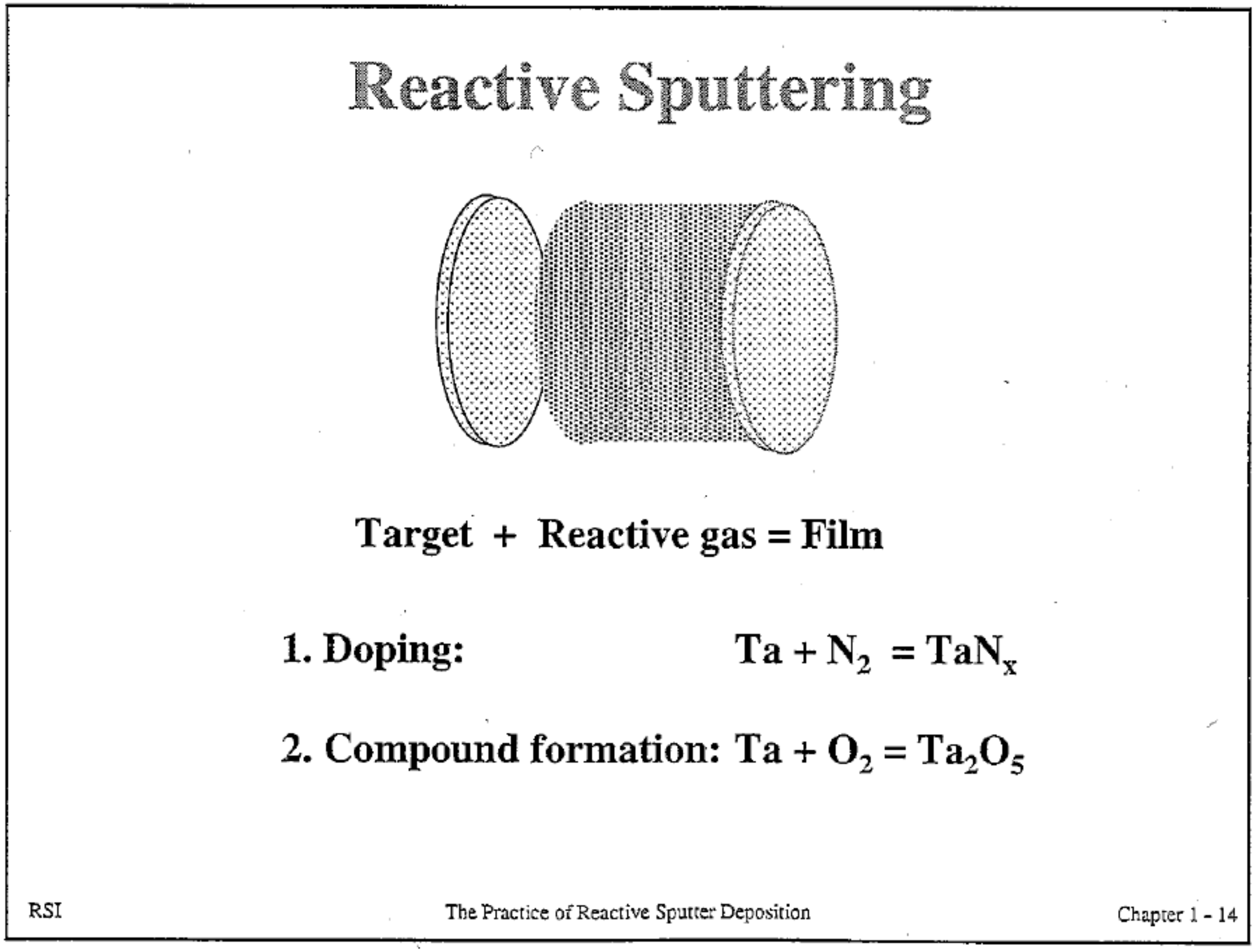
Reactive sputtering



Reactive Sputtering

- Sputtering of an elemental target in the presence of a gas (in addition to the inert gas) that will react with the element to form a compound
  - Examples:
    - $Al + O_2$ to form Al_2O_3
    - $Ti + N_2$ to form TiN
- Purposely add the reactive gas
- Outgassing can be a factor

Reactive sputtering



Reactive Sputtering

Target + Reactive gas = Film

1. Doping: $Ta + N_2 = TaN_x$

2. Compound formation: $Ta + O_2 = Ta_2O_5$

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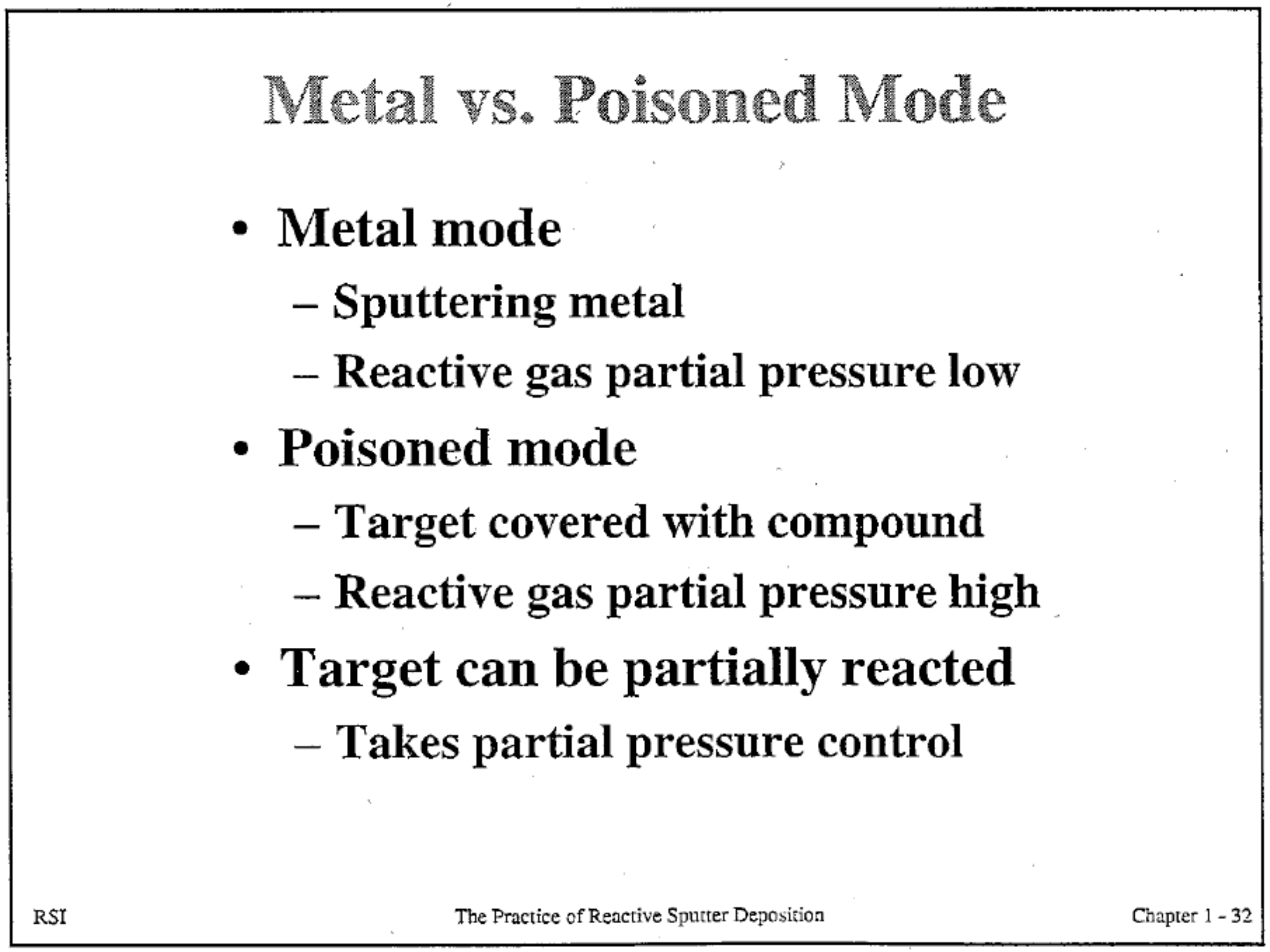
Reactive sputtering



Metal vs. Poisoned Mode

- Metal mode
  - Sputtering metal
  - Reactive gas partial pressure low
- Poisoned mode
  - Target covered with compound
  - Reactive gas partial pressure high
- Target can be partially reacted
  - Takes partial pressure control

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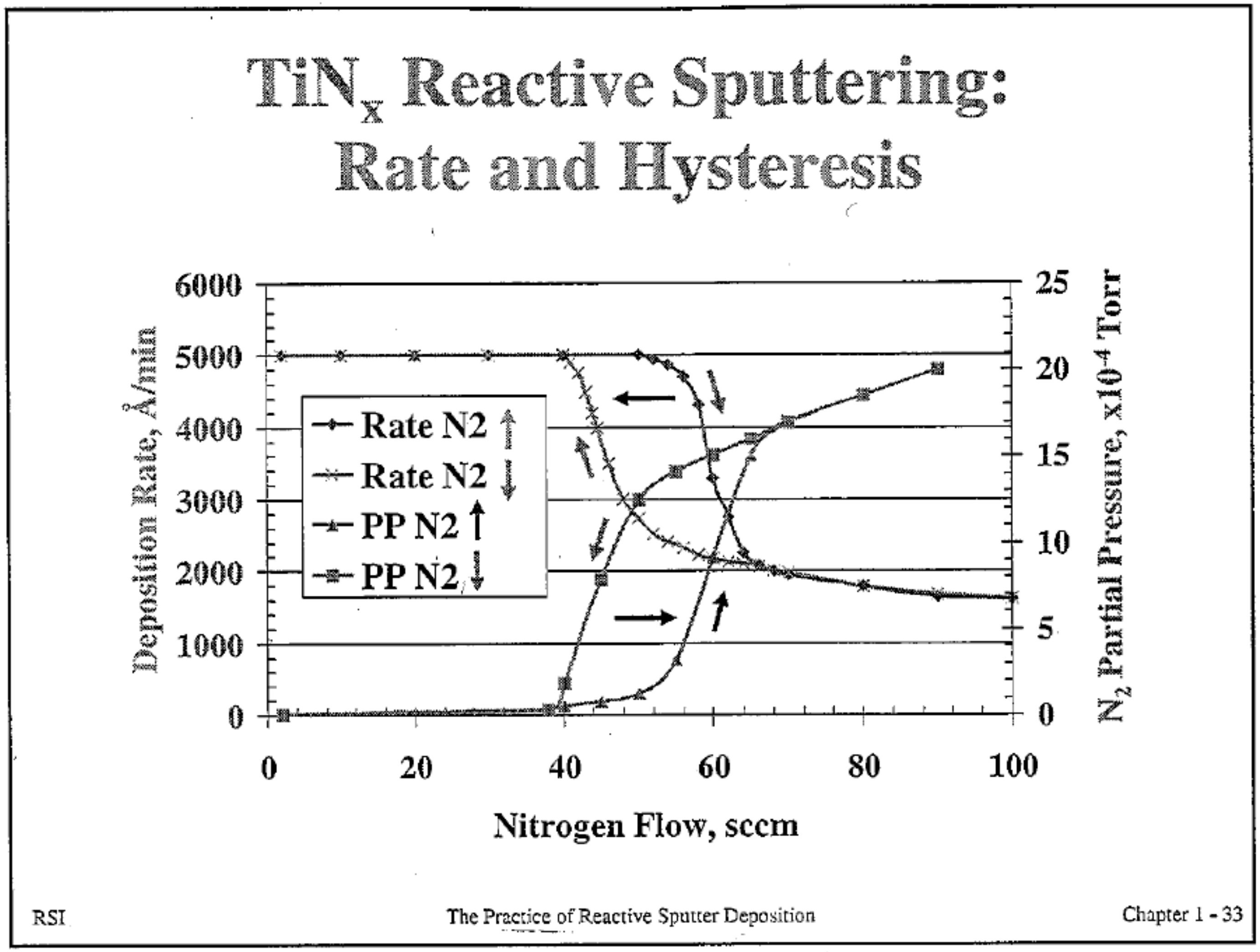
Reactive sputtering



TiN_x Reactive Sputtering: Rate and Hysteresis

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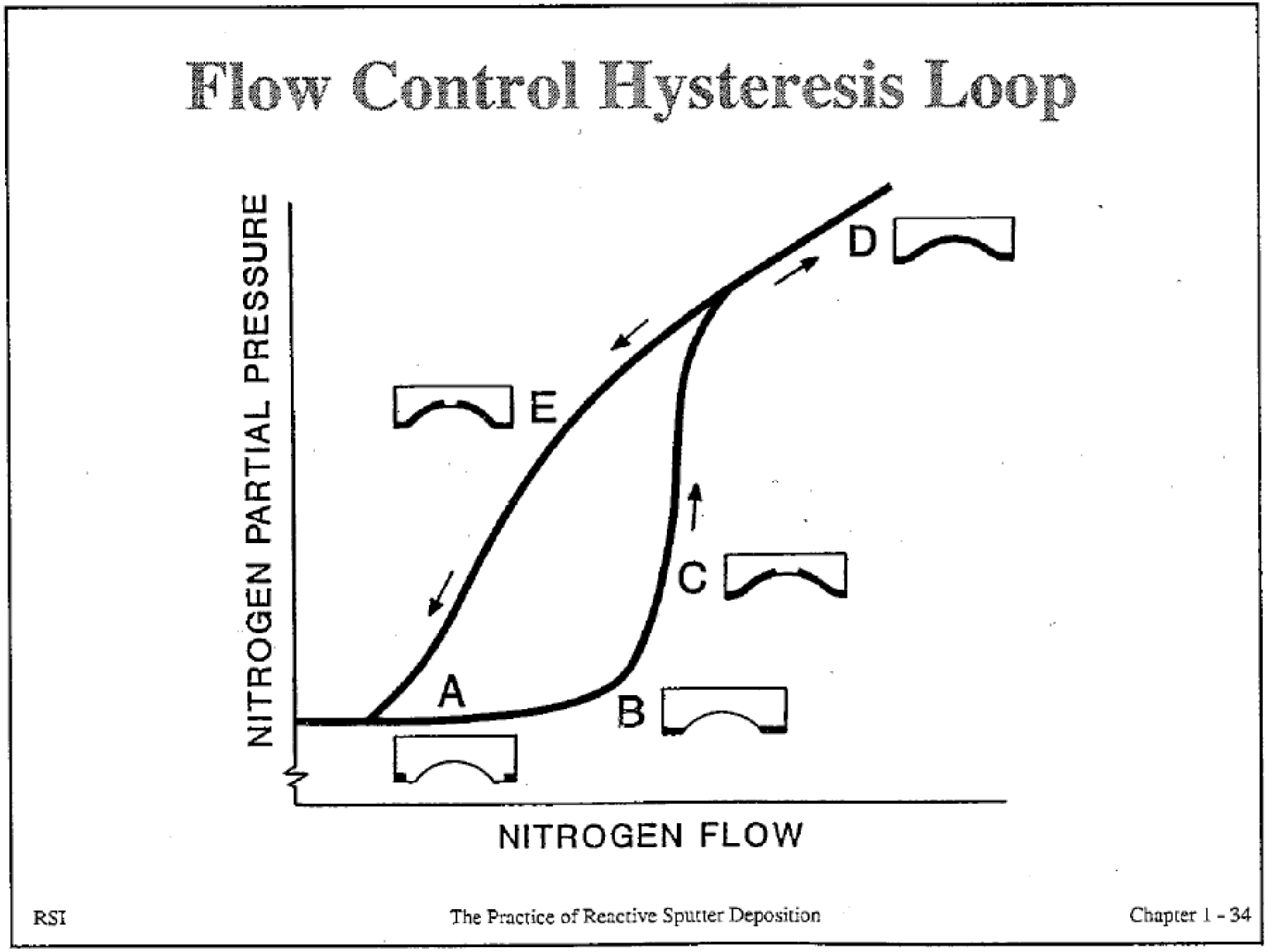
The Practice of Reactive Sputter Deposition

Chapter 1 - 33

Reactive sputtering



Flow Control Hysteresis Loop

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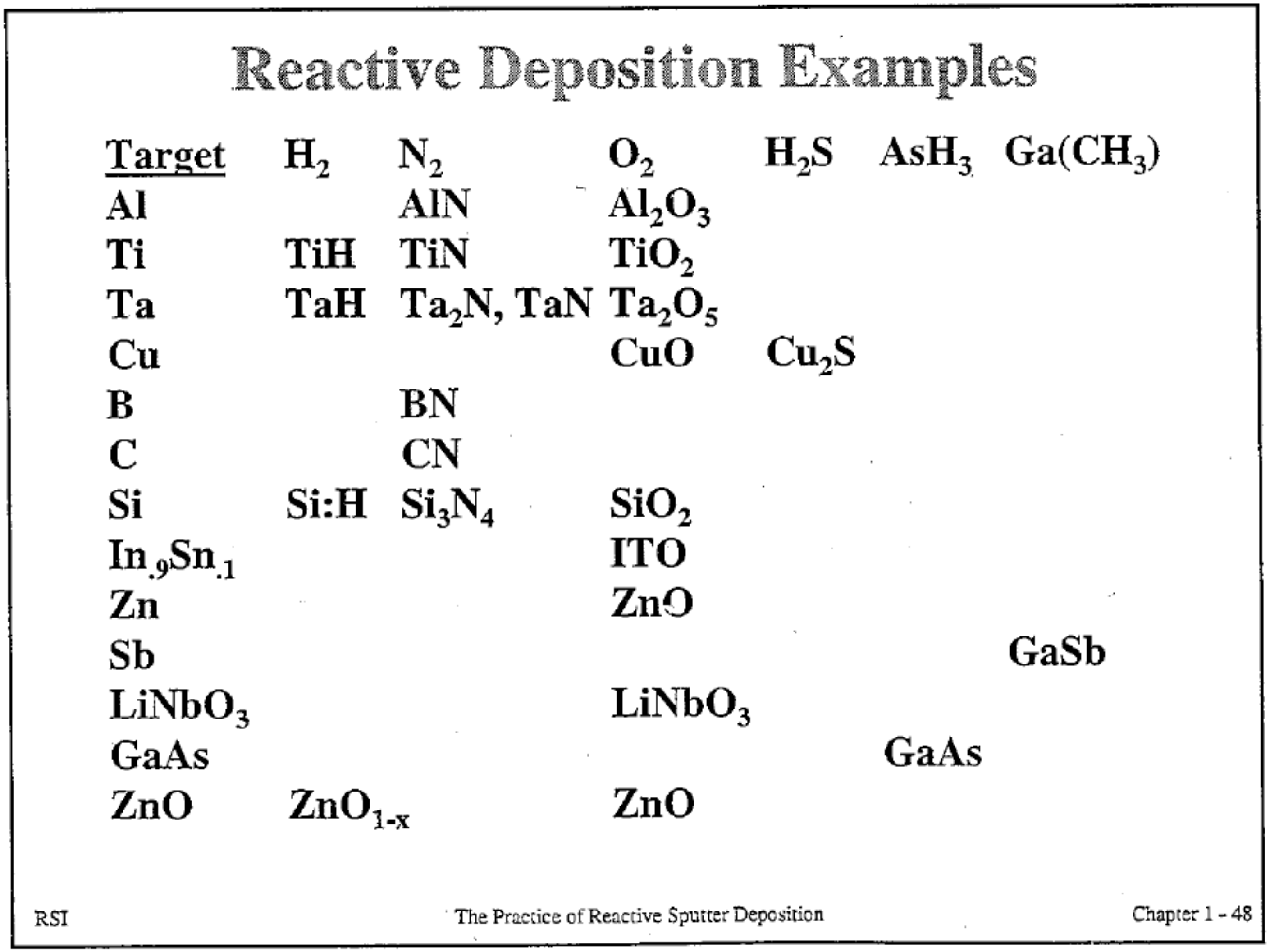
Reactive sputtering



Reactive Deposition Examples

Target	H_2	N_2	O_2	H_2S	AsH_3	Ga(CH_3)
Al		AlN	Al_2O_3			
Ti	TiH	TiN	TiO_2			
Ta	TaH	Ta_2N, TaN	Ta_2O_5			
Cu			CuO	Cu_2S		
B		BN				
C		CN				
Si	Si:H	Si_3N_4	SiO_2			
$In_{.9}Sn_{.1}$			ITO			
Zn			ZnO			
Sb						GaSb
$LiNbO_3$			$LiNbO_3$			
GaAs					GaAs	
ZnO	ZnO_{1-x}		ZnO			

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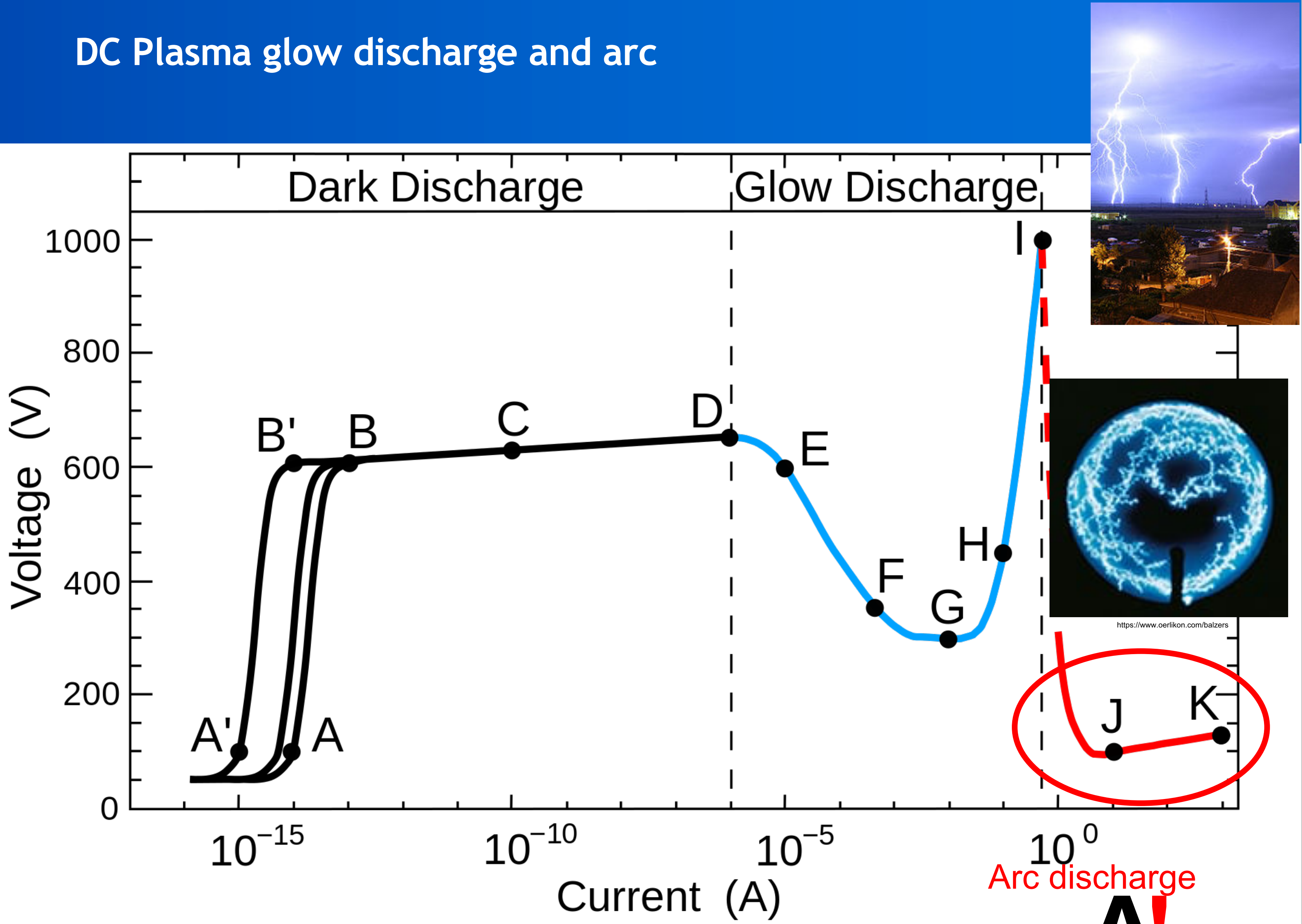
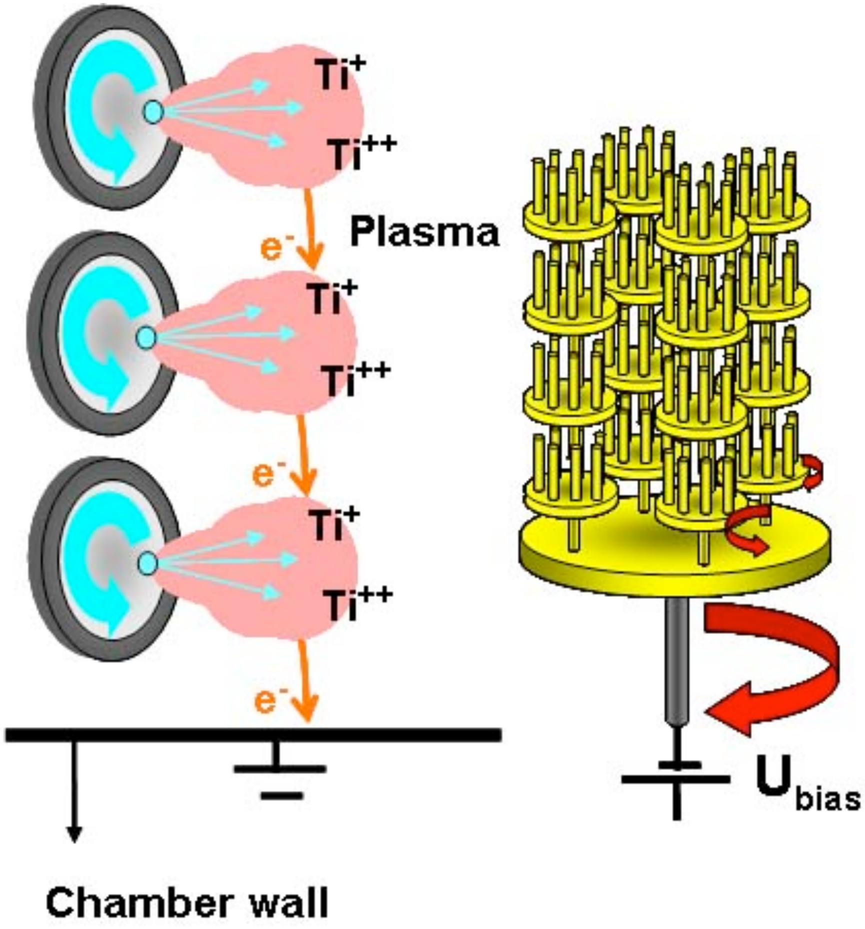
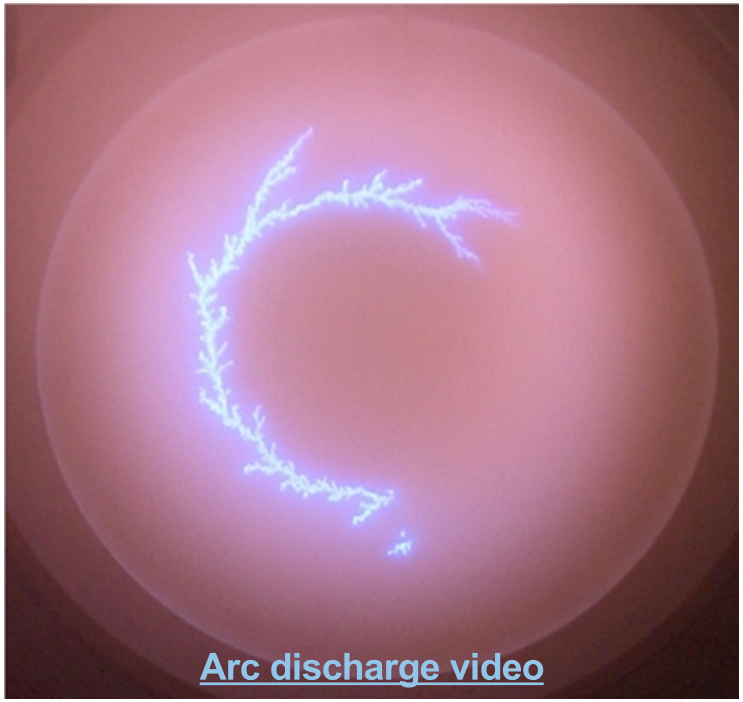
DC Plasma glow discharge and arc



https://www.oerlikon.com/balzers

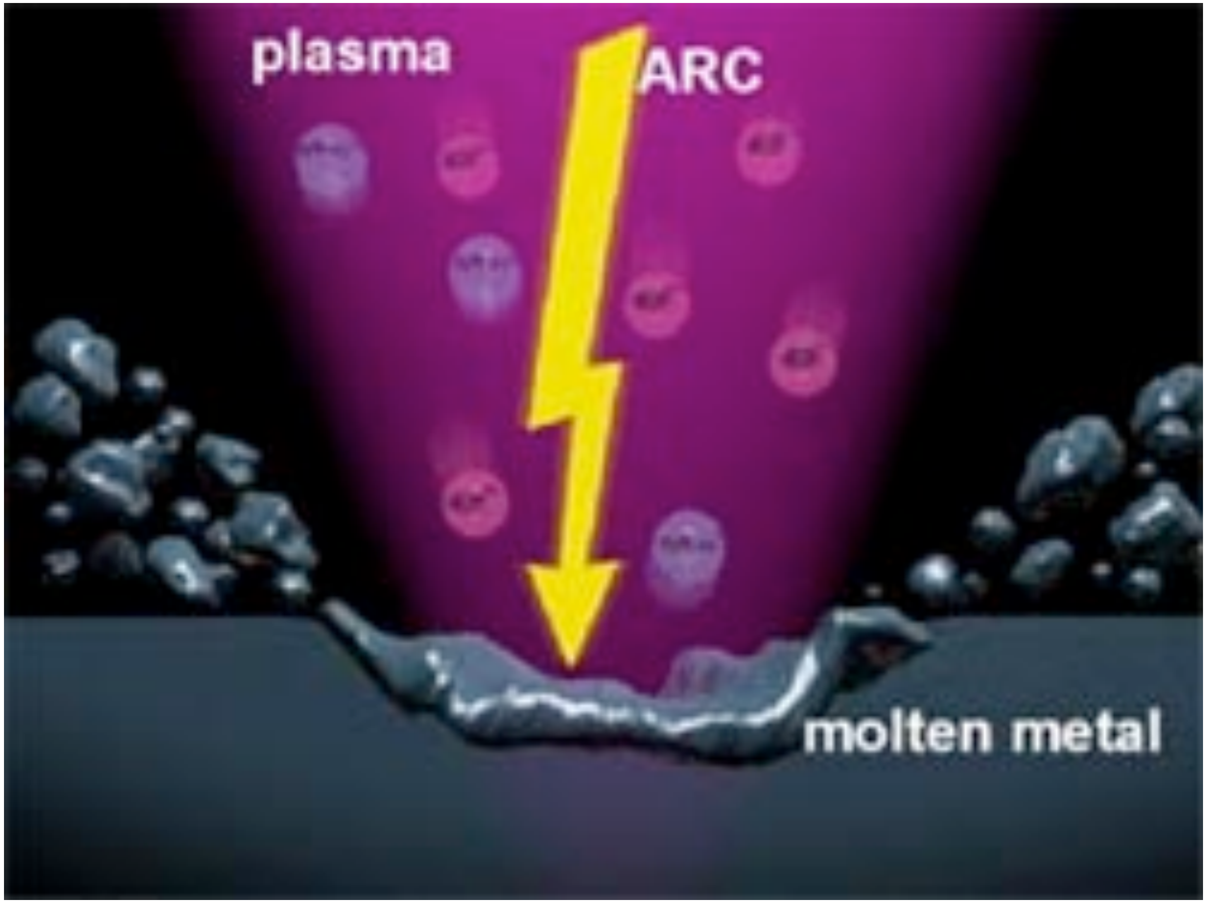
Arc discharge deposition





Arc discharge video

Arc disharge - cathode spot

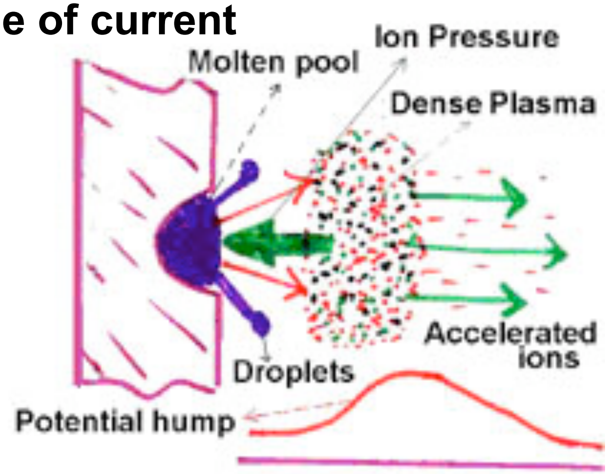


www.shm-cz.cz/files/schema01.jpg

Arc discharge process

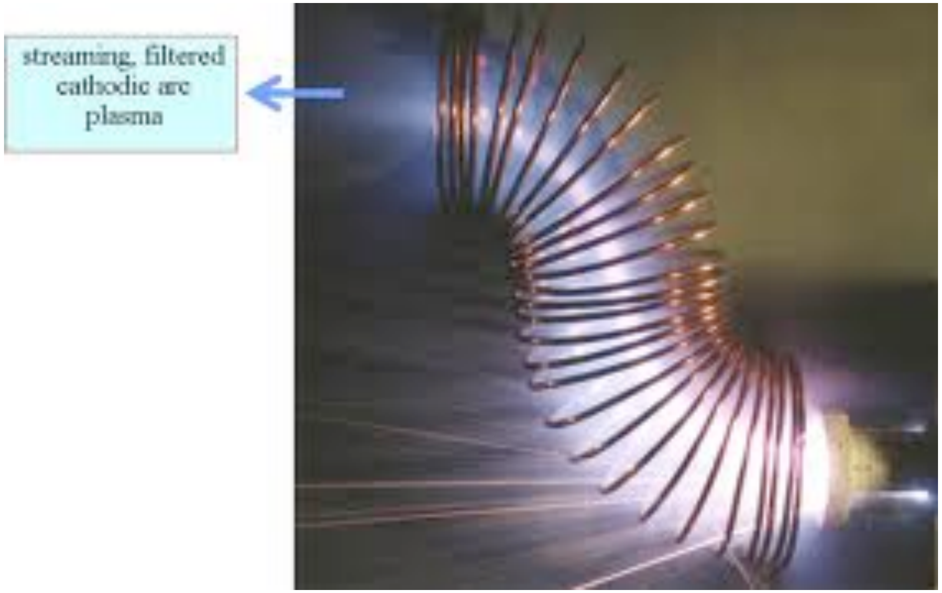
- arc current concentrated into filaments – arcs
- intense electron emission
- intense ion emission due to electron current (atoms/electrons – 1/100)
- ionization of atoms – formation of plasma
- flow of ions to cathode – intense sputtering of atoms
- 10^6 - 10^8 A/m^2
- overlapping thermal spikes
- materials is melted and sublimated in cathode spots
- cathode spots move randomly or could be steered by using magnets
- electons ionize vapor and create more electrons – increase of current
- ions accelerate
    - due to potential difference in plasma
    - due to multiple collisions with fast electrons
- macro particles (up to 10 µm diam.I are formed

Timko, Nordlund simulations
http://prb.aps.org/supplemental/PRB/v81/i18/e184109



Filtering of particles from vacuum arc plasma

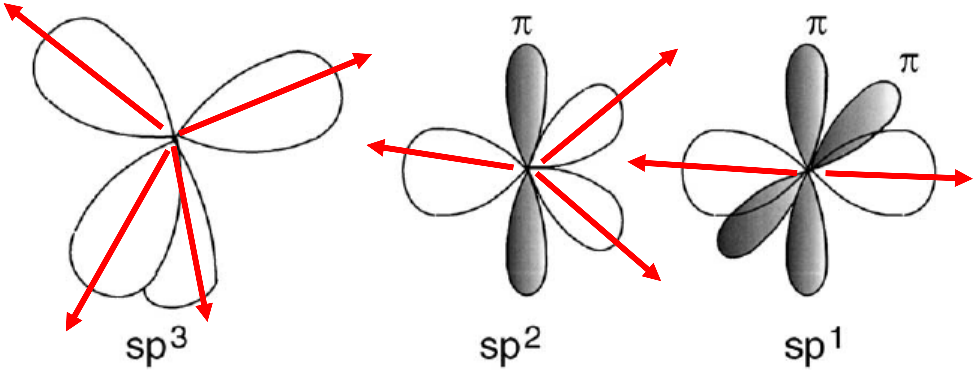
- plasma follows magnetic field lines
- plasma bent around corner
- particles go straight



streaming, filtered cathodic arc plasma

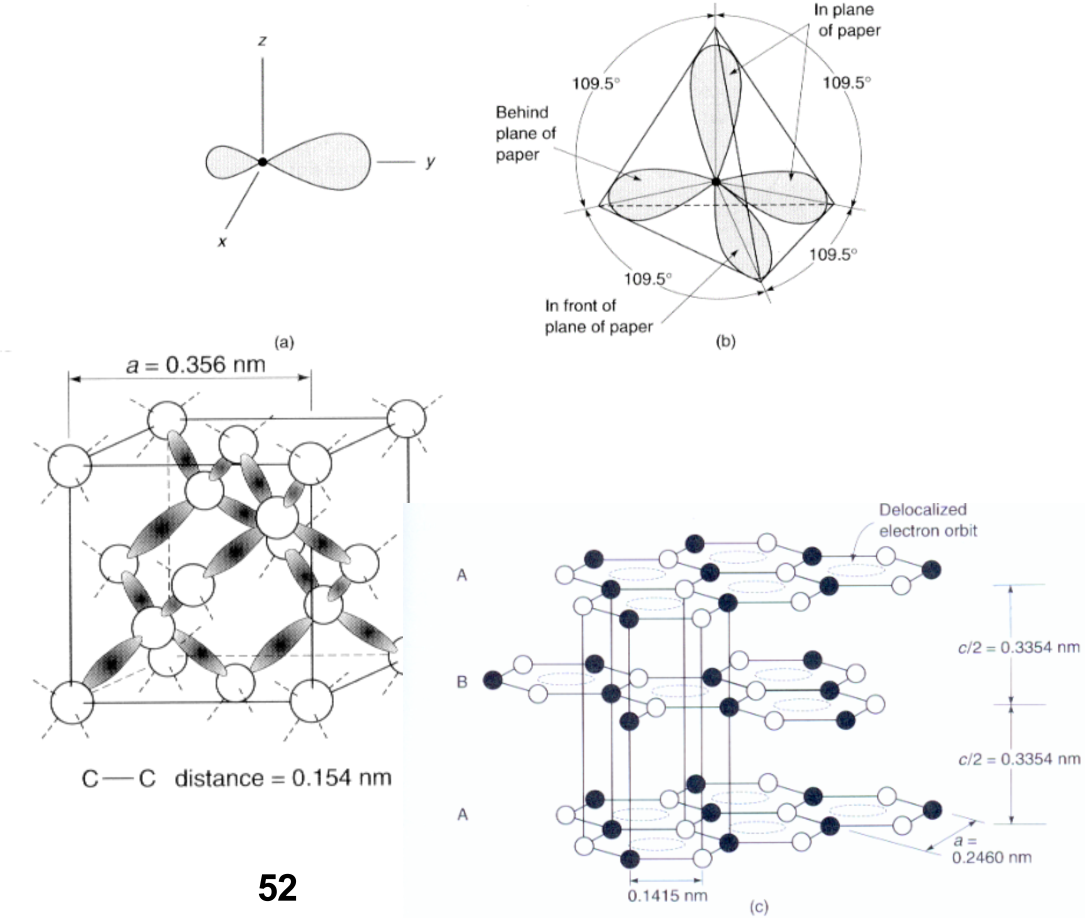
Andre Anders LBL

Three types of bonding of carbon atoms



- **sp^3**
  - Four string σ bonds in tetraedric directions
- **sp^2**
  - Two σ bonds in plane
  - One weekπ bond (non localised electron- conductivity)
- **sp^1**
  - Two σ linear bonds
  - Two week π bonds (non localised electrons- conductivity)

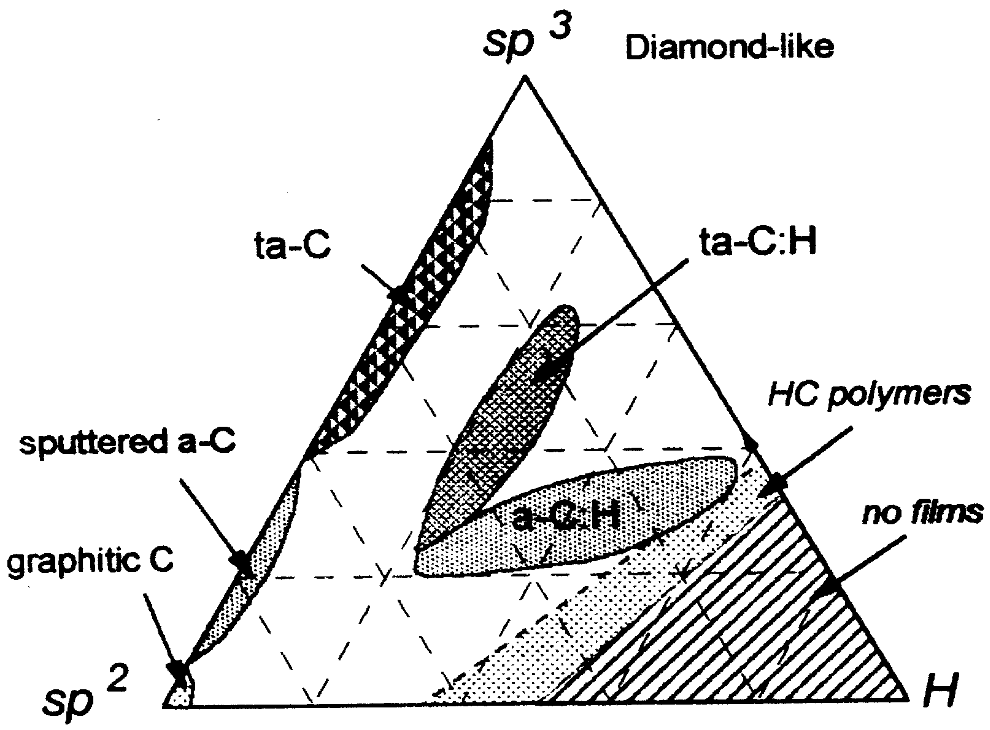
Carbon



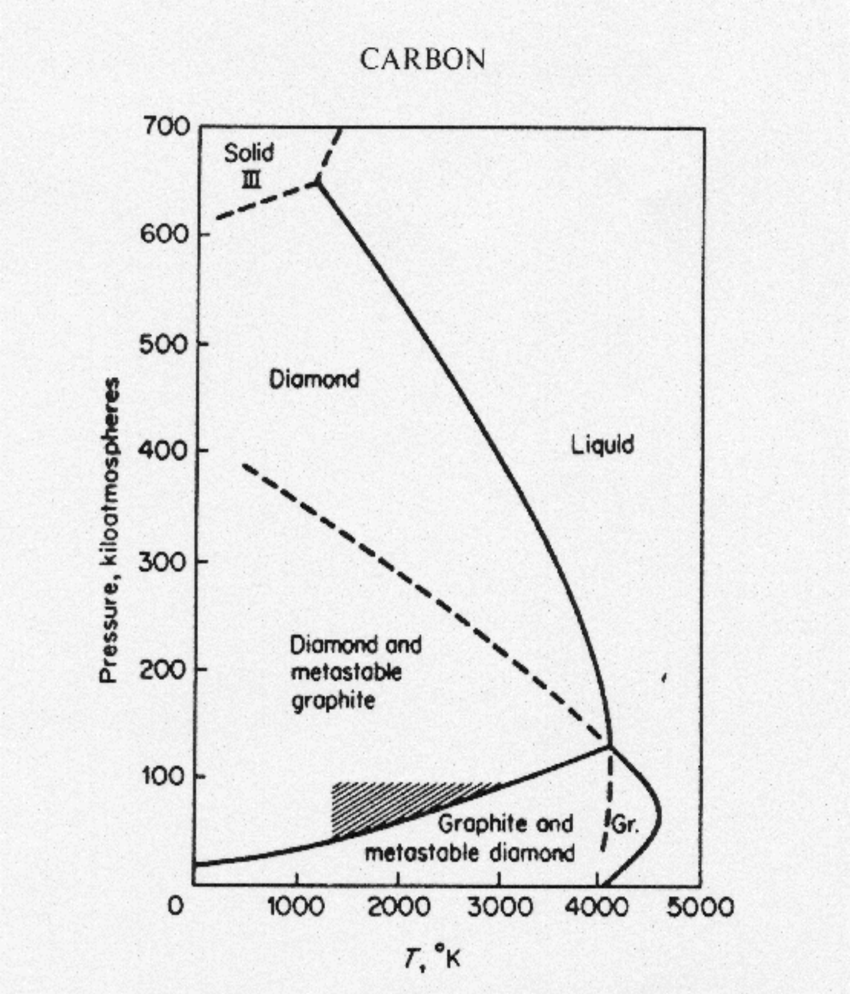
- **Carbon has 3 hybridised bondings sp^3, sp^2, sp^1**
- **sp^3 bondings form four equal carbon-carbon bonds producing tetrahedral structure of diamond**

Graphite has three sp^2 hybrid orbitals in plane

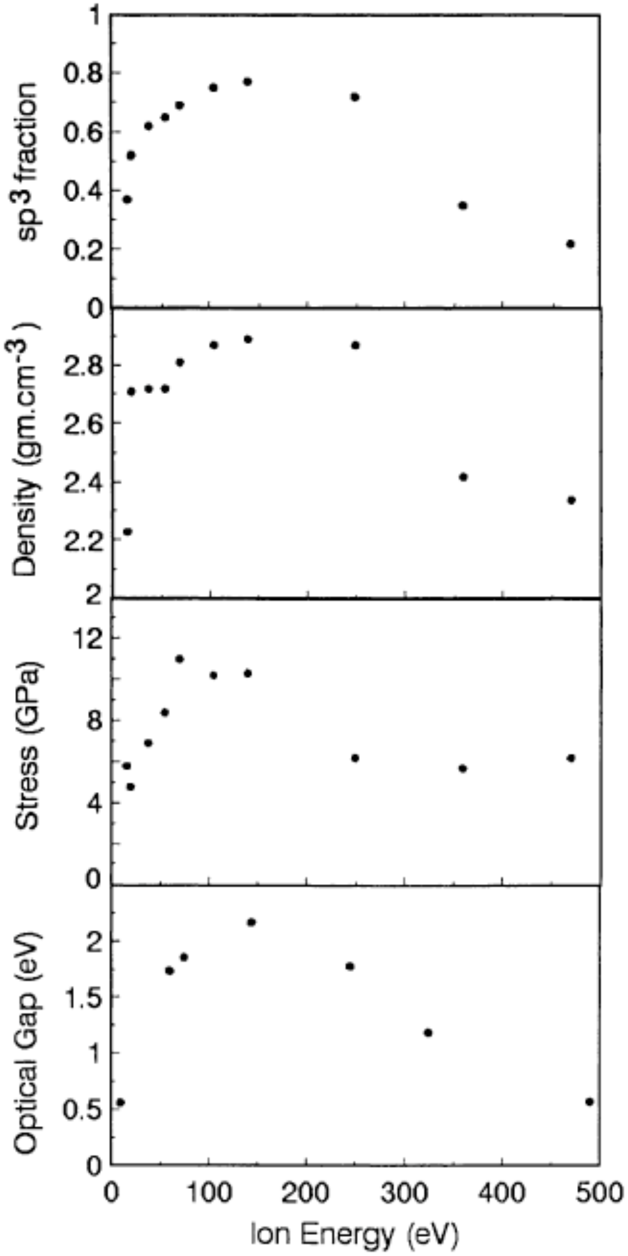
Diamond-like carbon (DLC)



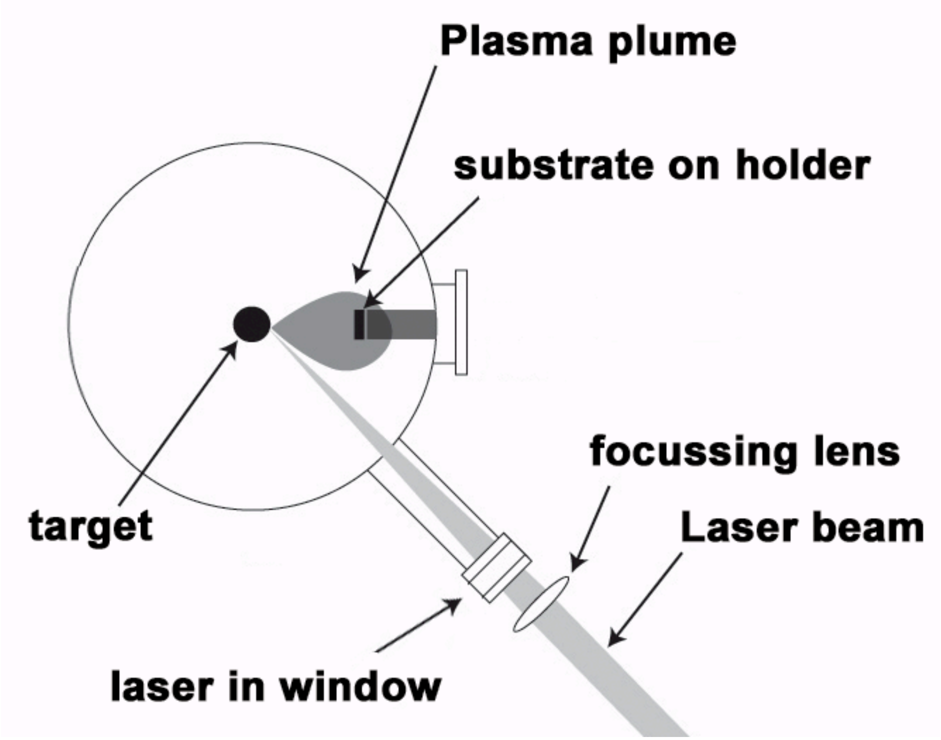
- Various forms of C-H alloys presented in a ternary phase diagram
- DLC is a metastable form of amorphous carbon
- DLC films have a mixed sp^3/ sp^2 structure with different sp^3 and sp^2 proportions depending on deposition technique and parameters


CARBON
700
600
500
400
300
200
100
0
1000
2000
3000
4000
5000
Pressure, kiloatmospheres
T, °K
Solid III
Diamond
Liquid
Diamond and metastable graphite
Graphite and metastable diamond
Gr.

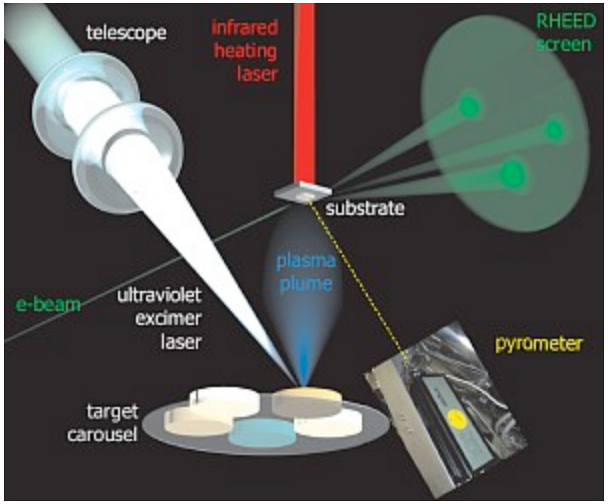
Properties of ta-C as function of E_i



Pulsed laser deposition PLD

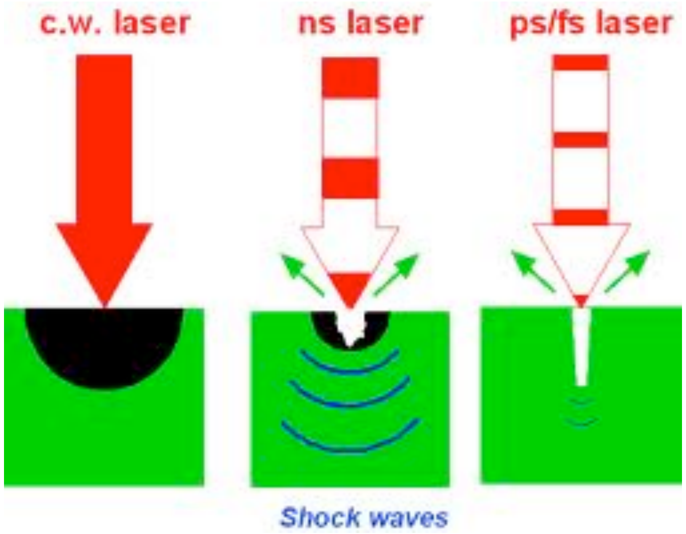


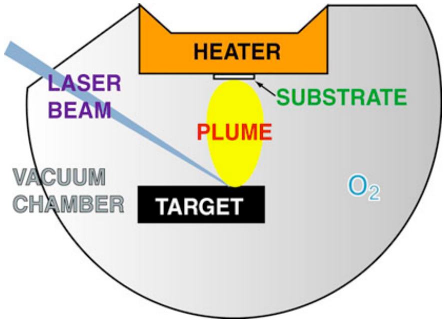
- high ionization
- evaporation of any material also in reactive gas
- stoichimetry of target to the surbstrate
- good control of depostion rate
- expensive lasers
- slow depostion rate
- not yet in industrial level



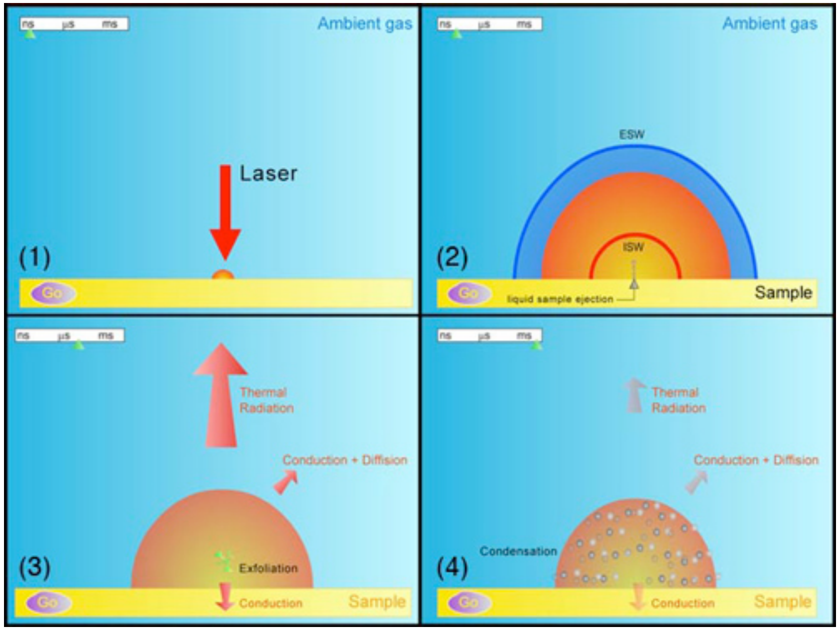
http://www.youtube.com/watch_popup?v=g9RM4QhBnL0&vq=medium#t=19

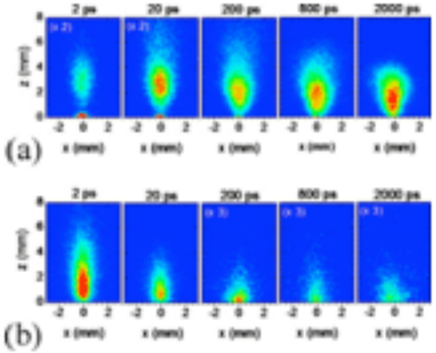
Laser ablation





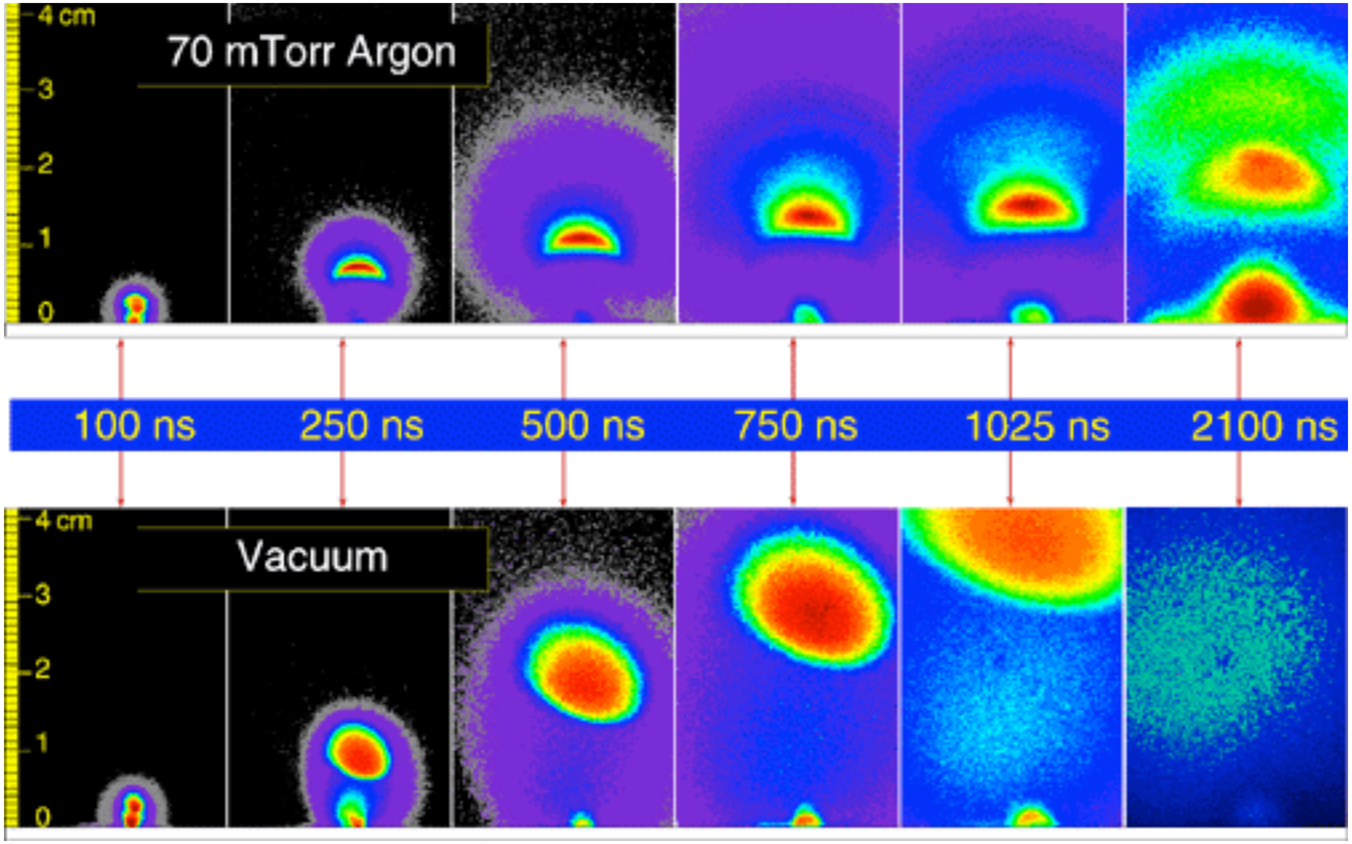
Plasma plume





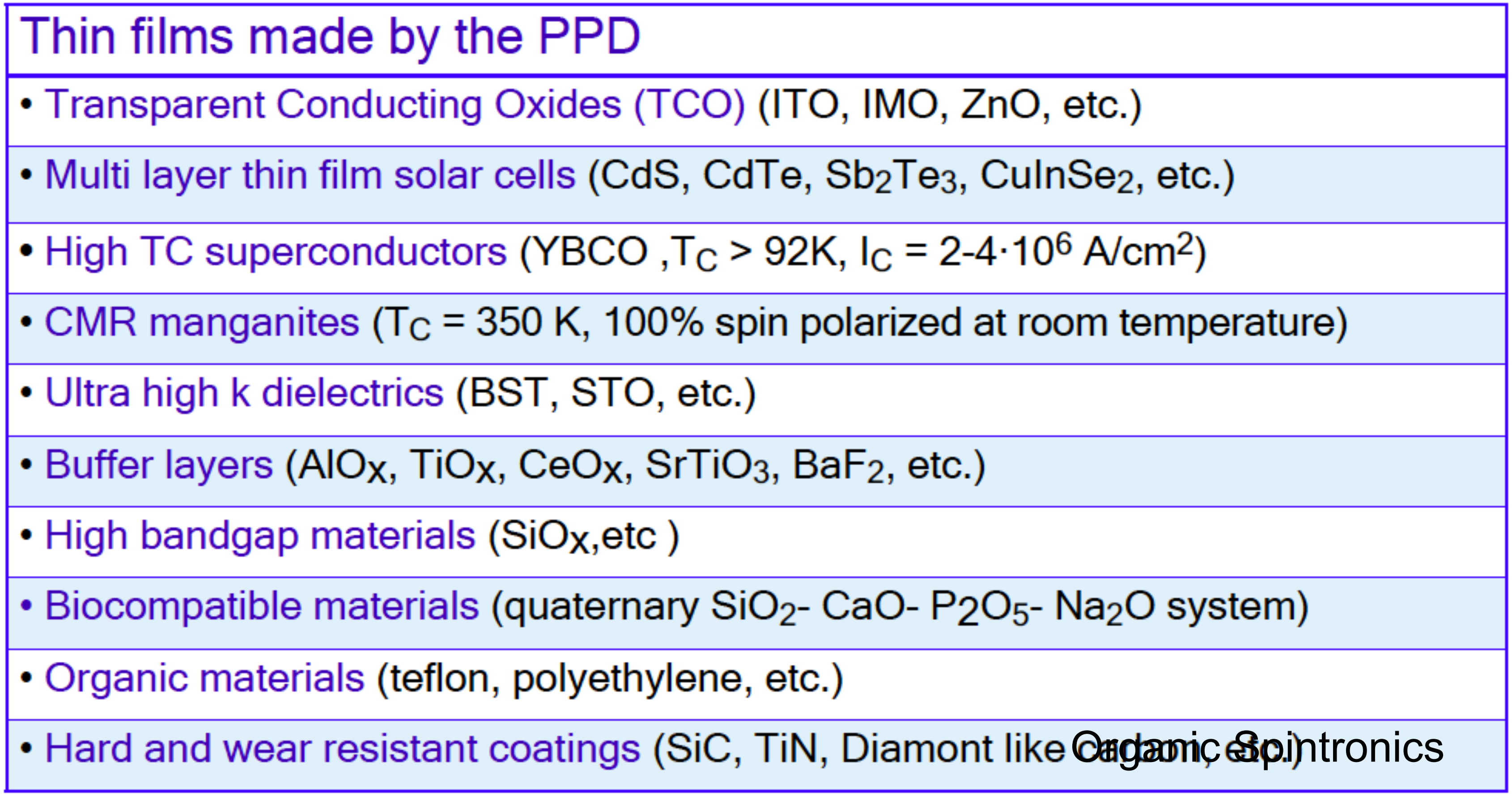
- Copper target

Laser plasma plume



- **Carbon plasma from graphite target**

Particularly suitable for alloyed materials



Thin films made by the PPD
• Transparent Conducting Oxides (TCO) (ITO, IMO, ZnO, etc.)
• Multi layer thin film solar cells (CdS, CdTe, Sb_2Te_3, $CuInSe_2$, etc.)
• High TC superconductors (YBCO ,T_C > 92K, $I_C = 2\text{-}4 \cdot 10^6$ A/cm^2)
• CMR manganites (T_C = 350 K, 100% spin polarized at room temperature)
• Ultra high k dielectrics (BST, STO, etc.)
• Buffer layers (AlO_x, TiO_x, CeO_x, $SrTiO_3$, BaF_2, etc.)
• High bandgap materials (SiO_x,etc)
• Biocompatible materials (quaternary SiO_2- CaO- P_2O_5- Na_2O system)
• Organic materials (teflon, polyethylene, etc.)
• Hard and wear resistant coatings (SiC, TiN, Diamont like Carbon, etc.)

Organic Spintronics

E_i as a function of laser pulse energy

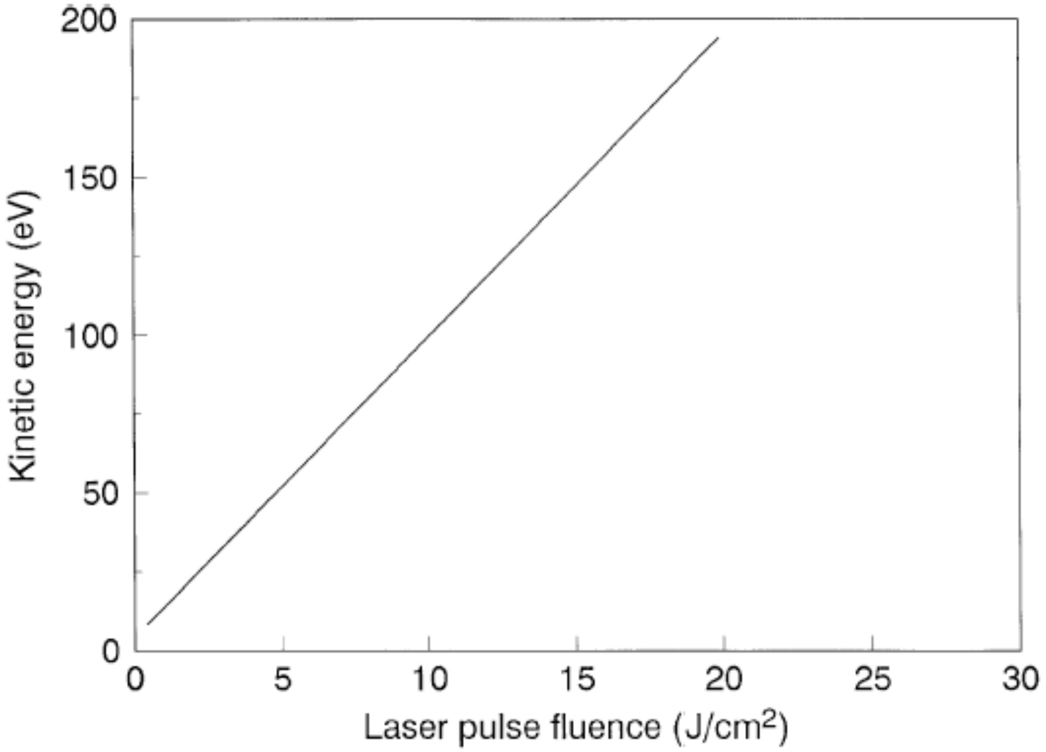
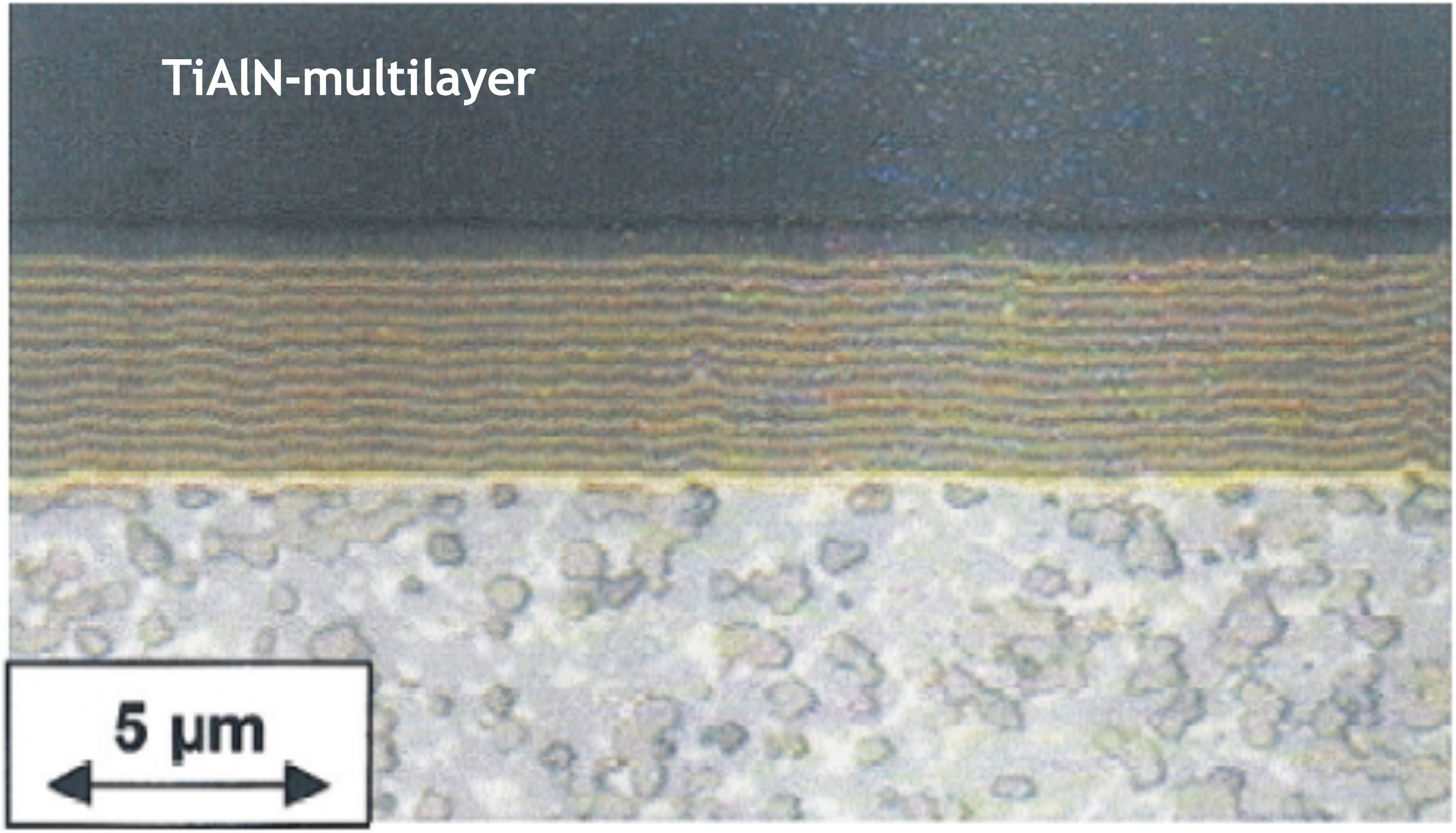


Fig. 6. Average ion energy vs. laser pulse fluence [9].

J. Robertson / Materials Science and Engineering R 37 (2002) 129–281

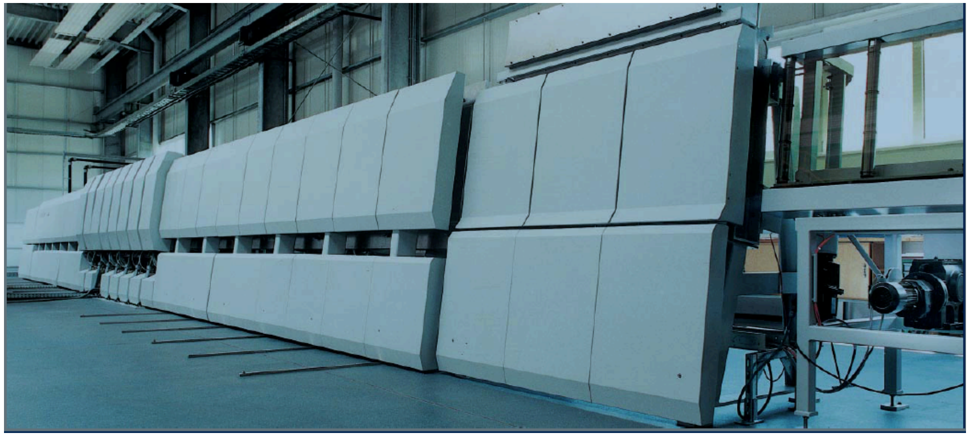
Multilayer coatings



Contents

- Plasma
- Ion surface interactions
- Film growth mechanisms
- Different PVD methods
- Commercial PVD coatings
- **Scale up**

Large volumes, up scaling
Heat reflecting, self cleaning, photo voltaic



/www. www.vonardenne.biz/

New emerging PVD methods

- vacuum polymer deposition (VPD)
- high-power pulsed magnetron sputtering (HPPMS or HIPIMS)
- filtered cathodic arc deposition
- glancing angle deposition (GLAD).