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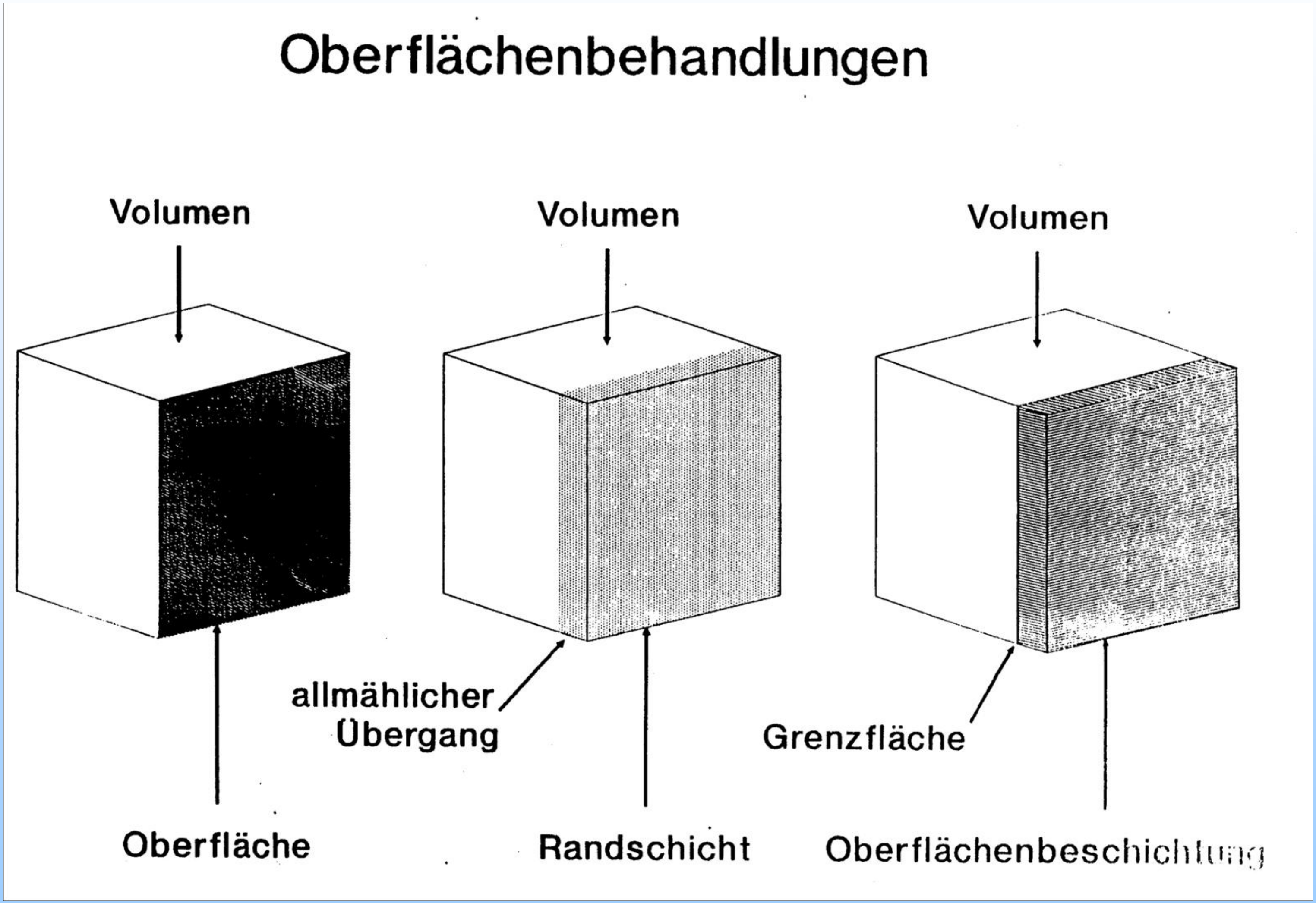
Oberflächenbehandlungen
Volumen
Volumen
Volumen
allmählicher Übergang
Grenzfläche
Oberfläche
Randschicht
Oberflächenbeschichtung

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Prinzipielle Möglichkeiten der Oberflächenbehandlung

- **Abtragen**
  - Mechanische Abtragen
  - Physikalische Abtragen:
    - Verdampfen
    - Zerstäuben
  - Reaktive (chemisch/elektrochemisch) Abtragen
- **Auftragen**
  - Großvolumige Teile
  - Schmelze/ Suspension/ Lösung
  - Tröpfchen
  - Atome/ Ionen
- **Modifizieren**
  - Verformen
  - Aufschmelzen
  - Umwandeln
  - Einbringen von Atomen

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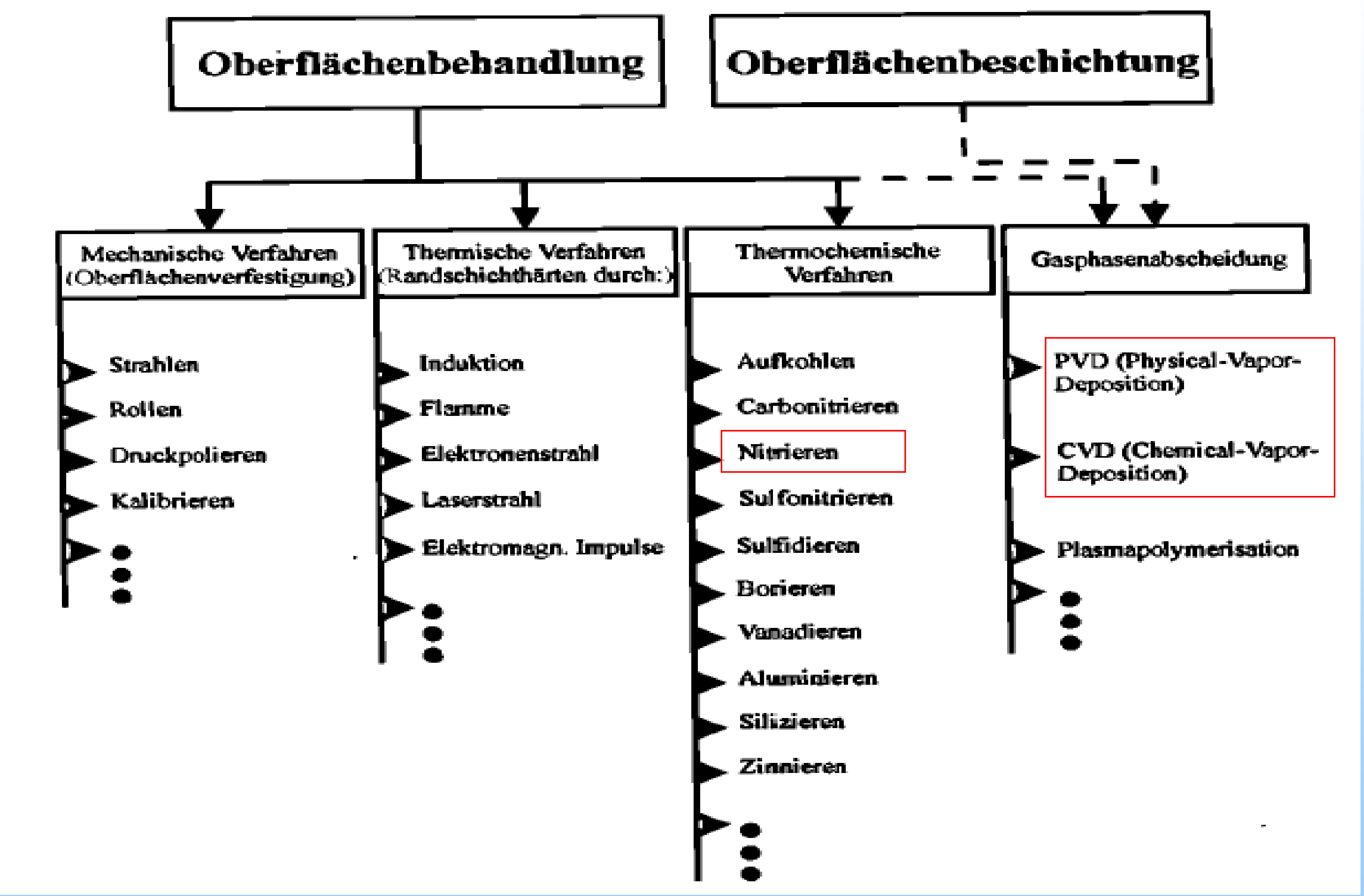
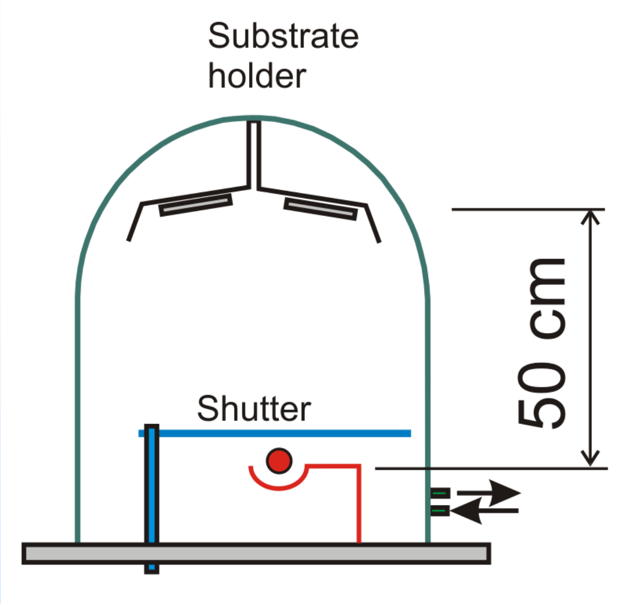
Oberflächenbehandlungsverfahren



Thermal Evaporation

- Deposition - a mix of applied science and art with physics.
- Deposition in vacuum environment.



Vacuum Environment

- Vacuum is complex - not inert.
- Deposition with awareness of the effect of vacuum upon the vapor flux and growing film.

The three most important parameters relevant to vacuum

- Pressure - the mean free path (MFP).
- Partial pressure of reactive gases in inert working gases.
- Film vapor arrival to reactive gas impingement rate ratio.

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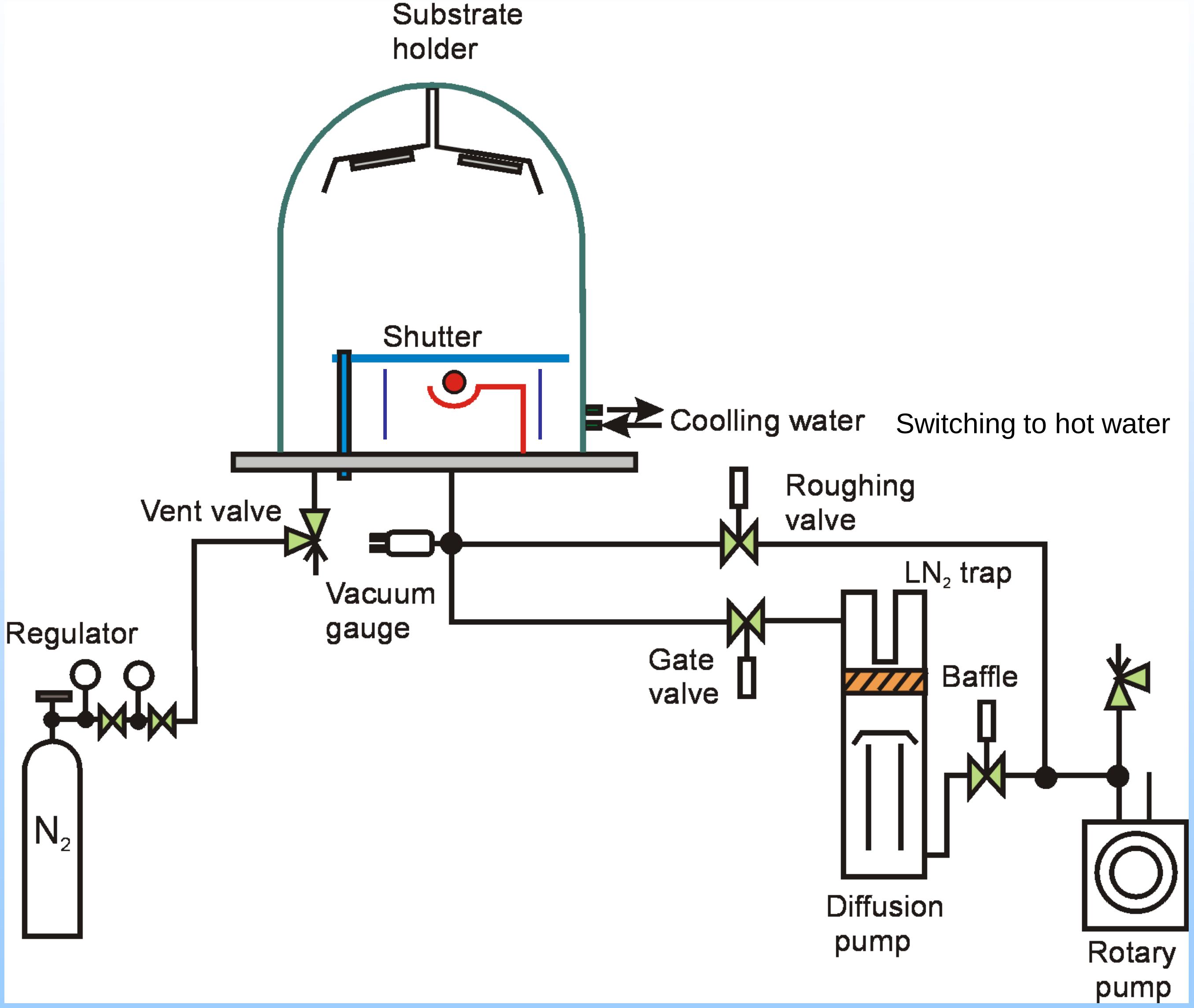
Evaporation System



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Notwendigkeit des Vakuums zur Verdampfung

Vermeidung von Reaktionen zwischen der Luft und den zu verdampfenden Materialien (Hochtemperatur), wodurch die Quellematerial verunreinigt wird

- Vermeidung von Zusammenstößen zwischen Molekülen verdampfter Substanzen und Molekülen der Luft im Dampfraum, wodurch die verdampften Moleküle das Substrat nicht erreichen können
- Vermeidung von Schichtverunreinigungen

Flächendichte der Oberflächenatomen $10^{14}/cm^2$. Bedeckung der Oberfläche dauert ca. 1 Sekunde bei 10^{-4} bis 10^{-5} mbar und bei 25 °C Hertz-Knudsen-Gleichung

$$J = \frac{dn}{dt} = n\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = \frac{1}{4} n\bar{v}$$

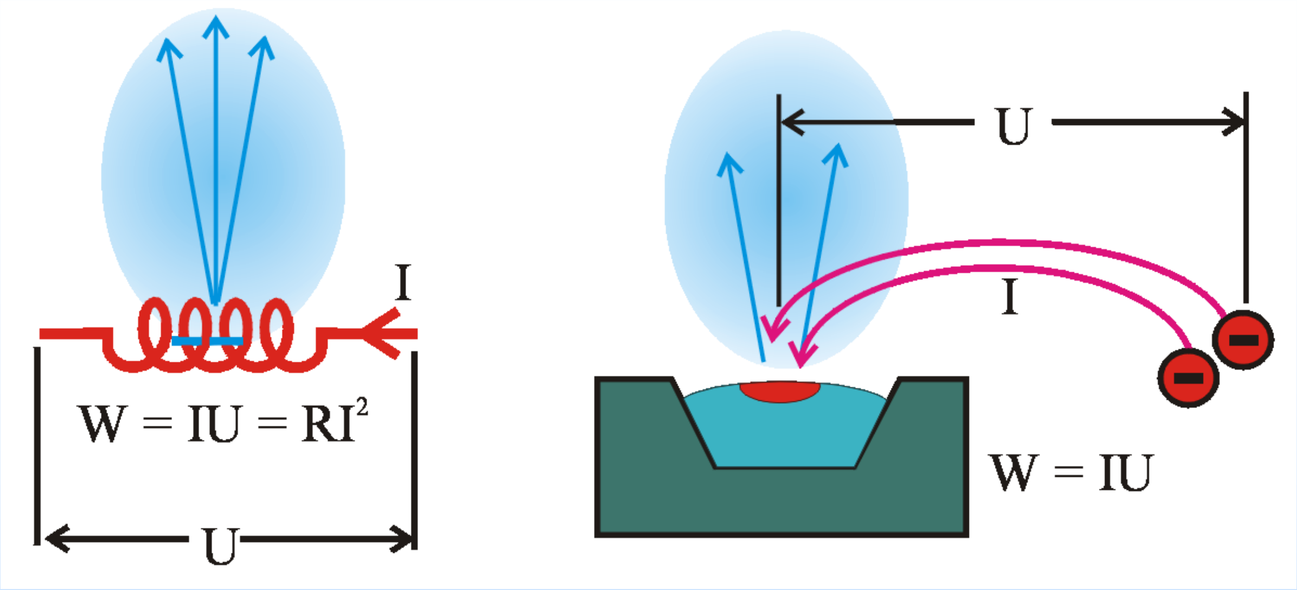
n - Konzentration

m - Masse

k - Boltzmann-Konst.

v - durchschnittliche Geschwindigkeit

Properties



- E-beam evaporation source - thermal evaporator
- It differs from resistance source
- Energy is supplied to the top of the evaporant - e-beam
- Evaporant is in a water cooled hearth
- Very local heat dissipates by radiation and conduction
- Reaction with hearth is mostly prevented
- EBE is universal source
- Allows deposition of materials with high melting points

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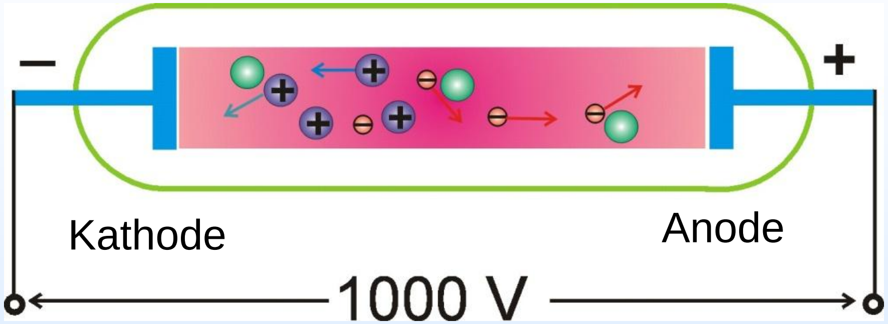
Erzeugung von Plasmen

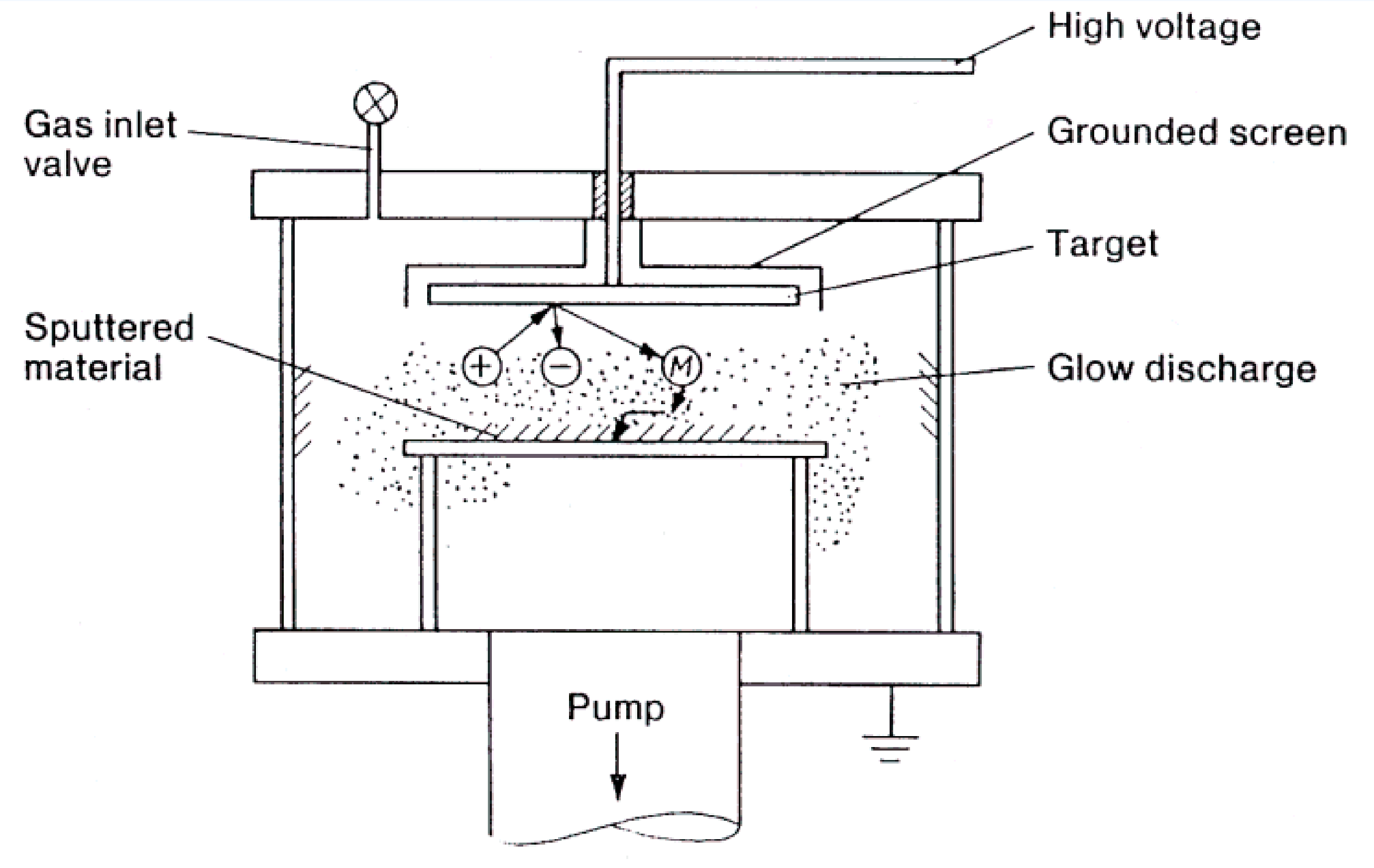


Entladungsrohr
niedriger Druck ≈ 1-5mbar (hPa)

Energiezufuhr
Resistiv (Gleichstrom, KHz, MHz)
Kapazitiv (KHz und MHz)
induktiv (Radiofrequenzen)
Wellenleiter (GHz, Mikrowellen)
Strahlungsquellen (Photonen, Laser UV)

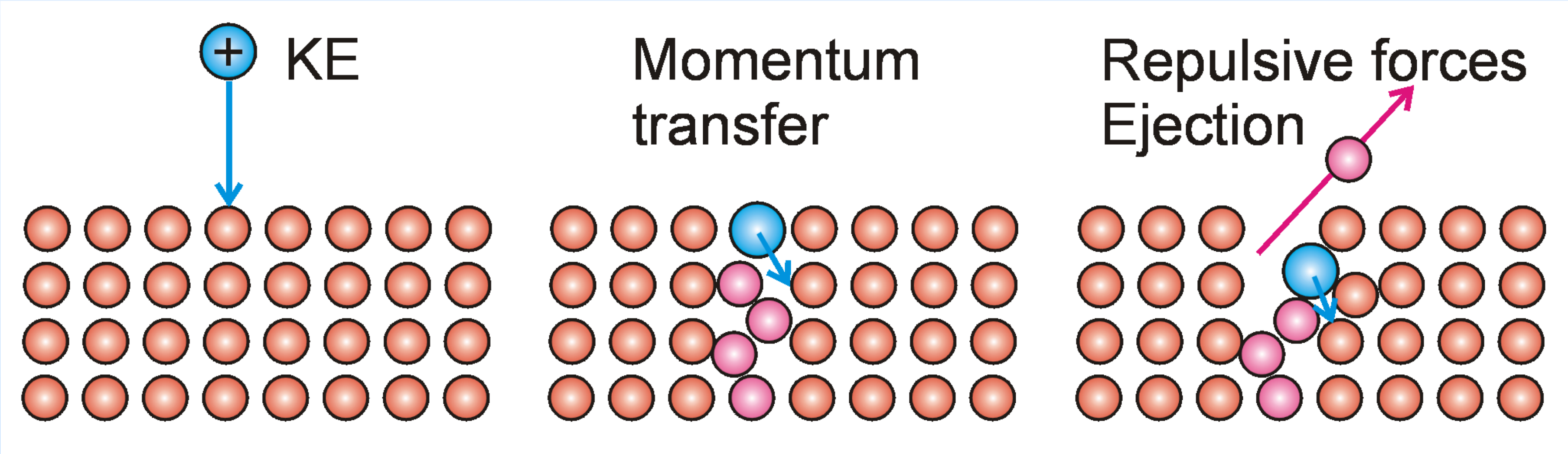
Plasma: Gemisch aus freien Elektronen, positiven Ionen und Neutralteilchen. Es ist quasineutral.
nt-Plasmen sind kalt. Neutralteilchen: RT
geladene Teilchen: E_{Kin}
Ladungsträger:
-aus der Kathode
-durch Stoßionisation im Gasraum

Simple diode type sputtering system

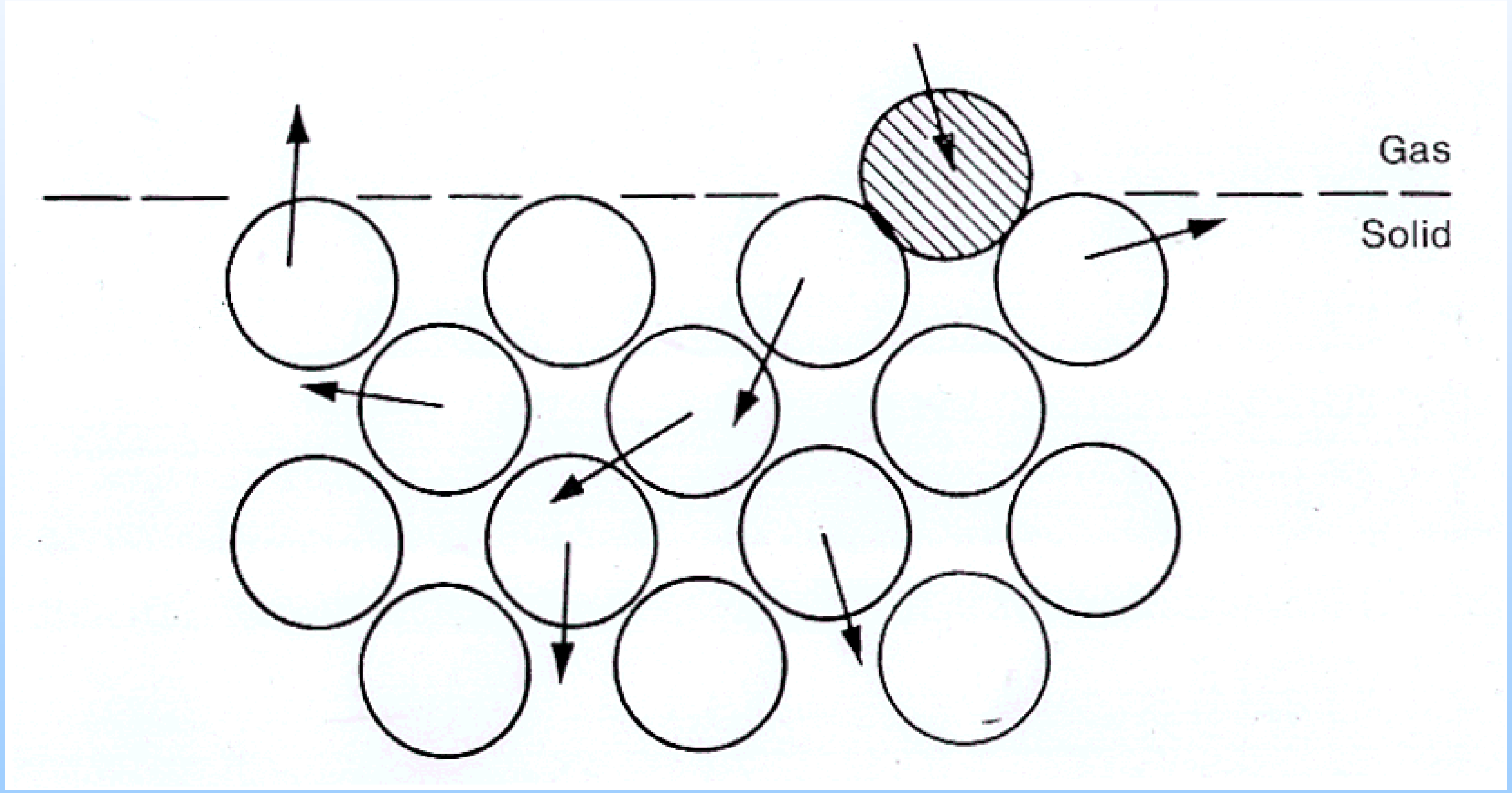


Sputtering

Ion bombardment - momentum transfer



Collision cascade in a condensed material during the ion bombardment with knocking out of two atoms



States of sputtered atoms and molecules

In general, the state of sputtered particles depends on the acceleration voltage (kinetic energy of incident ions) – the higher the KE is, the more the clusters

For example, Cu target sputtered with Ar ions
E_{Ar} = 100 eV, 5% Cu + Cu_2
E_{Ar} = 12 keV, Cu + Cu_2 + Cu^+_n (n = 1-11)
For Al target sputtered with Ar and Xe ions, Al_n (n = 1-7 and 1-18, respectively) will be sputtered.

Compounds:
GaAs sputtered with Ar ions, 99% are the Ga and As neutral atoms and 1% GaAs molecules.

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Definition of Sputtering Yield

- Number of atoms per incident ion
- **Sputtering Yield** is affected
  - Surface structure
  - Ion mass
  - Incident energy
  - Rather insensitive to temperature (in certain cases, decreasing sputtering yield with increasing target temperature

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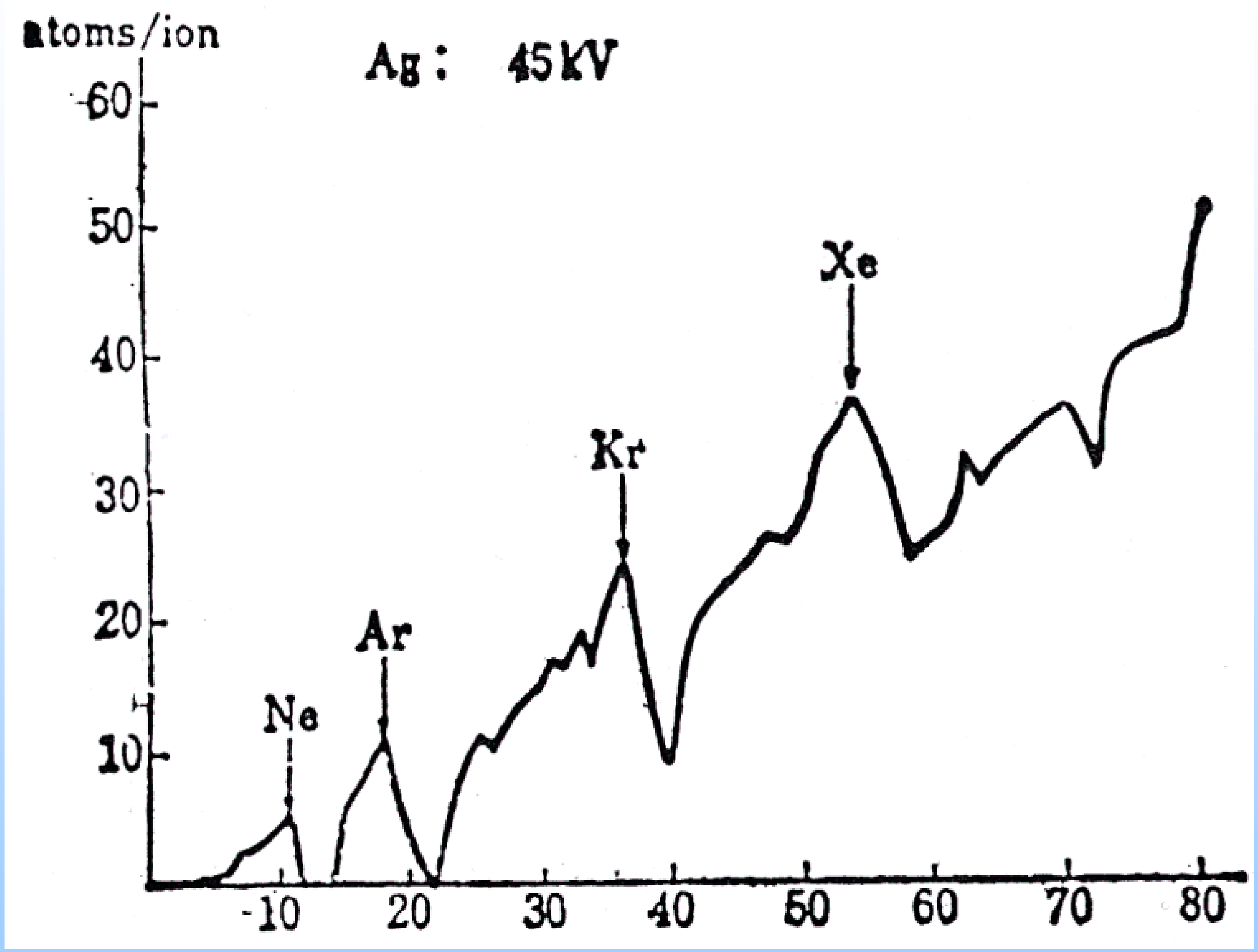

Atomic number

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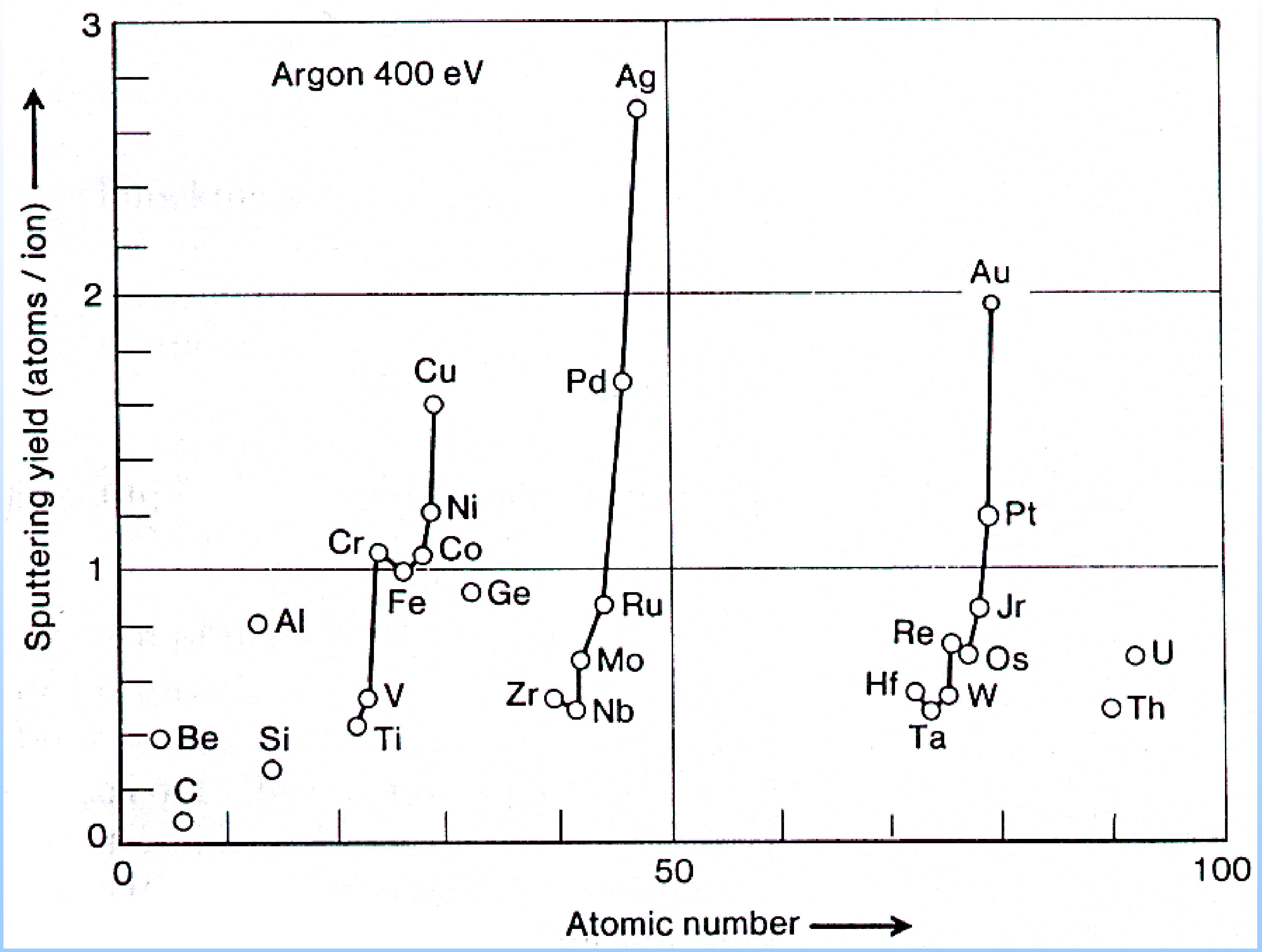

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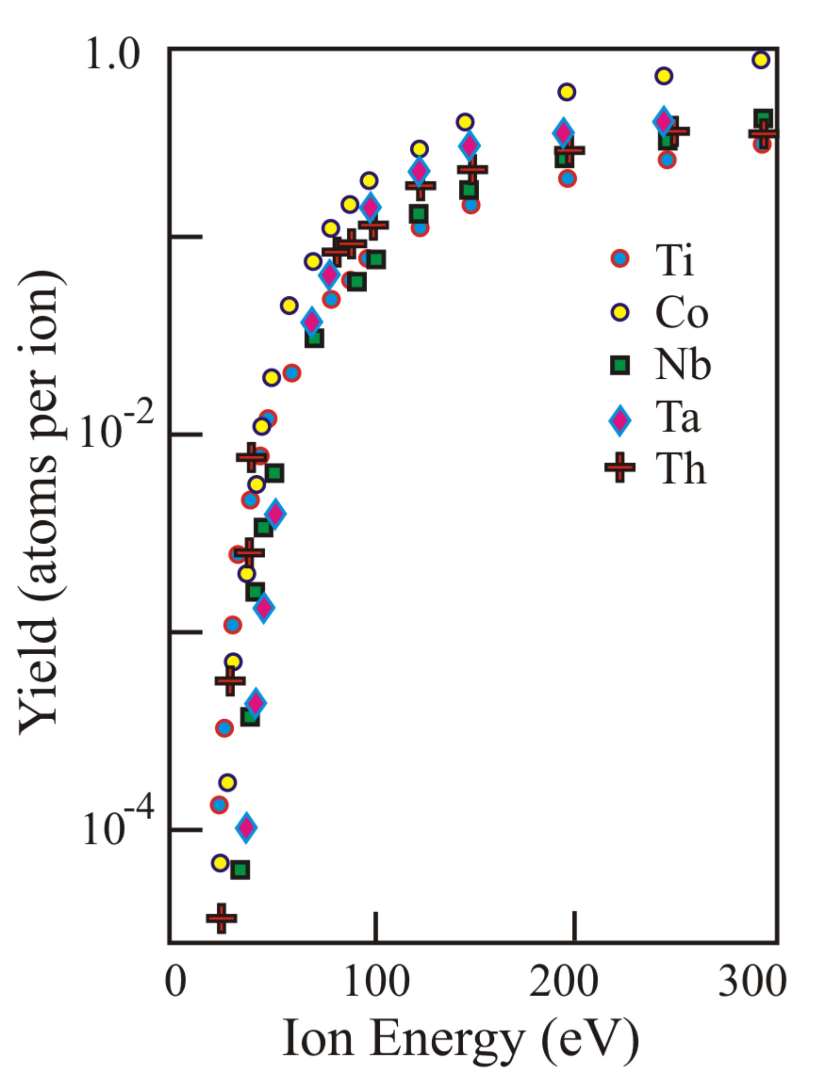
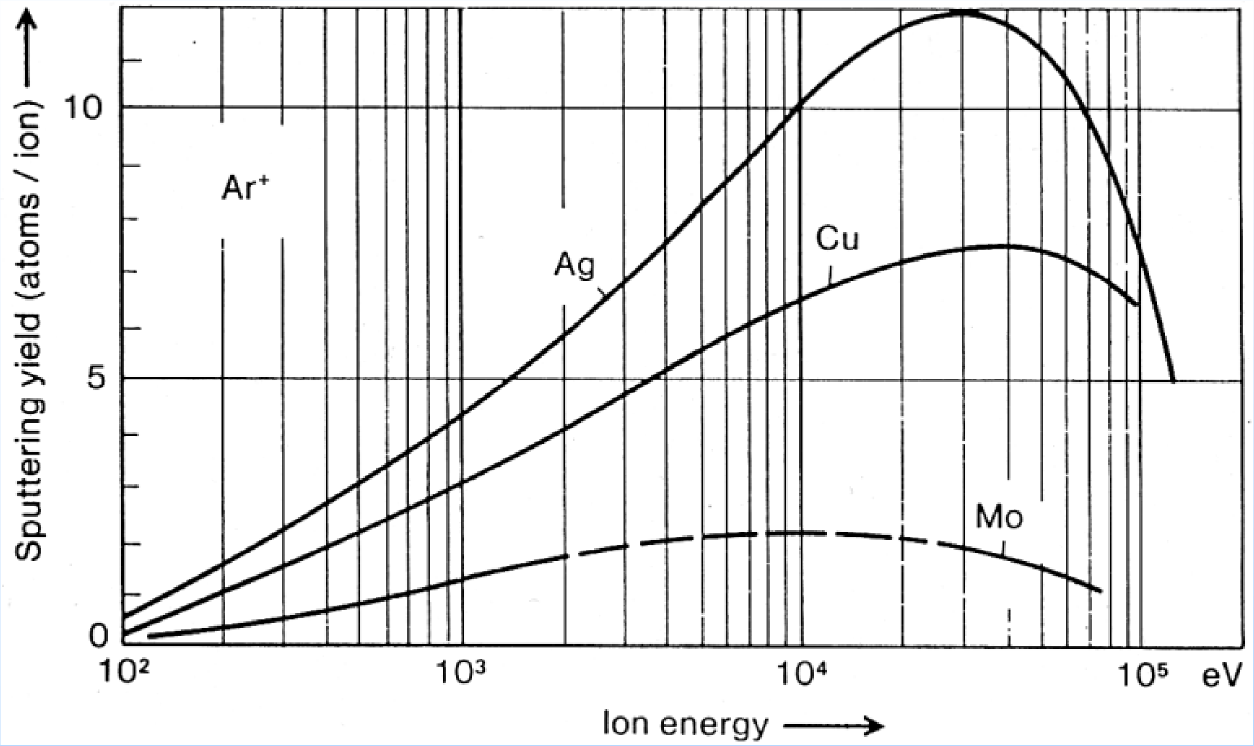
Sputtering Yield Depends on the Ion Energy (1)

- Rises rapidly from a threshold energy
- Threshold 10 - 30 eV for metals
- Above 100 eV, increases ~ linearly



Sputtering Yield Depends on the Ion Energy (2)



- Thereafter, a broad maximum and then decreases slowly
- Decrease with increasing ion energy – penetration depth too large to eject atoms from the deeper regions
- Light ions (H_2, He) maximum at a few thousand eV – large penetration depth. Heavy ions (Xe, Mg) - maximum at around 50 keV.

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Sputtering Yield for argon ion bombardment at 600 eV

Target	Yield	Target	Yield	Target	Yield	Target	Yield
Be	0.56	Mo	0.54	Al_2O_3	0.18	CdS	1.2
Al	0.83	Ru	0.67	SiO_2	1.34	GaAs	0.9
Ti	0.54	Rh	0.77	TiO_2	0.96	GaP	0.95
V	0.55	Pd	1.32	V_2O_3	0.45	GaSb	0.9
→ Cr	1.05	Ag	1.98	→ Cr_2O_3	0.18	InSb	0.55
Fe	0.97	Hf	0.39	Fe_2O_3	0.71	SiC	1.8
Co	0.99	Ta	0.30	ZrO_2	0.32		
Ni	1.34	W	0.32	Nb_2O_3	0.24		
Cu	2.00	Os	0.41	In_2O_3	0.57		
Ge	0.82	Ir	0.46	SnO_2	0.96		
Zr	0.42	Pt	0.7	Sb_2O_3	1.37		
Nb	0.42	Au	1.18	Ta_2O_5	0.15		

Ion Nitriding and Ion Carburizing

- Iron nitrides: γ'-Fe_4N, ε-$Fe_{2\text{-}3}N$, and ξ-Fe_2N are thermodynamically unstable.
- Nitriding of the Fe in ambient N_2 gas at atmospheric pressure does not take place.
- Hard Fe_4N layer can be formed by heating iron to ~ 500 ^{o}C in NH_3.
- Salt bath nitriding is an additional technique for surface hardening of iron and steel.
- Cold plasma is advanced nitriding technique for iron and steel used in industry.

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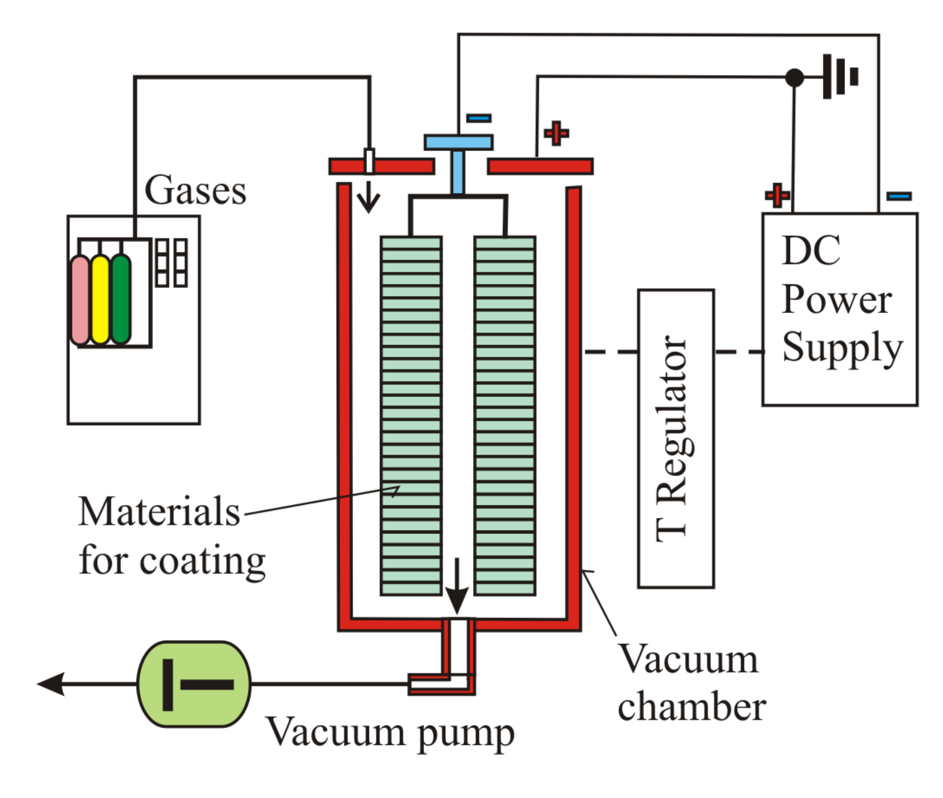
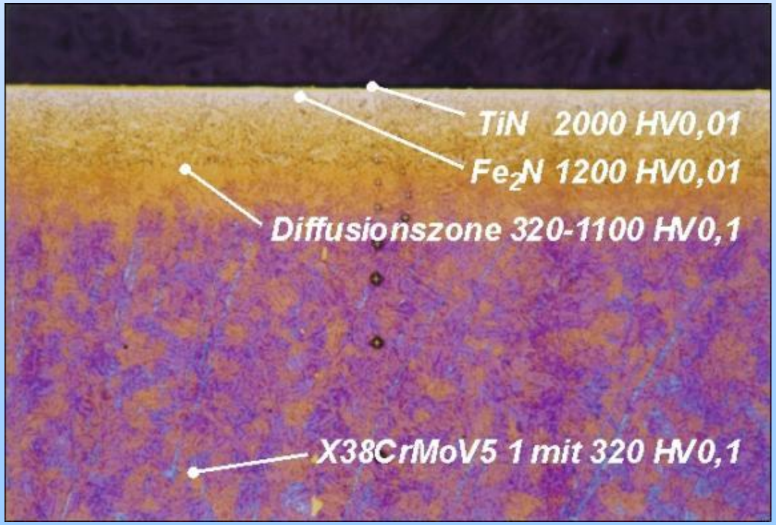
Ion Nitriding

- Pure N_2 or N_2-H_2 mixed gas at 0.5 –10 Torr.
- Abnormal DC glow discharge at 300 – 1200 V.
- Workpieces - cathode; chamber – grounded anode.
- Temperature ordinarily between 400 – 600 ^oC for steel.
- Iron nitrides are formed on the surface of steel substrate.
- Nitrogen diffusion layer exists in the bulk, below the compound layer.



- Compound layer thickness increases with increasing nitriding time.
- Nitriding rates are 2 – 2.5 - times larger than in ammonia gas nitriding at the same temperature.
- At temperatures higher than 500 ^{o}C, the thickness of the hardened layer increases but the surface hardness decreases.
- Chemical composition of the nitride layer (only a diffusion layer without a compound layer or a single phase compound layer of Fe_4N) can be controlled by changing the ratio of N_2 and H_2.
- Ion nitriding is effective not only for steel, but also for stainless steel.



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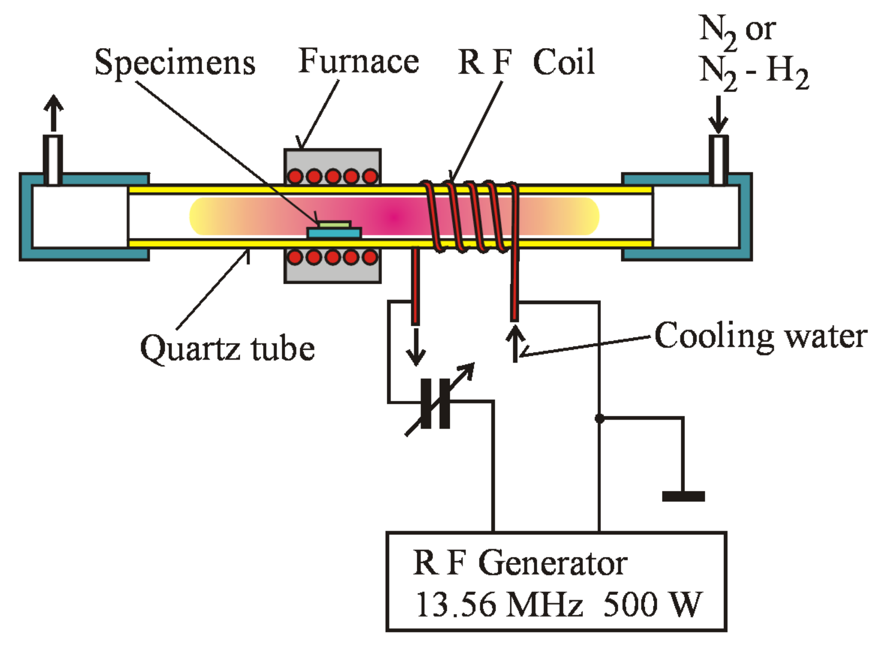
Plasma Nitriding

- Workpieces of metals at floating potential - nitrided in a RF plasma.
- N_2 or N_2-H_2 mixed gas employed as the nitriding agent.
- RF discharge between 5 and 20 Torr
- RF power between 200 and 300 W.
- Nitriding of Ti, Zr at 900 ^oC; Nitriding steel at 550 ^oC.
- Modified layer as large as 50 μm.



Plasma Oxidation and Plasma Anodization

- Surface oxidation of materials at a floating potential in a cold plasma is called **plasma oxidation**
- Plasma oxidation for materials at positively bias potential is called **plasma anodization**
- Plasma anodization is employed for obtaining a thick oxide layer
- Both techniques provide dense oxide films on solid material surfaces at < 300 ^{o}C
- High oxidation rate can be achieved by plasma anodization
- Oxide film thickness and oxidation rate can be controlled by bias voltage and /or current

- These techniques have been applied for the formation of electrically insulating films on either metals and semiconductors surfaces (Al, Si, Nb, GaAs, InP).
- Disadvantages of conventional high temperature oxidation: (for Si): oxidation-induced staking faults, excessive diffusion of dopants, evaporation of elements (from InP, GaAs) such as As, and P during oxidation.
- Low temperature plasma processing is an alternative.
- Good insulating pinhole free films with high breakdown voltages, can be formed at low temperatures on semiconductors.
- In high temperature superconducting oxides, plasma oxidation techniques are applied to improve the oxygen incorporation.

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Hydrogen Neutralization in Semiconductors

- Interest in the effect of hydrogen plasma exposure on properties of semiconductors.
- Hydrogen passivates deep level defects in semiconductors and improves the performance of electronic devices.
- Numerous types of plasma systems (RF, microwave discharges) have been used for hydrogen plasma exposure.
- Sample which is normally placed at floating potential: directly immersed in the plasma or immersed in the downstream afterglow.
- The depth of passivation shows characteristic diffusion limited $t^{1/2}$ dependence - sample temperatures: 100 – 350 °C to permit diffusion of hydrogen.
- Pure hydrogen plasma
- Small amounts of (0.1 – 0.3 %) of H_2O or O_2 can be added into an hydrogen plasma.

- Oxygen addition drastically increases the steady-state H atom concentration and oxygen does not diffuse into Si under conditions of shallow impurity passivation.
- Hydrogenation of InP shows very significant surface degradation due to P loss and subsequent In droplet formation.
- It is necessary to provide a simultaneous P overpressure, or to protect the InP surface with a thin H permeable cap layer.