2. Deposition Methods

2.1. PVD (Physical Vapor Deposition)

The processes of depositing materials directly from the vapor phase (Physical Vapor Deposition) comprise the following methods: evaporation, sputtering and ion plating as well as the reactive types of these processes.

Amongst others, PVD methods exhibit the following characteristics:

…the multitude of substrate materials which can be coated: metals, alloys, ceramics, glass, polymers etc.

…basically unlimited choice of coating materials: metals, alloys, semiconductors, metal oxides, carbides, nitrides, cermets, sulfides, selenides, tellurides etc.

…excellent coating adhesion.

…easy tuning of the microstructure by the choice of the coating parameters

There are, however the following disadvantages of PVD methods:

…relatively low deposition rates and film thicknesses

…technologically demanding processes (vacuum based)

…coating of geometrically complex parts is complicated

The main areas of application for PVD processes are thin films used in optical, optoelectronical, magnetic and microelectronic devices. Other applications may be found in the areas of tribology, corrosion protection, thermal insulation, decorative coatings amongst others.

A dedicated example shall elucidate the economic importance of thin film technology: cutting tools such as spiral drills, inserts and cutting bits are coated with TiN or TiC by reactive ion plating at T<500°C. This allows for an increase of tool life by a factor of 10 or even more, for a reduction of cutting forces and therefore for a significant increase in productivity. As a side benefit, the golden tint of TiN gives the tool a more "valuable" appearance. The annual turnover of such tools is located within the region of some 10 billion US-Dollar.

2.1.1. Evaporation

2.1.1.1. Introduction

For the evaporation process the substance to be evaporated is heated in a dedicated container (ceramic crucible, Ta boat, W spiral wire etc.) by the introduction of energy (electrical current, electron beam, laser, arc discharger etc.) to a suitable temperature. The thermally released atoms or molecules leave the surface of the evaporated material and form a coating on the substrate or on the surrounding walls. As the process is usually conducted under High Vacuum (HV, $p<10^{-5}$ mbar = 10^{-3} Pa) the coating particles basically move from the source to the substrates on straight trajectories, i. e. without collisions with residual gas atoms

To guarantee well defined film properties the substrate temperature often has to be as high as some 100°C. This can be achieved by using heating rods or quartz lamps. Employing glow electrodes allows for a cleaning of the substrate by ion or electron bombardment which is extremely important for a good coating adhesion. A suitable vacuum system equipped with gas inlets and different mechanical devices (screening arrangements, shutter, motor powered substrate movement) has to be available to perform an evaporation process (see Fig. 2.1.)

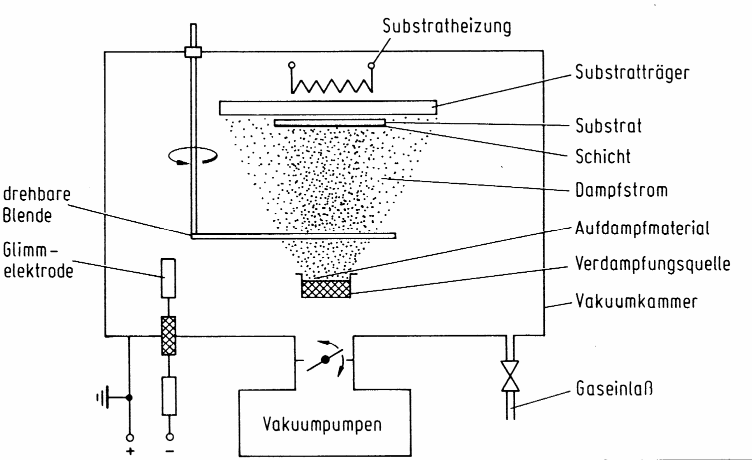


Abb. 2.1.: Schematic of an evaporation plant [1, p. 73]

2.1.1.2. Fundamentals of Evaporation

Residual Gas Pressure:

For evaporation under HV the pressure p of the residual gas has to fulfill two conditions:

1. The film forming particles have to move on straight lines to allow the production of straight edges by evaporating through a mask.
2. The ratio between residual gas particles and evaporated particles has to be reasonably small at the substrate to allow for the deposition of a clean coating.

ad **1**: The collision free fraction N of a particle stream consisting of N_0 particles, which progresses along a direction x in a gas is given by

$$N = N_0 e^{-x/\lambda} \tag{2.1}$$

with

$$\lambda = (n\sigma)^{-1} \tag{2.2}$$

λ = mean free path [m], n = particle density [m^{-3}], and
σ = interaction cross section [m^2].

The mean free path λ pf gases frequently encountered in vacuum technique (e. g. Oxygen, Nitrogen, Water Vapor) is approximately given by

$$\lambda p = 5\text{mmPa} \tag{2.3}$$

Approximately this is also valid for the film forming particles moving in a residual gas at the pressure p:

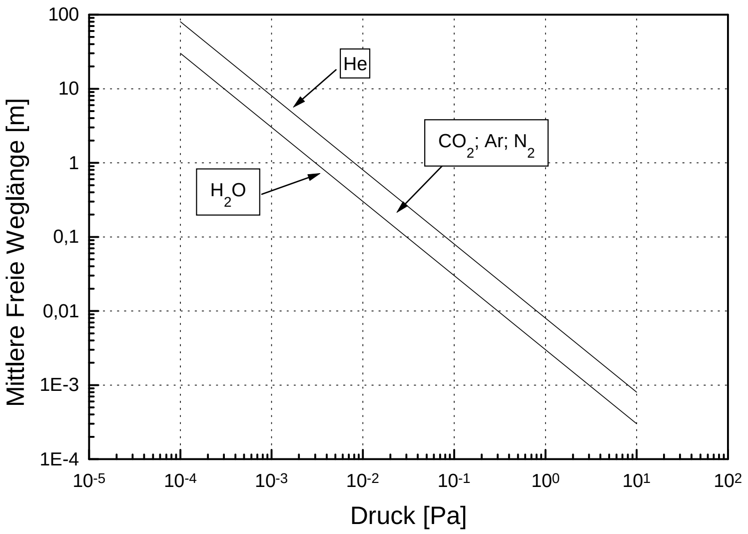


Abb. 2.2.: Mean free path as a function of pressure and of the kind of gas

At $p = 10^{-4}$mbar (10^{-2}Pa) λ = 500mm, which means that e. g. at a distance of $x = 150$mm between source and substrate approx. 74% of all coating particles reach the substate without collision. Ar $p = 10^{-5}$mbar (10^{-3}Pa) it is already a fraction of 97%. From this a demand to the base pressure of $p < 10^{-3}$mbar (10^{-1}Pa) can be derived.

ad **2**: Kinetic gas theory yields the aerial collision rate ν_g of the residual gas particles:

$$\nu_g = \frac{p}{\sqrt{2\pi m k_B T}} \quad [m^{-2}s^{-1}] \tag{2.4}$$

The aerial collision rate ν_d of the vapor particles at the substrate is given by

$$\nu_d = \frac{\rho \cdot a_W}{m_d} \quad [m^{-2}s^{-1}] \tag{2.5}$$

with

$$a_w = \frac{dm}{A\rho dt} \tag{2.6}$$

The ratio of the two collision rates is

$$\frac{\nu_g}{\nu_d} = \frac{m_d\, p}{a_w\, \rho \sqrt{2\pi m k_B T}} \tag{2.7}$$

with:

p = pressure [Pa]
m = molecular or atomic mass of the residual gas [kg]
m_d = molecular or atomic mass of the vapor (coating material) [kg]
k_B = Boltzmann's constant ($1.38 \cdot 10^{-23}$JK^{-1})
T = temperature [K]
a_w = deposition-(growth)rate [ms^{-1}]
ρ = density of the coating material [kgm^{-3}]
m = total mass of the coating [kg]
A = coated area [m^2]

Given air as a residual gas at T = 293K and Aluminium as coating material with ρ = 2700kgm^{-3} and the molar mass M_d = 27kgkmol^{-1}, the ratio of the collision rates is: ν_g/ν_d ~ 5.10^{-7}p/a_w. Typical growth rates range from 1 und 100nms^{-1} which finally yields ν_g/ν_d = 0,5 - 0,005 at a pressure p of 10^{-3}Pa.

Apart from ν_g/ν_d also the kind of residual gas and the substrate temperature influences the residual gas content of the coating. For chemically inert residual gas atoms (N_2, Ar) the sticking coefficient is very small so that ν_g/ν_d ~ 1 can generally be accepted. The sticking coefficient of O_2, H_2O and oil vapors, on the other hand, is close to 1. For these residual gas components ν_g/ν_d <<1 has to be demanded. This can be reached by employing vacuum technical features such as the construction of the evaporation chamber, the choice of the pumping system, and by knowing the out gassing rates of the used materials.

Evaporation Rate and Vopor Pressure:

In a homogenous system consisting of a vapor of pressure *p* and its condensate the number of evaporating and condensing particles is equal in thermodynamic equilibrium. From kinetic gas theory the expression of Hertz and Knudsen for the evaporation of solids or liquids into vacuum can be derived:

$$\frac{dN}{Adt} = \frac{p}{\sqrt{2\pi m k_B T}} \quad [\,m^{-2}s^{-1}\,] \qquad (2.8)$$

Also for non-equilibrium conditions a slight modification of eqn. (2.8) can be considered as valid:

$$\frac{dN_e}{Adt} = a_v \frac{(p^* - p)}{\sqrt{2\pi m k_B T}} \quad [\,m^{-2}s^{-1}\,] \qquad (2.9)$$

N_e = number of evaporated atoms [dimensionless]
A = area of the evaporation source [m^2]
a_v = evaporation coefficient [dimensionless]
p^* = saturation vapor pressure of the evaporated material [Pa]
p = vapor pressure of the evaporated material in the vacuum chamber [Pa]
m = molecular or atomic mass [kg]
k_B = Boltzmann's constant ($1.38\cdot10^{-23} JK^{-1}$)
T = temperature [K]

The evaporation coefficient a_v strongly depends on the contamination of the surface of the evaporated material. For very clean surfaces a value of 1 is reached. For light metals evaporated by an electron gun even values of up to 3 can be observed. This is caused by the strong movement of the melt due to the high energy density of the electron beam which leads to a higher effective surface of the evaporated material.

In the appendix one can find vapor pressure curves for many important evaporation materials. Different materials exhibit extremely different vapor pressures at equal temperatures:

Example: T = 2000K; $p^*(W) = 10^{-11}$mbar
$p^*(In) = 10^3$mbar

The vapor pressures of Tungsten and Indium therefore differ by 14(!) orders of magnitude. Selenium, Potassium and Zinc exhibit even higher vapor pressures than Indium thu sleading to a range of vapor pressuere which covers 17 orders of magnitude.

Evaporation Mechnaism:

In the simplest approach the atoms of the evaporation material can be considered as system of coupled oscillators in which the particles at the phase boundary are chemically bonded with the sublimation energy E_V. For a surface atom the transition into the gas phase is possible if its oscillatory energy E exceeds E_V. In addition it is assumed that all surface atoms have the same binding energy and can change into the gas phase with the same probability.

If evaporation is considered as thermally activated process the vapor pressure p^* can be expressed by:

$$p^* = p_0 e^{-(E_v/kT)} \tag{2.10}$$

From eqn (2.10) it is visible that the number of particles in the vapor beam is exponentially dependent on the source temperature and the sublimation energy. As it will be shown later, for the sputtering process the evaporation probability is only inversely dependent on the sublimation energy.

Spatial Distribution of the Vapor Current Density:

If a mass m_1 is evaporated from a plane source with a small area a quantity

$$dm = \frac{m_1}{\pi} \cos\alpha \; d\omega \tag{2.11}$$

will be emitted into the solid angle $d\omega = dA/r^2$ under the angle α relative to the surface norma. Eqn (2.11)is the analogy to the well known Lambert law of optics (see Fig. 2.7).

The spatial distribution of the vapor current density $\Phi(\alpha)$ (= mass current per solid angle) is then given by

$$\Phi(\alpha) = \frac{m_1}{\pi} \cos\alpha = \Phi_0 \cos\alpha \tag{2.12}$$

with

$$\Phi_0 = \frac{m_1}{\pi} \tag{2.13}$$

□ *$\Phi(\alpha)$ only represents the matter current emitted into the solid angle element. To obtain the film thickness distribution on a substrate which is arbitrarily tilted in respect to the source one has to consider two additional facts: the distance of the substrate from the source and the tilt of the substrate in respect to the source. This situation is sketched in Fig. 2.3..*

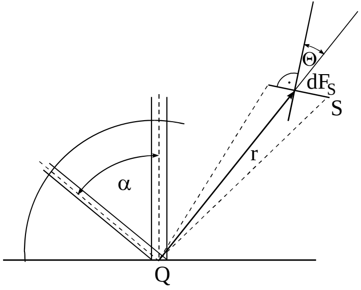


Abb. 2.3.: *Geometric situation for the determination of the film thickness distribution for evaporation processes; **Q**: source, **S**: substrate, **r**: distance source/substrate; **dF$_S$**: infinitesimal area alement of the substrate Θ: tilt angle of the substrate relative to the source*

Considering the geometry given in Fig. 2.3. the impingement rate in an arbitrary point of the substrate is given by the expression

$$R = \Phi(\alpha)\frac{\cos\Theta}{r^2} = \frac{m_1}{\pi}\frac{\cos\alpha \cdot \cos\Theta}{r^2} \tag{2.14}$$

Eq. (2.14) is also sometimes termed "Hertz Knudsen Law" and allows the determination of rate distributions (and, if the deposition rate is constant, of film thickness distributions) for any evaporation geometry. This shall be demonstrated for three simple examples in the following.

Case 1: Infinite, plane substrate (Fig. 2.4.)

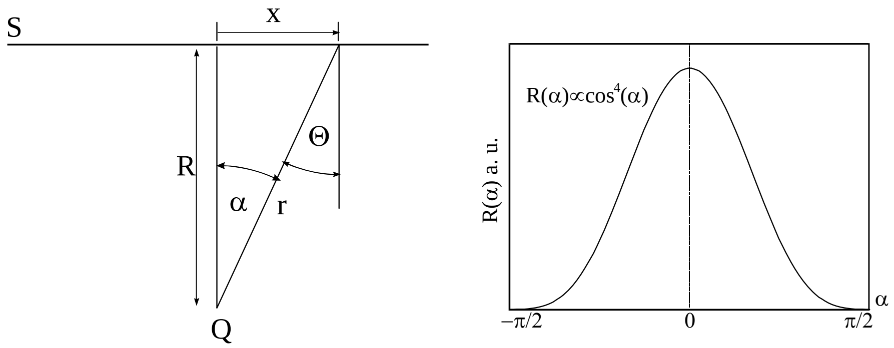


Fig. 2.4.: Geometry for the determination of the film thickness distribution on a plane infinite substrate; **Q**: source, **S**: substrate, **R**: normal distance source/substrate; **r**: distance source/substrate;

Using $\alpha=\Theta$, $r^2 = x^2 + a^2$ and $\cos^2\alpha = 1/[(x/R)^2 + 1]$ yields the rate distribution as

$$R(\alpha) = \frac{m_1}{R^2\pi}\cos^4\alpha\ . \tag{2.15}$$

Case 2: Hemispherical substrate with source in the center (Fig. 2.5.)

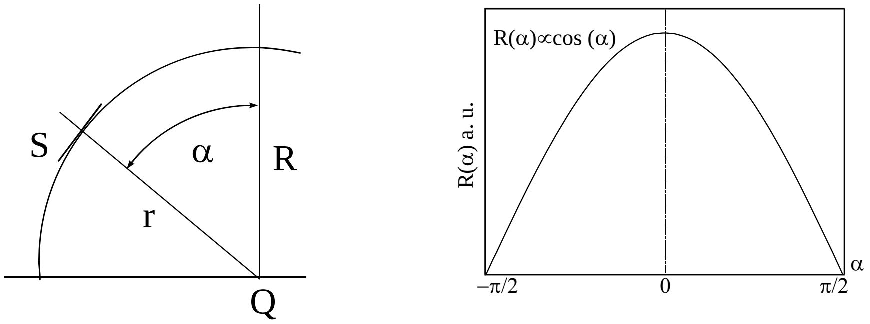


Fig. 2.5.: Geometry for the determination of the film thickness distribution on a hemispherical substrate; **Q**: source, **S**: substrate, **R**: radius of hemisphere; **r**: distance source/substrate;

Using $\Theta=0$ und $R=r$ yields the rate distribution as

$$R(\alpha) = \frac{m_1}{R^2\pi}\cos\alpha\ . \tag{2.16}$$

Case 3: Spherical substrate with source in one pole ("Knudsen-sphere", Fig. 2.6.)

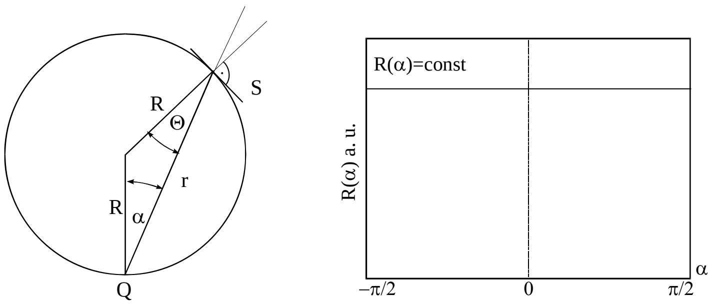


Fig. 2.6.: Geometry for the determination of the film thickness distribution for the "Knudsen-Sphere" **Q**: source, **S**: substrate, **R**: radius of hemisphere; **r**: distance source/substrate;

Using $\alpha = \Theta$ und $r = 2R\cos\alpha$ yields the rate distribution as

$$R(\alpha) = \frac{m_1}{4R^2\pi} = const. \tag{2.17}$$

The above case studies have shown that the film thickness on the plane substrate and on the hemisphere with the central source is not uniform. For the Knudsen-sphere, on the other hand, the deposition rate is constant and, resulting from this, the film thickness is uniform. This special geometry is preferred in commercially available deposition plants which have to guarantee highly uniform coating thicknesses, as e. g. in the optical industry. Usually not the whole sphere is charged with substrates, but only the upper polar calotte to avoid a grazing incidence of the vapor beam which has a negative influence on the coating microstructure.

Deviations from the cosine law are observed for evaporation sources with a non negligible area. In this case the total angular distribution of the emitted particles can be calculated by superimposing of the angular distributions of several point sources. For evaporators with the evaporation surface below the rim of the crucible the emission under high angles α is cut off. This type of deviation is significant for electron beam evaporators ("electron guns") because a crater forms beneath the focal spot which leads to a highly directional emission characteristic.

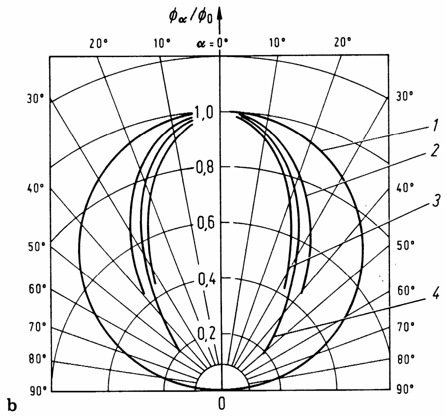


Fig. 2.7.: Vapor density distribution above a small area source with the characteristic $\Phi(\alpha) = \Phi_0 \cos^n \alpha$, Curve 1: n = 1; Curves 2-4: n > 1 [1, p. 77]

In the polar chart (Fig. 2.7) the evaporation characteristic $\Phi(\alpha)$ assumes a flattened shape when compared to the cosine law. For α <~ 30° this may be expressed by

$$\Phi(\alpha) = \Phi_0 \cos^n \alpha, \quad n>1 \tag{2.18}$$

Also the vapor beam density characteriatic of a 5 kW electron gun with *n* approx. 3,5-4 is visible in Fig. 2.7. (Curve 4).

Film Thickness Uniformity and Substrate Holder

As it has been shown in the last section the film thickness on a specific substrate depends on it's location on the substrate holder. To guarantee a high thickness uniformity on one or more substrates often rotating substrate holders are employed. The rotation periodically moves substrates from positions near the source to locations far away from the source. In addition one can use small adjustable carriers which may be tuned in respect to the evaporation characteristic.

2.1.1.3. Evaporation Sources

Evaporation sources can be categorized by the method of energy supply. One has also to consider that not each material can be evaporated from each source. Chemical reactions between crucible and evaporation material are possible which can lead to impurities in the film and/or to the destruction of the evaporation source. In addition the power density in different source types may vary strongly.

Direct Resistive Heating: Some (electrically conductive) elements which exhibit a vapor pressure >10^{-2} mbar (1Pa) below their melting point can be evaporated by sublimation. The evaporation material has the shape of wires or rods and is directly heated by a high electrical current. This method is not frequently employed since it is limited to only few materials (e. g. C, Cr, Fe, Mo, Ni, Pd, Rh, Ti, Al).

Indirect Resistive Heating: The principle of this frequently employed method is to put the evaporation material on or into a container (called "boat"), spiral wire, ribbon or crucible made from W (or Mo, Ta, C, Pt, BN, TiB_2) which is heated by a high electrical current and to evaporate it from there (Fig. 2.4.).

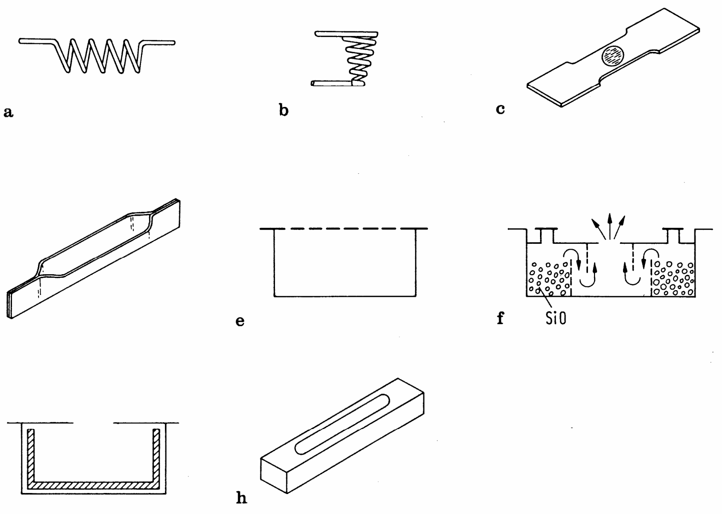


Abb. 2.8.: Different Indirectly heated evaporation sources [1, p. 86]

Inductive Heating: In this case the evaporated material is heated by high or low frequency induction. The evaporated material has to be conductive.

Electron Evaporator: Apart from a high power density which can be achieved there is also practically no reaction between the evaporation material and the crucible in these devices. The reason for this is that the evaporated material is kept in a water cooled Cu-crucible. Therefore highy reactive materials (Ta, Ti, Zr) and refractory metals (W, Mo, Pt, Rh) can be evaporated. Also dielectric substances can be deposited at high rates and high purity. Because of these properties electron beam evaporation has established itself as a universal method for the deposition of high quality coatings in large quantities. (Fig. 2.9:)

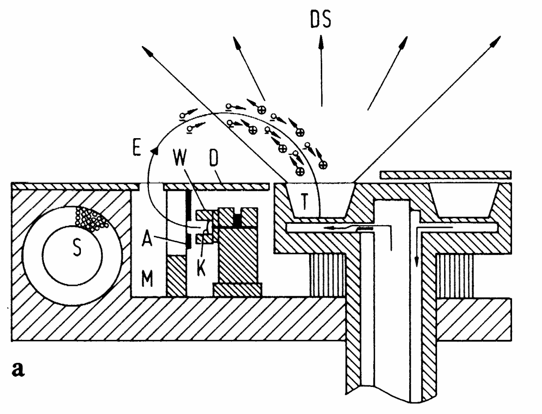


Fig. 2.9.: Electron beam evaporation source: **A** anode, **K** cathode, **W** Wehnelt blind, **S** coil, **M** pole shoes, **D** cover plate, **E** electron beam, **DS** vapor beam, **T** crucible [1, p. 88]

Arc Discharges: Arc discharges (Hollow Cathode Arc, Low Voltage Arc, Thermionic Arc) are extremely important for ion plating processes and will be treated in detail there.

Laser Evaporator or Laser Ablation: The continous interaction of laser radiation with matter can lead to thermal evaporation. Pulsed laser beams, on the other hand, may release particles from the solid by alternative mechanisms because of their low pulse duration and high power density. Local plasmas and explosive evaporation play an important role. The use of pulsed lasers, termed "laser ablation", has gained considerable importance in the field of PVD methods starting in the 1990s.

2.1.1.4. Evaporation Materials

Solid coating materials can be used for evaporation in the form of elements, alloys, compounds and finely dispersed mixtures. They have to exhibit a defined grade of purity in respect to the demands on the process employed. A multitude of materials is commercially available in a variety of purity grades.

2.1.1.5. Special Evaporation Methods

Multiple Sources

The single components (elements or compounds) are evaporated from separated crucibles to condense on the substrate together. Controlling the evaporation rates (e. g. by the source temperature) is a demanding task. It is slightly less problematic to use separate electron beam evaporators which are controlled by in-situ rate monitors.

Flash-Evaporation

The evaporation material (element, alloy, compound or mixture) is delivered to an extremely hot evaporator block in small portions and evaporates instantly. The evaporator temperature lies significantly above common crucible temperatures so that different vapor pressures of the constituents are irrelevant.

Reactive Evaporation

The evaporated material reacts with a gas (p = approx. $10^{-4}...10^{-3}$mbar) within the recipient and forms the desired compound at the substrate. The first application for this process was the deposition of oxides (TiO_2, SiO_2) as optical coatings. Meanwhile also Carbides and Nitrides (TiC; TiN) are manufactured this way.

Activated Reactive Evaporation

As early as 1960 the proposition was made to "activate" the reactive gas by a gas discharge to increase the reaction efficiency as compared to conventional reactive evaporation. For the activation especially methods are beneficial which lead to the excitation, dissociation or ionization of the reactive gas or vapor.

Different technologically feasible systems for reactive evaporation are displayed in Fig. 2.10.

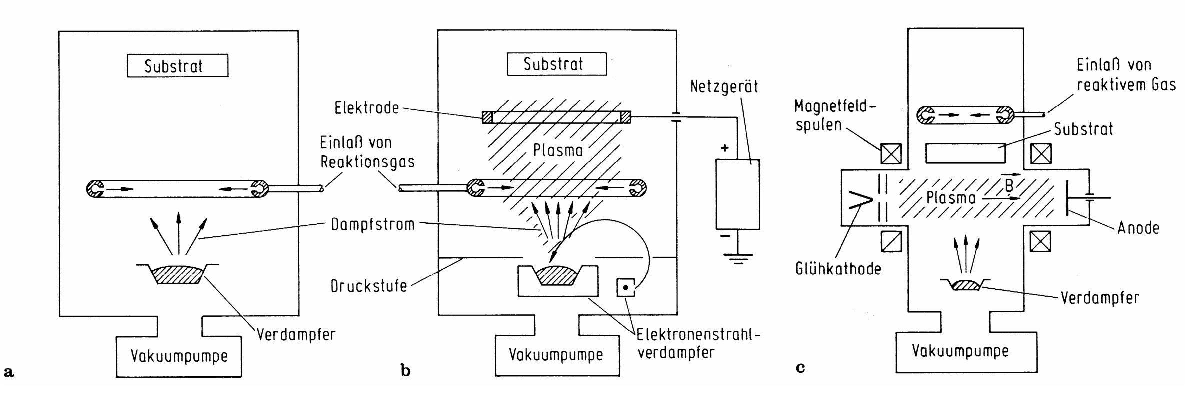


Fig. 2.10.: Systems for reactive evaporation [1, p. 84]

2.1.2. Sputtering

2.1.2.1. Introduction

If ions hit the surface of a solid then, amongst other possible interactions, neutral atoms, clusters, molecules or ions of the bombarded material can be emitted. This emission of particles is the basis of the widely spread sputter deposition process.

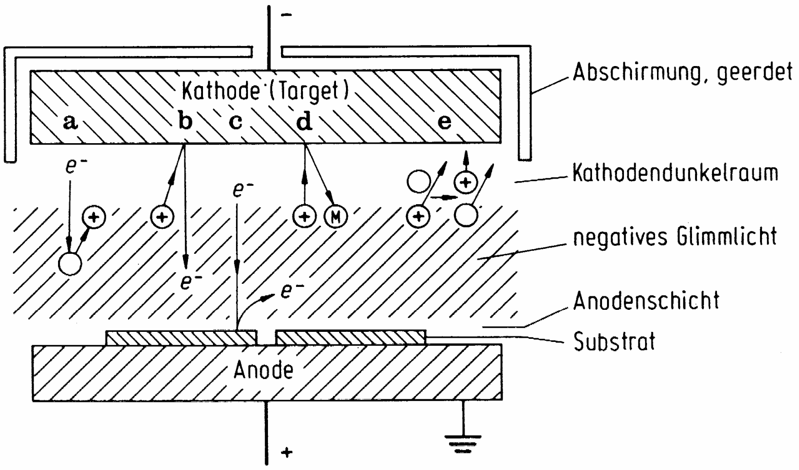


Abb. 2.11.: Schematic of the sputtering process in a planar geometry [1, p. 95]
a ionization,
b electron emission from the target,
c electron emission from the anode,
d emission of neutral particles from the target,
e charge reversal

In a typcal sputtering set up (see Fig. 2.11.) a target (=source of the coating material) is introduced into a HV chamber together with the substrates. The easiest method to generate an ion bombardement is to ignite aan anomal glow discharge with the target as cathode and the substrate serving as anode.

An attractive property of sputtering is it's universal applicability. Since the coating material is transferred into the gas phase by impulse transfer and not by thermal excitation, basically each substance can be sputtered.

2.1.2.2. Fundamentals of Sputtering

Sputter Yied

The sputter yield *Y* is the mean number of particles emitted by impinging ion. *Y* depends on the target material, the kind and energy of the used ions and on the angle of ion impingement.

Dependence on the Target Material

If the yield *Y* is plotted against the atomic number of the target elements at given ion energy and ion kind (Fig. 2.12.) one obtains a periodic characteristic which corresponds to the groups of the transition metals. An analogous periodicity can be found if one plots the inverse sublimation energy E_0 of the target material. This is a sign for an interdependence of *Y* and E_0 which was briefly mentioned already in section 2.1.1.2. and which will be dealt with in more detail in the present chapter.

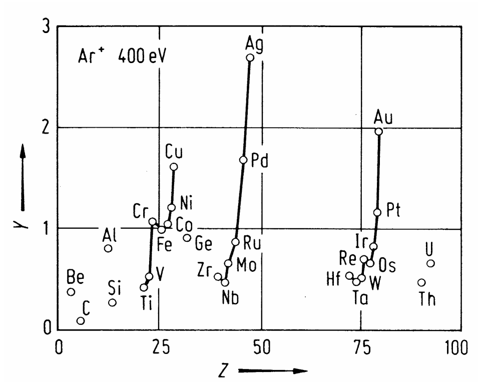


Abb. 2.12.: Sputter yield *Y* in dependence on the atomic number *Z* of the target material [1, p. 97]

Dependence on the Ion Mass

The yield *Y* reaches a maximum at a given ion energy of some 100 eV if the ion mass M_i approximately equals the target mass M_t. The optimum ratio of M_i/M_t shifts towards values slightly higher than 1 for higher bombardement energies (Fig. 2.13.).

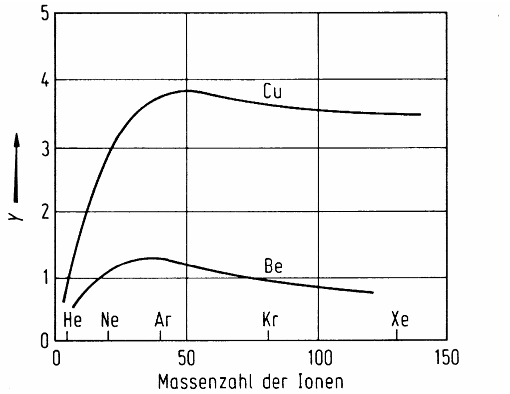


Abb. 2.13.: Dependence of the yield *Y* on the ion mass [1, p. 97]

Dependence on the Ion Energy

Sputtering starts at e threshold energy of approximately 10 - 30 eV which has a characteristic value for each combination of target material and used ions. At normal ion incidence *Y* at first increases linearily with the ion energy E_i, then reaches a maximum at values of E_i of some 10^4 eV and finally decreases again with increasing E_i due to the larger penetration depth of the ions and the resulting implantation phenomena (Fig. 2.14.).

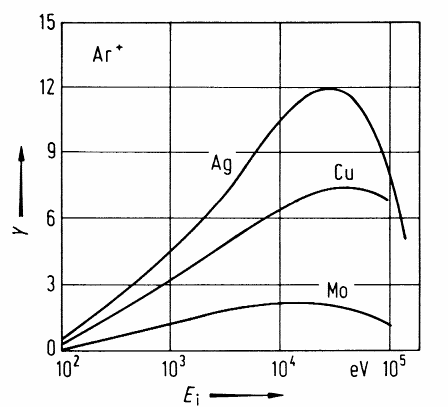


Abb. 2.14.: Sputter yield *Y* in dependenceon the ion energy E_i [1, p. 97]

Dependence on the Impingement Angle of the Ions

With the ion impingement angle Θ (measured from the surface normal) increasing from zero the yield *Y* grows first because the directional change of the impulse of an ejected atom is smaller than in the case of normal ion incidence. For small angles Θ *Y* increases with $cos^{-1}\Theta$. At larger Θ ion reflection becomes dominant and *Y* decreases again (Fig. 2.15.).

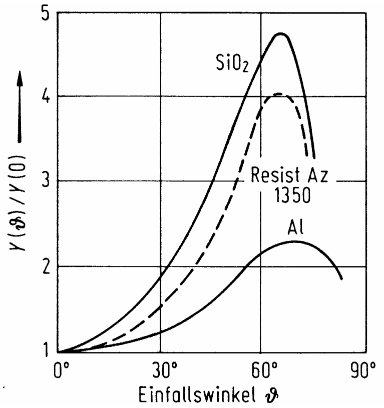


Abb. 2.15.: Sputter yield *Y* in dependence on the ion impingement angle Θ [1, p. 97]

Types of Sputtered Particles

Sputterd particles are mostly neutral atoms. A small fraction (<1%), however, may be negative or positive ions or atom clusters.

Sputter Rate

At normal ion incidence a target is eroded with the rate *x*.

$$x = \frac{Y(E_i)\, j_i\, M}{\rho e N_A} \qquad [ms^{-1}] \qquad (2.19)$$

with:

Y = sputter yield [dimensionless]
E_i = ion energy [eV]
M = molar mass of the target [kgkmol^{-1}]
ρ = target density [kgm^{-3}]
j_i = ion current density [Am^{-2}]
eN_A = 9,649.10^7 [Askmol^{-1}]

For most metals the sputter yield is in the order of 1. Sputter rates are therefore quite independent on the quantities discussed above, as opposed to evaporation rates which can cover many orders of magnitude in dependence on the source temperature or on the evaporated material. This fact is beneficial in respect to the deposition of alloy coatings or multicomponent films.

Energy Distribution of Ejected Atoms

Sputtered atoms leave the solid by impuls transfer and therefore have relatively large energies of approx. 5 - 40 eV. This is different from evaporation where the evaporated atoms only have energies ranging form 0,2 - 0,3 eV. The energy of the sputtered atoms can be described by the so called Sigmund-Thompson energy distribution which differs from the Maxwell-Boltzmann distribution in three major points (i) sputtered particles exhibit a maximum energy of several 100 eV which is determined by the impingement energy of the ions; (ii) at higher energies the Sigmind-Thompson distribution shows a quadratic decay and (iii) at low particle energies there is a linear increase. (Fig. 2.16.).

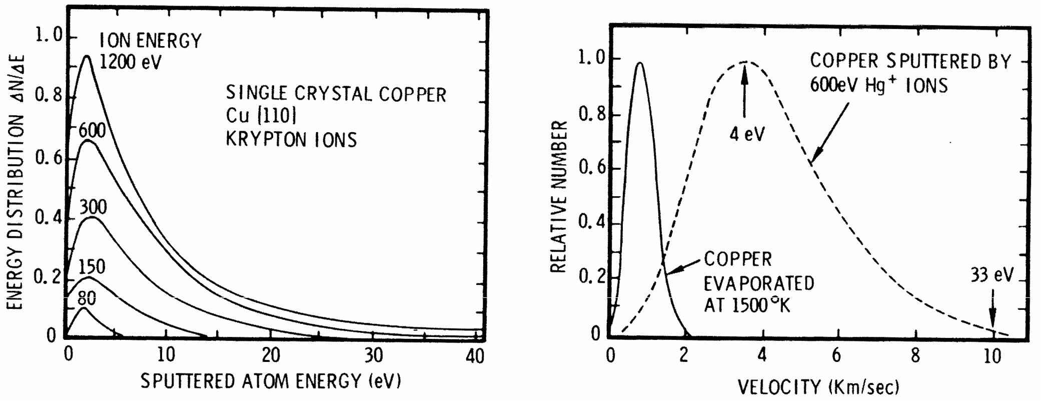


Abb. 2.16.: Energy distribution of sputtered particles [2, p. 188]

Sputtering Mechanisms

The fundamental mechanism of sputtering is the collision interaction between the impinging ions and the lattice atoms of the target. The ion dissipates it's energy in collision cascades. Impulse reversal is achieved by collisions between target atoms. The ejection depth of the target atoms is approx. 1 nm.

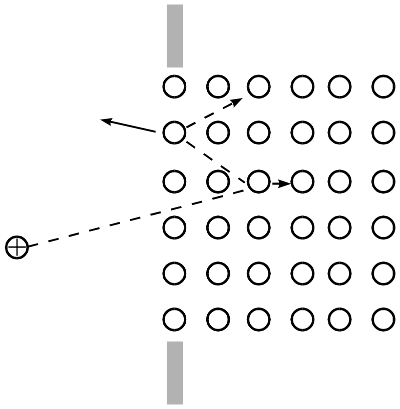
For quantitative statements one has to apply the formalism of transport theory to the mechanism of a collision cascade: Additional assumptions have to be made about the specific potential of binary collisions. At ion energies E_i *< 1keV the Born-Mayer potential may be used, at* E_i *> 1 keV the Thomas-Fermi potential is valid. In this framework the sputter yield can be expressed as*

$$Y = \frac{3\alpha}{4\pi^2} \frac{4M_i M_t}{(M_i + M_t)^2} \frac{E_i}{E_0} \qquad (2.20)$$

with M_i *= ion mass;* M_t *= atom mass of the target. The quantity* α *is a function of the ratio* M_t/M_i *which does not strongly vary for technically relevant materials. The material dependence mainly enters via the sublimation enthalpy* E_0 *of the target material. Contrary to thermal or chemical processes, which exponentially depend on the activation energy, sputtering only shows an energy dependence in a power law of the first order.*

In dependence on the ion energy three sputtering regimes can be distinguished:

Single-Knock-on-Regime



Ion energy small and/or ion mass small

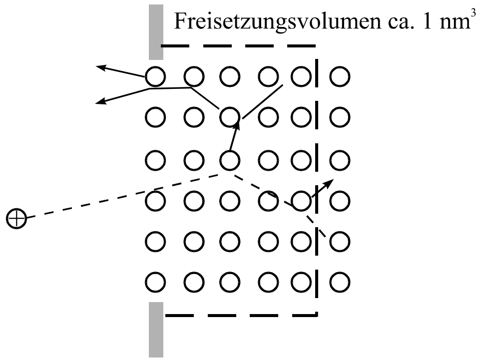
$$M_i < \quad : Y \propto 10^{-1} \qquad (2.21)$$

$$E_i < 10eV \quad : Y \propto \frac{E_i}{U_0} \qquad (2.22)$$

U_0 *= Surface binding energy*

In addition ions with energies close to the threshold energy E_{thres} *(i. e the minimum ion energy which allows for sputtering,* $E_{thres} \propto U_0$*) may also trigger evaporation processes because the thermal energy of the impinging ions is close to the thermal energy of the target atoms.*

Linear Collision Cascade

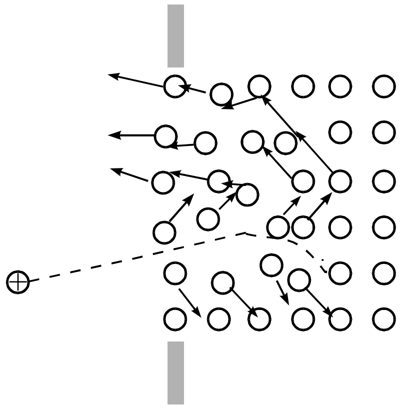


Ion energy 0.1 - 10 keV
Collision potentials:
E^+ 0.1 - 1 keV: Born-Mayer
E^+ 1 - 10 keV: Thomas-Fermi

$$Y \propto \frac{4 M_i M_t}{\left(M_i + M_t\right)^2} \frac{E_i}{U_0} \qquad (2.23)$$

M_t = Mass of target atoms

Thermal Spike Regime



Ion energy > 10 keV

$$Y \propto e^{\left(-\frac{U_0}{k_B T}\right)} \qquad (2.24)$$

i. e. am evaporation characteristic of the emission volume

Sputtering of Alloys

If an alloy consisting of components with different yields is sputtered the component with the lower yield is accumulated on the target surface. Since diffusion processes are suppressed due to efficient target cooling mass conservation requires a stationary state after a certain transient time ("conditioning phase"). Within the stationary state the product of surface concentration and sputter yield is proportional to the concentration of the respective component in the target. Therefore the current of deposition particles has the same composition as the target material. These processes occur within a surface zone of the target with a thickness of approx. 5 - 10 nm (see Fig. 2.17.).

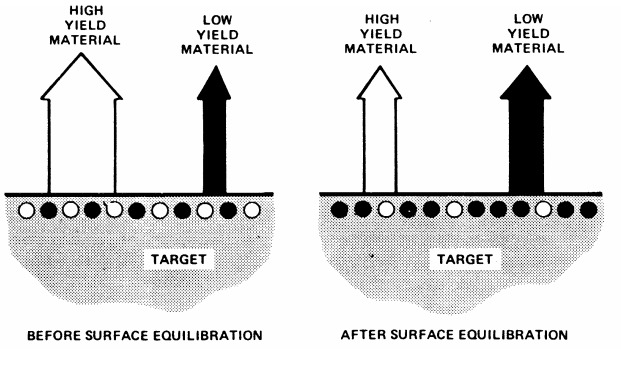


Abb. 2.17.: Sputtering of alloys [2, p. 184]

Additionally, the total sputter yield Y_{tot} of an alloy or of a material combination is generally lower that the sum $\sum a_i Y_i$ which results from the yields Y_i of the pure components and their molar fraction a_i. The reason for this is that the component with the lower yield (i. e. with the higher sublimation energy E_0) is accumulated on the surface. So the average E_0 is increased and, consequently, the total yield Y_{tot} is decreased.

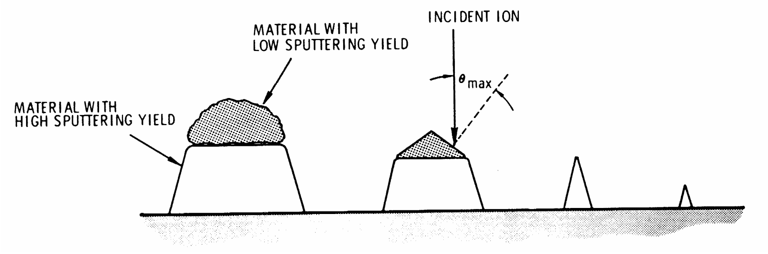


Abb. 2.18.: Sputtering of alloys (cone formation) [2, p. 184]

The total sputter yield Y_{tot} may even be considerably lower than the above sum. This effect is pronounced if the Y_i values of the components differ strongly. Atoms with small Y_i form islands on the surface of the matererial with the high sputter yield. Therefore the portions beneath the islands are shielded from sputtering. This leads to the formation of cones with an opening angle which corresponds to the impingement angle Θ_{max} of the maximum yield (see Fig. 2.18.). The sputter yield of a surface covered with such cones is close to the value Y_i of the component with the lower yield.

Sputtering of Chemical Compounds

Chemical compounds are sputtered either as molecules or as molecular fragments. The latter is often observed for oxides (e. g. $Ta_2O_5 \rightarrow Ta, TaO \text{ and } O$). The oxide is generally sputtered stronger than the pure metal, with a promonent exception being Al_2O_3.

2.1.2.3 Practical Aspects of Sputtering

Direct Current (DC) Sputtering

In this case an anomalous glow discharge is sustained between the electrodes.

Typical operational parameters:
pressure p = 10Pa (Ar)
voltage U = 3000V
current density j = 1mAcm^{-2}
deposition rate r = 40nmmin^{-1}

This "prototype" of the sputtering process has many disadvantages:

... low deposition rates

... high thermal load of the substrate due to energetic electrons

... sputtering of insulators is impossible due to charging of the target

... scattering of deposition particles at working gas atoms leads to energy loss of the film forming atoms which can lead to low quality coatings.

... incorporation of working gas atoms into the film.

These disadvantages could be counteracted by the development of several new process types which make sputtering technology to one of the most versatile deposition tools today.

Radio Frequency-(RF)-Sputtering

The advantage of RF sputtering is the possibility to sustain a gas discharge at much lower pressures (0,5 - 2 Pa) with a high frequency alternating voltage (13,56 MHz, free industry frequency) than with a DC voltage. A scond important feature is the possibility to sputter semiconductors and insulators.

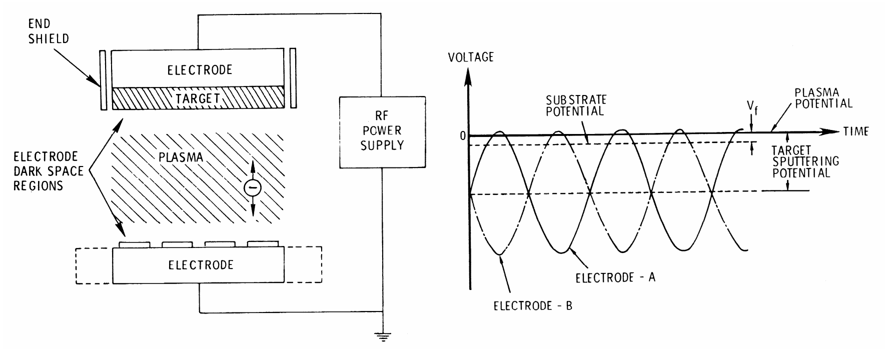


Abb. 2.19.: RF sputtering [2, pp. 206 & 207]

Sputtering in an RF discharge is based on the fact that each surface which is capacitively coupled to the plasma will be charged negatively in respect to the plasma. In Fig. 2.19. the target *T* of of a planar diode assembly is coupled via a capacity to the pole of an RF source. The other pole of the RF source is coupled to the plasma via a metallic counter electrode (substrate holder *S*). This assembly has the effect that during the positive half wave significantly more electrons can reach the target because of their low mass (i. e. high mobility) than ions during the negative half wave. The condition of quasi-neutrality demands that an electrode, which is insulated in respect to DC currents, has to be hit by an equal number of electrons and ions in the temporal average. Therefore a negative DC voltage ("Self Bias") in respect to the plasma is formed by the excess electrons.

In the stationary state the magnitude of the DC bias voltage U_t may be only insignificantly lower than the RF amplitude of the voltage drop between plasma and target, if the matching network is correctly adjusted. The frequency of the RF signal is chosen so high that the ions cannot follow the voltage variation while the electrons can still do this (f>1Mhz; usual: 13,56Mhz). In this case ions are flowing to the target during the whole RF period. In the short time in which the target is charged positively in respect to the plasma a relatively large electron current is flowing.

Bias-Sputtering

In this case the substrate holder is not kept at ground potential but is insulated towards ground and is supplied with a defined voltage. In most cases a negative potential (-50 to -200V) is used. This triggers an ion bombardement to the substrate which removes loosely bound impurities and may have a positive influence on the coating structure.

Triode System

In this system a discharge is maintained at low pressures (0,05 - 0,1 Pa) with the help of a glow filament which deivers electrons by thermal emission (see Fig. 2.20.). Radial plasma losses are reduced by an axial magnetic field. Advantages like a high deposition rate at low pressures are counteracted by the high sensitivity of the filament to reactive gases and impurities which may drastically reduce the lifetime of the assembly.

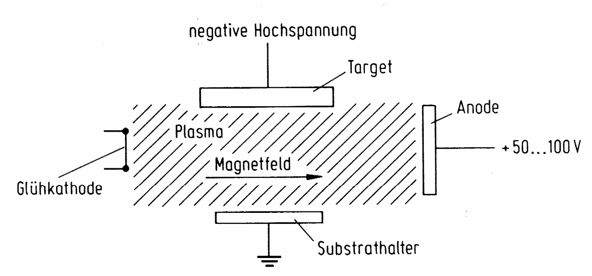


Abb. 2.20.: Triode sputtering system [1, p. 105]

Magnetron Sputtering

The scope of applications especially in the fierld of high technology significantly could be widened by the introduction of the so-called magnetron sources. Magnetron systems allow for the achievement of high deposition rates at low working gas pressure (even below 0,1 Pa) and at low substrate heating.

In principle a magnetron works as follows: Above the cathode (target) a so-called "electron trap" is generated by a magnetic field ***B*** which is transversal to the electric field ***E***. Within this region a closed annular current is formed by the trapped electrons due to the ***E***x***B***-drift. The magnetic field ***B*** has a strength of some 10 mT (= 100 G) and therefore does not influence the heavy ions but only the electrons with their low mass.

In their general appearance magnetron discharges are similar to a common glow discharge. Cathode dark space, plasma and anode fall are observable. An electron emitted from the target by an ion collision has an initial energy of some eV. After leaving the target it will describe a cycloidic arc and will only stay free if, within the first cycloidic arc, it suffers a collision with an energy loss which is larger than the initial energy (see Fig. 2.21.). Each time the electron loses energy by a collision a new cycloidic trajectory is started and the electron proceeds radially towards the anode. Therefore, within the ***E***x***B***-direction a currnt with the density $j_{e\vartheta}$ is generated.

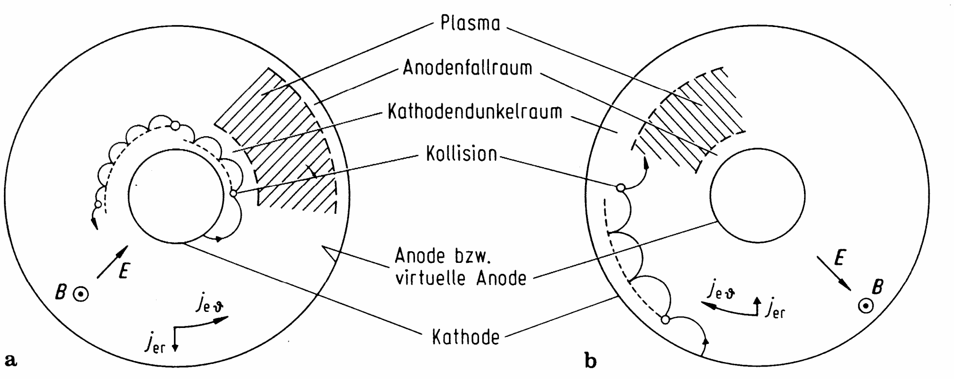


Fig. 2.21.: Schematic of electron movement within a cylindrical magnetron
a: post cathode magnetron; **b:** hollow cathode system [1, p. 107]

Technologically relevant set-ups for planar magnetrons are given in Fig. 2.22., cylindrical types are displayed in Fig. 2.23. and specially shaped variants are given in Fig. 2.24.

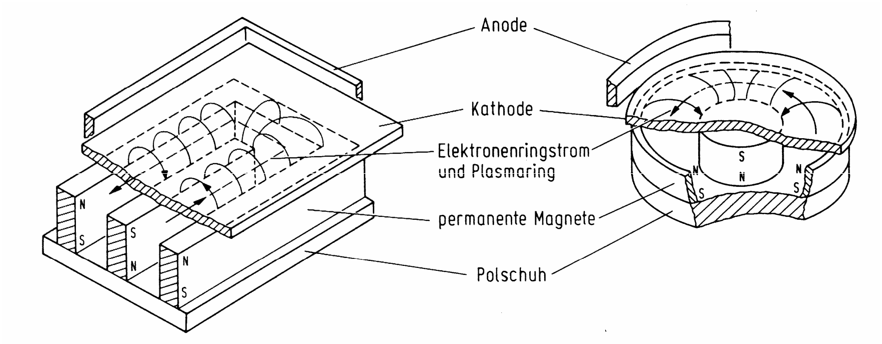


Fig. 2.22.: planar magnetrons [1, p. 109]

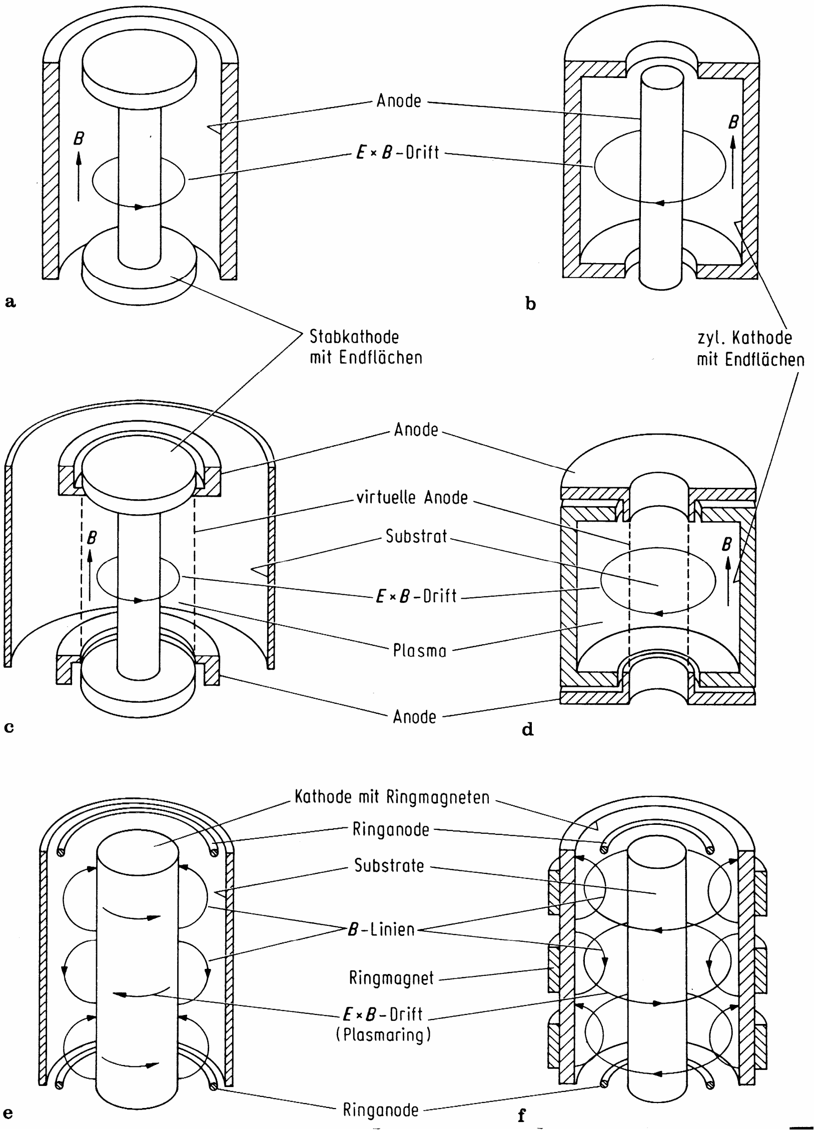


Fig. 2.23.: Cylindrical magnetron arrangements [1, p.106]
Left hand side: Post-Magnetrons
Right hand side: inverse magnetron ("hollow cathode")

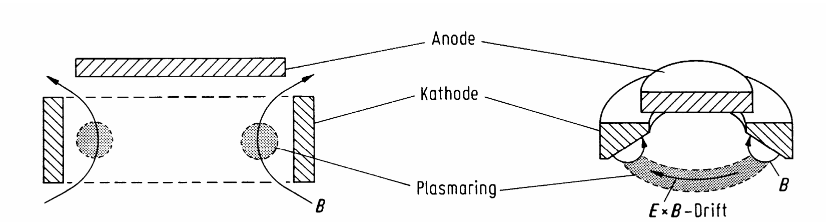


Fig. 2.24.: Special magnetron arrangements ("Sputter-Gun"; "S-Gun") [1, p. 109]

Planar and sputter-gun magnetrons are the magnetron sources mostly employed today. Also cylindrical magnetrons gain importance as e.g. sources for the coating of plain bearings (**MIBA**, upper austria) or as rotatable magnetrons for coating large glass panels for electronical (flat screens) and architecturtal (thermal management panes) applications.

Also rectangular planar magnetrons can be manufactured in dimensions of up to 5 - 8 m length, They are also used for coating large flast surfaces as e. g. glass panes. Deposition rates of more than 1 µm/min and film thickness uniformities of ±5% can be achieved. Finally it has to be mentioned that the magnetron set-up can be combined with other types of sputtering processes such as bias sputtering and RF sputtering in both, planar and cylindrical geometry.

Typical process parameters of a magnetron discharge:

Pressure $p = 10^{-1}$Pa
Magnetic field $\boldsymbol{B}$ = some 10^{-2}T
Voltage U = 800V
Current density j = 20mAcm^{-2}
Deposition rate r = 1µmmin^{-1}

A comparison with the process parameters of a common diode discharge (see Fig 2.26.) shows the advantages of magnetron sputtering.

Ion Beam Sputtering

Ion beam sputtering (see Fig. 2.25.) has the following advantages when compared to the previously described tgechniques:

1. low pressure (<10^{-3}Pa) in the region between target and substrate
2. no interaction between substrate and plasma
3. The energy E_i and the current density j_i of the ions can be varied independently in a wide range

The above points and the fact that ion beam systems only exhibit very low sputtering rates confine them, to applicatioins in R&D.

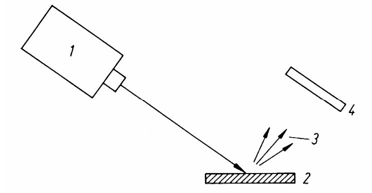


Fig. 2.25.: Ion beam sputtering system: **1** on beam source, **2** target, **3** sputtered particles, **4** substrate [1, p. 111]

Current Voltage Characteristics

From the current voltage characteristics of a gas discharge (see Fig. 2.26.) it is possible to draw conclusions on the ionization degree, on the efficiency of the electron enclosure and on other plasma features. For the determinationn of the erosion rate of the target and, following from this, of the deposition rate at the substrate at different process parameters it is necessary to know the current voltage characteristic of the given set-up.

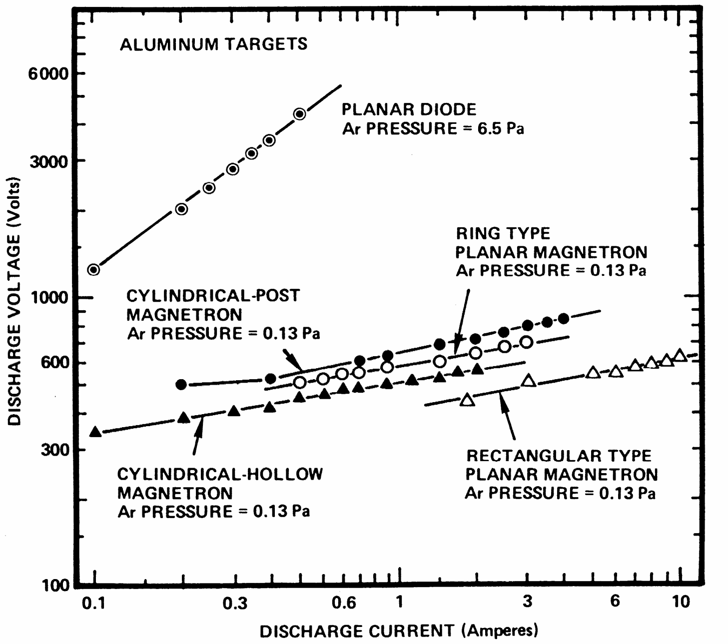


Fig. 2.26.: Current voltage characteristics of different sputtering systems [2, p. 201]

Film Thickness Uniformity

For various applications in thin film technology a high film thickness uniformity over the whole extension of the substrate is paramount. Due to the finite size of the target there may, however, be thickness gradients on large or complexly shaped substrates. As mentioned before in the case of evaporation, special constructions like e. g. moveable substrate holders or optimized distances between target and substate can provide thickness uniformities better than ±2%.

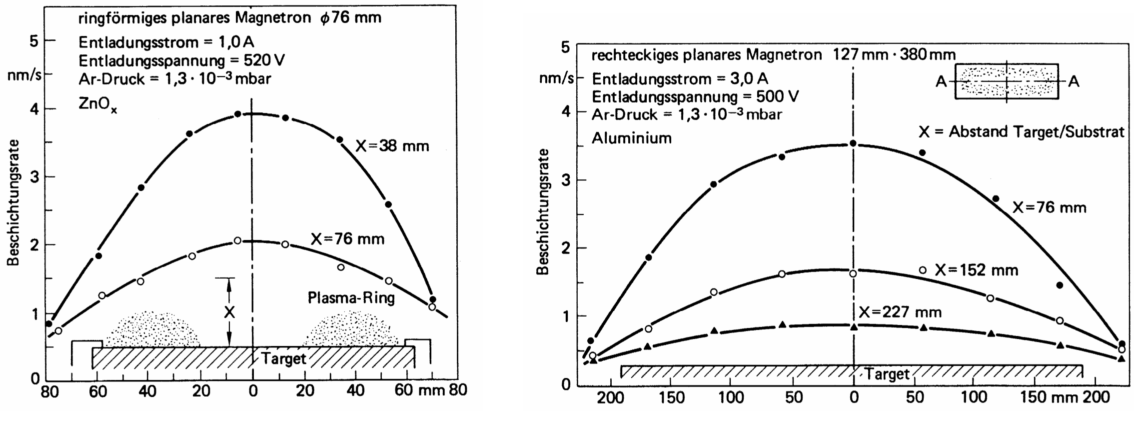


Abb. 2.27.: Schichtdickenverteilung für Planar-Magnetrons [3, p. 125]

Sputter Targets

For basically each kind of sputtering geometry a large choice of materials (pure elements, alloys and compounds) is commercially available as sputtering targets in different grades of purity.

Targets can be manufactured by:

... common melting and casting

... vacuum melting

... powder metallurgical processes

... coating (e. g. thermal spraying)

2.1.3. Ion Plating

2.1.3.1. Introduction

Ion plating is a vacuum based deposition process during which the substrate surface and/or the growing film is subjected to an intensive bombardement of particles. The particles have sufficient energy to influence the interface between substrate and coating and the growing film (as compared to the situation without particle bombardment).

Ion plating consists of two fundamental phases:

1. Sputter cleaning of the substrate surface

2. Coating under the influence of energetic ions

After evacuating the deposition chamber below 10^{-3} Pa (10^{-5} mbar) an inert gas (mostly Ar) is introduced at reduced pumping speed. At approx. 5 Pa a glow discharge is ignited at the substate by a negative high voltage (see Fig. 2.28.) The substrate is cleaned by the ion bombardement. After this phase the substrate is coated in the presence of the discharge. Process parameters have to be adjusted in a way which leaves the deposition rate at the substrate higher than the resputtring rate.

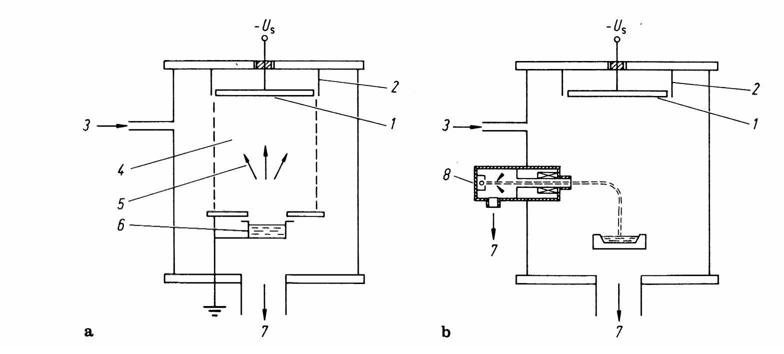


Fig. 2.28.: Ion plating set-ups: 1 Substrate holder; 2 screen (grounded); 3 gas inlet; 4 plasma; 5 vapor beam; 6 evaporator; 7 vacuum system; 8 electron gun [1, p. 122]

Since approximatly 1980 HSS tools for machining, cutting and forming are coated with hard materials (TiN, TiC). For tis purpose mostly ion plating processes are employed. Apart from functional coatings also decorative films gain importance: gold tinted extremely hard, abrasion and corrosion resistant TiN-films are attractive coatings for commodities like watch casings, eyeglass frames, jewellery etc.

2.1.3.2. Influence of Particle Bombardement on Interface and Film Properties

Sputtering: Particle bombardement first leads to the desorption of loosely bound (<1eV) adsorbates. Then contaminant films and reaction layers as e. g. oxides with thicknesses of 1 - 10 nm are removed and finally the substrate material is sputtered. Additionally, during the coating process the coating material is partially removed by sputtering.

Temperature increase: If less than 25 eV are transferred to a lattice atom this energy is converted into phonon oscillations and leads to a temperature increase. This process is valid for most of the impinging particles.

Lattice distortion: Collision cascades within the substrate and the growing film lead to a high defect concentration which can trigger amprphization in extreme cases. For instance, at an energy transfer to a lattice atom of more than 25 eV a point defect is created.

Changes in surface topography: Because of different sputter yields in the presence of more than one component canges in surface topography may occur (see e. g. cone formation, section 2.1.2.).

Changes in chemical composition: Because of different sputter yields and temperature induced diffusion changes in composition may occur.

Implantation of gas atoms: After losing it's energy and charge a neutralized ion may be incorporated into the film as a defect.

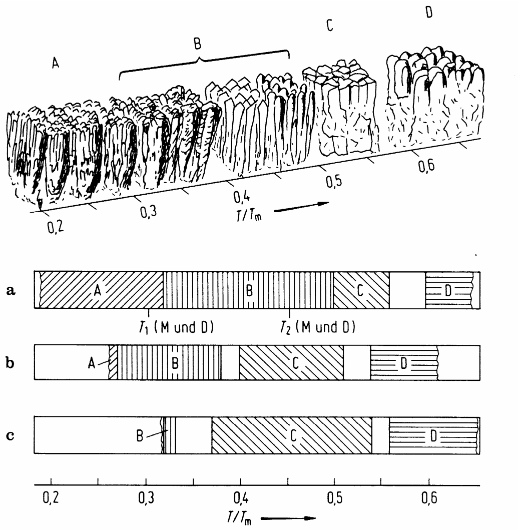


Fig. 2.29.: Influence of the substrate temperature *T* and the bias voltage U_b at the substrate on the film structure of Ti. **a:** U_b = 0; **b:** U_b = -5kV; **c:** U_b = -10kV; Argon-pressure: 2,7Pa; [1, p. 24]

Formation of the interface: When the vapor source is put into operation also neutral, excited and ionized vapor particles hit the substrate in addition to the gas particles. Processes like implantation of energetic vapor particles, recoil implantation of surface atoms and backscattering of sputtered substrate or coating particles lead to an intermixing between substrate material and coating material. The diffusion layer formed by this process is responsible for the excellent adhesion of ion plated coatings.

Formation of nuclei: A surface which is bombarded by energetic particles exhibits a higher number of positions with increased binding energy (=nucleation sites) because of its distorted lattice structure when compared to an unbombarded surface. In comparison to evaporation a higher nucleation density and an earlier coalescence (growing together) of nuclei and islands to a continous film is observed. Also the increased nucleus density is responsible for the better adhesion.

Influences on the film structure: As mentioned before the ion bombardement generates point defects and increases the nucleation density on the substrate. Also the energy transfer from the energetic ions increases the transient mobility of adsorbed atoms. This transient mobility cannot be explained by temperature increase alone. Compared to the situation without ion bombardement a film structure of small, densly packed crystallites is formed. In Fig. 2.29. a schematic of film structures achieved for different bias voltages is given.

The dense structure of evaporated films at high substrate temperature differs from the microstructure of ion plated films: in the case of evaporation at high substrate temperature the structure is a result of recrystallization and grain growth triggered by volume diffusion. In the case of ion plating volume diffusion is less important due to the relatively lower substrate temperature. The intensive ion bombardement, on the other hand, continuously forms new nuclei which leads to the fine grained, dense structure.

Incorporation of foreign atoms: During all deposition processes foreign atoms are incorporated into the film either as impurity or intentionally to achieve special film properties. In the case of ion plating especially the formation of carbides and nitrides has found a broad range of application.

2.1.3.3. Practical Aspects of Ion Plating

As for sputtering technology also ion plating allows the operation of nearly any possible combination of partial processes in reactive mode. A few ion plating set-ups shall be discussed as special examples taken from the large possible scope of ion plating plants:

Ion plating with DC-glow discharge: A schematic of this simplest set-up of an ion plating plant is given in Fig. 2.28.

Ion plating with separate ion source: Here, vapor and ion currents are produced in separate regions (see Fig 2.30a.).

Ion plating with RF discharge: (see Fig 2.30b.)

Ion plating with low voltage arc discharge: This process which is used for the coating of tools with high quality hard material films on an industrial scale is displayed in Fig. 2.31. From a low votage arc discharge (6) an electron beam (11, U=70V; I=140A) is extracted which hits the material to be evaporated with a power density of approx. 10 kWcm^{-2}. The resulting vapor is ionized to approx. 50% and ion currents of 15 - 30 A flow to the substrate (1) at a bias voltage of -200V.

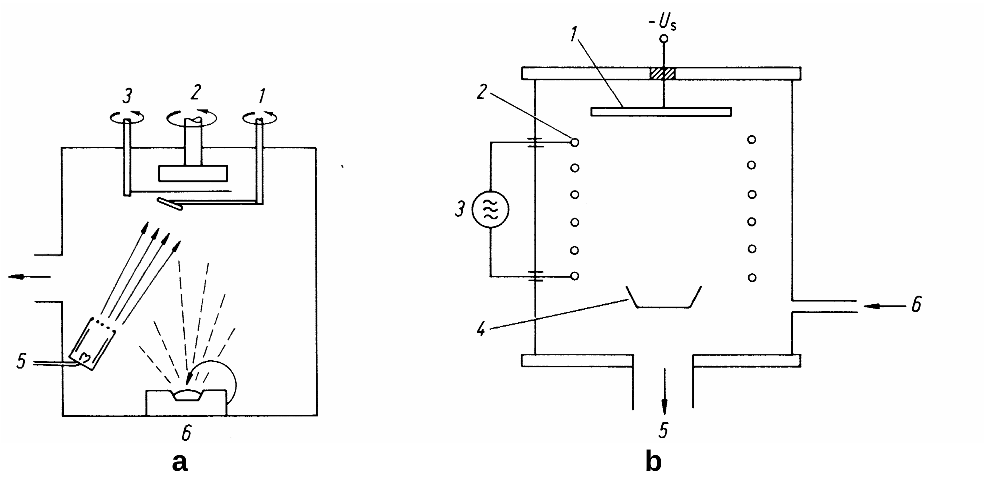


Fig. 2.30.: **a:** Ion plating with separate ion source: **1** ion probe, **2** substrate holder, **3** orifice, **4** pumping system, **5** ion source, **6** evaporator
b: Ion plating with RF discharge: **1** substrate holder, **2** RF-coil, **3** RF-generator, **4** evaporator, **5** pumping system, **6** gas inlet [1, p. 127]

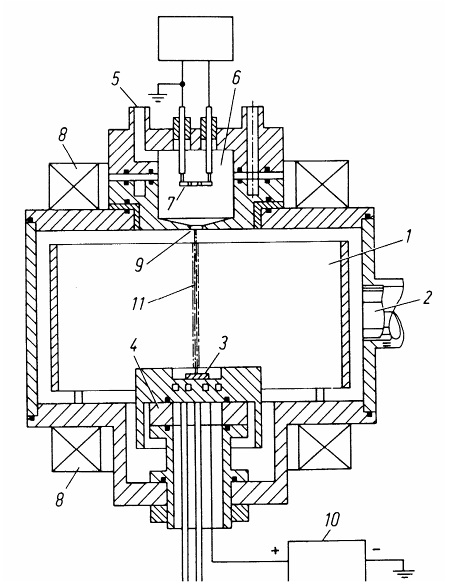


Fig. 2.31.: Ion plating with low voltage arc discharge: **1** substrate holder, **2** pumping system, **3** anode (evaporated material), **4** water cooled crucible, **5** gas inlet, **6** low voltage arc discharge, **7** glow cathode, **8** magnet coil, **9** electron-extraction orifice, **10** power supply, **11** electron beam [1, p. 135]

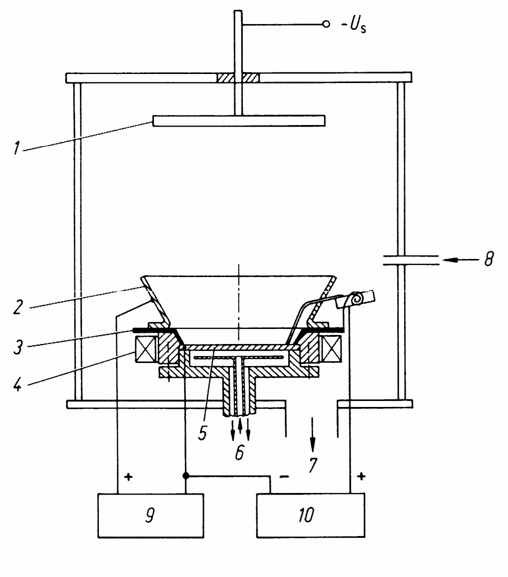


Fig. 2.32.: Ion plating with thermionic arc (Arc-technique)
1 substrate holder, **2** anode, **3** insulator, **4** magnet coil, **5** cathode, **6** cooling water, **7** pumping system, **8** gas inlet, **9** power supply, **10** arc generator
[1, p. 136]

Ion plating with thermionic arc: An arc with constantly moving arc spots is ignited between the material to be evaporated (cathode) and an anode. Because of the high energy densitiy (10^7Wcm^{-2}) within the arc spot material is evaporated in this region. The ionization degree of the evaporated material can reach up to100%, but also significant droplet formation is observed. Despite this effect this method has found wide acceptance (see Fig. 2.32)

2.2. CVD (Chemical Vapor Deposition)

CVD (Chemical Vapor Deposition)-processes use chemical reactions in the vapor phase which proceed at pressures between 0,01 and 1 bar and at temperatures from 200°C to 2000°C under the presence of thermal and/or radiation energy. To form a CVD coating the respective process has to form a solid product along with a volatile by product.

The gaseous precursor components are introduced into the reaction chamber together with an inert carrier gas (mostly Ar). In the chamber the solid is formed either by a heterogenous reaction as a coating and or as a powder if a homogenous reaction is involved.

Four basic types of reaction can be distinguished:

1. Chemosynthesis (Reactions with gases)
   [z.B.: $TiCl_4(g) + 1/2N_2(g) + 2H_2(g) \xrightarrow[\text{10-900mbar}]{\text{600-1000°C}} TiN(s) + 4HCl(g)$]

2. Pyrolysis (Thermal decomposition)
   [z.B.: $SiH_4(g) \overset{<650°C}{\leftrightarrow} Si(s) + 2H_2(g)$]

3. Disproportionation
   [z.B.: $2GeJ_2(g) \Longleftrightarrow Ge(s) + GeJ_4(g)$]

4. Photopolymerization

CVD processes are used for manufacturing coatings of refractory and other metals, of semiconductors, of borides, carbides and nitrides as well as of oxides. The advantage that many materials can be deposited close to their theoretical density with high purity, good adhesion and high thickness uniformity is counteracted by the fact that no chemical reaction may be existent for selected materials, that the substrate has to withstand (mostly) high reaction temperatures and that it has to be chemically stable against the presence of the reaction partners.

Fig 2.33. shows a typical reactor which is used for the deposition of TiN- and TiC-coatings on tools.

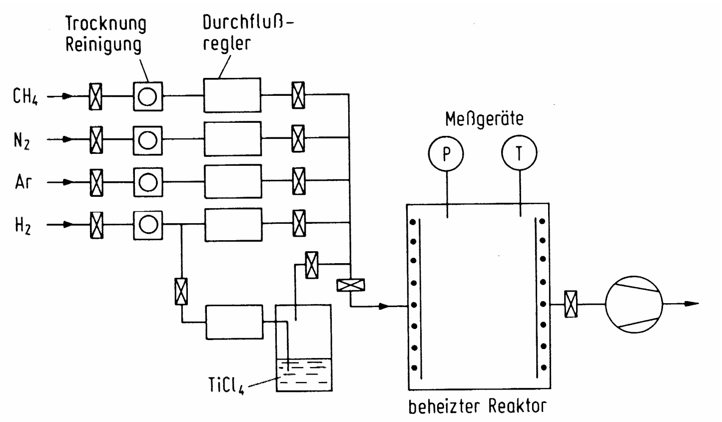


Fig. 2.33.: CVD-plant (reactor) for the production of TiN or TiC-coatings [1, p. 147]

Prior to the deposition process the reaction chamber is cleaned by purging with inert gas. To increase the coating adhesion often Hydrogen is flowed over the substrates.

The reaction gas is flowing through the chamber in a laminar current. A turbulent current would yield higher deposition rates but leads to a deterior utilization of the reaction partners because of high flow rates and to an ununiform film thickness. Coating uniformity can also be achieved by substrate movement and/or flow mechanical optimization.

Substrate heating can be accomplished by radation heating, by resistive heating or by inductive heating of the substrates or of the substrate holder.

2.2.1. PACVD (Plasma Assisted Chemical Vapor Deposition)

2.2.1.1. Introduction

PACVD is a method for the deposition of solid films from a precursor gas which is supplied with energy by a plasma. The gas molecules which are intended to be partners in the reaction can be dissociated in the plasma, radicals can be formed and/or excited states are produced. All these reactive species undergo chemical reactions at temperatures much lower than expected from thermodynamics. Therefore thermally more sensitive substrates can be coated by PACVD as compared to conventional CVD. Additionally, cooling to room temperature produces less thermal stress due to the lower temperature difference. Prior or during deposition the substrates can be cleaned by ion bombardement.

Compared to the plasmas used in sputtering and ion plating the following differences exist:

1. The multiatomic molecules used in PACVD have lower ionization potentials than inert gases (e. g. Argon).

2. Many reactive gases, especially Halogens can easily catch electrons.

3. Generally the pressures are higher (10 - 100 Pa as opposed <1Pa for sputtering). Therefore the mean free path of particles within the plasma is significantly lower.

Fig. 2.34. shows a comparison of the deposition rates of Si on Si(111) for CVD and PACVD in dependence on the substrate temperature *T* at a pressure of *p* = 533 Pa.

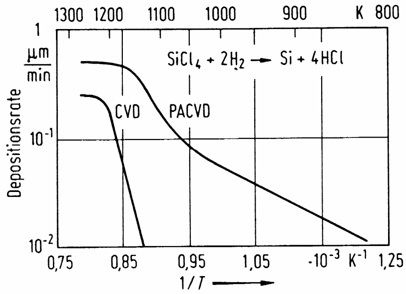


Fig. 2.34.: Comparison CVD-PACVD [1, p.163]

The plasma used in PACVD can be generated either by DC voltage or by RF voltage. DC plasmas are mostly produced in a hollow cathode magnetron like assembly. RF plasmas allow the deposition on electrically insulating substrates or of insulating materials and have therefore found high acceptance in industrial manufacturing. The RF energy can be coupled into the chamber capacitively or inductively, either from outside or inside of the chamber.

2.2.1.2. Praktcal Aspects of PACVD

Fig. 2.35. shows a reactor in the shape of a planar diode arrangement for the production of semiconductor films. The gas flow is directed from the periphery of the electrodes along the surface of the substrates and exits via the center of the chamber. The rarification of reactive substances within the way of the gas along the substrates is compensated by the simultaneous decrease in flow velocity and gas current density. This leads to a good uniformity in deposition rate.

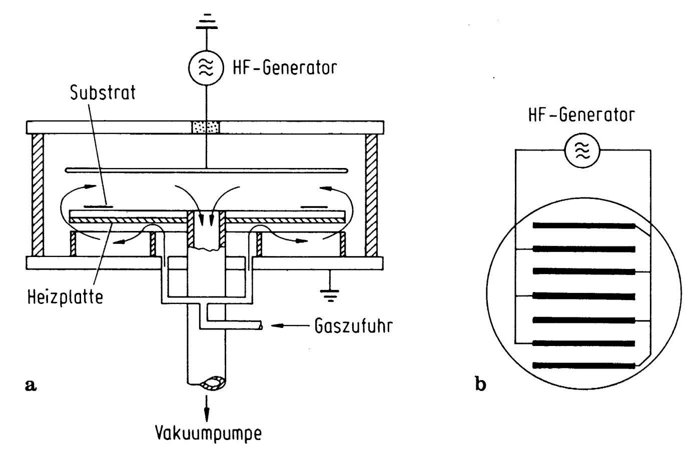


Fig. 2.35.: Reactor for a PACVD-process [1, p. 169]

The pressures during deposition are in the region of 10 to some 100 Pa. The pumpung speed of the vacuum pumps is approx. 100 - 500 m^3/h. Magnetron assemblies allow coating at pressures below 1 Pa. Similar to the CVD process gas supply systems, pumping systems and exhaust assemblies are necessary because the used gases may be toxic, flammable in air or self igniting. The dwell time of the reaction partners within the chamber is usually 1 s. The mass transport to the substrate is based on diffusion for high pressures (100 Pa) and on molecular flow at low (1 Pa) pressures.

2.3. Other Coating Methods

2.3.1. Plasmapolymerisation

Plasma polymerization is a process in which organic or anorganic polymerisates (as opposed to conventional polymers) are condensed from a monomer vapor with the aid of ions, electrons and photons generated in a gas discharge. Plasma polymerization is no conventional polymerization process where a polymer is formed by cross linking monomer molecules as e. g. the formation of Polyethylene from Ethylene molecules. In Plasma polymerization the precursor molecules are not conserved but precursor fragments serve as the source for building the polymerisate.

The polymerization process follows the steps below:

1. Reactions in the gas phase: reactive species are formed as excited and ionzed molecules or molecule fragments. These fragments link to chains, clusters and free radicals.

2. The species formed in phase 1 as well as intact monomer molecules are adsorbed at the substrate surface.

3. Particles and fragments are polymerized at the substrate surface.

A quanitative description of all involved mechanisms mostly yields no satisfactory correspondence to the experiment. Nonetheless it is possible to form polymer coatings reproducibly with well defined properties, as high density, excellent adhesion and absence of pinholes. Since in most cases insulating layers are deposited, RF discharges are used. Reactors are operated at pressures of 10 - 10^3 Pa. The gaseous monomer is frequently mixed with a carrier gas (e. g. Ar). This mixture laminarily flows through the chamber (see Fig. 2.36). Deposition rates range from 0,3 to 100 µmh^{-1}.

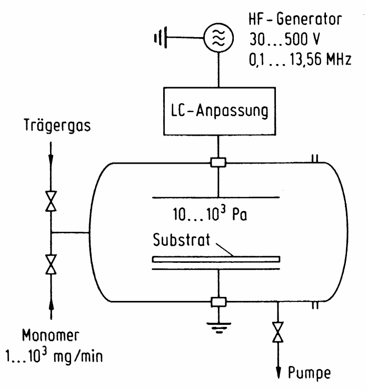


Fig. 2.36.: Plasmapolymerization plant [1, p. 179]

Polymer films are used in the following fields: membranes for inverse osmosis (desalination of sea water), optical coatings (protective and anti reflex coatings on polymers), electronics (protective coatings for sensitive devices), adhesion promoters on polymers, bio medicine (coatings on implants), dielectrics in microelectronic devices.

2.3.2. Electrochemical and Chemical Deposition

2.3.2.1. Introduction

Electrochemical and chemical processes used for the deposition of coatings can be devided into galvanics, anodic oxidation and chemically-reductive (electroless) deposition:

Galvanics

Galvanics comprises the deposition of metals and alloys on a metallic substrate in a suitable electrolyte by current flow. The substrate serves as the cathode. Exposed points and edges of the substrate experience higher deposition rates than holes (see Fig. 2.37a.) due to the tip effect (higher current density due to a larger electric field). A uniform coating thickness can be achieved by a suitable arrangement of anodes and shields.

Anodic Oxidation

The electrochemical formation of coatings by current flow in a suitable electrolyte with the substrate serving as anode is termed anodic oxidation ("anodization"). The coating uniformity is better than in galvanically deposited coatings but still edges and holes experience lower deposition rates (see Fig. 2.37b.).

Chemically Reductive Deposition

In this case the deposition happens without an exterior current source ("electroless"). The electrons necessary for the deposition of the metal from the electrolyte are provided by suitable reducing agents. Because of the absence of an exterior current source, which would lead to ununiform current densities, the coating thickness even on edges and in holes is very uniform (see Fig. 2.37c). Therefore it is possible to coat parts with complex geometries very uniformly.

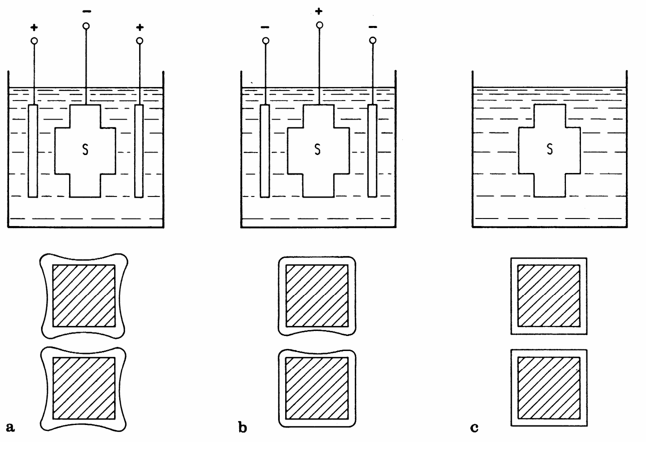


Abb. 2.37.: a galvanics; **b** anodic oxidation; **c** chemically reductive deposition;
Upper row: experimental set-up;
Lower row: film thickness distribution at edges and holes (schematic)
[1, p. 187]

2.3.2.2. Fundamentals of Galvanics

Electrochemical reaction/Faraday Law

The decomposition of an electrolyte with the help of an electrical current can be considered as a redox reaction which happens at the electrodes of the electrochemical cell. The electrodes are connected to a DC source. The positive metal ions which are solved in the electrolyte M^{n+} are supplied with *n* electrons by the electrical current. The metal ion is discharged and condenses at the cathode: $M^{n+} + ne \rightarrow M$.

The quantity of material transformed *m* and the quantity of carge *q* are connected by the Faraday law:

$$m = \frac{\nu q M}{nF} \qquad (2.25)$$

with
m = mass of deposited material [kg]
M = molar mass of deposited metal ions [kgkmol^{-1}]
n = charge number of ions
F = Faraday constant = $N_A.e$ = 9,65.10^7 [Askmol^{-1}]
q = charge quantity [As]
ν = yield factor [<1]

Electrochemical Double Layer

If a metal *M* is immersed into a solution containing M^{n+} ions small quantities of M^{n+} ions are transferred from the metal to the solution until a dynamic equilibrium $M \leftrightarrow M^{n+} + ne$ is established. The metal is therefore charged negatively when compared to the solution and the solution gains positive excess charge. Theis leads to a potential difference between metal and solution, the so called electrode potential, which is characteristic for the metal and depends on the concentration of metal ions in the solution and the temperature. It can be calculated by Nernsts eqation.

The surplus charges of opposite polarity which are present on both sides of the phase boundary form an electrochemical double layer of about 1 nm thickness. The space between the two layers contains oriented H_2O diploes and the surface at the side of the solution (the so called Helmholtz surface) contains hydratized metal ions. The concentration of excess ions decays exponentially and approaches zero within the solution. This decay region is called diffuse region of the double layer.

Electrode Polarization

Each electrode exhibits an equilibrium electrode potential towards the electrolyte if no material or energy is transformed. If, on the other hand, current is flowing the voltage between the electrodes has to be higher then the additive value of the electrode potentials to sustain the current flow. This excess voltage is called electrode polarization and results from the inhibition of the partial processes which combinedly form the electrochemical reaction.

In the case of cathodic deposition the metal ions have to

1. reach the double layer from the electrolyte, i. e. they have to pass the diffuse region and have to be incorporated into the Helmholtz surface and

2. finish the charge transfer to the cathode, be discharged subsequently and be incorporated into the lattice of the growing film finally.

2.3.2.3. Practical Aspects

Elektrolytes

In most cases the electrolyte is an aqueous solution which can be alcalic-cyanidic, alcalic-cyanide free or acidic and which contains the metal to be deposited as a salt (e. g. Cu from Cu-sulfate). Recently the interst in the deposition of metals from the melt also has increased. The number of accessible electrolytes is approx. 1000 where approx. 300 serve for the manufacturing of noble metal and alloy films. In many cases, mostly organic or colloidal, additives are added in concentrations of mg to g per dm^3. These additives can lead to an increase in film brightness, to a reduction of the grain size or can decrease the residual stress in the deposited films.

Current Shape

Regularily DC voltage is employed but also the application of other current shapes such as DC with superimposed AC, periodically reversed DC or pulsed DC (Hz to kHz) gains importance. The current profile influences the deposition rate, the microstructure and other film properties. The formation of amorphous Ni-alloys with thicknesses of 30 - 300µm coud be achieved by a so called "Pulse Plating" process. These films have interesting magnetic, mechanic and catalytic properties combined with good corrosion resistance.

Mechanical Agitation

The material transport can be enhanced by the agitation of the bath. The electrolyte may be agitated by:

1. Ultrasound with frequencies up to 30 kHz and power densities up to 0,5 Wcm^{-2}

2. intensive electrolyte currents generated by nozzles directed towards the cathode.

3. movement of the substrate with high velocity.

Pre- and Post Processing

The substrates have to be mechanically, chemically and/or electrochemically cleaned prior to deposition. Affter deposition the coated parts have to be rinsed and neutralized to avoid negative influences on the material of the coating. In other cases a stabilization of the film properties may be necessary (e. g. conservation of the brightness of Ag films or of the corrosion resistance of Zn or Cd films by the so-called chromatizing in a solution of chromic acid.).

2.3.2.4. Applications

Chromium Coatings

Important applications of Cr coatings are related to the fields of: combustion engines (piston rings, pistons, cylinder linings), mechanical engineering, aerospace industry, printing and paper industry (rolls in paper mills). The so called hard chrome plating is used for decorative coatings with thicknesses of 0,2 - 2 µm and for engineering purposes with thicknesses from 20 - 500 µm. The formation of thick coatings is limited by residual stresses.

Copper Coatings

Cu coatings are used for electrically conductive coatings with thicknesses from 10 - 100 µm.

Nickel-Coatings

Ni coatings are used for decorative purposes with thicknesses from 10 - 50 µm. Coatings with a thickness from 0,2 - 2 mm are used on parts which are subjected to severe corrosion.

Zink- and Cadmium-Coatings

They are used in corrosion protection. Approximately 40% of the world production of Zn is used for the corrosion protection of steel.

Tin- and Tin-Lead-Coatings

They are deposited on steel, Cu and Cu alloys. Steel sheets coated with 0,5 - 1,5 µm Sn are used for manufacturing tin cans. Steel sheets with a 5 - 20 µm Sn coating deposited on a Cu interlayer which serves as diffusion barrier exhibit a surface which can be soldered and are also used for manufacturing corrosion resistant food containers. Lead bronze coatings (the binary system Sn10-Pb90 or the ternary system Sn15-Pb65-Cu20) are used as plain bearing coatings due to their resistance against wear and fatigue.

Lead-Coatings

Pb coatings can be deposited with thicknesses from 10 - 500 µm. They are used in chemical engineering due to ther resistance against certain chemicals and also for manufacturing accumulators.

Noble Metal and Noble Metal Alloy Coatings

The metals Au, Pt, Pd and Rh serve as protective materials against high temperature corrosion in aerospace devices and as electronic contact materials. Au, Ag and Pt also find applications in the jewellery industry as materials for noble metal coatings.

2.3.2.5. Fundamentals of Anodization

Anodic oxidation is an electrochemical conversion process in which the surface of a body serving as anode is transformed to one if tis chemical compounds by immersion into a suitable electrolyte. In acids and bases oxides are formed and in NH_3 nitrides. The industrial applications are mainly directed towards the anodization of Al and its alloys. In addition Ta is anodized for the construction of thin film condensers and anodized Nb is used for applications in superconductivity.

Al which was previously cleaned and etched reacts as anode in a suitable electrolyte with oxygen which is produced by the flowing current. Al_2O_3 is formed in a certain quantity according to Faradays law following the chemical reaction $2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3 + 1700kJ$. Because Al_2O_3 with a band gap of 7 eV between valence and conduction band is an insulator only a small electron conduction can be achieved. Therefore one would expect the oxide growth to come to a halt in a short time after only a thin film has formed. But this is not observed since the high electrical field strength of approx. 10^9 Vm^{-1} triggers ion conduction in the porous oxide coating. Al, O, H and impurity ions take part in this process. So a charge and mass transport through the film takes place and the oxide is growing at the expense of the underlying Al which serves as substrate.

The achieavable oxide thickness *d* is proportional to the anode potential *U* according to the relation *d/U* approx. 1,3nm/V. Therefore, at U = 100 V approx. 0,13 µm oxide can be produced basically independent on the concentration or the temperature of the electrolyte.

2.3.2.6. Fundamentals of Chemical-Reductive Deposition

This method is an immersion technique in which the substrate is dipped into a solution and is coated by a chemical reaction. While in electrochemical processes the metal ions are reduced by the incorporation of electrons from an external current, chemical reactive deposition does not involve any external current. Therefore electrons have to be provided from the electronic system of a reducing agent. The reaction does not take place homogenously in the whole space filled by the electrolyte but only on catalytic metal surfaces. Depositing material on insulating surfaces which are not catalytically active requires a so called activation. This activation can be accomplished by pre-treatment with $SnCl_2$ or $PdCl_2$ soutions from which catalytically active Pd or Sn nuclei are deposited on the surface.

The advantages of this electroless, autocatalytic deposition process as compared to galvanics are: coatings exhibit high thickness uniformity and follow even complex contours, low porosity, which means high corrosion resistance, is achieved and the possibility to coat insulators is given. Disadvantages are the low deposition rates (a factor of 10 as compared to galvanics) and the higher costs which result from the reducing agents which may be quite expensive.

2.3.3. Thermal Spraying

2.3.3.1. Introduction

Thermal spraying methods allow the coating of components with metals, ceramics, cermets and other special materials. The coating material is supplied as powder or wire and is molten within a heat source of high power density. Fine droplets of the completely or partially molten material are accelerated towards the substrate by suitable means. The substrate is kept at temperatures below 200°C and is roughned by sand or glass blasting to increase adhesion.

Upon impact on the surface the droplets are flattened and cooled by heat transfer to the substrate. Usually no metallurgical interconnection (intermixing by diffusion) is observed even if the combination coating/substrate has the inclination do interdiffuse or to weld. The coatibg adheres locally by mechanical interlocking and chemical or Van der Waals bonding. The excellent adhesion is caused by the shrinking of the cooling droplets onto the roughness peaks of the surface.

The advantages of thermal spraying are:

1. Compared to PVD and CVD methods the deposition rates are higher by two orders of magnitude. Coating Thicknesses of some mm can readily be achieved.

2. The process is suitable for mass production, but also for coating single components. Apart from vacuum plasma spraying parts can be coated in the lab as well as in the field (e. g. dredger buckets).

3. Since the substrates are not highly thermally loaded also Al, Sn or Zn based alloys as well as some polymers can be coated without shape change, oxidation or changes in microstructure.

4. The deposition of coatings consisting of metals, ceramics cermets, hard materials as well as of selected polymers is possible.

Disadvantages which are present especially for flame, arc and plasma spraying are:

1. The coatings are very porous and can only be densified by certain post treatments e. g. (re-melting or sealing).

2. The strength of the coatings is lower than the strength of the bulk material.

3. Sometimes there may be low adhesion strength.

These disadvantages are not relevant for detonation spraying and vacuum plasma spraying.

2.3.3.2. Practical Aspects of Thermal Spraying

Flame Spraying

A combustion gas/oxygen flame acts as heat source. Metals (in the shape of wires or powders) and selected ceramic materials are molten and transported to the substrate by a compressed air stream (see Fig. 2.38.).

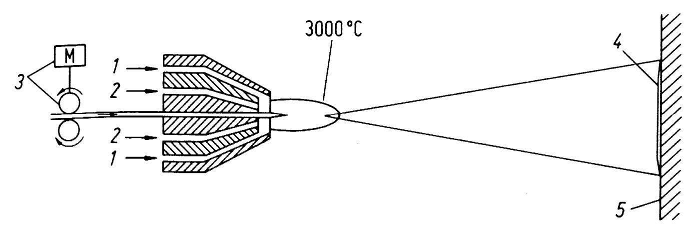


Fig. 2.38.: Flame spraying: **1** compressed air, **2** Acetylene-Oxygen mixture, **3** wire feeder, **4** coating, **5** component (*T*<250°C) [1, p. 217]

Detonation Spraying

This method works with a detonation gun which consists of a water cooled pipe (approx. 1 m length and 25 mm diameter) into which a powder mixture and a Ethine/Oxygen mixture is introduced. After ignition a detonation wave is generated which accelerates the powder to a velocity of approx. 800 ms^{-1}. During this phase the powder is also heated to its melting point (see Fig. 2.39.).

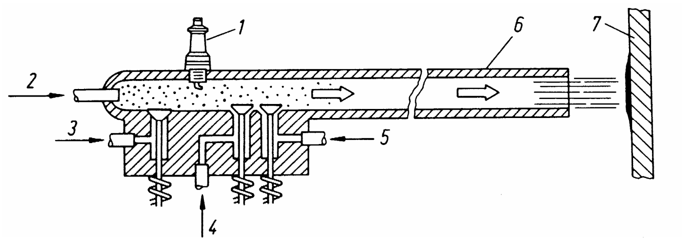


Fig. 2.39.: Detonation spraying: **1** spatk plug, **2** powder, **3** Nitrogen, **4** Ethine (Acetylene), **5** Oxygen, **6** pipe, **7** component [1, p. 218]

Vacuum Plasma Spraying

Coating Materials with a high affinity to O_2 and N_2 such as Ti, Ta, Nb etc. form coatings of poor quality if sprayed under air (oxide inclusions, porous structure, low adhesion). These troubles can be circumvented if the plasma spray process is performed under vacuum (approx. 80 mbar, see Fig. 2.40).

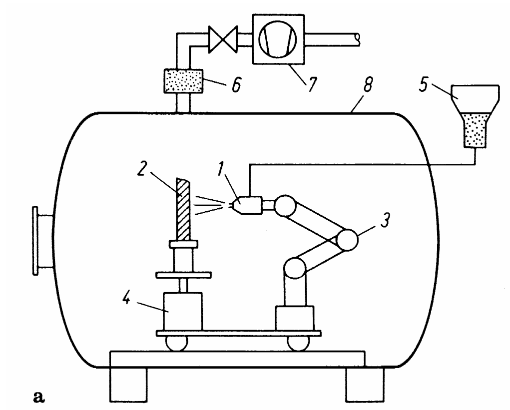


Fig. 2.40.: Vacuum plasma spraying: **1** plasma torch, **2** components, **3** robot arm, **4** turntable, **5** powder feed, **6** filter, **7** vacuum pump, **8** vacuum chamber [1, p. 223]

Spraying Materials

Materials suitable for spraying have to be meltable. In addition it has to be possible to heat them in the liquid state without risking decomposition or chemical reactions (oxidation). Also the material has to be available in a suitable shape (i. e. as flexible wire or as easily trickling powder of a defined grain size).

Powders for plasma and detonation spraying have grain sizes of 5 to 50 µm. Flame spraying allows for coarser powders. At present more than 100 different spraying materials are commercially easily available. Regarding pure materials especially refractory metals (e. g. Ti, V, W) are used. Concerning alloys a focus can be put on the so called "Super Alloys" as e. g. $CoCrAlY/ZrO_2Y_2O_3$. Hard materials are deposited as nitrides, carbides and silicides. Apart from oxide ceramics (e. g. Al_2O_3, ZrO_2) also pseudo alloys (e. g. a mixture of Cu and W) and composites (e. g. WC/Ni) are used.

Coating structure

If they are not subjected to thermal treatment the coatings exhibit a lamellar structure. The lamellae are constituted from thin lenticular structures with a thickness of approx. 5 µm and a diameter of 10 to 60 µm. They form during the impact of the droplets. The high cooling rate to which the particles are subjected may lead to te amorphization of the material.

Reactions which occur during the transport of the droplets from the source to the substrate may influence the chemical composition of the coating. Selective evaporation of some volatile components can occur. The formation of oxides, nitrides and hydrides has also to be taken into account.

The packing density of the films is 70 - 90% for flame spraying, 80 - 95% for plasma spraying in air and above 99% for detonation spraying and vacuum plasma spraying. Nonetheless, some applications may even require a certain porosity (e. g. bearings, where pores may act as lubricant reservoirs).

Surface Constitution

All coatings produced by thermal spraying exhibit a high surface roughness of 5 to 30 µm which can be reduced to values below 0,2 µm by grinding and polishing if the application requires this. No post treatment is necessary for flame sprayed Al coatings on steel constructions which serve as corrosion protection because they make an excellent primer for impregnating lacquers.

Adhesion Strength

The adhesion mechanism for thermally untreated sprayed coatings is mostly considered to be the mechanical interlocking of the film with the roughness peaks generated by sand blasting. If, on the other hand, refractory metals with high melting point and a high heat capacity are condensed on steel, Ni or Cu then there also a metallurgical bond by diffusion may be formed. The highest adhesion values are achieved for vacuum plasma spraying due to the possibility of cleaning the substrate surface by ion bombardement prior to deposition.

2.3.3.3. Applications

Thermal spraying is employed

for manufacturing protective layers against wear, corrosion and heat.

for producing surfaces with special properties (e. g. electrical insulation).

for special applications (e. g. for manufacturing hollow bodies made of refractory metals on soluble cores).

for repairing used or faulty components or for renewing eroded coatings (e. g. dredger buckets).

2.3.4. Build up Welding and Cladding

2.3.4.1. Introduction

Build up welding is the coating of metallic components by welding based methods. It can be sub-devided according to the type of heat source used - flame, arc, plasma beam or Joule heat. Using these heat sources the coating material as well as a thin surface layer of the substrate are molten so that a well adhering, pore free coating is generated by diffusion and intermixing.

The melting of the substrate surface and the partial intermixing with the coating material is the main difference of build up welding to thermal spraying.

Cladding is the joining of two or more relatively thick metal layers (>50 µm) by the exposure to heat and/or pressure. There are the following differences to build up welding:

1. The coating material is fed as compact layer in the case of cladding while it is introduced as powder or molten droplets for build up welding.

2. Energy is provided as thermal energy, mechanical energy (of a roll, press or explosion) or as reaction enthalpy of a chemical reaction in the case of cladding. Build up welding, on the other hand, only uses heat sources such as flames, arcs, plasmas or Joule heat.

Both methods have in common that relatively thick coatings up to 10 mm can be produced and that the layers are bonded to the substrate by a welded joint.

2.3.4.2. Practical Aspects

To achieve film thicknesses of 1 mm and more the energy source (flame, arc or plasma torch) is moved over the substrate surface in an oscillatory motion. The coating is applied in several layers. The coating materials which consist of alloys or composites are supplied in the form of rods, wires, bands, powders or pastes.

Applications comprise the coating and repair of components subjected to wear and corrosion as well as plating in the field of half finished products.

In Figs. 2.41. to 2.44. the most important methods of build up welding are displayed schematically.

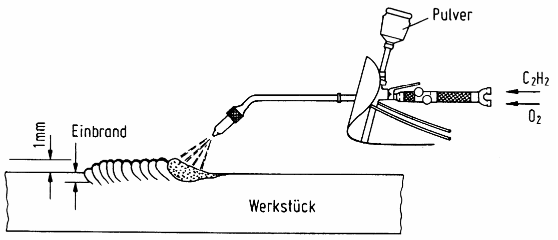


Fig. 2.41.: Flame build up welding: gas-powder-process [1, p. 244]

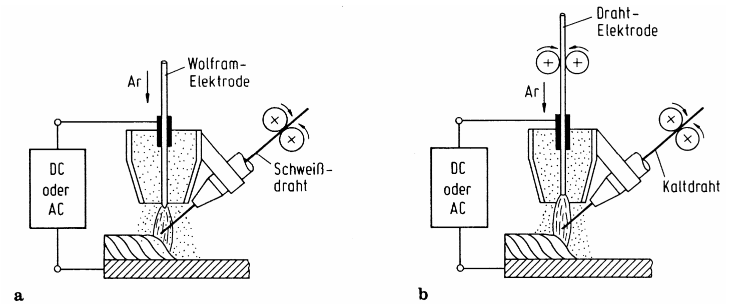


Fig. 2.42.: Arc build up welding: **a** Tungsten-inert gas (WIG)-method
b Metal-inert gas (MIG)-method [1, p. 244]

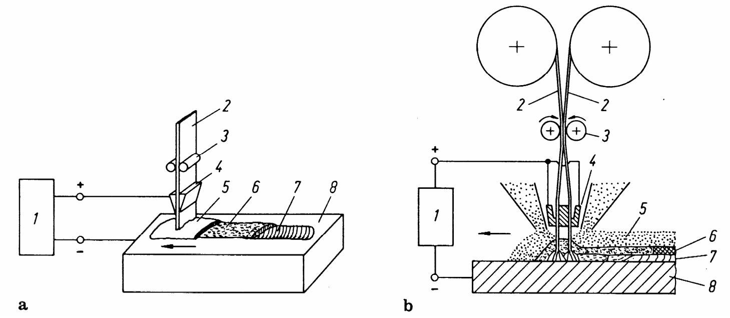


Fig. 2.43.: Under powder (UP) build up welding: **a** with band electrode; **b** with double band;
1 current source, **2** band electrode, **3** band feed, **4** conbtact clamps,
5 powder bed, **6** cinder, **7** coating, **8** substrate [1, p. 246]

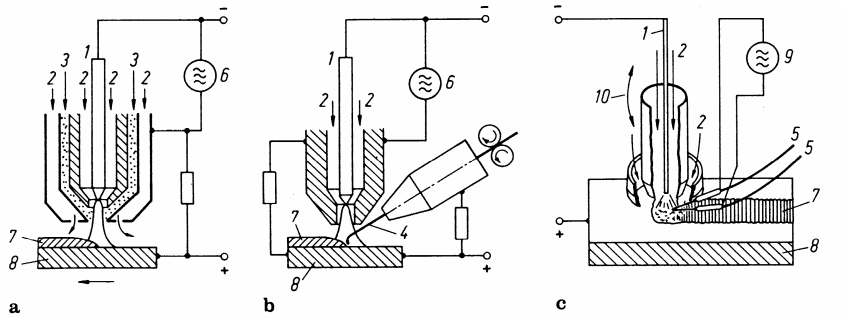


Fig. 2.44.: Plasma build up welding: **a** with powder; **b** with wire, plasma-MIG-method,
c plasma hot wire method; **1** tungsten cathode, **2** argon,
3 welding powder, **4** welding wire, **5** hot wire, **6** RF-generator for ignition,
7 coating, **8** substrate, **9** hot wire current source, **10** oscillatory motion [1, p. 247]

In Figs 2.45. and 2.46. two important plating methods are displayed schematically.

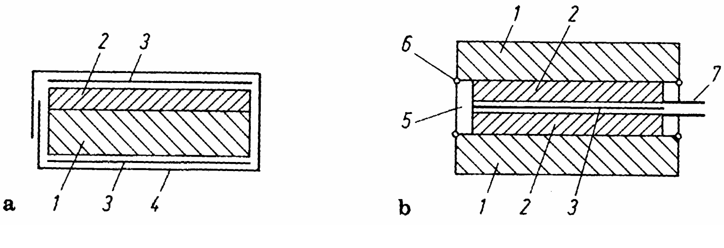


Fig. 2.45.: Preparation for roll cladding: **a** packaging in protective sheets;
b welding into distance frame; **1** base material, **2** cladding material, **3** separation layer (glass wool fabric, MgO- or Al_2O_3-casings, **4** protective sheet, closed by bending or welding, **5** welded distance frame, **6** weld seam, **7** evacuation port [1, p. 252]

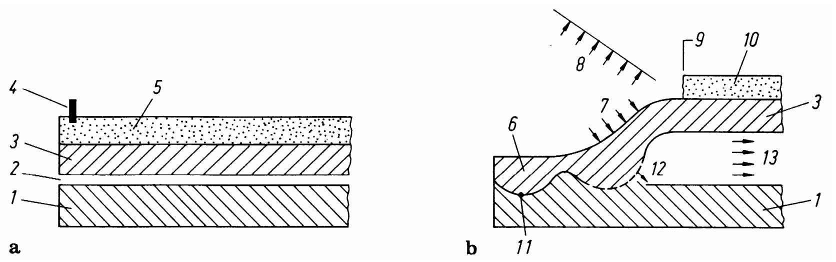


Fig. 2.46.: Detonation cladding: **a** preparation; **b** after ignition (schematic);
1 base material, **2** distance, **3** cladding material, **4** ignition device,
5 explosive layer, **6** cladded material, **7** accelerated cladding material,
8 detonation by-products, **9** detonation front in the explosive, **10** unburned explosive,
11 wave shaped transition zone, **12** high velocity material flow, **13** shock front in air
[1, p. 253]

2.3.5. Melt Dipping

Melt dipping of components and half finished products is important in respect to corrosion protection of steel. Mostly Al, Pb and Sn are used as coating materials. In the melt bath steel forms an alloy film with these materials (except with Pb) at its surface which is responsible for the excellent adhesion.

For pre treatment the components to be coated are cleaned thoroughly by sand blasting, de greasing and bating. Then the components are coverd by a flux material to ensure uniform wetting (see Fig. 2.47.).

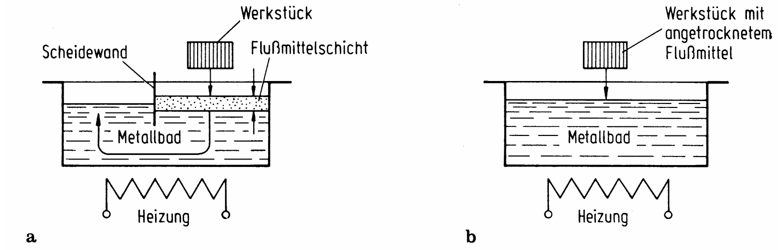


Fig. 2.47.: Schematic of melt dipping: **a** dipping of the component through a flux material film, **b** dipping of the component which was covered by flux material previously. [1, p. 256]

One can distinguish discontinous (for small parts as screws, fittings, pipes and containers as well as for large components such as steel assemblies for bridges etc.) and continous (for sheets, bands and wires) melt dipping processes.

Example: The production of "hot dip galvanized" steel sheets which is used for manufacturing parts ranging from rain pipes to car bodies world wide grosses approx. 25 million tons per year. The corrosion protection of Zn on steel works in two ways: on the one hand a film of Zn carbonate and Zn oxide forms at exposure to the atmpsphere which exhibits self terminated growth and is insoluble in water. On the other hand steel is protected in the presence of an electrolyte (industrially polluted air, SO_2!) because within the pores of the coating Zn goes into solution and not Fe due to its position in the electrochemical series. On the average the mean annual erosion rate amounts to 2 µm/year on the countryside, 4 µm/year in an urban environment and up to 8 µm/year in heavily contaminated industrial sites.

2.3.6. Emulsions and Pastes

The band width of these coating processes spans from the formation of monomolecular layers (Langmuir-Blodgett method) to the application of colors and lacquers by brushes and rollers. Organic polymer coatings are produced from lacquers which are applied to the substrate as liquid, powder or paste. Subsequently they are transformed to a solid film ba a chemical reaction and/or a physical treatment. Lacquers are disperse systems which contain solvents, pigments, fillers and activators apart from an organic binder.

Fillers are added to the lacquer to obtain certain film properties (corrosion protection or electrical conductivity). By the addition of pigments lacquers for opaque paintworks are manufactured. As binders Acryl, Alcyle, Epoxide, Phenole, Polyester and Poyurethane resins are available. Natural resins (Shellack, Colophonium) only have little importance. Solvents are Alcoholes, Xylol, Toluole, Trichlorethene and other chlorated carbohydrates. Since only in Europe approximately 6 million tons of laquers were consumed per year before 1990 and half of this mass was evaporated into the atmosphere as solvent the development of water based lacquers was enforced after 1990. Unfortunately their ageing resistance is still lower that that of lacquers basend on conventional solvents.

Regarding coating formation it is important that the binder within the liquid lacquer goes through certain chemical reactions upon the evaporation of the solvent. These take the binder from a low molecular state to the state of a strongly linked polymer. The linking can be achieved by polyaddition or polycondensation reactions which are triggered chemically, catalytically, thermally or by UV radiation.

Langmuir-Blodgett films: by this method organic polymers are solved in a suitable solvent. The solution is put on the surface of high purity water in exactly dosed amounts. After the evaporation of the solvent monolayer by monolayer is deposited on a substrate which is subsequently and very carefully dipped into and lifted out of the water (see Fig. 2.48.).

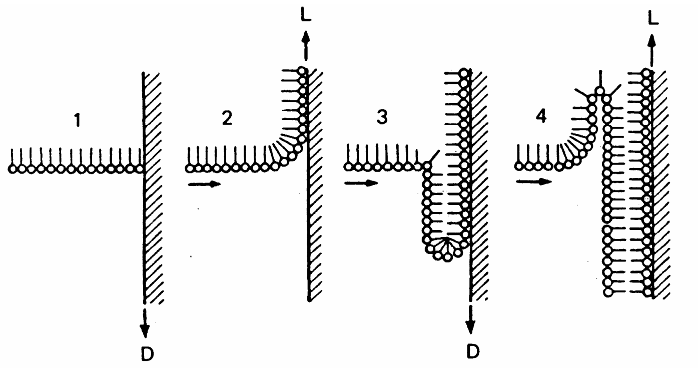


Fig. 2.48.: Production of Langmuir-Blodgett films: **D** = Dipping, **L** = Lifting [4, p. 115]

o = polar group
of an organic molecule
| = non polar part