Chapter 1

Overview of Processes

1.1 Evaporation

1.1.1 Kinetická teorie plynů

Maxwell-Boltzmannovo rozdělení rychlostí

$$f(V) = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mV^2}{2kT} \right).$$
(1.1)

Předpokládáme, že $\mathbf{u} = 0$ nebo se pozorovatel pohybuje střední rychlostí plynu $\Rightarrow \mathbf{v} = \mathbf{V}$:

$$f(v)d^3v = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) d^3v.$$
(1.2)

Protože M.-B. rozdělení je izotropní, můžeme definovat rozdělení *velikosti rychlosti* $v \equiv |\mathbf{v}|$. Přejdeme do sférických souřadnic

$$d^3v = v^2 \sin\theta d\theta d\phi.$$
(1.3)

Rozdělovací funkce rychlostí $F(v)$

$$F(v)dv = \int_\theta \int_\phi f(v) v^2 \sin\theta d\theta d\phi dv$$
(1.4)

a tedy

$$F(v) = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp v^2 \left(-\frac{mv^2}{kT} \right)$$
(1.5)

Střední hodnota velikosti rychlosti

$$< v > = \frac{1}{n} \int_v f v d^3v = \frac{1}{n} \int_0^\infty F(v) v dv$$
(1.6)

a po výpočtu

$$< v > = (8/\pi)^{1/2} (kT/m)^{1/2}.$$
(1.7)

Tok částic

$$\Gamma_n = n < v_n > = \int_v f \mathbf{v} \cdot \vec{\mathbf{n}} d^3v$$
(1.8)

je pro náhodný pohyb částic roven nule. Jaký je tok na jednu stranu myšlené plochy?

$$\Gamma = n \left(\frac{kT}{2\pi m} \right)^{1/2} = \frac{1}{4} n < v >$$
(1.9)

Stavová rovnice

$$\frac{pV}{T} = N k_{\mathrm{B}} \rightarrow \frac{p}{T} = n k_{\mathrm{B}} \tag{1.10}$$

Z této rovnice dosadíme za n v (1.9) a dostáváme

$$\Gamma = p(2\pi k_{\mathrm{B}} T m)^{-1/2} \tag{1.11}$$

1.1.2 General Considerations

Thermal evaporation or vacuum evaporation (purely physical process) is composed of following sequential basic steps:

1. Generation of Vapor by sublimation or evaporation of solid or liquid material, respectively $\Rightarrow$ heating to sufficiently high temperatures.

2. Transportation of vapor from the source to a substrate.

3. Condensation of vapor as a solid film on a cooler substrate surface.

Thin films of carbon deposited by evaporation inside an electric bulb were probably first observed by Edison. Historically, however, the deposition of a metal film from a wire exploded by a high current density is attributed to Faraday, and by vacuum evaporation to Nahrwold, Pohl and Pringsheim.

Because of collisions with ambient gas atoms, a fraction of the vapor atoms will be scattered and hence randomized in direction in a distance d during their transfer through the gas. The flux of particles at the distance d that did not undergo any collision is given as

$$\Gamma(d) = \Gamma_0 \exp(-d/\lambda). \tag{1.12}$$

Here λ is the mean free path of gas atoms which for air molecules at 25 °C and pressures 10^{-2} and 10^{-4} Pa is about 60 and 6000 cm. Thus, *p*ressures lower than 10^{-3} Pa are necessary to ensure a straight-line path for most of emitted vapor atoms, for substrate-to-source distances of $\approx$10 to 60 cm in a vacuum evaporator.

The rate of free evaporation of vapor atoms from clean surface of unit area in dimensions $\mathrm{m}^{-2}.\mathrm{s}^{-}1$ is given by the **Langmuir expression**:

$$\Gamma_{\mathrm{evap}} = p_{\mathrm{ev}}(2\pi k_{\mathrm{B}} T_{\mathrm{ev}} m_{\mathrm{ev}})^{-1/2} \tag{1.13}$$

where p_{ev} and T_{ev} are equilibrium vapor pressure and temperature of evaporated material, respectively, m_{ev} is mass of vapor molecules and k_{B} is Boltzmann constant. It is the same equation as for the flux of particles (1.11) because of particle conservation law.

The rate of evaporation can be alternatively expressed in dimensions $\mathrm{kg.m}^{-2}.\mathrm{s}^{-}1$

$$\Gamma'_{\mathrm{evap}} = p_{\mathrm{ev}} \left(\frac{m_{\mathrm{ev}}}{2\pi k_{\mathrm{B}} T_{\mathrm{ev}}} \right)^{1/2} \tag{1.14}$$

Deposition rate from clean, uniform emitting *p*oint source onto a plane receiver varies as $\cos\theta/r^2$ (Knudsen cosine law), where r is the radial distance of the receiver from the source and θ is the angle between the radial vector and the normal to the receiver direction. If t_0 and t are the thicknesses of deposits at the receiver vertically below the source at a distance h, and a at a horizontal distance x from the vertical line, respectively, then the deposit distribution (assuming the same condensation coefficient) is given by

$$\frac{t}{t_0} = \frac{1}{[1 + (x/h)^2]^{3/2}}. \tag{1.15}$$

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For evaporation from a small area onto a parallel plane receiver, the deposition rate is proportional to $\cos^2\theta/r^2$ and the thickness distribution is given by

$$\frac{t}{t_0} = \frac{1}{[1 + (x/h)^2]^2}.$$
(1.16)

In both cases, the thickness decreases by about 10% for $x = h/4$.

A parameter of interest in understanding the influence of ambient gases on the properties of films is the impingement rate of gas atoms or molecules. This is given by the kinetic theory of gases under equilibrium conditions (1.11)

$$\Gamma_{\mathrm{g}} = p_{\mathrm{g}}(2\pi k_{\mathrm{B}}T_{\mathrm{g}}m_{\mathrm{g}})^{-1/2}.$$
(1.17)

The Table **??** lists the mean free paths, impingement rate and other related quantities for air molecules at different pressures. Note that at constant gas and evaporation temperatures, the ratio $\Gamma_{\mathrm{g}}/\Gamma_{\mathrm{evap}} \approx p_{\mathrm{g}}/p_{\mathrm{evap}}$. From Table **??** implies that under commonly employed experimental conditions of vacuum $(\sim 10^{-3})$ and deposition rate $(\sim 1 \mathring{A}/\mathrm{s})$, the impingement rate of gas atoms is relatively quite large, so that if the sticking coefficient of gas atoms is not negligible small, a considerable amount of gas sorption could occur.

1.2   Chemical Reactions

Chemical reactions can involve gas, liquid or solid phases. The reaction is called homogeneous if the reactants are in the same phase, while heterogeneous reactions have reactants in two or more phases. Reactions that take place on the surface of a catalyst of a different phase are also heterogeneous. A reaction between two gases, two liquids or two solids is homogeneous. A reaction between a gas and a liquid, a gas and a solid or a liquid and a solid is heterogeneous.

1.2.1   Reaction Rate

We consider an isolated volume in the reactor. This volume contains one single fluid (gas or liquid) phase only. It is uniform in composition and temperature. If the reactor is spatially uniform, the representative volume is the total volume; if not, the representative volume is limited to a differential element.

The rate of a homogeneous reaction is determined by the composition of the reaction mixture, the temperature, and the pressure. The pressure can be determined from an equation of state together with the temperature and composition. Thus, we focus on the influence of latter factors.

Consider the reaction

$$aA + bB \ldots \longrightarrow qQ + sS \ldots$$
(1.18)

It can be stated that A and B react at rate

$$r'_A = -\frac{dN_A}{dt} \quad r'_B = -\frac{dN_B}{dt}$$
(1.19)

and Q and S are formed at rates

$$r'_S = -\frac{dN_S}{dt} \quad r'_Q = -\frac{dN_Q}{dt}$$
(1.20)

where N_j represents the molar amount of one of the chemical species in the reaction (from here in kmol), and t is time.

The following equalities exist between the different rates

$$-\frac{1}{a}\frac{dN_A}{dt} = -\frac{1}{b}\frac{dN_B}{dt} = \frac{1}{q}\frac{dN_Q}{dt} = \frac{1}{s}\frac{dN_S}{dt}.$$
(1.21)

Each term of these equalities may be considered as the rate of the reaction.

This can be generalized to the case of N chemical species participating in M independent chemical reactions,

$$\alpha_{i1}A_1 + \alpha_{i2}A_2 + \ldots + \alpha_{iN}A_N = 0 \tag{1.22}$$

nebo

$$0 = \sum_{j=1}^{N} \alpha_{ij}A_j \quad i = 1, 2, \ldots M \tag{1.23}$$

with the convention that the stoichiometric coefficients α_{ij} are taken positive for products and negative for reactants.

The rate of reaction is generally expressed on an intensive basis, say reaction volume, so that when V represents the volume occupied by the reaction mixture,

$$r_i = \frac{1}{V}\frac{1}{\alpha_{ij}}\left(\frac{dN_j}{dt}\right)_i. \tag{1.24}$$

For the simpler case,

$$r = \frac{-1}{aV}\frac{dN_A}{dt} = \frac{-1}{aV}\frac{d}{dt}(C_A V) = \frac{-1}{aV}\left(V\frac{dC_A}{dt} + C_A\frac{dV}{dt}\right) \tag{1.25}$$

where C_A represents the molar concentration of A ($kmol/m^3$). When the reaction volume does not vary

$$r = \frac{-1}{a}\frac{dC_A}{dt}. \tag{1.26}$$

In this case it suffices to measure the change in concentration to obtain the rate of reaction.

1.2.2 Conversion and Extent of Reaction

Conversions, rather than concentrations, are often used in the rate expressions, as follows:

$$x'_A = N_{A0} - N_A \quad x'_B = N_{B0} - N_B \tag{1.27}$$

or for constant volume

$$x''_A = C_{A0} - C_A \quad x''_B = C_{B0} - C_B. \tag{1.28}$$

Most frequently, fractional conversion are used

$$x_A = \frac{N_{A0} - N_A}{N_{A0}} \quad x_B = \frac{N_{B0} - N_B}{N_{B0}} \tag{1.29}$$

which show immediately how far the reaction has progressed.

One must be very careful when using the literature because it is not always clearly defined which kind of conversion is meant. The following relations may be derived easily from Eqs. (1.27)–(1.29):

$$x'_j = N_{j0}x_j \tag{1.30}$$

$$\frac{x'_A}{a} = \frac{x'_B}{b} = \ldots = \frac{x'_Q}{q}\ldots \tag{1.31}$$

$$x_B = \frac{b}{a}\frac{N_{A0}}{N_{B0}}x_A \tag{1.32}$$

An alternate but related concept to the conversion is the extent or degree of advancement (stupeň rozvoje reakce) of the general reaction Eq. (1.23), which is defined as

$$\xi = \frac{N_j - N_{j0}}{\alpha_j} \tag{1.33}$$

a quantity that is the same for any species. Also,

$$N_j = N_{j0} + \alpha_j \xi \tag{1.34}$$

where N_{j0} is the initial amount of A_j present in the reaction mixture. For multiple reactions,

$$N_j = N_{j0} + \sum_{i=1}^{M} \alpha_{ij} \xi_i. \tag{1.35}$$

Eqs. (1.29) and (1.34) can be combined to give

$$N_j = N_{j0} + \alpha_j \frac{N_{A0}}{a} x_A. \tag{1.36}$$

If species A is the limiting reactant (present in least amount), the maximum extent of reaction is found from

$$0 = N_{A0} + \alpha_A \xi_{\max} \tag{1.37}$$

and the fractional conversion defined by Eq.(1.29) becomes

$$x_A = \frac{\xi}{\xi_{\max}}. \tag{1.38}$$

Either conversion or extent of reaction can be used to characterize the amount of reaction that has occured. For industrial applications, the conversion of a feed is usually of interest, while for other scientific applications, the extent is often more useful.

In terms of the extent of reaction, the reaction rate Eq. (1.24) can be written

$$r_i = \frac{1}{V} \frac{1}{\alpha_{ij}} \left(\frac{dN_j}{dt} \right)_i = \frac{1}{V} \frac{d\xi_i}{dt}. \tag{1.39}$$

With this rate, the change in moles of any species is, for a single reaction,

$$\frac{dN_j}{dt} = \alpha_j V r \tag{1.40}$$

and for multiple reactions

$$\frac{dN_j}{dt} = \sum_{i=1}^{M} \alpha_{ij} V r_i = V R_j. \tag{1.41}$$

1.2.3   Order of Reaction

Based on experimental observation and later explained by the collision theory, it is found that the $r$ate of reaction in Eq. (1.18) can be expressed as

$$r = k_c C_A^a C_B^b. \tag{1.42}$$

The proportionality factor k_c is called the rate coefficient, or rate constant. By definition, this rate coefficient is independent of the quantities of the reacting species, but is dependent on the

other variables that influence the rate. When r is expressed in kmol m^{-3} hr^{-1}, then k_c has dimensions

$$(\text{kmol/m}^3)^{1-(a+b+\ldots)}\,\text{hr}^{-1} \tag{1.43}$$

The dimensions of the rate coefficient used with the conversions are the same as those given for use with the concentrations. Partial pressures may also be used as a measure of the quantities of the reacting species,

$$r = k_p p_A^a p_B^b. \tag{1.44}$$

In this case the dimensions of the rate coefficient k_p are

$$(\text{kmol/m}^3)\,\text{hr}^{-1}\text{Pa}^{-(a+b+\ldots)} \tag{1.45}$$

According to the ideal gas law

$$C_i = \frac{p_i}{RT} \tag{1.46}$$

so that

$$k_c = k_p(RT)^{a+b+\ldots}. \tag{1.47}$$

The powers a, b, ... are called "partial orders" of the reaction with respect to A, B... The sum $a + b + \ldots$ may be called the "global order", or generally just "order" of the reaction. In reality, the orders in the above equations should be replaced by the quantities a', b', ... that do not necessarily coincide (only for elementary processes) with the stoichiometric coefficients a, b, ... but has to be determined experimentally. Only for elementary reactions does the order have to be 1, 2, or 3. When the stoichiometric equation (1.18) is only an "overall" equation for a processes consisting of several mechanistic steps, the order cannot be predicted on the basis of this stoichiometric equation.

For an irreversible first-order constant volume reaction, we have

$$r_A = -\frac{dC_A}{dt} = kC_A. \tag{1.48}$$

When the rate coefficient k (hr^{-1}) is known, Eq. (1.48) permits the calculation of the rate r_A for any concentration of the reacting component. Conversely, when the change in concentration is known as a function of time, Eq. (1.48) permits the calculation of the rate coefficient. This method for obtaining k is known as the "differential" method. Integration of Eq. (1.48) leads to

$$kt = ln\left(\frac{C_{A0}}{C_A}\right) \tag{1.49}$$

and a semilog plot of C_{A0}/C_A versus t gives k.

1.3 Interaction of Ions with Solid

Chapter 2

Interaction of ions with solids

Interaction of ions or atoms with solids is a part of many material processing techniques because it can result in structural changes of the material, implantation of incident particles or sputtering of the material. Additionally, several physical methods of material and surface characterization are based on detection of reflected or released particles resulting from ion/atom bombardment. The emitted particles include atoms or ions of the material, electrons, photons and products of nuclear reactions. All the processes initiated by an impact of ion or atom projectile are schematically shown in Fig. **??**.

The processes caused by impact of an ion or an atom on a surface depend on several parameters such as the energy of incident projectile ($E_{i,0}$), angle of incidence with respect to the surface normal, incident flux (γ_i), mass and atomic number of the projectile (M_i and Z_i, respectively), mass and atomic number of the target atom (M_t and Z_t, respectively), and the charges of the projectile and target atom. At the conditions relevant to the material processing, the interaction of the projectile with the solid can be divided in two different mechanisms

- nuclear collisions, i. e., elastic collisions with atoms

- electronic collisions, in which electrons are excited or ejected from the material.

At high energies ...nuclear reaction have to be taken into account.

2.1   Ion stopping

As mentioned above the projectile penetrating a solid is slowed down by interactions with the electrons and atoms of the material. The energy lost per unit path length dx

$$S = -\frac{dE}{dx} \tag{2.1}$$

is called stopping power or, less frequently, specific energy loss. The stopping cross section is defined as

$$\mathcal{S} = -\frac{1}{n}\frac{dE}{dx} \tag{2.2}$$

or

$$\mathcal{S} = -\frac{1}{\varrho}\frac{dE}{dx} \tag{2.3}$$

where n is the volume density in atoms/cm^3 and ϱ is the mass density in kg/cm^3. The quantity $\mathcal{S}$ is called sometimes also the stopping power.

Generally, the total energy loss experienced by the projectile moving through the material is obtained as a sum of nuclear and electronic contributions:

$$S = S_n + S_e. \tag{2.4}$$

At projectile velocities $v_{i,0}$ significantly lower than the Bohr velocity of the atomic electrons (v_0), the projectile carries its electrons and, in case of ion, it tends to become neutralized by electron capture. At these velocities elastic collisions with the target nuclei, i.e., the nuclear energy losses, dominate. As the velocity is increased the interaction with the material electrons leading to inelastic collisions (electronic stopping) becomes more important. The term inelastic is used to signify that the collisions may result both in excitations of bound electrons of the medium, and in excitations of the electron cloud of the ion.

2.1.1 Nuclear Stopping

Kinematics of Binary Elastic Collision

In nuclear collisions the mass of the incident particle is comparable with the mass of target atom. Therefore, the elastic nuclear collision can involve significant discrete losses of projectile energy, a significant angular deflection of projectile trajectory and a creation of energetic recoil atoms. It implies from the energy and momentum conservation laws that the energies of the projectile and the recoil atom after the collision, $E_{i,1}$ and E_t, respectively, are given by

$$E_{i,1} = KE_{i,0} \tag{2.5}$$
$$E_t = (1 - K)E_{i,0} \tag{2.6}$$

where K is the kinematic factor determined by the relative mass M_i/M_t and the laboratory angle θ_i of scattered projectile. If the mass of incident particle exceeds the mass of the target atom, $M_i/M_t > 1$, the kinematic factor is given by:

$$K = \left[\frac{\cos\theta_i \pm \left(\frac{M_t}{M_i}^2 - \sin^2\theta_i \right)^{1/2}}{\frac{M_t}{M_i} + 1} \right]^2 . \tag{2.7}$$

If $M_i/M_t \leq 1$ the expression is reduced to

$$K = \left[\frac{\cos\theta_i + \left(\frac{M_t}{M_i}^2 - \sin^2\theta_i \right)^{1/2}}{\frac{M_t}{M_i} + 1} \right]^2 . \tag{2.8}$$

The energy transfered to the target atom can be expressed by simplification of Eq. (**??**) as

$$E_t = \frac{4M_iM_t}{(M_i + M_t)^2} \sin^2\frac{\theta_c}{2} \, E_{i,0} \tag{2.9}$$

where θ_c is the center-of-mass scattering angle.

Dynamics of Binary Elastic Collisions and Scattering Cross Section

Irradiation of material by ions or atoms is the interaction of many particles. Therefore, it is conveniently described by a statistical approach that introduces a measure of scattering probability. We consider the particles incident at a distance b off-center from the target particle. The situation of the scattering event is depicted in Fig. **??**. The quantity b is the impact parameter and particle flux will be denoted as Γ. The conservation of particle flux requires that the particles incoming through the differential area $b\,db\,d\phi_i$ leave, after the scattering, through the differential solid angle proportional to $d\Omega$ defined by the scattering angle θ_i and the orientation of the scattering plane ϕ_i as

$$d\Omega = \sin\theta_i d\theta_i d\phi_i. \tag{2.10}$$

The proportionality constant is the differential scattering cross section $\sigma(\theta_i, \phi_i)$:

$$\Gamma b db d\phi = \sigma(\theta_i, \phi_i) \, \Gamma d\Omega. \tag{2.11}$$

Since both sides of Eq. (2.11) are equal to the number of particles scattered per unit time, dN/dt, the differential scattering cross section is the number of particles scattered per unit time and unit incident flux into the solid angle $d\Omega$:

$$\sigma(\theta_i, \phi_i) = \frac{dN}{dt \, \Gamma \, d\Omega} \tag{2.12}$$

The differetial scattering cross section is obtained from Eqs. (2.10) and (2.11) as

$$\sigma(\theta_i, \phi_i) = \frac{b}{\sin \theta_i} \left| \frac{db}{d\theta_i} \right|. \tag{2.13}$$

The quantity $db/d\theta$ is determined from the scattering force. The absolute value is used since θ normally decreases with increasing b whereas $\sigma(\theta_i, \phi_i)$ is inherently a positive quantity.

We can calculate the total scattering cross section σ_t by integrating σ over the solid angle

$$\sigma_t = \int_\Omega \sigma(\theta_i, \phi_i) d\Omega = \int_0^{2\pi} \int_0^\pi \sigma(\theta_i, \phi_i) d\theta d\phi. \tag{2.14}$$

Both $\sigma(\theta_i, \phi_i)$ and σ_t depend on the magnitude of relative particle velocity. In the case of central force, the interaction potential depends only on the particle separation r. Such potential is isotropic and the differential scattering cross section is independent of ϕ:

$$\sigma_t = 2\pi \int_0^\pi \sigma(\theta_i) d\theta. \tag{2.15}$$

Namely, this is the case of Coulomb force.

Consider static target particles having density n_t. For infrequent collisions within dx, the number of incident particles per unit volume at x that undergo an interaction within a differential distance dx, removing them from the incident beam is according to Eq. (2.12)

$$dn = -\sigma_{\text{tot}} n n_t dx. \tag{2.16}$$

When studying the nuclear stopping it is useful to know the probability that a projectile with energy $E_{i,0}$ will transfer an amount of energy between E_t and $E_t + dE_t$ to a target atom. Such probability function defines the differential energy-transfer cross section $\sigma_E(E_t)$ that is related to $\sigma(\theta_i, \phi_i)$ by

$$\sigma_E(E_t) dE_t = \sigma(\theta_i, \phi_i) d\theta_i d\phi_i. \tag{2.17}$$

In order to determine differential cross section from Eq. (**??**) it is necessary to establish a relation between the impact parameter b and the scattering angle θ_i. We can derive a general formula without knowledge of an exact expression of the interaction force for the force acting along a straight line joining the two particles. Such central force $\mathbf{F}(r) = F(r)\hat{\mathbf{r}}$ is related to the potential energy $U(r)$ by

$$\mathbf{F}(r) = -\nabla U(r) = -\frac{dU(r)}{dr}\hat{\mathbf{r}}. \tag{2.18}$$

Then, the scattering angle θ_i is expressed by

$$\theta_i(b, v) = \pi - 2 \int_{r_{\min}}^\infty \frac{b}{r^2} \left[1 - \frac{b^2}{r^2} - \frac{2U(r)}{\mu v^2} \right]^{-1/2} dr \tag{2.19}$$

where v is relative velocity of interacting particles and $r_{\min}$ is the distance of the closest approach given by

$$r_{\min} = b \left[1 - \frac{2U(r_{\min})}{\mu v^2} \right]^{-1/2}. \tag{2.20}$$

Interatomic Potentials

The interaction of two atom nuclei is described by Coulomb potential energy

$$U_{\mathrm{C}}(r) = \frac{1}{4\pi\varepsilon_0} \frac{Z_{\mathrm{i}} Z_{\mathrm{t}} e^2}{r}. \tag{2.21}$$

However, the interaction of two atoms involves also influence of atomic electrons in dependence on the interatomic distance. There are two useful reference points that scale the problem, the Bohr radius of the hydrogen atom, a_0,

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}, \tag{2.22}$$

and the spacing between neighboring atoms in the crystal, r_0. The Bohr radius, $a_0 = 0.053$ nm, indicates the extent of the atomic electron shells. The spacing between atoms, typically $r_0 = 0.25$ nm, is the distance between two bonded atoms related to the minimum potential energy of the crystal. The nuclear charges are well screened by atomic electrons at the distances $r \gg r_0$. As the atoms come closer to each other the valence shells begin to overlap and there may be attractive interaction of the type forming the bonds. At the extreme case of $r \ll a_0$, the nuclei become the closest pair of charged particles in the system and since their Coulomb interaction dominates, the potential energy of interaction is well defined by Eq. (2.21). At the intermediate distances $a_0 < r \leq r_0$, a positive interaction energy, resulting in repulsive force, has two components (i) the electrostatic repulsion between the positively charge nuclei and (ii) the increase in energy caused by Paulli exclusion principle.

Although the description of the interatomic interaction involves complicated effect of atomic electrons we can see from the above discussion that a reasonable choice is the Coulomb interaction given by Eq. (2.21) moderated by a proper function. Thus, the atomic interaction is generally described by the screened Coulomb potential energy

$$U(r) = \frac{1}{4\pi\varepsilon_0} \frac{Z_{\mathrm{i}} Z_{\mathrm{t}} e^2}{r} \chi(r) \tag{2.23}$$

where χ is the screening function. Under ideal circumstances, $\chi(r)$ should tend to zero or unity for large or very small distances, respectively.

Basically, there are two approaches to express the screening function, (i) the simple statistical and (i) the quantum-mechanical Hartree-Fock atomic models. The statistical, Thomas-Fermi (TF), description assumes that the electrons behave as an ideal gas of particles of energy E obeying Fermi-Dirac statistics and fill the potential well around the positively charged core. Clearly, this model does not take into account the different electron shells.

Accurate solutions of the TF model of the screening function are typically obtained through numerical approaches as discussed by Torrens [**?**]. However, for many applications it would be desirable to have available an analytical expression that approximately satisfies the TF equation. The earliest and best known of these analytical expressions is the Sommerfeld asymptotic form:

$$\chi(x) = \left[1 + \left(\frac{x}{a} \right)^\lambda \right]^{-c} \tag{2.24}$$

where the constant a, λ and c were chosen as $a = 12^{2/3}$ and $c\lambda = 3$. The normalized interatomic distance $x = r/a_{\mathrm{TF}}$ is scaled by the TF screening radius for collision between the atoms

$$a_{\mathrm{TF}} = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{3/2} \frac{a_0}{Z_{\mathrm{eff}}^{1/3}} \tag{2.25}$$

where Z_{eff} is the effective charge number in the interaction of two unlike atoms

$$Z_{\text{eff}} = (Z_i^{1/2} + Z_t^{1/2})^2. \tag{2.26}$$

Sommerfeld found that at large x the appropriate values for λ and c are $\lambda = 0.772$ and $c = 3.886$.

Another often used approximation to the TF screening function was given by Moliere in the form of three exponentials:

$$\chi(x) = 7p\exp(-qx) + 11p\exp(-4qx) + 2p\exp(20qx) \tag{2.27}$$

where $p = 0.05$ and $q = 0.3$. Mathematically simple analytical expression of the screening function can be constructed using inverse powers of $x = r/a_{\text{TF}}$ with exponent differening in different ranges of r/a_{TF}:

$$\chi(r) = \frac{k_s}{s} \left(\frac{a_{\text{TF}}}{r}\right)^{s-1} \tag{2.28}$$

with $s = 3/2, 2, 3 \ldots$ and a constant k_s.

A screening function based on quantum mechanically derived charge distribution gives rise to what is commonly referred to as the *universal interatomic potential*. The extensive work of Ziegler, Biersack and Littmark (ZBL) [?] and Wilson *et al.* [?] produced the ZBL universal screening function

$$\chi_{\text{U}} = 0.1818\exp(-3.2x) + 0.5099\exp(-0.9423x) + 0.2802\exp(-0.4028x) + 0.02817\exp(-0.2016) \tag{2.29}$$

where the reduced distance x is given by

$$x = \frac{r}{a_{\text{U}}} \tag{2.30}$$

and a_{U}, the universal screening length, is defined by

$$a_{\text{U}} = \frac{0.8854a_0}{Z_i^{0.23} + Z_t^{0.23}}. \tag{2.31}$$

The application of the power law screening function, Eq. (2.28), to the scattering process results in a power law differential cross section [?]

$$\sigma_E(E_i) = \frac{C_m}{E_i^m E_t^{1+m}} \tag{2.32}$$

where $m = 1/s$ in Eq. (2.28) and the constant C_{m} is given by

$$C_{\text{m}} = \frac{\pi}{2}\lambda_m a_{\text{TF}}^2 \left(\frac{Z_i Z_t e^2}{2\pi\varepsilon_0 a_{\text{TF}}}\right)^{2m} \frac{M_1}{M_2}^2 \tag{2.33}$$

where λ_{m} is given by [?]

$$\lambda_{1/3} = 1.309 \quad \lambda_{1/2} = 0.327 \quad \lambda_{0.5} = 0.5. \tag{2.34}$$

Winterbon et al. []

Nuclear Stopping Cross Section

The average energy loss by the moving particle in the distance dx is obtained with the help of differential energy-transfer cross section σ_E defined by Eq. (2.17) as

$$\langle \frac{dE}{dx} \rangle = n \int_{E_{t,min}}^{E_{t,max}} E_t \sigma_E dE_t \tag{2.35}$$

where $E_{t,min}$ and $E_{t,max}$ are minimum and maximum energies transferred to the target atom, respectively.

Applying the power law differential cross section given by Eq. (**??**), the power law nuclear stopping cross section is [?]

$$S_n(E) = \frac{C_m E^{1-2m}}{1-m} \left[\frac{4M_i M_t}{(M_i + M_t)^2} \right]^{1-m} \tag{2.36}$$

where C_m is defined by Eq. (**??**).

The nuclear stopping cross section increases in the range of low energies reaching the maximum at some keV or hundreds of keV for light or heavy ions, respectively. It may be calculated at the ion energy E (in keV) from Ziegler *et al.* [?] as

$$\mathcal{S}_n = \frac{8.462 Z_i Z_t S_n(E_r)}{(M_i + M_t) + (Z_i^{0.23} + Z_t^{0.23})} \mathrm{eV cm^2}/10^{15} \mathrm{atoms} \tag{2.37}$$

where E_r is the reduced energy defined by

$$E_r = \frac{32.53 M_t E}{Z_i Z_t (M_i + M_t) Z_i^{0.23} + Z_t^{0.23})} \tag{2.38}$$

and $S_n(E_r)$ is the reduced nuclear stopping given as

$$S_n(E_r = \frac{\ln(1 + 1.1383 E_r)}{2(E_r + 0.01321 E_r^{0.21226} + 0.19593 E_r^{0.5})} \qquad \text{for} \qquad E_r \leq 30 \, \mathrm{keV} \tag{2.39}$$

or

$$S_n(E_r = \frac{\ln E_r}{2 E_r} \qquad \text{for} \qquad E_r > 30 \, \mathrm{keV}. \tag{2.40}$$

Above 200 keV/amu the nuclear stopping contribution is small, typically below 1 % of the electronic stopping.

2.1.2 Electronic Stopping

Since the number of collisions an ion experiences with electrons is large, and since the charge state of the ion while traversing the medium may change frequently, it is very difficult to describe all possible interactions for all possible ion charge states. Instead, the electronic stopping power is often given as an average taken over all energy loss processes for different charge states. It can be theoretically determined to an accuracy of a few percent in the energy range above several hundred keV per nucleon from theoretical treatments, the best known being the Bethe formula:

$$S = \frac{4\pi}{m_e c^2} \frac{nz^2}{\beta^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \left[\ln(\frac{2m_e c^2 \beta^2}{I(1-\beta^2)}) - \beta^2 \right] \tag{2.41}$$

where v is the velocity of particle, c is the speed of light, $\beta = v/c$, ze is particle charge, m_e is the rest mass of electron, $n = N_A Z \rho / A$ is electron density of the target and I is the excitation potential of the target. For lower energies

At energies lower than about 100 keV per nucleon, it becomes more difficult to determine the electronic stopping theoretically [**?**].

In the velocity range from $\approx 0.1v_0$ to $Z_i^{2/3}v_0$ the electronic energy loss is approximately proportional to $E^{1/2}$ as derived by Lindhard et al. [**?**, **?**]. At higher velocities $v_{i,0} \gg v_0$ the charge state of the projectile increases and finally it becomes fully stripped of its electrons. At a given velocity the energy loss is proportional to the square of ion charge.

2.2 Sputtering

The yield, Y, describes how many atoms are ejected during the sputtering event. The total yield is defined as the average number of atoms ejected per incident ion.

The collective response of the atoms in the target to the strike of energetic atom or ion can be divided into five distinct groups according to E_i, Z_i and M_i, Z_t and M_t. These 3D regions are demonstrated by two plane cross-sections with $E_i = 50$ keV and $Z_t = 50$ in Figure **??**a and **??**b, respectively [**?**]. The response that can be described by a linear cascade theory [**?**,**?**,?,**?**], is depicted by an unshaded area. In this theory the incident particle shares its kinetic energy with target atoms initially at rest in a series of binary collisions and produces fast recoils. These, in turn, set other target atoms in motion and a continuously increasing number of progressively slower atoms participate in created isotropic cascade. About 1–5×10^{13} s after impact, the recoil energies at the edges of the cascade have become less than the threshold energy to displace an atom, which is of the order of some 10 eV. The cascade is damped by energy dissipation through, e. g., , phonon-assisted processes. Using this approach, the sputter yield can be described by an analytical formula [?, ?]

$$Y(E_i, \theta_i) = \frac{K_{it}}{U_0} \, S_n(E_i/E_{it}) \, f(\theta_i) \qquad (2.42)$$

where U_0 is the surface binding energy (in eV), K_{it} and E_{it} are scaling constants dependent on the initial target and projectile species, $S_n(E_i/E_{it})$ is the reduced nuclear stopping cross section ($\epsilon = E_i/E_{it}$ is reduced energy) and $f(\theta_i)$ is the angle-of-incidence function.

It primarily occurs at intermediate energies (5 to 100 keV). A cascade of recoil atoms is produced along the path of the incident ion. The number of atoms produced at any point depends linearly on the amount of energy lost by the incident ion at that point. The energy loss is due to electron drag from the free electrons in the solid and screened Coulomb interactions with the nuclei. i. e., analytical expressions for sputter yield

2.3 Plasma processes

2.4 Processes in glow discharge plasmas

The electrons couple to the applied electric field which powers the discharge, thus gaining energy. Any ions present are relatively unaffected because of their much heavier mass. The accelerated free electrons lose little energy in elastic collisions with atoms or molecules because of the large difference in mass. Furthermore, they initially lose little energy in inelastic collisions (e. g., excitation and ionization) until their energies reach the corresponding threshold energies (e. g., 11.56 eV excitation and 15.8 eV ionization for argon). Consequently, these free electrons gain relatively high energy quickly from the field. This energy is transfered to the gas by electron-gas collisions that produce excited and ionized species. The latter generating additional electrons which are in turn accelerated by the field. For a plasma to be sustained, the electron must be produced by the ionization and emission from positive ion bombardment on the electrodes and walls at a rate equal to that of electron and ion losses by plasma-phase and surface recombination.

Since plasma-phase recombination is a three-body reaction which is slow at the low pressures used in glow discharges, the majority of recombination occurs at the surfaces.

A broad range of chemical and physical reactions occur in a plasma. Listed below are some of the more significant electron-gas and gas-gas reactions:

Excitation	$A_2 + e^- \rightarrow A_2^* + e^-$
Dissociation	$A_2 + e^- \rightarrow 2A + e^-$
Electron Attachment	$A_2 + e^- \rightarrow A_2^-$
Dissociative Attachment	$A_2 + e^- \rightarrow A^- + A$
Ionization	$A_2 + e^- \rightarrow A_2^+ + 2e^-$
Photoemission	$A_2^* \rightarrow A_2 + h\nu$
Abstraction	$A + B_2 \rightarrow AB + B$

where A_2^* is excited molecule A_2.

The rate at which free radicals, ions, or other excited states are formed by electron impact in a plasma can be quantified in terms of a chemical reaction rate expression,

$$d[n_j]/dt = k_{ij}[e^-][n_i] \tag{2.43}$$

where $d[n_j]/dt$ is the rate of formation of species n_j from precursor n_i, $[e^-]$ is the concentration of electrons, and $[n_i]$ is the concentration of the neutral precursor species. The rate coefficient k_{ij} can be calculated from the collision cross section $\sigma_{ij}(E)$ specific to the reaction. The cross section is proportional to the probability that a given j^{th} process will occur upon collision between n_i and an electron with an energy E. If the electron has an energy lower than that required for j^{th} process, the cross section equals zero. The collision cross section is a function of the electron energy E, and thus k_{ij} is:

$$k_{ij} = \int_0^\infty \sqrt{\frac{2E}{m_e}} \sigma_{ij}(E) f(E) dE \tag{2.44}$$

where f(E) is the electron distribution function which describes the fraction of free electrons with a given energy, and m_e is the electron mass. The Maxwell-Boltzmann distribution is usually used to approximate the energy distribution, i. e., a large fraction of the electrons have an energy at or below the average electron energy, but the fraction of electrons at higher electron energies decays exponentially with increasing electron energy. In the glow discharge, the electrons attain high average energies, typically 1–10 eV, with the fastest electrons having energies as high as 10-30 eV [?].

The energy of the electrons is primarily dissipated through inelastic collisions with gas molecules give rise to reactive species, such as excited neutrals and free radicals. In this manner the energy of the electrons, which is acquired from the applied electric field, is used to create highly reactive species without significantly raising the gas temperature. PECVD uses these highly reactive species to deposit thin films at lower temperatures than are possible with thermally driven CVD. Furthermore, the ion bombardment of the any surface in the touch with the plasma that is result of different potentials, as discussed in section **??**, can induce several specific processes during the film deposition:

- The ion may be reflected, probably being neutralized in the process.

- The impact of the ion may cause the target to eject an secondary electron.

- The ion may become buried in the target. This is the phenomenon of ion implantation.

- The ion impact may also be responsible for some structural rearrangements in the growing material. Rearrangement may vary from simple vacancies (missing atoms) and interstitials (atoms out of position) to more gross lattice changes like recrystallisation.

- The ion impact may set up series of collisions between atoms of the surface, possibly leading to the ejection of one of these atoms. This ejection process is know as sputtering.

Chapter 3

Overview of Material Processing Methods

There are basically three different activities applied within material processing

- removal of material,

- deposition of thin films,

- modification or forming of material.

The removal of thin layers of material, as for example in lithography, can be achieved by (i) sputter etching using inert ions, i. e., purely physical processes, (ii) by chemical etching, i. e., purely chemical processes, or (iii) by the combination of both, i. e., by reactive ion etching (RIE). The advantage of RIE is the significant enhancement of removal rate as compared to the pure chemical or physical processes. The processes requiring interaction of ions with solids can be achieved either by using ion beam or plasma techniques. Thus, the first and the last method of material removal fall either into ion beam or plasma processing technology and can be further divided according to the ion or plasma source used. Similar sources can be also applied to the film deposition.

The general clasification of the technologies for the deposition of films, a few nanometers to about ten micrometers thick, is similar to that of material removal. Thin film deposition techniques are (i) purely physical, such as vacuum evaporation and ion beam or plasma sputter deposition, (ii) purely chemical, such as gas- and liquid- phase chemical processes and (iii) a considerable number of methods combine both, physical processes and chemical reactions. The physical-chemical approaches include the ion beam method combined with the chemical processes and various modifications of the chemical vapor deposition (CVD) in which a certain physical process helps to initiate the chemical reactions. A wide range of CVD methods are based on electrical discharges and they create their own extensive group called plasma enhanced chemical vapor deposition (PECVD). A brief survey of all the deposition methods classified according to the general processes is given in Tables 3.1 and 3.2.

Methods for the modification or forming of materials cover many different phenomena. They include thermal or plasma forming processes such as oxidation or nitridation. They are applied in the processing of polymers such as polymer cross-linking, surface modifications for variation of surface free energy or grafting of new functional groups. They cover ion beam processes like ion implantation or ion beam modifications.

As mentioned above, plasma processing technologies can be used in sputter etching, reactive ion etching, sputter deposition, PECVD and plasma surface modifications. They have already established a key role in many industrial products such as microelectronic devices, solar cells,

Table 3.1: First part of the survey of technologies for thin film deposition classified according to general processes applied: evaporative, MBE, liquid-phase chemical, gas-phase chemical and gas-phase physical-chemical techniques (except ion beam and plasma processes).

evaporative techniques:	
method/processes	specification
thermal (vacuum) evaporation	resistive heating
	flash evaporation
	arc evaporation
	exploding-wire technique
	laser evaporation
	rf heating
	electron-beam evaporation
molecular beam epitaxy (MBE)	
liquid-phase chemical techniques:	
method/processes	specification
electro processes	electroplating
	electrolytic anodization
mechanical techniques	spray pyrolysis
liquid phase epitaxy	
gas-phase chemical techniques:	
method/processes	specification
chemical vapor deposition (CVD)	CVD epitaxy
	metalorganic CVD (MOCVD)
	low-pressure CVD (LPCVD)
	atmospheric-pressure CVD (APCVD)
	atomic layer deposition (ALD)
gas-phase physical-chemical techniques:	
(except plasma and ion beam)	
method/processes	specification
modifications of CVD	hot filament CVD (HFCVD)
	laser-induced CVD (PCVD)
	photo-enhanced CVD (PHCVD)
	electron enhanced CVD

protective or anticorrosion coatings on machining tools or automobile parts. In many other cases, it is still an emerging technology with a large potential for further grow. However, there is always a need for better understanding of plasmachemical processes and testing different deposition conditions as well as new mixtures and multi-step procedures [**?**].

One of the most important plasma processing techniques is PECVD. It is very complex method combining physical and chemical processes in the plasma phase as well as at plasma-solid interface. It is based on the molecule dissociation in the gas phase by impact of energetic electrons and atoms in metastable states followed by chemical reactions of gas radicals. As compared with classical chemical methods PECVD has several advantages: low substrate temperature (necessary condition in many applications), possibility to produce materials of new properties and to vary the film properties simply by changing some deposition parameters, film production without toxic by-products, ozone and the like.

Table 3.2: Second part of the survey of technologies for thin film deposition classified according to general applied processes: ion beam and plasma techniques.

method/processes	*plasma techniques:* specification
sputter deposition	
	dc sputtering
	rf diode sputtering
	magnetron sputtering
PECVD in low temperature discharges	
	dc discharge
	rf capacitively coupled plasma (CCP)
	rf inductively coupled plasma (ICP)
	microwave ECR deposition
	microwave resonantor reactor
	atmospheric pressure dielectric barrier discharge (DBD)
	atmospheric pressure glow discharge (APGD)
	atmospheric pressure surface barrier discharge
	etc.
plasma processing in high temperature discharges	
	vacuum arc
	dc torch
	microwave torch
	etc.
method/processes	*ion beam techniques:* specification
sputter deposition	
	ion beam sputtering
	reactive ion beam sputtering
ion deposition	
	ion beam deposition
	ionized cluster beam deposition (ICB)
dual processes	ion beam assisted deposition (IBAD)
	dual ion beam sputtering

Chapter 4

Evaporative Technologies

4.1 Thermal Evaporation

Thermal evaporation or vacuum evaporation (purely physical method) is one of the oldest techniques used for depositing thin films. It is still widely used in the laboratory and in industry for depositing metals and metal alloys.

There are several evaporation methods:

- **Resistive Heating.** This method consists of heating the material with a resistively heated filament or boat, generally made of refractory metals such as W, Mo, Ta and Nb, with or without ceramic coatings.

  - Direct heating is obtained when evaporant

    * hangs for example on the wire spiral in the form of U-shaped staples (the evaporant has to be able to wet the wire so to be able to cling to the wire after melting),
    * is inserted into a basket shaped wire (it need not wet the wire because it will coalesce into a blob that will not flow out through the spacing)
    * is placed in dimpled boat. The dimple is about 0.3 cm deep, and the overall dimensions of the boat are about 10 cm long and 1 or 2 cm wide. Power requirements for these sources are appreciably higher than for wire sources but thicker coatings can be deposited.
    * or is inside a closed source design (furnace) developed to prevent evaporant specks from being ejected and striking the substrates. The furnace chamber is filled with evaporant vapours that streams out of the holes.

  - Crucibles of quartz, graphite, alumina, beryllia and zirconia are used with indirect heating.

$\Rightarrow$ *Sublimation.* If a material has a sufficiently high vapour pressure before melting occurs, it will sublime, and the condensed vapours form a film (low deposition rates).

$\Rightarrow$ *Multiple-component Evaporation.* When multicomponent alloys or compounds are thermally evaporated, the component may evaporate at different rates because of their different vapour pressures, their different tendencies to react with the support material, and possible thermal decomposition of the parent material. Due to vapour pressure difference alone, the ratio of the evaporation rates of components A and B of an alloy may be obtained from Langmuir's expression (1.13) by assuming that the vapour pressure of each component is

depressed by an amount proportional to the relative concentrations C_A, C_B:

$$\frac{j_A}{j_B} = \frac{C_A p_A}{C_B p_B} \sqrt{\frac{m_B}{m_A}}. \tag{4.1}$$

A point of technical interest is that the higher the evaporation temperature of an alloy of widely different vapour-pressure components is, the closer is the composition of the film to the bulk alloy.

- **Flash Evaporation.** A rapid evaporation of a multicomponent alloy or compound, which tends to distill fractionally, may be obtained by continuously dropping fine particles of the material onto a hot surface so that numerous discrete evaporations occur.

- **Arc Evaporation.** By striking an arc between two electrodes of a conducting material, sufficiently high temperatures can be generated to evaporate refractory metals such as Nb and Ta. This method is also widely used for evaporation of carbon for electron-microscope specimens.

- **Exploding-Wire Technique.** This technique consists of exploding wire by a sudden resistive heating of the wire with a transient high current density approaching 10^6 A/cm^2. This is achieved by discharging a bank of condensers (≈ 10 to 100 μF), charged to a voltage ≈ 1 to 10 kV, through a metallic wire.

- **Laser Evaporation.** The enormous intensity of a laser may be used to heat and vaporize materials by keeping the laser source outside the vacuum system and focusing the beam onto the surface of the evaporant.

- **RF Heating.** The rf induction heating may be supplied to the evaporant directly or indirectly from the crucible material

- **Electron-Beam Evaporation.** The simple resistive heating of an evaporation source suffers from the disadvantages of possible contamination from the support material and the limitations of the input power, which make difficult to evaporate high-melting-point materials. $\Rightarrow$ Overcome with electron bombardment of the material.

The simplest arrangement consists of a heated W filament to supply electrons which are accelerated by applying a positive potential to the material for evaporation. The electrons lose their energy in the material $\Rightarrow$ molten drops, evaporation.

4.2   Molecular Beam Epitaxy

MBE is a sophisticated, finely controlled method for growing single-crystal epitaxial films in a high vacuum (10^{-9} Pa). The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film onto substrates held at an appropriate temperature. MBE deposition equipment consists of:

- **Vacuum system construction** closely follows this of surface analysis equipment - standard UHV practises are employed. A typical current MBE system is composed of four separate vacuum chambers: a load-lock for substrate entry and exit, a growth chamber, an auxiliary chamber for analysis or metallization and an intermediate or "buffer" chamber for pregrowth processing.

- **Sources** are key elements of any MBE system. They must be designed to supply the needed uniformity and material purity.

  - *Knudsen Cells* are standard thermal evaporation sources. They are deep crucibles in furnaces with cooled shrouds, equipped with a thermocouple. Construction materials are usually refractory metals such as Ta and Mo and insulators like alumina.

  - *Solid Source Cracking Cells.* Some materials, As and P, evaporate in more than one molecular form. Often the larger molecule will have a higher vapour pressure and a lower sticking coefficient for a given substrate temperature than the smaller molecules. $\Rightarrow$ the efficiency can be improved by cracking the larger molecule at the source. Source construction follows standard K-cell with the addition of a secondary heat zone at the source exit for cracking.

  - *Continuous Sources.* Sources which can be maintained in a liquid state (e.g., mercury).

  - *Electron Beam Heated Sources* are used for materials with very high melting temperatures (W, Co, Ni, Si, Ge).

  - *Implantation Sources.* The gas is ionised, optionally mass separated and the ions are accelerated towards the substrate.

  - *Source Shutters.* One of the main virtues of MBE originates from the fact that fast acting shutters coupled with a slow growth rate allow for monolayer film growth control. Shutter actuation times below 0.1 s are nominal.

- **Sample Manipulation.** MBE samples are mounted to Mo holders using In solder. At film growth temperatures, In is liquid and provides adequate attractive force and good thermal conductivity. Sample temperature can be set and maintained by either thermocouple or pyrometer feedback. Standard practise with large substrates (> 5 cm) is to rotate the wafer during the deposition.

Chapter 5

Gas-Phase Chemical Processes

Methods of film formation by purely chemical processes using the gas or vapour phase reactants on the one hand side and the solid phase reactants on the other hand side. It includes chemical vapour deposition and thermal forming processes.

5.1 Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is a materials synthesis processes whereby constituents of the vapour phase react chemically near or on a substrate surface to form a solid product. Most CVD processes are chosen to be **heterogenous** reactions. Undesirable **homogeneous** reactions in the gas phase nucleate particles that may form powdery deposits and lead to particle contamination.

Both chemical composition and physical structure can be tailored by control of the reaction chemistry and deposition conditions. Fundamental principles of CVD encompass an interdisciplinary range of gas-phase reaction chemistry, thermodynamics, kinetics, transport mechanisms, film growth phenomena and reactor engineering.

- chemical reactions in CVD: pyrolysis (thermal decomposition), oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reactions, chemical transport. A sequence of several reaction types may be involved.

- deposition variables: temperature, pressure (from low pressures, i.e., 10–1000 Pa - LPCVD, up to atmospheric pressures - APCVD), input concentration, gas flow rates, reactor geometry, operating principles. Kinetics of the reactions may depend on such factors like substrate material, structure and orientation.

- starting materials: inorganic, organometallic and organic reactants. Gases are preferred because they can be easily handled and distributed to the reactor. Liquid and solid reactants must be vaporized without decomposition at suitable temperatures and transported with a carrier gas through heated tubes to the reaction chamber.

- thin film materials: broad range of elements and compounds. Materials deposited at low temperatures (bellow 600 °C for silicon) are generally amorphous. Higher temperatures tend to lead to polycrystalline phases. Very high temperatures (typically 900–1100 °C in the case of silicon) are necessary for growing single-crystal films.

- applications:

  - fabrication of solid-state devices - dielectrics (oxides, silicates, nitrides), elemental and compound semiconductors (Si, GaAs, etc.), conductors (W, Mo, Al, refractory metal silicides),

  - tool technology - hard and wear resistant coatings such as boron, polycrystalline diamond, borides, carbides and nitrides,

  - metallurgical applications - corrosion resistant coatings for protection of metals, especially oxides and nitrides

Chemical reactors must provide several basic functions:

- transport of the reactant and diluent gases to the reaction site,

- provide activation energy to the reactants (heat, radiation, plasma),

- maintain a specific system pressure and temperature,

- allow the chemical processes for thin film deposition to proceed optimally,

- remove the by-product gases and vapours.

Reactor geometry affects the gas flow characteristics which, in turn affect the properties of the deposited layer. Two basic flow type reactors:

- Displacement or **plug flow reactor** in which the entering gas displaces the gas already present with no intermixing of successive fluid elements. Plug flow is a simplified and idealized picture of the motion of a fluid, whereby all the fluid elements move with a uniform velocity along parallel streamlines. Mass balance for reactant A involved in a single reaction is very simple: $F_A - (F_A + dF_A) = r_A dV$.

- **Perfectly mixed flow reactor** is the opposite extreme from the plug flow reactor. To approach the ideal mixing pattern, the feed has to be intimately mixed with the contents of the reactor in a time interval that is very small compared to the mean residence time of the fluid flowing through the vessel. The essential feature is the assumption of complete uniformity of concentration and temperature throughout the reactor.

There are different types of CVD techniques:

- CVD epitaxy and metal-organic CVD
  CVD epitaxy or vapour-phase epitaxy (VPE) and metal-organic chemical vapour deposition (MOCVD) are used for growing epitaxial films of e.g. silicon or compound semiconductors. Layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.

- low pressure and atmospheric pressure CVD
  These two methods are used for deposition of polycrystalline or amorphous materials like polysilicon, silicon nitride and Low Temperature Oxide (LTO). The deposition of thin films for semiconductor device manufacture by CVD at atmoshperic pressure (APCVD) was a widely accpeted process in 1976 when equipment for low-pressure CVD (LPCVD) was introduced into the marketplace. At that time, the 3-inch wafer was the predominantly wafer size used in production with some residual presence of smaller wafers and the 4-inch wafer just being introduced into advanced lines. In the next few years, the LPCVD process became the preferred method for chemical vapour deposition of thin films. The transformation to a new technology that required massive capital expenditure for new equipment took place at a rapid rate throughout the industry. The reason for this rapid change were: (1) a superior film quality, (2) a greatly reduced processing cost, and (3) greatly increased thtoughput per unit of capital investment. Improved film quality also means increased yields and decreased unit costs in an industry that was becoming increasingly competitive.

5.1.1 Epitaxy by Chemical Vapour Deposition

The world epitaxy is derived from the Greek "epi" - upon and "taxis" - to arrange. Thus, epitaxial deposition requires the ability to add and arrange atoms upon a single crystal surface. Epitaxy is a regularly oriented growth of one crystalline substance upon another. Specific applicat ions require controlling the crystalline perfection and the dopant concentration in the added layer. Two different kinds of epitaxy are recognized:

- Homo-epitaxy is growth in which the epitaxial layer is of the same material as the substrate.

- Hetero-epitaxy is growth in which the layer is a different material than the substrate.

Epitaxial layers can be prepared by a wide range of techniques including evaporation, sputtering and molecular beams. Epitaxial deposition by CVD uses a gaseous transport and chemical reactions. Important application of CVD epitaxy is a production of crystalline silicon (c-Si). With the **silicon epitaxy** radical changes in material properties can be created over small distances within the same crystal. This capability permits the growth of lightly-doped single c-Si on the top of heavily-doped c-Si, n-type Si over p-type Si and vice versa, Si layer with controlled dopant profiles etc. Successful silicon epitaxy depends upon having:

- high surface mobility for arriving atoms,

- numerous, equivalent growth sites,

- commercially significant growth rates.

For deposition of epitaxial c-Si films, chlorosilanes ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2) and SiH_4 are used in H_2 atmosphere. The heterogenous reaction involves the following steps:

- Arrival

  - bulk transport of reactants into the process volume
  - gaseous diffusion of reactants to the surface
  - adsorption of reactants onto the surface

- Surface reaction

  - surface reaction (reaction can also take place in the gas volume immediately above the surface)
  - surface diffusion
  - crystal lattice incorporation

- Removal of reactant by-products

  - reaction by-product desorption
  - gaseous transport of by-products
  - bulk transport of by-products out of process volume

The rate of CVD is primarily controlled by one of the following major groups of process steps:

- rate of arrival of reactants,

- surface reaction rate,

- rate of removal of by-products.

For typical epitaxy process (the best crystal quality), the reaction conditions are established so that the rate of arrival of the reactants controls the growth rate. The crystal quality of the epitaxial layer is controlled primarily by

- nature of the surface prior to the epitaxial growth: If the surface has a contamination, such as oxides or if the crystal is defective $\Rightarrow$ crystal defects. Surface is prepared by chemical/mechanical polishing and native oxide etching. H_2 bake at 1150 °C for 10 min remove a native oxide. The heating-up and etching with gaseous HCl/H_2 (0.1% HCl/H_2 mixture at 1150 °C $\Rightarrow$ 0.1–0.3 μm/min) can etch the silicon. However, if the etching rate is too high for given temperature the surface will be pitted instead of being polished.

- arrival rate relative to the surface diffusion rate: If the rate of arrival reactants greatly exceeds the surface diffusion rate, then diffusing atoms cannot move to the positions of the lowest energy $\Rightarrow$ deffects.

- nature of the lattice incorporation: the rate of lattice incorporation is a function of crystal orientation because the density of atomic sites is a function of crystallographic faces. The low growth rate for (111) planes encourages a defect called faceting or orange peel. To prevent faceting, (111) surfaces are cut a few degrees off the (111).

The conditions for acceptable commercial silicon epitaxy:

variable	horizontal	cylinder	bell jar
tilt angle	major	major, fixed	not applicable
gas inlet	minor	major	varies
wafer/carrier	recessed	recessed	recessed
wafer/wall	major	major	minor
exhaust pressure	minor	major	minor

In the *horizontal reactor* it is useful to break the thickness profile in the direction of gas flow into the front and back half. Each half can then be described as thick or thin in front, or thick or thin in back. The adjustments for thickness uniformity are divided in the same manner.

In the *cylinder reactor*

- Thickness is increased in the front (top of carrier) by increasing temperature and/or concentration of reactant

- and in the back by increasing the total flow rate, directing the gas jets in a more downward direction, reducing the process pressure (slower heating of gas) and bringing the back pressure toward a more positive value.

- Thickness uniformity is improved within a wafer from left to right by balancing the two jet flows, by lowering the temperature (controlled by surface reactions) and by increasing the distance between the wafer and the walls.

- Thickness variation at any distance along the carrier is averaged by rotation.

In the *bell jar* reactor the uniformity at any radius is averaged by rotation of the susceptor. The radial variation is a function of total flow rate:
low flow rate $\rightarrow$ thin outside, high flow rate $\rightarrow$ thick outside $\Rightarrow$ optimum value

Adjustment parameters for the *tapered cavity reactor* follow those for the horizontal reactor. Rotation of the circular cluster of tapered cavities averages the initial velocities and concentrations from multiple gas inlets.

Control of operator variables

- *Leak testing* includes bubble testing with sensitive detergent solutions, He mass spectrometers, high sensitive combustile gas detectors and pressure decay techniques

$$\text{leak rate \{sccm\}} = \frac{\Delta p}{\Delta t} \frac{V}{p_{\text{atm}}} \tag{5.1}$$

- *Gas flow control* is possible by four different methods

    - fixed or variable orifices
    - ball-in-tube flowmeters. The calibration is a function of pressure in the gauge tube

$$\frac{\text{actual flowrate}}{\text{calibrated flowrate}} = \sqrt{\frac{\text{actual pressure}}{\text{calibrated pressure}}} \tag{5.2}$$

    - mass flow controllers are based on the principle of measuring mass flow using gas heat capacity. There is the possibility of a back-loop control.
    - source controllers for liquids (bubblers). In this case a gas (e.g. H_2) is bubbled through a liquid (e.g. $SiCl_4$)

$$Q(SiCl_4) = \frac{Q(H_2) \ p(SiCl_4) \ [\text{eff.}]}{p_{\text{total}}} \tag{5.3}$$

    Bubblers require a constant temperature and pressure. Bubbler efficiency is fixed primarily by the size of the bubbles and the path lenght the bubbles travel through the liquid.

- Higher *temperature* is achieved by the heating systems:

    - Induction heating, using frequencies 3–400 kHz, with coils located internally or externally to the process chamber.
    - Radiative heating, using high intensity infrared heating lamps, located externally.
    - Resistance heating, using heaters located internally.
    - Combination of the above.

and controlled by the measurements. For Si epitaxy it has to be controlled with a precision of a few °C in the range 900–1300 °C and the only convenient method is radiation pyrometry (thermocouples are not stable in H_2 environment)

    - Disappearing filament pyrometers: brightness within a narrow wavelength range (650 nm) of a heated filament of known temperature is matched with the brightness of the target.
    - Electronic pyrometers: intensity of light within a narrow range of wavelenght is directly measured by a photovoltaic cell (Si photocells - 0.8 μm, PbS photocell - 2.2 μm) or a thermopile (assemplies of thermocouples on which the radiation is focused - broad band detectors).

- *Pressure* from the range 5–760 Torr implies viscous gas flow and for the constant mass flow rate, there is a little effect on the rate of arrival of reactants $\Rightarrow$ the effect of gas flow on the uniformity is the same. The number of volume changes per unit time is inverse proportional to the pressure $\Rightarrow$ strong effect on the material properties (dopant incorporation, crystal perfection).

Defects in epitaxy layers

- *Haze*, as revelaed by reflected light, is a fine pitting or slightly texture surface caused by oxidizer in the process sapce or by subsurface crystal damage in the substrate

- *Pits* are localized etching of substrate defects or local inhibition of epitaxy growth, often caused by contamination left on the surface prior to heat-up.

- *Orange peel* is a roughened surface appearance caused by having the growth rate too high for the deposition temperature. Subsurface crystal damage can also cause orange peel.

- *Faceted growth* is irregular, stepped growth over the surface caused by growing on (111) faces.Si should be cut 3–5° off the (111) plane towards the nearest (110) plane.

- *Edge growth* occurs when the growth rate at the edge of the wafer greatly exceeds that over the rest of the wafer surface.

- *Etch pit* are created by decorative etch technique and reveal crystal dislocations produced by slip, as well as other defects.

- *Crystallographic slip* is dislocation motion in response to thermall stress during epitaxy.

- *Stacking faults* are geometric defects nucleated at crystallographically disturbed sites on or near the growth surface. A uniform size of stacking faults indicates that the disturbance was all at the original surface prior to epitaxy.

- *Spikes and hillocks* are severe defects also caused by crystallographically disturbed sites. The larger defects are usually the result of particle contamination.

- *Shallow pits or haze* are revealed by decorative etching alone or etching followed by an oxidation cycle and indicate the presence of heavy metal precipitates.

Stavová rovnice:

$$\frac{pV}{T} = nR = \frac{N}{N_A}R = N\,k \tag{5.4}$$

kde $k = 1.38\mathrm{x}10^{-23}$ J.K^{-1}, $N_A = 6.022\mathrm{x}10^{23}$ mol^{-1}

5.2 Thermal Forming Processes

In the gas phase, thermal oxidation and nitridation is a chemical thin-film forming process in which the substrate itself provides the source for the metal or semiconductor constituent of the oxide and nitride, respectively. This technique is obviously much more limited than CVD.

5.2.1 Thermal Oxidation

The thermal oxidation has extremely important applications in silicon device technology where very high purity oxide films with high quality Si/SiO$_2$ interface are required. **Thermal oxidation of silicon** surfaces produces glassy films of SiO$_2$ for protecting highly sensitive p-n junctions and for creating dielectric layers for MOS devices. The temperature for this process lie in the range of about 700 °C to 1200 ∘C with either dry oxygen or water vapour (steam) as the oxidant. Steam oxidation proceeds at a much faster rate than dry oxidation. The oxidation rate is a function of the oxidant partial pressure and is controlled essentially by the rate of oxidant diffusion through the growing SiO$_2$ layer interface, resulting in a decrease of the growth rate with increased oxide thickness. The process is frequently conducted in the presence of hydrochloric acid vapours or vapours of chlorine-containing organic compounds. The HCl vapour formed acts as an effective impurity getter, improving the Si/SiO$_2$ interface properties and stability.

Silicon **oxidation under elevated pressure** is of technological interest where the temperature must be minimized, such as for VLSI devices. Since the oxidation rate of silicon is approximately proportional to pressure, higher product throughput and/or decreased temperatures can be attained. The oxidant in commercial systems is H_2O, which is generated pyrogenically from H_2 and O_2. Pressures up to 10 atm are usually used at temperatures ranging from 750 °C to 950 ∘C.

Gas-phase **oxidation of other materials** is of limited technical importance. Examples include metallic tantalum films converted by thermal oxidation to tantalum pentoxide for use as antireflection coating in photovoltaic devices and as capacitor elements in microcircuits. Other metal oxides grown thermally have been also used as capacitor dielectrics in thin-film devices, to improve the bonding with glass in glass-to metal seals and to improved corrosion resistance.