Basics of Molecular Beam Epitaxy (MBE)

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A brief introduction to the MBE technique is presented with main attention to the elemental source MBE. A discussion on the effusion cell as beam source is shortly given starting from ideal cases to real cells homogeneity problems. A short review regarding the thermodynamic approach to the MBE is pointed out. Focusing on the possibility that, despite the fact that MBE processes occur under strong nonequilibrium conditions, for the III/V elements, a thermodynamic approach can be used on the basis of equations for mass action in combination with the equations describing the conservation of the mass of the interacting elements.

1. Introduction

Molecular beam epitaxy is a technique for epitaxial growth via the interaction of one or several molecular or atomic beams that occurs on a surface of a heated crystalline substrate. In Fig. 1 a scheme of a typical MBE system is shown. The solid sources materials are placed in evaporation cells to provide an angular distribution of atoms or molecules in a beam. The substrate is heated to the necessary temperature and, when needed, continuously rotated to improve the growth homogeneity.
According to Fig. 2, the molecular beam condition that the mean free path λ of the particles should be larger than the geometrical size of the chamber is easily fulfilled if the total pressure does not exceed 10^{-5} Torr. Also, the condition for growing a sufficiently clean epilayer must be satisfied, e.g. requiring for the monolayer deposition times of the beams t_b and the background residual vapor t_res the relation $t_\mathrm{res} < 10^{-5}\, t_\mathrm{b}$. For a typical gallium flux Γ of $10^{19}\,\mathrm{atoms\,m^{-2}s^{-1}}$ and for a growth rate in the order of $1\,\mu$m/h, the conclusion is that $p_\mathrm{res} \leq 10^{-11}$ Torr. Considering that the sticking coefficient of gallium on GaAs atoms in normal operating conditions is approximately unity and that the sticking coefficient of most of the typical residual gas species is much less than 1, the condition above results to be not so strict, nevertheless ultra high vacuum (UHV) is required. Thus, UHV is the essential environment for MBE. Therefore, the rate of gas evolution from the materials in the chamber has to be as low as possible. So pyrolytic boron nitride (PBN) is chosen for the crucibles which gives low rate of gas evolution and chemical stability up to 1400° C, molybdenum and tantalum are widely used for the shutters, the heaters and other components, and only ultrapure materials are used as source. To reach UHV, a bakeout of the whole chamber at approximately 200° C for 24 h is required any

time after having vented the system for maintenance. A cryogenic screening around the substrate minimizes spurious fluxes of atoms and molecules from the walls of the chamber. Despite this big technological problems, MBE systems permit the control of composition

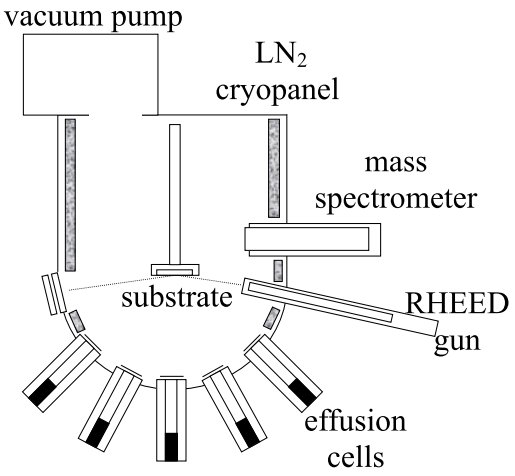

Fig. 1: A typical MBE system.

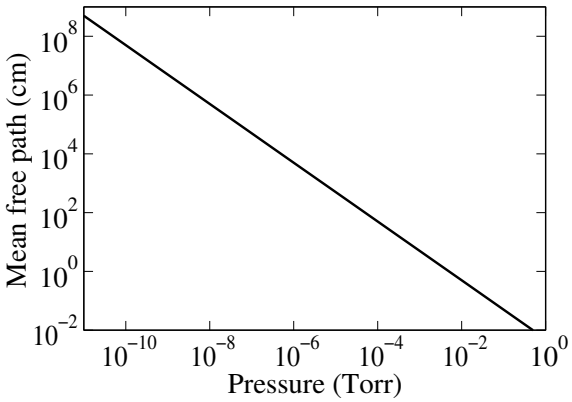

Fig. 2: Mean free path for nitrogen molecules at 300K.

and doping of the growing structure at monolayer level by changing the nature of the incoming beam just by opening and closing mechanical shutters. The operation time of a shutter of approximately 0.1 s is normally much shorter than the time needed to grow one monolayer (typically 1–5 s). Careful variation of the temperatures of the cells via PID controllers permits the control of the intensity of the flux of every component or dopant of better than 1 %. The UHV environment of the system is also ideal for many in-situ characterization tools, like the RHEED (reflection high energy electron diffraction). The oscillation of the RHEED signal exactly corresponds to the time needed to grow a monolayer and the diffraction pattern on the RHEED window gives direct indication over the state of the surface as can be seen in Fig. 3.

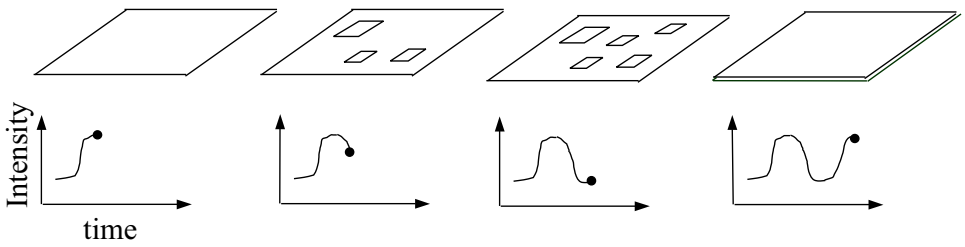

Fig. 3: RHEED oscillations.

2. Effusion Cells

The effusion cells used in MBE systems exploit the evaporation process of condensed materials as molecular flux source in vacuum. The understanding of the properties of real effusion cells is complicated and not straightforward, so easier models are needed and just the main complications are subsequently added.
In a closed enclosure, for pure substances, an equilibrium is estabilished between the gas and the condensed phase. Such systems have only one degree of freedom f, that means that the pressure p_{eq} is a function of the temperature T and can be approximately expressed by the Clapeyron equation [1]

$$p_{\mathrm{eq}}(T) = A \exp\left(-\frac{\Delta H}{k_{\mathrm{B}} T}\right). \tag{1}$$

Where in (1) ΔH is the evaporation enthalpy and k_{B} the Boltzmann constant. Under this equilibrium condition, we observe that when the p_{eq} is very low, it is possible to treat the incoming and the outcoming flux independently. A close look to the fluxes of particles having a mass m on the condensed phase surface shows that the maximum value for the evaporated flux Γ_{m} is

$$\Gamma_{\mathrm{m}} = \frac{p_{\mathrm{eq}}}{\sqrt{2\,\pi m\, k_{\mathrm{B}} T}}. \tag{2}$$

This assumes that each molecule from the gas phase is always trapped by the surface and an equal opposite flux of material must leave the condensed phase to maintain the equilibrium pressure. Considering now that the impinging beam is partially reflected and only a fraction a is accommodate on the surface, the complete expression for the flux leaving the surface can be easily found as

$$\Gamma = a\,\Gamma_{\mathrm{m}}. \tag{3}$$

The factor a is dependent on the microscopic status of the surface and is strongly unpredictable and because of (3) the flux of material. The Knudsen evaporating method overcome this problem providing a molecular beam that is independent of a. An ideal Knudsen cell is composed of a large enclosure were the condensed material is in thermodynamic equilibrium with the gas phase and of an orifice so small that the equilibrium pressure p_{eq} is not perturbed. The orifice geometry has to fulfill two additional conditions, one for the diameter d, that fullfils $d \ll \lambda$ at p_{eq} and one for its wall thickness L, assumed to be vanishingly thin. Under these conditions, the orifice is a surface with an evaporant pressure p_{eq} and has not the ability to reflect any of the incoming molecules resulting in $a = 1$ and the number of molecules per time unit of the created beam is $A\,\Gamma_{\mathrm{m}}$, where A is the orifice area.
The ideal Knudsen cell exhibits an angular distribution of the evaporated particles that follows a cosine law, where the angle θ is referred to the normal to A.

$$\frac{d\Gamma_\theta}{d\Omega} = \frac{\Gamma_{\mathrm{m}}}{\pi}\cos\theta, \tag{4}$$

so that the flux at distances much bigger than the orifice dimensions is proportional to $\cos\theta$. Using Clausing's model [2] for the conductance of a molecular flow in a cylindrical tube, Dayton has studied the deviation from ideality given when L/d is not longer 0. In this calculations a model is necessary to describe the interaction of the molecules with the orifice walls. Random reflection is the simplest approach, but also more complicated ones are possible involving also temporary adsorption and surface diffusion [3]. However, an estimation of a for the surface of the condensed material is not required. When L/d increases, the beam is more focused on the normal direction and for $L/d = 1$ the deviation from the cosine law is relevant. These models are important tools to measure p_{eq} and so thermodynamic quantities related with (1). When it is not possible to consider the enclosure as infinitely large and when it is therefore important to consider the influences of the main body of the cell, the value of the a coefficient is needed [4]. This is also the case of cylindrical and conical cells, that are widely used in MBE systems, there is no thermodynamic equilibrium between condensed and gas phase and therefore the value of a is necessary to calculate the emerging flux. Nevertheless, assuming for a a homogeneous distribution on the condensed phase material surface, it is possible to estimate the shape of the outcoming vapour beam using all the modelling discussed before. Many variables

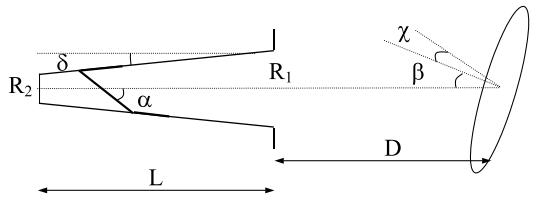

Fig. 4: Example of the geometrical configuration for a conical effusion cell.

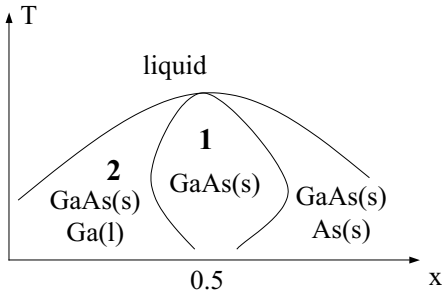

Fig. 5: Simplified phase diagram (T–x section) for GaAs. (s) is the solid and (l) is liquid phase. A gas phase is always present.

are involved in this problem, like shown in Fig. 4. For example, very often the source material is in liquid form (Ga, Al, In) and so an additional angle α is required to set up the geometry of the system. Some materials wet the crucible surface (e.g. aluminum in PBN crucibles), so other variables are needed to specify the position of the evaporating surface. A complex work of optimization is therefore necessary in relation to the fact that in a MBE system many cells must operate and for each one a suitable geometrical configuration cell substrate must be properly chosen. Control and homogeneity of the cells temperature are crucial, because of the strong dependence of the flux on temperature. W-Re thermocouples are used for the chemical stability at high temperatures and for the very low outgassing rate. Tantalum heater elements and radiative shields are chosen for the excellent refractory properties. These elements are often self-supporting preventing the use of material that does not have such low rate of gas evolution. Great care is

also needed to decrease the temperature difference between heater and crucible. This is necessary to avoid very high temperature outgassing from tantalum, and to reduce the dissipated heat which causes possible uncontrolled outgassing from other parts of the vacuum chamber.

3. Thermodynamic Approach

In the past there was a lot of controversy concerning the possibility of applying thermodynamics to the growth processes in MBE. In the 1980s, MBE was developing experimentally very successfully, and most of the problems particularly regarding AlGaAs and InGaAlAs materials were solved empirically. In recent years, the need for MBE grow with newer materials revealed the importance of a closer theoretical modeling of the growth processes. In the case of MBE, it seems that the system cannot be described by a thermodynamic representation, because the different parts like sources, substrate, and walls are at different temperatures. However, it is possible to assume that the temperature of the system is the temperature of the substrate if the thermalization time is much shorter than the time required to grow a monolayer. So we consider an equilibrium state in which the partial pressures are the ones relative to fluxes of atoms or molecules leaving the substrates surface at its temperature.
The validity of this assumption is confirmed by two facts. First that the fluxes of atoms or molecules leaving the substrate have its temperature irrespective of the temperature of fluxes arriving at the surface. Second, the nature of the arsenic molecules, e.g. in the GaAs system, leaving the substrate is independent of the nature of the arsenic molecules reaching the surface. In this case, we have to consider the following reaction with the associated mass action equation [5]

$$2\mathrm{As_2(g)} \rightleftharpoons \mathrm{As_4(g)} \quad \text{and} \quad p_{\mathrm{As_2}}^2\, p_{\mathrm{As_4}}^{-1} = 3.98 \cdot 10^8 \exp\left(-\frac{2.35}{k_\mathrm{B}T}\right), \tag{5}$$

where the pressures are measured in atmospheres and $k_\mathrm{B}T$ in eV. The dimeric fraction of arsenic molecules leaving the substrate exactly follows the temperature behaviour predicted by (5) [6]. Starting by these assumptions it is possible to model the basic behavior of the III/V binary compounds in MBE conditions. For a binary compound, a phase diagram like the one sketched in Fig. 5 must be considered. In the region labeled with 1 GaAs(s) is present in equilibrium with Ga(g) and $\mathrm{As_2(g)}$ and $\mathrm{As_4(g)}$(with just a small deviation, exaggerated in the figure, from the $\mathrm{Ga_{0.5}As_{0.5}}$ stoichiometry possible via point defect, but always much smaller than 10^{-4} even at high temperatures). Using the Gibbs' Phase Rule $f = c - p + 2$ [7] that relates the number of components c and the number of different phases p to the number of degrees of freedom f, it is easy to recognize that in the region 1 of the phase diagram $f = 2$. So temperature and pressure are independent. In the region 2, liquid gallium is present and therefore $f = 1$ as 3 phases are present. Hence a function $p = p(T)$ exists. In the region 1, the reactions between the components are

$$\mathrm{GaAs(s)} \rightleftharpoons \mathrm{Ga(g)} + \frac{1}{2}\mathrm{As_2(g)} \quad \text{and} \quad 2\mathrm{As_2(g)} \rightleftharpoons \mathrm{As_4(g)}. \tag{6}$$

The mass action equation is

$$p_{\mathrm{Ga}}\, p_{\mathrm{As_2}}^{\frac{1}{2}} = K_{\mathrm{GaAs}} = 2.73 \cdot 10^{11} \exp\left(-\frac{4.72}{k_{\mathrm{B}}T}\right). \tag{7}$$

Under normal MBE growth conditions, when $T > 450^{\circ}\,\mathrm{C}$, it is possible to neglect the $p_{\mathrm{As_4}}$ contribution to the total pressure. Therefore the total pressure is given by

$$p_{\mathrm{T}} = p_{\mathrm{Ga}} + p_{\mathrm{As_2}} = \frac{K_{\mathrm{GaAs}}}{p_{\mathrm{As_2}}^{\frac{1}{2}}} + p_{\mathrm{As_2}}. \tag{8}$$

The gallium pressure is maximum on the left side of the diagram, where it approximately corresponds to the gallium pressure on pure liquid gallium, moving to the right, because of (7), this partial pressure will decrease while the arsenic pressure is increasing. For some range in temperature, the pressure shows a minimum for a suitable stoichiometry of the solid phase. This is the condition that has to be applied to find the flux in free sublimation, i.e. sublimation in vacuum. The reason for the minimum condition is very general [8]. In a compound A_xB_{1-x}, the pressure is the sum of the pressures of its components. If the partial pressure of the component B is bigger than the one of the component A, the composition of the condensed phase will be enriched with A, moving the system to a lower partial pressure. If a minimum for a certain x exists, this will be asymptotically reached. In this point the sublimation is congruent. In our case the equation for a minimum of the pressure is

$$\frac{dp_{\mathrm{T}}}{dp_{\mathrm{As_2}}} = \frac{dp_{\mathrm{T}}}{dp_{\mathrm{Ga}}} = 0. \tag{9}$$

Solving this with the (8) will bring the result

$$p_{\mathrm{Ga}} = 2\, p_{\mathrm{As_2}} = (2\, K_{\mathrm{GaAs}}^2)^{\frac{1}{3}}. \tag{10}$$

This corresponds to congruent sublimation of GaAs. When the temperature increases over a certain temperature T_{max}, the pressure of the more volatile component, in this case arsenic, increases faster and there will be no minimum in the region 1. Under this condition, a liquid gallium phase is created. The temperature T_{max} is called "temperature of maximum sublimation". T_{max} is calculated imposing p_{Ga} from (10) equal to the value of the gallium pressure over the liquid gallium

$$p_{\mathrm{Ga}}^{\mathrm{L}} = 2.88 \cdot 10^{5} \exp\left(-\frac{2.74}{k_{\mathrm{B}}T}\right). \tag{11}$$

The value of T_{max} is approximately $630^{\circ}\,\mathrm{C}$. The free sublimation rate is so given by

$$v = -\,V\, \frac{p_{\mathrm{Ga}}}{\sqrt{2\,\pi m_{\mathrm{Ga}}\, k_{\mathrm{B}}T}}, \tag{12}$$

where p_{Ga} is defined by (9) and V is the volume occupied by a pair of gallium and arsenic atoms in GaAs. When an external As_2 flux is supplied, so that $p_{\mathrm{As_2}}^{\mathrm{ext}} \gg p_{\mathrm{As_2}}$, for the (7) we will obtain a reduced Ga evaporated flux

$$p_{\mathrm{Ga}}^{\mathrm{red}} = \frac{K_{\mathrm{GaAs}}}{(p_{\mathrm{As_2}}^{\mathrm{ext}})^{\frac{1}{2}}}. \tag{13}$$

Thereby a suppression of the sublimation occurs. The rate of evaporation inversely proportional to the square root of the arsenic flux to the substrate is experimentally observed in MBE systems. For an external As_4 flux in (13), $p^{\text{ext}}_{\text{As}_2}$ must be exchanged with $2\,p^{\text{ext}}_{\text{As}_2}$. It is important to emphasize that in the previous calculations we have used the fact that the sticking coefficient of gallium on GaAs is ≈ 1, because the outcoming flux, and so the related pressure, is always given by (3).
When an external gallium flux is added the growth rate can be expressed by

$$v = -V\,\frac{p_{\text{Ga}} - p^{\text{ext}}_{\text{Ga}}}{\sqrt{2\,\pi m_{\text{Ga}}\,k_{\text{B}}T}}. \tag{14}$$

Just considering that the arsenic flux is always much bigger than the one of gallium, neglecting the fraction of arsenic that will take part in the growth process, and considering always the condition $p_{\text{As}_2} \gg p_{\text{As}_4}$, for the growth rate we get

$$v = C\,\left[p^{\text{ext}}_{\text{Ga}} - \frac{K_{\text{GaAs}}}{(p^{\text{ext}}_{\text{As}_2})^{\frac{1}{2}}}\right]. \tag{15}$$

Also the temperature dependence implicit in (15) was experimentally found [9]. So for the typical $p^{\text{ext}}_{\text{As}_2}$ with a value of $10^{-6} - 10^{-4}$ Torr which is used, the growth rate is mainly controlled by the gallium flux. A solid arsenic phase is never formed in MBE system because the typical arsenic pressure would be for this temperature, T > 500° C, in Torr range. The excess arsenic flux fixes a point in the phase diagram and so determines the type and concentration of point defects. This considerations are valid for many III/V compounds [10].

Compounds	$K_{\text{III/V}}$	$T_{\max}(^\circ\,\text{C})$
AlAs	$1.63 \cdot 10^{10} \exp\left(-\frac{5.39}{k_{\text{B}}T}\right)$	902
GaAs	$2.73 \cdot 10^{11} \exp\left(-\frac{4.72}{k_{\text{B}}T}\right)$	630
GaP	$2.26 \cdot 10^{11} \exp\left(-\frac{4.71}{k_{\text{B}}T}\right)$	571
InAs	$7.76 \cdot 10^{11} \exp\left(-\frac{4.34}{k_{\text{B}}T}\right)$	508
InP	$8.34 \cdot 10^{11} \exp\left(-\frac{4.02}{k_{\text{B}}T}\right)$	268

For each compound equations like (11) can be used to calculate the $T_{\max}$. Extremely interesting is an overview on the ternary compounds. $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, $Al_xIn_{1-x}As$ were successfully analyzed. The problem in a ternal compound is the estimation of the activities coefficient γ that take the nonideal nature of the alloy into account. $Al_xGa_{1-x}As$ is a special case having $\gamma_{\text{GaAs}} = \gamma_{\text{AlAs}} = 1$. In other cases, e.g. $GaAs_xP_{1-x}$ we can write the following equations

$$p_{\text{Ga}}\,p^{\frac{1}{2}}_{\text{As}_2} = \gamma_{\text{GaAs}} K_{\text{GaAs}} x \quad \text{and} \quad p_{\text{Ga}}\,p^{\frac{1}{2}}_{\text{P}_2} = \gamma_{\text{GaP}} K_{\text{GaP}} (1-x) \tag{16}$$

together with the (5) and another mass action equation for the reaction $2P_{2(g)} \rightleftharpoons P_{4(g)}$. Considering that again the dimers are the dominating species, for $T > 500^\circ C$, and neglecting the amount of group-V elements that take part in the growth process we can find for the resulting final composition of $GaAs_xP_{1-x}$

$$x = \frac{1}{\left(\frac{\gamma_{GaP} K_{GaP}}{\gamma_{GaAs} K_{GaAs}}\right)\left(\frac{p^{ext}_{P_2}}{p^{ext}_{As_2}}\right)^{\frac{1}{2}} + 1} \tag{17}$$

Even neglecting the influence of the activity coefficients in (17), a good qualitative agreement can be found with the experimental data [11].

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