

Thermodynamic models of molecular beams

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The thermodynamic models of the molecular beams currently used in the MBE systems are developed. The main difference with respect to traditional thermodynamic models resides on the consideration of physical behavior of the molecules of the beams. Usually the beams are considered as particles in a vapor phase, with three translational degrees of freedom. However the molecular beams emerging from the conventional and Knudsen effusion cells have different behavior. In the developed models, the beams emerged from the conventional cells as well as desorbed fluxes in the molecular beam epitaxy are considered as canonical ensembles of the one-dimensional ideal gas moving in a given direction. The thermodynamic characteristics of the molecules in the beams emerging from the cracking and Knudsen effusion cells are described by the velocity distribution law. These differences impact on the results of the thermodynamic models as compared with those in the literature. In this work the chemical potential of the conventional effusion and the Knudsen effusion cells considering their own characteristics are shown.

Keywords: Molecular Beam Epitaxy (MBE); Adsorption/desorption Kinetics; Physics of Crystal Growth

1. Introduction

The molecular beam epitaxy (MBE) is one of the most important technologies of the modern solid state electronics [1-3]. In MBE, the epitaxial films are formed from the molecular beams emerging from the two types of the effusion cells and spreading in ultrahigh vacuum (UHV) environment. The conventional effusion cells of modern MBE have a large aperture design for growth on substrates of 2-4 inches in diameter. Therefore, the formation process of the flux from these MBE cells is close to the free evaporation. The already developed models of MBE consider the molecules in the incident fluxes as species of the vapor phase [1-3]. However, the one direction movement of the particles in the fluxes after free evaporation are distinct from the species of the vapor phase having three translational degrees of freedom. Therefore, the kinetic energy as well as the entropy of the particles emerging from the conventional MBE cells and in the vapor phase are different one from another [4]. Therefore is reasonable to represent the free evaporated particles as species of a one-dimensional gas moving in a given direction [4]. Moreover, the desorbed fluxes in the UHV of the MBE equipment may be described by the same way.

The emergent molecular beams emerging from the Knudsen cells and spreading in UHV have been studied in some aspects. The intensity and shape of the fluxes, velocities of the particles of the molecular beams emerging from the Knudsen effusion cells having the small aperture are described in [5]. The modern MBE cracking cells having a set of the small apertures can be considered as Knudsen cells [3]. However, any thermodynamic characteristics of the beams emerged from the Knudsen cells are known yet. The vapor in the Knudsen cell with a

small aperture is in thermodynamic equilibrium with the evaporated material. The small aperture selects the highly energetic particles of the vapor in the flux. Thus, the mean velocity of the particles in the emergent flux from the Knudsen cell is larger than the mean velocity of the particles inside the same cell.

The characteristics of the one-dimensional ideal gas are different from those of the emergent molecular beam from the cell with a small aperture [4-5]. The mean velocity of the particles in the molecular beams described in [5] are in $3\pi/4$ times more than that of the particles of the one-dimensional ideal gas moving in a given direction [4]. The substantial difference in the mean velocity is produced by two causes. At first, the mean velocity of the particles emerging from the small aperture is larger than that of the vapor particles at the same temperature. At second, the vapor particles have three translational degrees of freedom in comparison with the particles of the one-dimensional ideal gas that have one translational degree of freedom. Thus, the kinetic energy for the particles of a emergent molecular beam from the cell with a small aperture is substantially larger than that of the particles of the ideal gas at the same temperature. The distinct mean velocity will also lead to the different entropy of these two types of the molecular beams having the same fluxes and temperature.

The thermodynamic models of the beams can be used in order to describe the non-equilibrium MBE growth runs [5]. The deviation from thermodynamic equilibrium of processes is usually estimated by the affinity of reaction [6]. The affinity is the difference between the chemical potentials multiplied by the coefficients of the reaction equation. Thus, in order to describe the affinity of the MBE growth run it is necessary to know the chemical potentials of the particles in the beams. It is reasonable to

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consider desorption of the particles physisorbed from the fluxes as a quasiback reaction with respect to physisorption of the same particles.

Crystal growth theory suggests to use a chemical potential difference as a general measure for the driving force. Obviously, this would facilitate a confrontation between theory and experiment[6].

The aim of the study is the development of the thermodynamic models of the molecular beams.

2. Molecular Beams Emerging from the Conventional MBE cells

The incident and desorbed fluxes in the MBE are presented as a set of the one-dimensional ideal gases with the particles moving in a given direction. The consideration of the fluxes as a set of the one-dimensional ideal gases is used due to the small density of the particles in the fluxes and absence of the interactions between the fluxes.

The thermodynamic characteristics of the particles in a flux can be described by the partition function of the one-dimensional ideal gas with the particles moving in a given direction. Let us consider the steady state of the free linear movement of the particles in the one-dimensional space with the distance L . In such a case, the flux can be considered as a canonical ensemble since temperature, distance and number of particles in the flux are given values. The partition function of a particle of the one-dimensional ideal gas moving in a given direction represented as a canonical ensemble is written as[4]:

$$q = \frac{\sqrt{2\pi mk_B T} \sigma e l}{h} \quad (1)$$

where k_B and h are the Boltzmann and Plank constants, respectively, m and σ are mass and internal partition function of particle, respectively, l is the mean distance between the nearest particles, e is the base of natural logarithm and T is the temperature in Kelvin. The partition function of the flux in this case is given as $Q = q^N$, where N is the number of particles in the flux. The thermodynamic functions of the one-dimensional ideal gas moving in a given direction are expressed by the partition function of the flux as:

The energy:

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_L.$$

The entropy:

$$S = k_B \left[\ln Q + T \left(\frac{\partial \ln Q}{\partial T} \right)_L \right].$$

The Helmholtz free energy:

$$F = -k_B T \ln Q.$$

The one-dimensional pressure:

$$P = - \left(\frac{\partial F}{\partial L} \right)_T.$$

The Gibbs free energy:

$$G = F + PL.$$

The chemical potential:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,L}.$$

Thus, the chemical potential of a particle of the one-dimensional ideal gas (μ^{OD}) moving in a given direction[4] can be written in according with [1] as:

$$\mu^{OD} = -k_B T \ln \left(\sigma l \frac{\sqrt{2\pi m k_B T}}{h} \right) \quad (2)$$

The part of the free energy for a particle of the flux depending on the internal degrees of freedom may be estimated by the interpolation expression for the chemical potential of a particle of the concrete ideal gas as:

$$-k_B T \ln \sigma = \mu^{OG} + k_B T \ln \left[\frac{\sqrt{(2\pi m k_B T)^3}}{h^3} \times \frac{k_B T}{P_{St}} \right], \quad (3)$$

where μ^{OG} is the chemical potential of the particle of the gaseous phase in the standard state, P_{St} is the standard pressure equal to 1 atm. The mean distance between the particles in the flux is equal to the ratio between the mean velocity of the particles of the one-dimensional ideal gas that move in a given direction[4] and the flux per surface site. The mean velocity of the particles of the one-dimensional ideal gas moving in a given direction is written as:

$$\bar{v}_{od} = \frac{\int_0^{\infty} v \exp \left\{ -\frac{mv^2}{2k_B T} \right\} dv}{\int_0^{\infty} \exp \left\{ -\frac{mv^2}{2k_B T} \right\} dv} = \sqrt{\frac{k_B T}{2\pi m}} \quad (4)$$

Thus, the mean distance between the particles is given as:

$$l = \sqrt{\frac{k_B T}{2\pi m}} \times \frac{N_S}{W}, \quad (5)$$

where N_S is the density of the surface sites, W is a flux. Hence, the chemical potential per particle of the one-dimensional flux may be written as:

$$\mu^{OD} = \mu^{OG} + k_B T \ln \left[\frac{\sqrt{(2\pi m k_B T)^3}}{h^3} \times \frac{h}{\sqrt{2\pi m k_B T}} \times \sqrt{\frac{2\pi m}{k_B T}} \times \frac{W k_B T}{P_{St} N_S} \right] \quad (6)$$

Therefore the chemical potential for a conventional effusion cell is expressed as:

$$\mu^{OD} = \mu^{OG} + k_B T \ln \left[\frac{\sqrt{(2\pi m k_B T)^3}}{h^2} \times \frac{W}{P_{St} N_S} \right] \quad (7)$$

The chemical potential obtained for the conventional effusion cell can be compared with the chemical potential for an ideal gas given as:

$$\mu^G = \mu^{OG} + k_B T \ln(P/P_{St}) \quad (8)$$

Using the one-dimensional analog for the ideal gas law in order to describe the pressure of the particles inside the chamber $W = \frac{P}{\sqrt{2\pi m k_B T}}$, we have:

$$\mu^{OD} = \mu^{OG} + k_B T \ln \left(\frac{2\pi m k_B T}{h^2 N_S} \right) + k_B T \ln \frac{P}{P_{St}} \quad (9)$$

Therefore in this particular case the chemical potential for the beam emerged from a conventional effusion cell is larger than the chemical potential for a gas with three translational degrees of freedom, this fact is consequence of the larger entropy in a gas with a Maxwellian behavior. This difference is important in order to correlate the theory with the experiment. The developed model expressed by Eq.(7) was used to explain some experimental results[8].

3. Molecular Beams Emerging from Cracking and Knudsen Effusion Cells

The sources in the early molecule beam experiments as well as the modern cracking cells consist of small chambers that contain the molecules in a gas or vapor at a few mm Hg pressure and have small apertures or cells with the Knudsen effusion regime[5]. In a volume of gas, such as these inside the source, the velocity distribution of the molecules is in accordance with the Maxwell distribution law. The Maxwell distribution law gives:

$$\frac{dN}{dv} = N f_{Maxll}(v) = \frac{4N}{\sqrt{\pi}} \sqrt{\left(\frac{m}{2k_B T} \right)^3} v^2 \exp \left\{ -\frac{mv^2}{2k_B T} \right\}, \quad (10)$$

where N is a total number of molecules of a gas, m and v are the mass and velocity of a molecule, $f_{Maxll}(v)$ is the Maxwell velocity distribution.

On a first instance one might expect that Eq. (10) would also be applicable to molecules from the Knudsen effusion cell since the molecules in the beam are obtained from a gas or vapor. However, such is not the case as it can be seen. In particular, the probability of a molecule emerging from the small source aperture is proportional to the molecular velocity[5]. Therefore, the velocity dependence

of molecules in the beam should be proportional to Eq. (10) multiplied by v . The constant of proportionality can then be obtained, as usually, by normalizing to the total number of molecules in a beam N . Thus, the velocity distribution of the particles in the beam from the Knudsen effusion cell is given as:

$$\frac{dN}{dv} = N f_{Knd}(v) = \frac{Nm^2 v^3}{2k_B^2 T} \exp \left\{ -\frac{mv^2}{2k_B T} \right\}, \quad (11)$$

where $f_{Knd}(v)$ is the velocity distribution in a Knudsen cell.

The different velocity distributions for molecules in a volume and in a beam from the Knudsen effusion cell lead to the different mean velocities in two cases that are written as:

In a volume gas the mean velocity is:

$$\bar{v}_{Maxll} = 2 \sqrt{\frac{2k_B T}{\pi m}}, \quad (12)$$

where \bar{v}_{Maxll} is the mean velocity in a volume of a gas.

In an emergent molecular beam emerged from the Knudsen effusion cell the mean velocity is:

$$\bar{v}_{Knd} = \frac{3\pi}{4} \sqrt{\frac{2k_B T}{\pi m}}, \quad (13)$$

where \bar{v}_{Knd} is the mean velocity in an emergent molecular beam from the Knudsen effusion cell.

The mean velocity of molecules in the beam from the Knudsen cell is larger than the mean velocity of molecules in a volume of a gas, at the same temperature. In fact, a small aperture of the Knudsen cell selects the higher energy molecules for the beam. Therefore, the velocity distribution of molecules in the beam from the Knudsen effusion cell does not correspond to the Maxwell distribution law. In consequence, the thermodynamic characteristics of the emergent molecule beam from the Knudsen cell cannot be described by the minimum condition of the free energy. Therefore is important to obtain a model for the description of the molecules emerging from a Knudsen cell.

The mean kinetic energy of an emergent molecule beam from the Knudsen effusion cell can be represented by the mean velocity as:

$$u_{Knd} = \frac{m \bar{v}_{Knd}^2}{2} = \frac{9\pi k_B T}{16}. \quad (14)$$

The entropy of the beam from the Knudsen effusion cell may be considered as the entropy of a non-equilibrium ideal gas[9]. The entropy of the non-equilibrium ideal gas is given as:

$$S = k_B \int n \ln \frac{e}{n} d\tau, \quad (15)$$

where n is the distribution density of the particles in the phase space, e is the base of the natural logarithm, $d\tau = \frac{dqdp}{h}$ is the number of quantum states in the element of the two-dimensional phase volume $dqdp$, q and p are the coordinate and momentum of a molecule on the two-dimensional phase space of molecules, respectively, and h is the Plank constant. The distribution density of the particles in the beam from the Knudsen effusion cell in accordance with (11) is written as:

$$n = h \frac{N}{L} \frac{p^3}{2m^2 k_B^2 T^2} \exp\left\{-\frac{p^2}{2mk_B T}\right\}, \quad (16)$$

where L is a size of the beam. Respectively, the entropy is given as:

$$S = k_B \int n \ln \frac{e}{n} d\tau = \quad (17)$$

$$= Nk_B \left\{ 2 + \frac{1}{2} C - 3 \left(\frac{h^2 N^2}{L^2 m k_B T} \right)^2 \left[\frac{11}{6} - C - \ln \left(\frac{L^2 m k_B T}{h^2 N^2} \right) \right] \right\},$$

where C is Euler's constant that is defined by the limit:

$$C = \lim_{s \rightarrow \infty} \left(\sum_{m=1}^{\infty} \frac{1}{m} - \ln s \right) = 0.577215.$$

The part of the chemical potential depending on the internal degrees of freedom can be described as before, so that:

$$-k_B T \ln \sigma = \mu^{OG} + k_B T \ln \left(\frac{\sqrt{8\pi^3 m^3 k_B^5 T^5}}{h^3} \right), \quad (18)$$

where σ is the internal partition function of molecule, μ^{OG} is the chemical potential of a particle of the gaseous phase in the standard state that is usually given as an explicit function of temperature.

The chemical potential of the molecule in the emergent beam from the Knudsen effusion cell is given as:

$$\mu_{Knd} = \mu^{OG} + k_B T \ln \left(\frac{\sqrt{8\pi^3 m^3 k_B^5 T^5}}{h^3} \right) + \frac{9\pi k_B T}{16} + \quad (19)$$

$$-k_B T \left\{ 2 + \frac{1}{2} C - 3 \left(\frac{h^2 N^2}{L^2 m k_B T} \right)^2 \left[\frac{11}{6} - C - \ln \left(\frac{L^2 m k_B T}{h^2 N^2} \right) \right] \right\}.$$

In order to compare the chemical potential for the beams emerging from a Knudsen effusion cell and a conventional effusion cell we need to use similar process conditions. Using the characteristics of the runs described in [10] we have estimated the beam equivalent pressure, (BEP), of the gallium atoms. Introducing this parameter in the equation (19), the number of particles (N) is obtained from the mean velocity of the particles in the beam, given in the equation (13) and the time to travel the reactor with a characteristic length L . The estimations show us that the chemical potential of the particles from a Knudsen cell is larger than the chemical potential of the particles from the conventional effusion cell. This result is in agreement with the fact that the mean velocity of the particles emerging from a Knudsen cell is larger than the particles in free evaporation, therefore the enthalpy is larger too.

4. Conclusions

The thermodynamic models of molecular beams emerged from the conventional effusion cells and from the Knudsen cells are developed. The molecular beams are represented as one-dimensional ideal gas and non-equilibrium ideal gases moving in a given direction. The thermodynamic characteristics of the molecules in the both types of the beams are described. The analysis of the chemical potential for both type of beams show us that this is larger for the molecular beams emerging from a Knudsen effusion cell. The chemical potential of both type of beams are larger than the chemical potential for a Maxwellian gas with three translational degrees of freedom. These results are a natural consequence of the intrinsic thermodynamic characteristics of the beams.

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