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On the Thermal Behaviour of Molecular Beam Effusion Sources

Molecular beam epitaxy (MBE) takes advantage of crucibles indirectly heated by an electric resistance heater. These thermal sources can be used to evaporate a great variety of materials. A precise control of the evaporation rate, however, requires a temperature stability of about 1‰. Therefore, a detailed knowledge on the thermal behaviour of the source is indispensible.

It is intended to present models describing the response of the source temperature to a step change in heating power and compare the results by experimental data.

Für die Molekularstrahlepitaxie (MBE) verwendet man Tiegel, die durch einen elektrischen Widerstandsheizer geheizt werden. Eine Vielzahl von Materialien läßt sich mit thermischen Quellen verdampfen. Die genaue Steuerung und Regelung der Verdampfungsrate erfordert jedoch eine Temperaturkonstanz von ungefähr 1‰. Deshalb sind genaue Kenntnisse des thermischen Verhaltens der Quelle notwendig.

Es werden einerseits Modelle zur Beschreibung des zeitlichen Verlaufes der Quellentemperatur nach sprunghafter Änderung der Heizleistung und andererseits experimentelle Ergebnisse zur Charakterisierung der Quelle vorgestellt.

1. Introduction

Since the beginning of this century electrically heated crucibles have been used for beam generation in physical vapour deposition (PVD) (KNUDSEN). Therefore it is not surprising that effusion sources became primary beam generators in molecular beam epitaxy (MBE). Thermal effusion sources could successfully defend their leading position in MBE among the gas sources (PANISH) and other ultra high vacuum (UHV) evaporators (HERMAN, SITTER; ZEHE). It should be taken into account that gas sources usually operate with poisonous and dangerous materials. Contrary to electron beam and laser evaporators thermal sources are simple, cheap and common in use due to their relatively easy control.

Compared to traditional PVD the effusion sources in MBE have to meet a new quality of requirements. (i) The ultraclean conditions of UHV-processing demand that the sources should not gas nor react with the substances to evaporate. This results in strong limitations for the crucible materials. Therefore pyrolytic boron nitride, high purity graphite, vitreous carbon and quartz are nearly exclusively in use (PARKER; ZEHE). (ii) The application of MBE to produce new types of microstructures such as superlattices and quantum wells needs a high degree of stability and reproducibility of the evaporation rate. Almost any physical property of ternary, quaternary and more complex compounds is sensitive to the chemical composition (SHIRAKI, SAKAKI). The particle flux is usually stabilized by a precise temperature control. But the temperature of the evaporation material cannot be changed without delay.

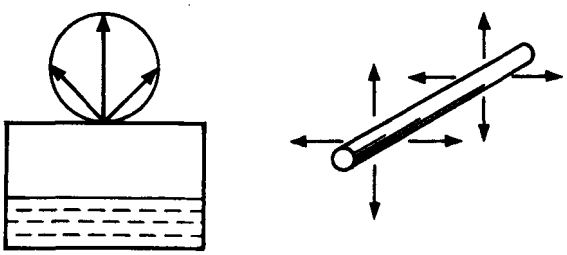

Fig. 1. The two extrema of vacuum evaporation: a) ideal Knudsen-evaporation (effusion through an orifice); b) Langmuir-evaporation (vaporizing wire)

2. Theoretical considerations

2.1. Temperature dependence of particle flux

The two extrema of thermal evaporation are the ideal Knudsen- and the Langmuir-evaporation, as illustrated in Figures 1a and b, respectively.

Langmuir-evaporation means that there are no interactions between the vapour particles and the liquid or solid material (vaporizing wire). On the other hand, the Knudsen-evaporation is characterized by strong interactions of the vapour, liquid and solid phase (equilibrium conditions) and only a small amount of the vapour leaves the reservoir through on orifice without any noticeable disturbance to the equilibrium.

In practice the evaporation is situated between these two extrema. Since the Knudsen-case can be easily described by means of the kinetic gas theory this situation is used for the following considerations although it is not realized in praxi.

The beam flux distribution can be written as

$$j(\vartheta, T) = j_0(T) f(\vartheta), \tag{1}$$

where $j_0(T)$ is the particle flux density on the beam axis and $f(\vartheta)$ describes the normalized angular distribution. Since j is given by

$$j = n\bar{v}/4 \tag{2}$$

(n particle density, $\bar{v}$ mean particle velocity),

$$\bar{v} = \sqrt{8kT/\pi m} \tag{3}$$

(T temperature, k Boltzmann-constant, m particle mass), and using the ideal gas law we get

$$j = p/\sqrt{2\pi m k T}\,, \tag{4}$$

where p is the equilibrium vapour pressure. It follows the exponential law

$$p = p_0 \exp(-\Delta H/RT) \tag{5}$$

(ΔH enthalpy of evaporation; R universal gas constant). Due to the proportionality

$$j \sim p/\sqrt{T} \tag{6}$$

one can obtain

$$dj/j = ((\Delta H/RT) - 1/2)\, dT/T = \alpha \cdot dT/T. \tag{7}$$

Normally the factor α ranges from 10 to 60 (RAMSEY; HONIG, KRAMER), so a temperature variation by 1 K at 1000 K (1‰) results in a flux alteration of 1 to 6%. Consequently temperature deviations should be smaller than 1‰ in practical application.

2.2 Effect of radiation shields

Only a small amount of the electric heating power is used for the evaporation process. Nearly all energy leaves the source by heat radiation.

The evaporation of aluminium, e.g., requires only a power of 0.3 W under typical MBE conditions. (It corresponds to a growth rate of about 1 monolayer per second.) Considering a nonshielded source with a surface area of 20 cm^2 at 1500 K, a power of about 400 W will be emitted (WOLF). Roughly spoken, less than 1% of the heating power contributes to the evaporation.

The power input can be considerably reduced by means of radiation shields. In common practice these shields are a set of coaxially arranged and isentropely separated metal foils.

Let us consider a pair of coaxial cylinders ("1" and "2") with the areas A_1 and A_2, the temperatures T_1 and T_2 and the emissivity ε_1 and ε_2, respectively. The power $\Delta\dot{Q}$ transferred by heat radiation between "1" and "2" is given by

$$\Delta\dot{Q} = \left(\frac{1}{\alpha\varepsilon_1} + \frac{1}{\beta\varepsilon_2} + \frac{1-\alpha-\beta}{\alpha\beta}\right)^{-1} \sigma\left(\frac{A_1T_1^4}{\alpha} - \frac{A_2T_2^4}{\beta}\right) \tag{8}$$

(α probability that heat radiation emitted by "2" strikes "1", β probability that heat radiation emitted by "1" strikes "2", σ Stefan-Boltzmann constant) (cp. MÜLLER).

If cylinder "1" is totally surrounded by "2", $\beta = 1$ is valid and we obtain:

$$\Delta\dot{Q} = \frac{\varepsilon_1 A_1(T_1^4 - T_2^4)}{1 + \alpha\varepsilon_1(1/\varepsilon_2 - 1)}. \tag{9}$$

Furthermore one can show that the use of n shields reduces the power approximately by a factor of $1/(n+1)$.

Summarizing we can state:

- The surface of the source should be as small as possible consistent with the application.
- The number of shields should be as large as technologically feasible.
- The emissivity of the shields should be as small as possible.
- The shields should be arranged as close as technologically possible.
- The source should be designed in such a way that the response time caused by the heat capacity of the source and the heat transfer inside the source is optimum.

From equation (8) we can also conclude that a water- or LN_2- cooled jacket cannot only

- improve the control of the evaporation rate,
- extent the life-time of the source,
- decrease the energy input into the chamber and
- minimize the contaminations produced by the source (NORRMAN et al.; ROULET, ALEXANDRE; BELLAMY, COLOMER; BOSACCHI et al.) but can also
- decrease the electrical power required for the source heating (MÜLLER).

2.3. A model describing the temperature dependence of the time constant

For an optimum temperature control a detailed knowledge of both the stationary and the time dependent thermal behaviour of the source is necessary. All parts of the source possess a heat capacity and a limited heat conductivity. Consequently, after changing the heating power or the radiative conditions (as e.g. by shutter motion) it will take some time before a new equilibrium is established. The term to characterize the transition between two stationary states is called jump response.

Let us consider a body of infinite heat conductivity with the temperature T inserted into a radiation field of a constant temperature T_0. According to the Stefan-Boltzmann-law the heat transfer dQ/dt is written

$$dQ/dt = \varepsilon\sigma A(T^4 - T_0^4)\,. \tag{10}$$

For small differences $\Delta T = T - T_0$ can be obtained as approximation

$$T^4 - T_0^4 = 4T_0^3(T - T_0)\,, \tag{11}$$

and therefore the heat transfer becomes

$$dQ/dt = 4\varepsilon\sigma A T_0^3(T - T_0)\,. \tag{12}$$

Replacing dQ by CdT (where C is the heat capacity) it follows

$$dT/dt = \gamma_r(T - T_0) \tag{13}$$

with the reciprocal time constant for radiation γ_r,

$$\gamma_r = 4\varepsilon\sigma A T_0^3/C\,. \tag{14}$$

The solution of the differential equation (13) is

$$T(t) = T_0 + (T_\infty - T_0)\,(1 - \exp(-\gamma_r t)) \tag{15}$$

(T_∞ source temperature at the new stationary conditions). Note that γ_r strongly depends on the temperature as

$$\gamma_r \sim T_0^3\,. \tag{16}$$

Though the heat conduction from the source to the UHV-chamber is negligible it is important inside the source. Considering a model similar to that mentioned above the energy transfer by heat conduction is given by

$$dQ/dt = g\lambda(T - T_0) \tag{17}$$

(g geometry factor, λ heat conductivity).

If we again substitute dQ by CdT and solve eq. (17) we can obtain

$$T(t) = T_0 + (T_\infty - T_0)\,(1 - \exp(-\gamma_c t)) \tag{18}$$

with the reciprocal time constant for heat conduction γ_c,

$$\gamma_c = g\lambda/C\,. \tag{19}$$

Eq. (18) has the same structure as eq. (15) but the time constant γ_c is not explicitly temperature dependent. An implicit dependence arises from the temperature dependence of the heat conductivity and to the heat capacity. This influence is however small.

Consequently, we can separate the radiation and conduction contributions to the heat transfer if only small temperature changes are considered, i.e. the relation

$$|(T - T_0)/T_0| \ll 1 \tag{20}$$

must be fulfilled.

3. Experimental

3.1. The thermal effusion source

A scheme of the MBE-source used for the experiments is shown in Figure 2. The crucible (3) made of high purity graphite and vitreous carbon, respectively, is indirectly heated by a tungsten wire (2) (0.2 mm in diameter, length about 1.1 m) separated by alumina tubes. The crucible and the heater are surrounded by 7 radiation shields (1) made of thin tantalum foils. A W5%Re–W20%Re thermocouple (4) is placed in a hole at the bottom of the crucible.

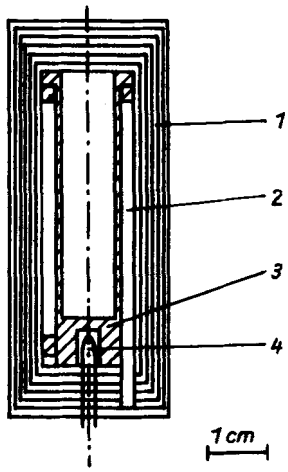

Fig. 2. The scheme of a thermal MBE-source. (1) cylindrical radiation shields (thin tantalum foils); (2) heater (tungsten) in alumina tubes; (3) crucible made of high purity graphite or vitreous carbon; (4) W5%Re–W20%Re thermocouple

3.2. Temperature measurement and the relation between source temperature and heating power

One of the most important difficulties is the determination of the source temperature. In order to get an idea about the temperature distribution of the source, the temperature of the brim and inside the crucible (P_B) and (P_C), respectively, was measured pyrometrically, and the temperature at the bottom was measured by the thermocouple (T) (cp. Fig. 3). Furthermore the temperature of the heating wire (W) was determined by its resistivity behaviour by means of published data (PIRANI). These measurements show that differences up to 400 K between the crucible and the heater may occur.

It is worth mentioning that the temperature inhomogeneity can be reduced by filling the crucible. This effect is greater for liquids than for sublimating solids. Moreover, we can conclude that in the case of sublimation the use of large grains with irregular shape should be avoided since temperature differences between the grains may happen. For this situation cylindrical ingots or fine powders are prefered.

A useful feature to characterize the source is the temperature power plot (cp. Figs 3 and 4). The logarithmically plotted data in Figure 4 demonstrate that above 600 °C the heat from the source is mainly emitted by radiation. It will be clear by comparing the rise of the curves with the value expected from the Stefan-Boltzmann law. The slope of the curve for the heating wire is steeper because the emissivity of tungsten increases as the temperature in the concerned range grows.

3.3. A search for an optimum radiation shielding of the source

The used source without shielding needs a heating power of 123 W to achieve a temperature of 1000 K. Both the top and the bottom emit 8 W each, while 107 W leave the cylinder in radial direction. After a

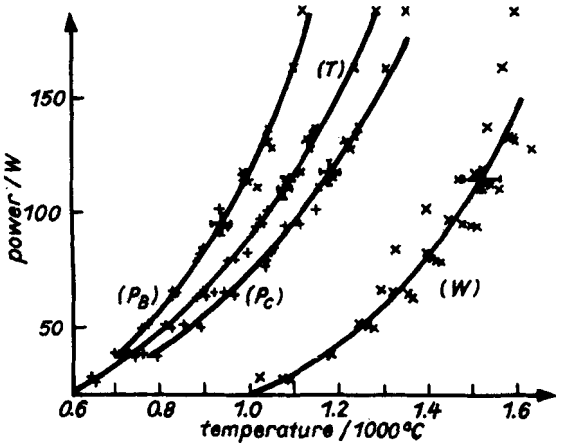

Fig. 3. Relationship between the electrical power required for the source heating and the temperature at four different positions within the source. (P_B) pyrometrically measured temperature at the brim of the crucible; (T) temperature measured with the thermocouple at the bottom of the crucible; (P_C) pyrometrically measured temperature inside the crucible; (W) temperature of the heating wire determined by its resistivity

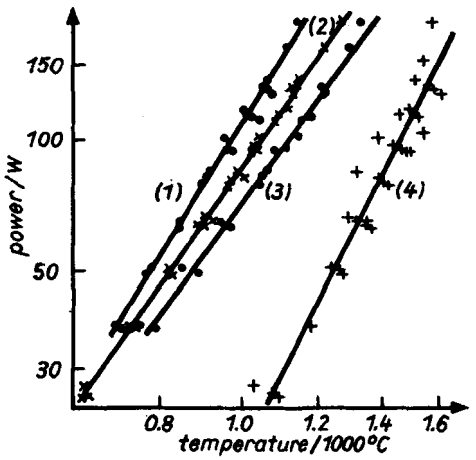

Fig. 4. Logarithmic plot of the relation between heating power and source temperature at four positions (cp. Fig. 3)

shielding according to Figure 2 the power was reduced to 31 W. It is worth noting that 13% of the surface area (top and bottom) emit more than 50% of the energy. These considerations show that the bottom of the source should be shielded, too. Furthermore we can state the number of shields in radial direction should not exceed about 10 because other shields would hardly reduce the emission but the control would become more difficult.

The top of the source (the orifice) can of course not be shielded, but it is necessary to look for a compromise on the area size of the orifice: on one hand the orifice should be as small as possible to minimize the emission and on the other hand as large as possible to minimize the source temperature for a given evaporation rate. The latter fact is important since the amount of contaminations produced by the source increases by an exponential law with the temperature.

Note that the design of the crucible considerably influences the angular distribution of the vapour particles, too.

The prefered material to build the shields are thin polished foils of tantalum, since tantalum has a low emissivity and is UHV-compatible in an excellent fashion. The tantalum shields reduce not only the energy input into the chamber but improve also the vacuum conditions because tantalum can getter gases such as H_2, O_2, N_2, and CO_2 very well (ESPE).

3.4. The response of the source temperature to a step increase in heating power

We investigated the behaviour of the source temperature by a step increase in heating power from P_1 to P_2. The corresponding temperatures under stationary conditions are called T_1 and T_2, respectively. Then the transition function $F(t)$ is given by

$$F(t) = (T(t) - T_1)/(T_2 - T_1)) . \tag{21}$$

A typical transition function obtained from an empty source is shown in Figure 5. Note that the thermal behaviour of such a MBE-source is comparable with other thermal systems, e.g. content thermometers (HUHNKE).

As shown in chapter 2.3., an exponential law like $F(t) = 1 - \exp(-t/\tau)$ could be a good approximation. But a good fit to the experimental data is only obtained using a second constant, e.g. the nearly temperature independent delay t_v (cp. Fig. 5). Contrary to t_v the time constant τ is not only temperature dependent (cp. chapter 2.3.) but depends on the heat capacity and the thermal resistance of the evaporation material, too. In oder to estimate both the temperature dependence and the influence on the heat capacity, the empty (leer) and the totally Ni-filled source (Ni) was investigated (cp. Fig. 6).

We chose Ni because of its very high heat capacity per volume. For an Al-source (Al) typical in MBE the time constant τ is situated between these two extrema. A computer treatment and the discussion of the experimental data is presented elsewhere (MÜLLER).

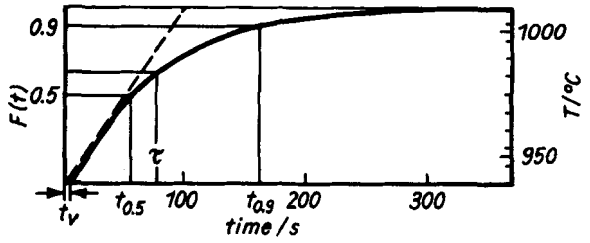

Fig. 5. Response of the source to a step increase in heating power from 63 to 77 W

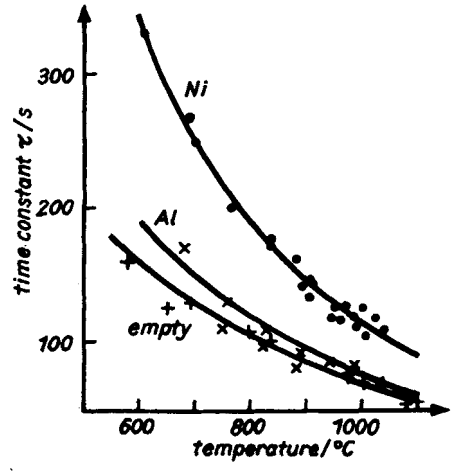

Fig. 6. Experimental relation between the time constant τ and the source temperature for the two extrema – the empty (leer) and the totally filled source with Ni(Ni) – and the source filled with Al typical in MBE(Al)

3.5. The influence of the shutter opening to the source temperature

Though not intended the shutter acts as a radiation shield. This could only be avoided if the shutter after absorbing all energy conducts it to the environment, i.e. in the cases "open" and "close" the emission of the source sould be the same. It cannot of course be realized completely. However, the idea involves a possibility to reduce the shutter motion induced temperature change. This effect is the more evident the better the shielding of the source is (cp. chapter 2.2.).

Our experiments of the effect mentioned above are summarized in Figure 7. The top curve shows the temperature decrease after opening the shutter measured by the thermocouple and the lower curve the related variation of the particle flux determined by a quartz crystal microbalance.

The time dependence of the temperature decrease is influenced by
- the emissivity of the surface,
- the heat conductivity and the heat capacity of the evaporation material, and
- the geometry of the crucible (cp. MAKI et al.).

The temperature decrease due to the changed energy balance is commonly a slow process. Therefore it can also be described in terms of the transition function introduced in chapter 3.4. for a step increase in heating power.

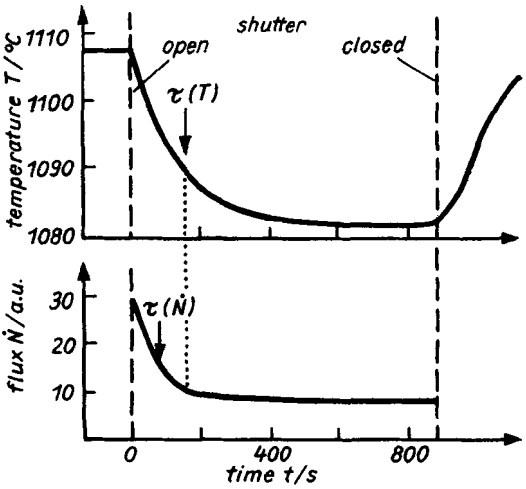

Fig. 7. Response of the source after shutter opening: upper curve: temperature change determined by means of the thermocouple; lower curve: variation in particle flux monitored with a quartz crystal microbalance

4. Summary

For a molecular beam effusion source it has been shown that a particle flux stabilization of 1% requires a temperature stability of 1‰ and better. At a source temperature of about 1000 °C (typical e.g. for Ga or In) deviations must not exceed 1 K!

Although the RHEED-intensity-oscillation technique allows a very precise determination of the deposition rate, reproducible and stable particle fluxes realized by a precise temperature control are still highly important. This is especially the case for well defined doping concentrations and mole fractions in complex compounds. An efficient temperature control requires data on both the stationary and dynamical thermal behaviour of the source.

The relationship between heating power and source temperature is an expressive one to characterize the stationary behaviour. Since the heating power is always connected with unintentional gas emission by an exponential law the power input should be as low as possible. The heating power to reach a certain source temperature can considerably be reduced by radiation shields. The efficiency of the shield ensemble depends on the number of shields, on their emissivity and on the arrangement of the shields.

The temperature transition function for a step increase in heating power furnishes the most important information about the dynamical behaviour of the source. It has been shown that for small temperature differences the transition can be approximated by an exponential law, if a constant delay time is taken into account. The time constant τ used for this law consists of a contribution related to the heat radiation (proportional to T^3) and a second one nearly temperature independent derived from the heat conduction. Other improvements of the control are the shutter cooling to reduce the influence of shutter operation and a cooled jacket around the source.

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