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K. GRASZA, W. PALOSZ*

Polish Academy of Sciences, Warsaw, Poland
*USRA-NASA, Huntsville, Alabama, USA

Some Aspects of PVT Low-Supersaturation Nucleation and Contactless Crystal Growth

The basic principles of the contactless growth of crystals from the vapor in combination with the process of low-supersaturation nucleation are discussed. The mathematical formulation of the morphological stability criterion in vapor growth systems is given and its implications for contactless growth technique are analysed. A diagram for selection of proper temperature conditions for growth of CdTe crystals is presented.

keywords: Theory and modeling of crystal growth, Growth from the vapor, Computational modeling, Cadmium telluride

1. Introduction

The "contactless" growth of crystals from the vapor is a technique which proved to be useful in technology of II-VI and IV-VI materials (MARKOV, DAVYDOV 1971,1975, GRASZA et al. 1992, GRASZA 1993). In this method the key issue is the thermal field in the system and the relation between the temperature of the ampoule walls and that of the crystal surface. The contactless growth conditions require that the walls of the growth ampoule are kept at temperatures sufficiently high relative to the crystal to prevent deposition of the material at undesired locations.

A significant addition to the contactless process is the low-superaturation nucleation (LSN) technique allowing for the formation of a high quality seed in the system. In the first stage of the LSN process a seed is grown on the body of the source material. As the process of nucleation progresses, the seed adheres to the crystal pedestal, then separates from the source and grows into a large crystal (GRASZA et al. 1992). The process of nucleation is controlled primarily by the temperature field in the system. Therefore, the understanding and control of the temperature field in the growth ampoule is critical for a successful control of the nucleation and growth process.

2. Basic principles of contactless growth technique

Figs. 1a - 1e show a typical ampoule used in LSN contactless crystal growth technique at different stages of the process. The source material placed originally at the bottom of the ampoule (Fig. 1a) undergoes a local resublimation and forms a cone with a nucleus at the top (Fig. 1b). Eventually the nucleus reaches the pedestal, separates from the source, and grows into a large crystal (Figs. 1c - 1e, respectively). The ampoule can be positioned in any orientation relative to the gravity vector. The conditions for the successful contactless

growth are discussed below.

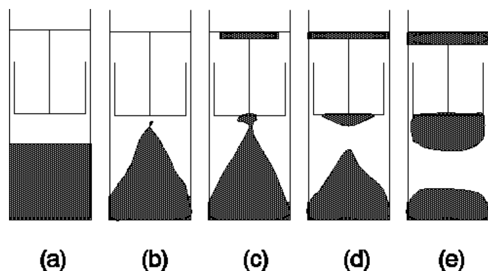

Fig. 1: Consecutive stages of the LSN process and crystal growth.

2.1. Relationship between partial pressures and temperature of the ampoule walls (the condition for "no deposition" in the gap)

Contactless growth conditions require that deposition takes place only on the crystal pedestal and at the very end of the ampoule (top of the ampoule in Fig.1). This requires that the vapors are undersaturated in all other locations. If the reaction of sublimation/condensation of a binary material is written in the general form

$$A_m B_n(s) = uC(g) + wD(g)\,, \tag{1}$$

(s - solid, g - gas), then the thermodynamic conditions for undersaturation at a given location l can be written as

$$K^*(l) < K(l) \tag{2}$$

where K* is the product of the *actual* partial pressures of the constituent components

$$K^*(l) = C(l)^u D(l)^w\,, \tag{3}$$

and K is the equilibrium constant of reaction (1). The condition (2) can be expressed alternatively by

$$T^*(l) < T(l)\,, \tag{4}$$

where T* is the temperature at which the product K* at location l is equal to the equilibrium constant K(T*).

The product K* of partial pressures in eq. (2) is dependent on the mass flow conditions, and changes most in narrow cross-sections of the system (here the gap between the ampoule wall and the crystal and pedestal's side surfaces). The right side of eq. (2), equilibrium constant K(l), is exponentially dependent on temperature as expressed by the formula

$$\ln K = B - \frac{A}{T}\,, \tag{5}$$

where A and B are constants. The relation between K and T is illustrated in Fig. 2 for a

standard parabola-like temperature profile required to conduct an effective LSN process. The equilibrium constant shows a relatively small change both at high temperature (where a quasi-isothermal "temperature plateau" exists) as well as at low temperatures (where steep temperature gradient is present). The largest change occurs in the range of a relatively minor thermal gradient near the maximum temperature in the furnace; Fig. 2. On the other hand, the change of K* is approximately linear along the gap (dotted line in Fig. 2). Therefore, in case of a larger temperature difference between the source and the cold end of the ampoule, particularly when only a short free space between the gap and the deposition in the back of the ampoule exists, the value of K* may exceed that of the equilibrium constant at the cold end of the gap and deposition of the material in that location may ensue. Another critical location where supersaturation of the vapors in the gap may occur lies just below the base of the crystal. Supersaturation in this location is dependent on several factors, most of all on thermal conductivity and length of the pedestal.

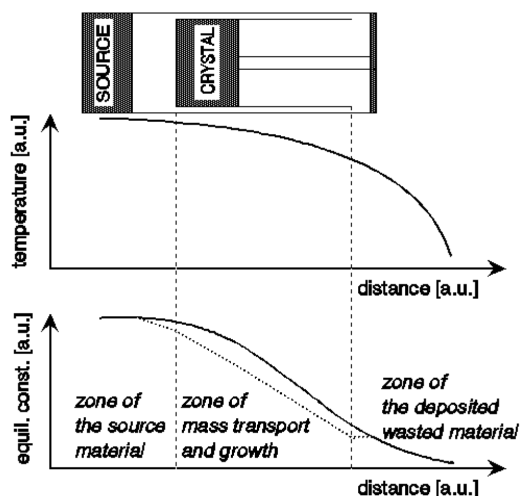

Fig. 2: Temperature profile in the furnace (upper graph) and the corresponding equilibrium constant and typical partial pressures product K* profile (solid and dotted lines, respectively, in lower graph).

2.2. Stability of the crystallization front

In Fig. 3 two equivalent descriptions of the crystal-vapor interface morphological stability phenomenon are presented. The shaded areas represent the solid (crystal) side of the interface. An unstable interface has a 'hill-and-valley' structure, represented in Fig. 3 by protrusions (solid and dotted sinusoidal curves) advanced into the vapor. Both the gradient of temperature dT/dl, and the gradient of the equilibrium constant dK/dl on the crystal side of the interface are lower than the dT^*/dl and dK^*/dl values on the vapor side of the interface. The incoming vapor is supersaturated more at the tip of the protrusion than at its base. Therefore, the tip grows faster than the surface behind, and growth proceeds with an unstable crystal-vapor interface.

It should be noted that, in contactless growth with constant width of the gap between the side of the crystal and the ampoule wall and no radial temperature gradient in that location, dK/dl and dK^*/dl represent the actual distribution of partial pressures in the gap and at the crystal front surface, respectively. dT/dl is the gradient of temperature along the side surface of the crystal, dT^*/dl is the hypothetical temperature gradient corresponding (see eq. 5) to the actual distribution of partial pressures at the front surface.

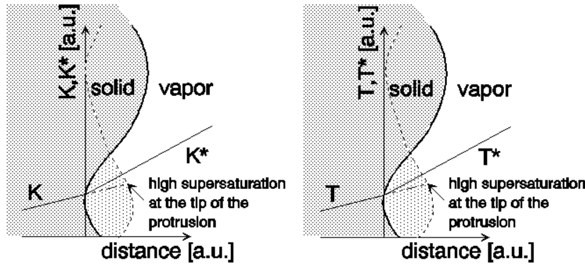

Fig. 3: Illustration of the stability criterion. See text for explanation.

For diffusive mass transport with fast surface kinetics the formula for stable growth conditions (independent of the specific vapor growth technique) takes the form (GRASZA and JEDRZEJCZAK 1996)

$$\frac{dT^*}{dl} < \frac{dT}{dl}, \tag{6}$$

where dT^*/dl is the axial tangent of T^* and dT/dl is the axial temperature gradient in the crystal at the crystal-vapor interface. Neglecting latent heat and assuming that heat transfer between the furnace and crystallization front is determined by radiation only, the temperature gradient in the crystal at the interface can be obtained from the radiative and conductive heat transfer balance (GRASZA 1993):

$$\frac{dT}{dl} = 4\sigma\frac{\varepsilon}{k}(T_f - T_i)\cdot T_i^3, \tag{7}$$

where σ is the Stefan-Boltzmann constant, ε is the average emissivity of the growing surface, k is the crystal heat conductivity, T_i is the average temperature of the crystallization front, and T_f is the effective average temperature of the elements (furnace, ampoule and source material) "seen" by the crystal-vapor interface (i.e. the temperature of a hypothetical isothermal opaque sphere surrounding the crystallization front).

The left-hand side of eq. (6) can be related to the thermochemical properties of the growth system. By differentiating equation (5) and rearranging we obtain

$$\frac{dT^*}{dl} = \frac{T^{*2}}{AK^*}\frac{dK^*}{dl}, \tag{8}$$

Assuming a uniform temperature T_i and taking into account that $T^* = T_i$ at the crystal-vapor interface, the stability criterion (6) takes the form

$$\frac{dK^*}{dl} \ \langle \ 4\sigma AK^*\frac{\varepsilon}{k}T_i(T_f - T_i)\cdot \tag{9}$$

It follows from eq. (9), that at a given temperature the morphological stability of a growing surface is easier to be achieved for: materials (1) having low thermal conductivity k, (2) grown at higher temperatures, and (3) with a temperature hump in front of the growing interface (larger T_f-T_i).

2.3. Selection of proper furnace temperature profile (the criterion of contactless growth)

In general, confinement of deposition area at the pedestal requires that its temperature is lower than that of the adjacent ampoule wall. The actual thermal field in the ampoule is a complex function of the system geometry and thermal properties of the materials. When the temperature of the pedestal is sufficiently low and the temperature of the crystal growth interface is lower than the temperature of the adjacent ampoule walls, growth proceeds with no contact with the ampoule wall and with convex solid-vapor interface. This can occur permanently when the axial temperature gradient at the crystal-vapor interface is lower or equal to the temperature gradient at the furnace wall at the corresponding axial location. Assuming the domination of radiative heat transfer between the furnace/ampoule and the crystallization front, this condition can be written in the form (GRASZA 1993):

$$\frac{\varepsilon}{k} \le N_{Gs} T_i^{-3}, \tag{10}$$

where

$$N_{Gs} = \frac{1}{4\sigma} \cdot \frac{1}{T_f - T_i} \cdot \frac{dT}{dl}. \tag{11}$$

The consequence of the relation (10) for growth of CdTe crystals is shown in Fig. 4. The line $N_{Gs} T_i^{-3}$ represents the maximum temperature at which growth with a convex/flat crystal-vapor interface and no contact of the crystal with the ampoule wall in a given experimental system (GRASZA et al. 1992) is possible. The maximum temperature at which the material (here CdTe) meets these conditions results from the intersection of this line with the curve representing the dependence of the ratio of emissivity and heat conductivity of the crystal material on temperature, $\varepsilon \backslash k$ (T). The temperature range suitable for contactless growth extends from this curve down to a temperature lower by some 200°C. The lower temperature limit is determined by the stability criterion (eq. (9)). The analysis of eq. (10) leads to the conclusion that the temperature range suitable for contactless growth conditions can be extended by some changes in the experimental conditions. Steeper temperature gradients and shorter high temperature zone in the furnace move the line $N_{Gs} T_i^{-3}$ to the higher temperatures (and vice versa).

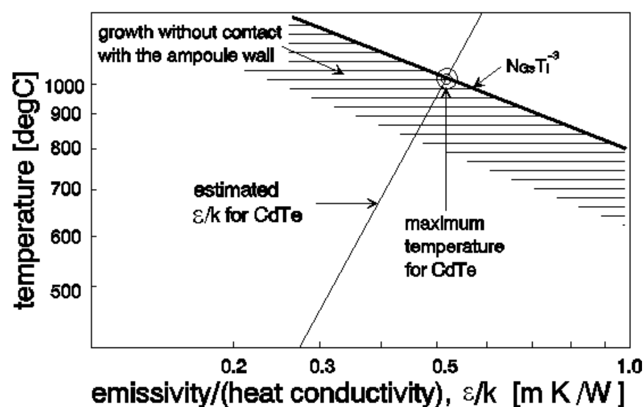

Fig.4: Region of contactless crystal growth for the experimental system presented in (GRASZA et al. 1992), used for growth of CdTe single crystals.

3. Discussion

Effective crystallization using LSN technique requires that the mass transport in the system does not reach extreme values. The transport rate is strongly dependent on the composition of the vapor phase in the system. This composition depends on the composition (stoichiometry) of the source material, temperature of the source, crystal and the cold end of the ampoule, and the amount of inert/residual gases present in the system. The composition of the vapor over II-VI compounds is particularly sensitive to that of the solid, since even a minor excess of one of the constituent components results in a corresponding, opposite change in the partial pressure of the other. Residual gas may significantly reduce the growth rate if its pressure is at least comparable to that of the excess pressure of the majority constituent species. If the total (constituent and residual) excess pressure is considerably higher than the equilibrium pressure over the source/crystal, the mass transport and the rate of the single grain selection in LSN process is very low. On the other hand, if the composition of the vapor is very close to the congruent sublimation conditions and the amount of inert gas is low, high mass transport rate and high gradient of the product K^* at the solid-vapor interface develops. The growth interface becomes unstable (see eq. (9)) and, thus, LSN process is not effective at all. In such cases, an appropriate amount of inert gas or excess constituent element has to be added to the system to reduce the mass transport rate.

Transport of vapors without condensation in the gap is possible if the whole crystal and the crystal holder are located in the range of the largest change of the equilibrium constant K corresponding to the temperature distribution along the ampoule wall (the zone of mass transport and growth in Fig. 2). The exponential dependence of the equilibrium constant on temperature (eq. (5)) limits the mass transport and growth to the central region of the furnace, where the temperature drops no more than about 200°C below that of the source. This limitation affects the maximum length of the crystal that can be grown by the contactless technique, and is particularly relevant in the growth of II-VI compounds due to their low thermal conductivity at the growth temperature (1 - 3 W/m K). Low thermal conductivity requires steep temperature gradients (eqs. (10) and (11)) and the 200°C drop occurs over a relatively short distance. In practice, the length of the contactless grown II-VI crystals does not exceed 3-5 cm. For materials with high thermal conductivities (for IV-VI compounds, k = 2 - 10 W/m K), the temperature gradient can be smaller and the crystal grown may exceed 10 cm. What is important, stationary system (no displacement of the furnace/ampoule) can be applied, and the rate of the loss of the material through the gap can be limited by increasing the length of the pedestal. However, as follows from the stability criterion (eq. (9)), higher thermal conductivity requires lower gradient of the K* product (i.e. reduced growth rate). This can be improved by placing a temperature hump in front of the growing interface i.e. an increase in (T_f- T_i), eq. (9), (Grasza et al. 1995).

4. Summary and conclusions

In this paper the principles of contactless crystal growth in conjunction with low-supersaturation nucleation process were presented. Relationship between partial pressures and temperature of the ampoule walls was analysed. The criterion of selection of proper furnace temperature profile was given. Morphological stability of the crystal-vapor interface and its dependence on the mass transport and thermal properties of the materials was discussed.

The stable contactless growth is possible for relatively short (3-5cm) II-VI compounds crystals, and longer (10cm) IV-VI compounds crystals. Temperature hump in front of the growing interface improves the growth conditions.

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Authors' addresses:

Dr. K. GRASZA
Institute of Physics, Polish Academy of Sciences
Al. Lotnikow 32/46
02-668 Warsaw, Poland
Tel. (48-22) 843-5626
Fax.(48-22) 843-0926
E-mail: grasza@ifpan.edu.pl

Dr. W. PALOSZ
USRA-NASA / Marshall Space Flight Center
ES75, Huntsville
Alabama 35812, USA