Journal of Optoelectronics and Advanced Materials Vol. 2, No. 5, 2000, p. 432-440

CRYSTAL GROWTH PROCESS ENGINEERING

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The research undertaken since 20 years in our laboratory is aiming to address the problem of the relationship between the crystal growth parameters (pulling rate, thermal gradients, set-up geometry, crucible ...) and the resulting crystal quality. All processes of crystal growth from the melt have been studied (Bridgman, Czochralski, Verneuil, Floating zone, shaping), applied to a variety of materials (semiconductors, oxides, halogenides). The various physical phenomena involved can be classified in: Heat transfer, which is responsible of growth rate and thermal gradients, hydrodynamics and transport, basis of intricate advection-diffusion-convection processes acting on the chemical homogeneity of the crystal, capillarity and interfaces, including crucible interactions, shape selection, nucleations... Mechanics of the solid crystal, including elasticity and plasticity, that often generate dislocations, grain boundaries, residual stresses and even cracks. A typical process engineering approach leaded to the establishment of order of magnitude relationships between the various parameters and the subsequent defects. Experiments, including growth under microgravity conditions and in a number of industrial set-ups, gave reference data. However, it was only when numerical simulation of the global process has been applied that it has been possible to understand and improve the real industrial crystal growth processes. A global approach of all the crystal growth techniques, applied to any kind of materials, has been used. Considering the inter-disciplinary frame, under very large time and length scales, the emergence of a crystal growth process engineering can be postulated.

Keywords: Crystal growth, Process engineering, Numerical simulation, Heat transfer, Hydrodynamics, Capillarity, Mechanics, Chemical segregation

1 Introduction

This paper is an immodest attempt to summarize 20 years of the author's work in the field of crystal growth engineering, limited to bulk crystal growth from the melt. At the beginning of this research, crystal growth, especially on the industrial point of view, was mainly considered as personal know-how rather than engineering science. This approach was also relevant in the scientific community: « The processes involved cannot yet be completely predicted » [1], « Much crystal growth is still art and technique rather than science » [2], see also the title of [3]. However all the physical phenomena involved and practically all the scientific concepts were known at that time. The difficulty was in the complexity of the relationships between the phenomena, which act on very large length and time scales, especially in the case of industrial processes. It will be shown that it is only with the help of powerful numerical simulation that both global and specific solutions of practical problems have been obtained.

The techniques of process engineering have been used in order to improve the scientific understanding of crystal growth processes. The general approach is simple: identify the parameters involved, then determine and quantify their effect on the crystal quality in order to optimise the growth process. All the crystal growth processes from the melt have been studied: Czochralski, Bridgman, shaping, Verneuil, zone melting and growth from a solution. Also, the growth of various materials has been studied: congruent and alloyed semiconductors, oxides and halogenides. However the main experimental, numerical and theoretical developments have been obtained in the case of the Bridgman growth of antimonide semiconductors, taken as model process and material, respectively.

Basically, optimisation of a crystal growth process can be summarized as the management of the defects involved in the crystal, with yield considerations in mind (essentially increase of growth rate and crystal size). Table 1 gives the defects sorted by dimensional classes, their origin and the growth parameters involved. Obviously the key of the problem is to quantify all the relationships between the growth parameters and the defects. However it can be seen in the table that different defects have common origins and that a given defect can have different origins. Indeed, relationships would be difficult to establish clearly in that way. Furthermore, it is empirically well known that a growth parameter, at a fixed value, can be beneficial at the beginning of the growth and detrimental at the end.

Table 1. Origin of the crystal defects. The effective parameters are those by which the crystal grower may have an effect on the defect density or occurrence.

Defect	Origin	Effective parameters
Punctual: interstitials, voids, impurities	Stoichiometry, pollution, initial composition, solidification path	Raw material, thermal field in the solid, crucible
Linear: dislocations	Seed, voids, plasticity due to thermal, chemical or sticking stresses	Thermal field in the solid, crucible, growth rate
Bi-dimensional: grain boundaries, twins	Spurious nucleation, dislocations, growth facets, impurities	Crucible, thermal field, temperature fluctuations, growth rate, raw material
Local three-dimensional: precipitates, bubbles	Pollution, impurities, chemical reactions, solidification path	Crucible, growth rate, thermal field in both solid and liquid
Diffuse three dimensional: residual stresses, chemical heterogeneity	Plasticity, convection and diffusion in the melt, solute rejection	Thermal field in both solid and melt, growth rate

In fact, the simplest way to address the problem is to discuss the occurrence of defects and their relationship with growth parameters in the frame of the main physical phenomena involved: heat transfer, hydrodynamics, capillarity and solid mechanics. The interdisciplinary relationships will be introduced through the use of global numerical simulation. Fig. 1 shows these interdisciplinary links and the relations between physical phenomena and crystal defects.

2 Heat transfer and solidification

Heat transfer is the motor of solidification because it determines the two fundamental growth parameters: the growth rate and the thermal gradients in the liquid and solid sample. Thermal gradients are of primary importance because they are the basis of natural convection in the liquid and of thermo-elastic stresses in the solid. It is therefore of interest to decrease the gradients, but on the other hand high thermal gradients stabilize the solid-liquid interface, evacuate the latent heat of solidification and then allow a higher growth rate. This is only one example of the numerous compromises existing in crystal growth engineering.

For dilute systems, the solid-liquid interface is an isotherm and heat transfer determines its position, velocity and shape. For concentrated alloys, the situation is more complex because the chemical composition, then the melting temperature, is likely to vary along the interface. The interface shape gives information on the thermal gradients directly acting on the solidification. A curved interface is the sign of radial thermal gradients, at the origin of buoyant convection in the melt and thermo-elastic stresses in the crystal. It is also associated to radial chemical segregation.

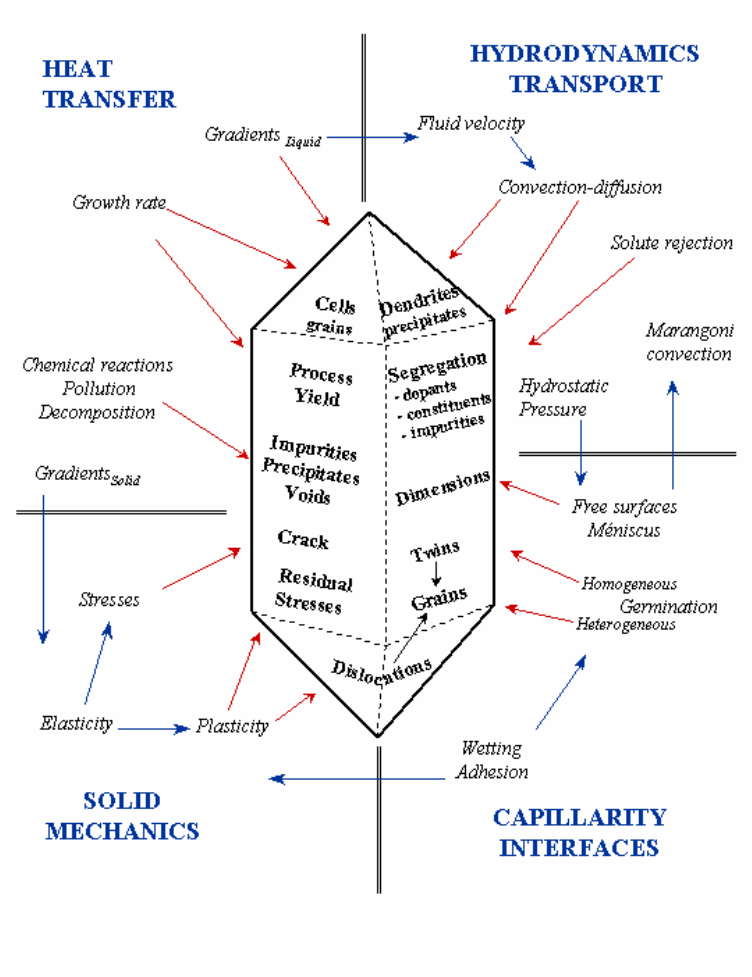

Fig. 1. Relationships between the various physical phenomena involved in crystal growth processes and their effect on the crystal.

The first step in the study of a crystal growth process will then be the determination of the velocity and shape of the interface and of the thermal gradients. Thermal gradients are obtained through classical temperature measurements and interface shapes and position versus time can be obtained by post-mortem metallography, after periodic perturbations of the growth of an alloy. Such perturbations could be performed through a mechanical or thermal change [4] or, in a more sophisticated way, through electric current periodically sent in the sample [5]. These methods have been used for semiconductors, but also for halogenides [6].

In the lack of experimental capabilities, the solid-liquid interface curvature can be calculated with the help of order of magnitude analysis [7]. Numerical simulation of local heat transfer around the interface is also a powerful tool to get gradients and information on the interface. However this can lead to complicated calculations, especially if transparent and semi-transparent samples are under interest [8]. It has also be shown that, in the case of crystal growth process under high pressure, the convection in the gas should be fully calculated [9] in order to get a reliable knowledge of the heat transfer.

3. Fluid mechanics and segregation

One of the consequences of the existence of thermal gradients in the liquid is the apparition of convective motion in the melt. These movements will act on the thermal transfer at the interface, generally decreasing the interface curvature. But the most important effect will be on the transport of chemical species in the melt, leading to a more or less heterogeneous crystal. Some processes, such as

the Czochralski technique, use forced convection in order to control these effects, but this has some drawbacks, especially the creation of dopant or chemical striations in the crystal and a strong effect on the interface curvature (Fig. 2).

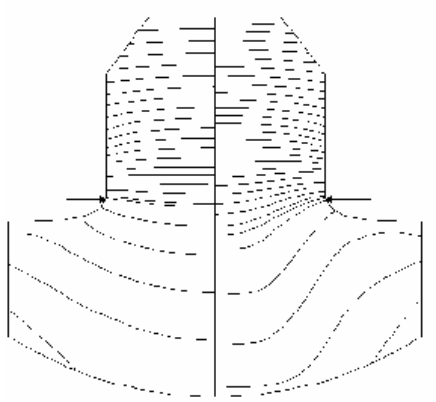

Fig. 2. Influence of the convection on the interface shape during Czochralski growth of InP crystals. This numerical simulation shows on the left the thermal field without convection and on the right the thermal field in the crystal and the flow field in case of convection in the liquid; arrows show the solidification isotherm (1335K).

Chemical heterogeneity is the source of numerous practical problems for crystal growers. For electronic wafers, this gives variations of electronic properties between wafers and in a single wafer. Some dopants have a strengthening effect on the semiconductor and the dislocation density is likely to vary with the chemical composition. The general problem is therefore to get an estimation of the axial and radial chemical heterogeneity in the crystal. In the case of forced convection, scaling laws permit the calculation of the flow field. For natural convection, order of magnitude analysis permitted to get the scaling laws of the chemical segregation in horizontal Bridgman growth [10]. For the vertical Bridgman case, these laws have been obtained with the help of numerical simulation, validated by experiments [11].

Four experiments under microgravity conditions have been devoted to the study of the effect of gravity, then buoyant convection, on chemical segregations, with the aim to validate the order of magnitude results. In the EURECA satellite, with a residual gravity 10^7 times lower than on the earth, the transport regime was purely diffusive, without noticeable convective effect [12] (see Fig. 3). The experiments onboard the space shuttle (where the gravity level is 10^5 times lower than on the earth) leaded to convective chemical segregation, in agreement with the order of magnitude analysis [13]. Other experiments permitted the study of the effect of Marangoni convection on the chemical segregation [14-15].

The general knowledge resulting from these analytical, experimental and numerical studies permitted to solve some applied heterogeneity problems and to design and patent new processes.

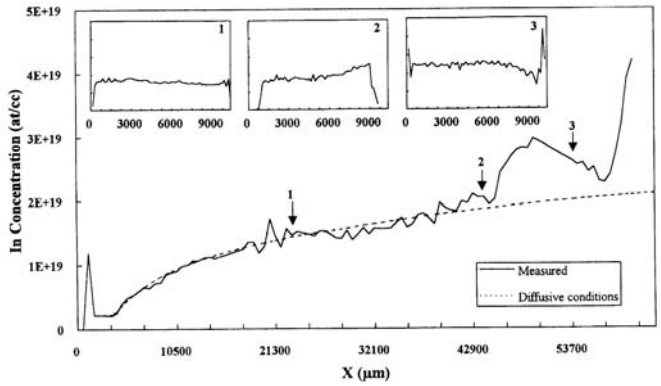

Fig. 3. Longitudinal segregation of In along the axis of a GaInSb sample grown onboard the EURECA satellite. The dotted line corresponds to the theoretical diffusive case. The perturbation at the end is in agreement with the modification of growth rate at that time.

4. Capillarity and interfaces

The case of Bridgman growth excepted, the crystal growth processes avoid the use of a crucible in contact with the grown crystal, in order to avoid the adhesion and differential dilatation problems. However this is paid by difficulties for the control of the crystal dimensions. This drawback is partially solved by the use of dies for the growth of shaped crystals but a special attention should be paid to the height and shape of the meniscus situated between the solid-liquid interface and the die. Unstable growth may result from inadequate dies or growth parameters and a careful stability analysis is necessary [16]. Another problem is associated to the a-priori calculation of the shape of the die in order to obtain a given crystal shape. Due to the highly non-linear equations involved, mathematical optimal control methods must be used to solve the problem [17].

Meniscus problems have also been surprisingly encountered during Bridgman space experiments. Indeed, most of the space crystal growth experiments have shown a detachment of the sample from the crucible. In some cases, the gap between the crystal and the crucible was extremely stable, of the order of tens of micrometers and the crystal structural quality was highly enhanced. The phenomenon, called de-wetting, has been explained in the case of rough [18] and smooth [19] crucibles (see Fig. 4). These models have been validated with dedicated space experiments [15, 20]. From this understanding, new processes have been designed in order to get the de-wetting phenomenon also on the earth, with the associated gain in structural quality [21].

Another problem linked to interfaces and capillarity concerns the sticking of the crystal on the crucible, which can be quantified through wetting measurements [22]. During subsequent cooling, differential dilatation occurs and stresses are created in the crystal, generating defects and detachment from the crucible when the temperature is low enough [23]. It has also been shown that spurious nucleation is linked to the difference of the interfacial energy between the liquid, the solid and the sample [24].

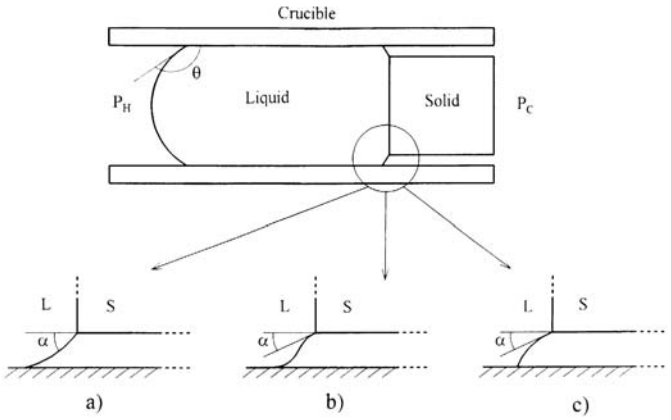

Fig. 4. Explanation of the dewetting process observed in space: the leading parameters are the liquid crucible wetting angle θ and the growth angle α. The value of the pressure difference PC-PH gives a number of meniscus configurations that lead to stable or unstable growth. Stable growth can be obtained on earth when the pressure difference corresponds to the hydrostatic pressure.

5. Solid mechanics and structural defects

Generally speaking, all structural defects in a crystal will have an incidence on the physical properties of the material. The decrease of structural defects is then a constant concern for the crystal grower. This is especially true in the case of dislocations.

Dislocations have various sources. They may come from the seed (necking is an efficient way to avoid the problem), or appear due to void diffusion and condensation (but this mechanism has been identified in the case of GaAs only) but the main mechanism of dislocation generation is

plasticity, which appears when stresses exceed a given limit, which is temperature and history dependant. In the case of GaSb, this limit has been estimated at about 0.5 MPa [24]. Fighting again dislocations is then reduced to find the way to decrease the stresses in the crystal. Sticking on the crucible has been discussed in the above paragraph and can be avoided by the use of encapsulation [25].

Thermo-elastic stresses are linked to the thermal field in the growing and cooling crystal and can be numerically calculated provided that a full knowledge of the thermal history is available. However the calculation of the dislocation number in a crystal necessitates further steps. After a careful analysis of the literature available on the plastic behaviour of the given material, comportemental laws are defined then solved numerically, including the projection of the calculated stresses on the gliding planes. It is then possible to compute the dislocation density in the various planes, the residual stresses and the strain all along the growth process. The numerical model is validated by comparison with reference mechanical tests. This approach has been applied to the growth of InP by the encapsulated Czochralski method [26], see Fig. 5.

A similar approach has been used for the growth of shaped sapphire hollow pieces that experienced cracking at some moment of the growth process. In that case, calculations were complicated by the three-dimensional geometry of the problem, but application of a visco-plastic model for sapphire permitted to understand the cracking mechanism and then to propose modifications of the growth parameters to cancel the problem [27].

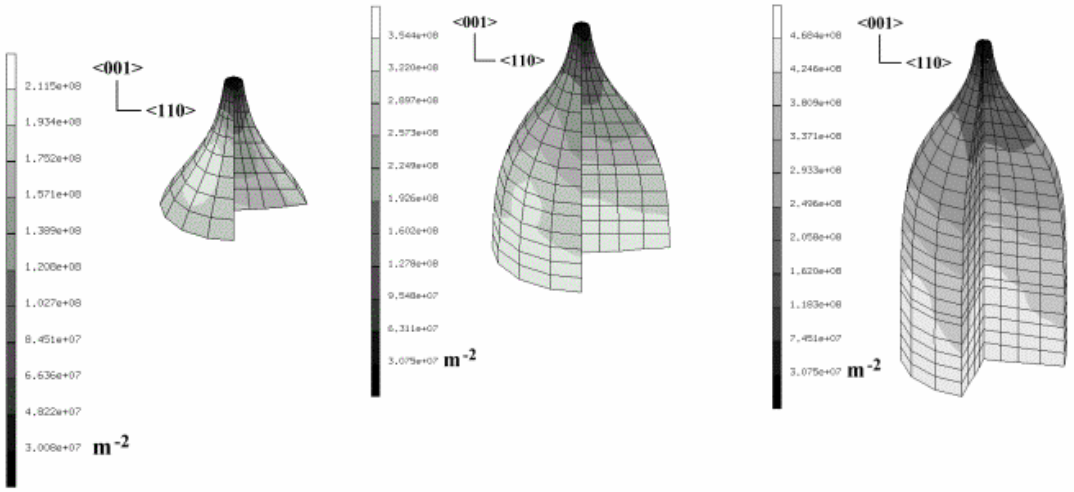

Fig. 5. Distribution of the dislocation density in an InP crystal, at three stages of the Czochralski growth.

6. Numerical simulations of crystal growth processes

Order of magnitude laws and calculations are useful for the dimensionalization of a process and in order to estimate the relative importance of physical phenomena. However in order to quantify the details of a process, numerical simulation becomes mandatory. Due to the complexity of the physical phenomena involved and to the three-dimensional and transient nature of the process, it is necessary, before simulation, to carefully study the process in order to identify the possible simplifications. In some cases, a simplified two-dimensional and stationary model may give a valuable knowledge of the process. Figure 6 gives the various phenomena that should be taken into account in order to fully simulate a process. Industrial software, thanks to their reliability and pre- and post-processing capabilities, are well fitted to such calculations. The general approach is to include progressively new physical phenomena in the numerical simulations, with careful experimental validation of the results [28].

Two approaches are possible, depending on the expected results. Global models are used when the whole crystal growth set-up is taken into account; boundary conditions are then the electrical power input in the furnace and the temperature of the cooling water. Local models are restricted to a region close to the crystal, in order to get accurate information, and boundary conditions are coming from experimental measurements or from a less accurate global model.

Simulation software are limited in practice due to the lack of physical models, or of physical material properties. Furthermore it is impossible to take into account all the geometrical details of a growth set-up and some expertise is needed to get a proper description of the process. Last but not least, tri-dimensional and transient models are the exception, due to limitations in computer power and memory.

Numerical optimisation of a crystal growth process is only possible up to now by solving the direct problem. This means that the geometry of the set-up and the growth parameters are input in the model which gives the critical parameters, such as chemical segregation, dislocation density, stresses... Then the parameters or the geometry are changed. This is a long and tedious process and there is no mean to know if the result is optimum. The so-called inverse problem consists in building a model in which the input is the property of the crystal to be grown and the model should determine automatically the optimal geometry and growth parameters. It has been demonstrated that a unique solution of such a problem exists, but the practical application has suffered from technical mathematical difficulties [29].

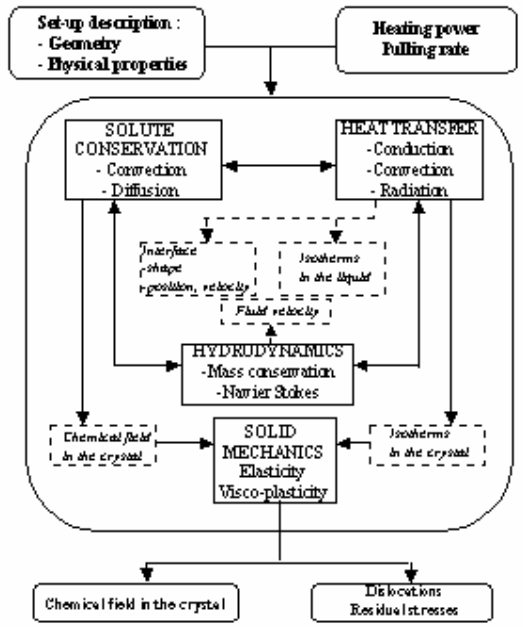

Fig. 6. The sequence of calculations necessary in order to study a full crystal growth process.

7. Conclusions

The approach used to study the crystal growth processes is an intimate mixing of experiments, understanding of physical phenomena and numerical modelisation. It has been shown that the tools developed through the deep study of the Vertical Bridgman process, applied to one material (GaInSb alloys), have been successfully used in the frame of totally different processes and materials. For example, the numerical software optimised and validated for the Bridgman growth of antimonides are now used for the shaping of sapphire or Czochralski growth of other oxides. This strengthens the assessment that *the physical phenomena involved in crystal growth are basically the same, whatever the process or the material.*

It has been shown that the basic concepts involved in this approach are related to heat, mass or momentum transfers, in a large inter-disciplinary frame and under very wide time and length scales. Bridges have been built between the laboratory (even under microgravity) and the industry, in full opposition with the classical approach of crystal growth: the notion of « know-how » linked to a given and unique « product ». In the continuity of the pioneering works of A. Witt and H. Gatos (MIT), D. T. J. Hurle (Cambridge Univ.) and G. Müller (Erlangen Univ.) *the existence of a crystal growth process engineering can now be postulated.*

It is nowadays possible to determine the growth conditions for a given material accurately enough to define the crystal growth set-up. However, this relies on the existence, or the accuracy, of the physical parameters to be used in the models. Also, it is not possible to ascertain the quality of the grown crystal because specific problems will be likely to necessitate complementary studies, see for example the problem of micro-bubbles in shaped sapphire. Then, *each material is unique and process engineering cannot a-priori address all problems, only the basic ones.*

There is also a lack of understanding of a number of physical phenomena involved in crystal growth. For example there is no general theory of the generation of dislocations due to plasticity and the cases of InP and sapphire have necessitated the establishment of empirical models. Concerning defects, there is no way up to now to calculate the number of grains or twins in a crystal obtained under given conditions. Software are limited too, and there is no tool available for the resolution of a transient problem including view factor recalculations in 3D. Such limitations are highly specialized and *future improvements will need the establishment of strong collaborations between basic research, specialists in crystal growth, in numerical processes and the industry.*

Crystals, due to their perfection, always fascinated human beings, including crystal growers. It will always be more touching to take a silicon crystal out of its furnace than a stainless steel ingot from its mould. However, industrial silicon crystal growth is, by far, better understood than steel moulding. This is the reason why crystal growth will probably remain an art for a long time, even after that science will solve all its mysteries.

Acknowledgements

Practically all the experiments involved in this study, in the space or on the earth, have been realised by Pierre Dusserre, with whom I experienced all the doubts and joy of experimental research. Thanks are also due to a number of people who helped, or worked, or managed the laboratory, in close relationship with this research: J .J. Favier, J.P. Nabot, J.L. Santailler, N. Giacometti, J. Abadie and numerous others. A special attention is devoted to the students who worked on their PhD in the frame of this program: a lot of thanks to Jean-Paul, Isabelle, Catherine, Philippe, Mathias, Carlos, Fred, Stéphane, Flori and Sylvain.

The Commissariat à l'energie atomique, the CNES and the ESA and practically all the French companies involved in crystal growth have supported this research program on crystal growth processes.

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