AIAA 2001-5002

SCIENCE OF DETACHED BRIDGMAN GROWTH AND SOLUTOCAPILLARY CONVECTION IN SOLID SOLUTION CRYSTALS

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ABSTRACT

Bridgman and float-zone crystal growth experiments are planned for NASA's Materials Science Research Rack using the European Space Agency's Materials Science Laboratory with the Low Gradient Furnace (LGF) and Float Zone Furnace with Rotating Magnetic Field (FMF) inserts, respectively. Samples will include Ge and Ge-Si alloys with up to 10 at% Si. The planned experiments in microgravity will provide information unattainable from Earth-based experiments. The Bridgman part of the investigation includes detached growth samples and microgravity will enhance the ability to study the science of detachment. Repeatable Earth-based experiments show promise that the method can be perfected for terrestrial use. This capability would greatly improve the crystalline quality of selected materials of substantial technological interest because it would eliminate contact between the solidified crystal and the container wall. For float-zone growth, microgravity experiments are the only way to separate the segregation contributions of soluto- and thermocapillary convection from buoyancy-driven convection. Thus, solutocapillary convection is frequently ignored or poorly estimated in modeling float-zone growth of alloys. Additionally, the size limitation of the zone height (and crystal diameter) of about 10mm under Earth conditions is only limited in space by the heater power and furnace geometry. Larger zones increase the accessible range of convection strength and thus enable the determination of critical values for convection.

INTRODUCTION

Experiment Team

This investigation is an international collaboration with two universities in Germany and the Marshall Space Flight Center (MSFC) along with one U.S. university and a small business enterprise. To reach the objectives of the investigation, flight experiments involving Bridgman crystal growth and float-zone crystal growth must be completed. In terms of planning, cooperation, and sharing of information, the U.S. and German teams participate fully and equally in all aspects. Electronic and verbal communication between the investigation teams is open and frequent; there have been numerous visits, including extended stays, between the teams. With respect to resources, the German and U.S. investigations are independent and parallel. To minimize duplication of effort and to take best advantage of available resources including personnel and equipment, the Bridgman part of the investigation is being led by the NASA team and the float-zone part of the investigation is being led by the German team funded by the German Space Agency, Deutsches Zentrum für Luft- und Raumfahrt (DLR) * with the flight opportunities provided by the European Space Agency (ESA) †.

Apparatus and Experiments

The proposed experiments are divided into three subsets:

a) Detached Bridgman experiments

b) Bridgman experiments with wall contact

c) Float zone experiments

We plan to use Ge-Si samples with the same diameter (18 to 20mm) in all cases.

A suitable furnace for a) and b) is the Low Gradient Furnace (LGF) because of the availability of a rotating magnetic field. The LGF is being built by ESA for incorporation into the ESA Materials Science Laboratory (MSL) in the First Materials Science Research Rack (MSRR-1) on the International Space Station. The U.S. National Aeronautics and Space Administration Marshall Space Flight Center is responsible for the MSRR-1. For c), the Float Zone Furnace with Magnetic Field (FMF), which will be developed by the German DLR as an insert module for the MSL will be well-suited for the FZ experiments on the ISS.

The materials that will be used for these experiments include germanium and germanium-silicon alloys with silicon concentrations up to 10 at%. Ge or GeSi seeds will be utilized, seed orientation will be <111> or <100>. The feed material will either be pre-synthesized or we will apply an adequate rotating magnetic field during the homogenization period to ensure a homogeneous silicon and/or dopant distribution.

We expect to show whether detached Bridgman or float-zone processing can produce lower defect germanium-silicon crystals and to quantify the difference. To do this requires the development of improved numerical techniques for heat and mass transport and stress analysis, and, for detached Bridgman growth, a complete and accurate model that includes stability analysis.

BRIDGMAN GROWTH

Detached Bridgman Growth

Crystals grown without contact with a container have far superior quality to otherwise similar crystals grown in direct contact with a container[1,2,3,4,5,6]. In addition to float-zone processing, detached Bridgman growth is often cited as a promising tool to improve crystal quality, without the limitations of float zoning. Compared to Earth-based experience, detached growth has been found a much higher percentage of the time during microgravity Bridgman growth experiments (see e.g. review article ref. 7) and considerable improvements of crystal quality have been reported for those cases. However, no thorough understanding of the process or quantitative assessment of the quality improvements exists so far.

Detached growth can take place when the sum of the contact angle between the sample and container plus the growth angle of the sample are larger than 180°[8,9]. This condition can be relaxed to some extent if the pressure in the volume around the solidified crystal $p2$ is larger than the sum of the hydrostatic pressure and the pressure exerted on the free surface of the melt $p1$. See figure 1.

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* The title of the German project is: „Einfluß von Wandkontakt und Konvektion auf die Einkristallzüchtung von Halbleitermaterialien“ (i.e. “Influence of wall-contact and convection on the growth of semiconductor single crystals”), project number 50WM9503-5.

† The proposal was submitted in response to the ESA 1998 AO under the title “Influence of Containment on Defects in GeSi Crystals: Comparison of Detached Bridgman and Floating-Zone Growth”. The proposal is registered under the reference number AO-99-034. It was evaluated as “Highly recommended – Priority 1” and is the highest ranking selection in the crystal growth section.

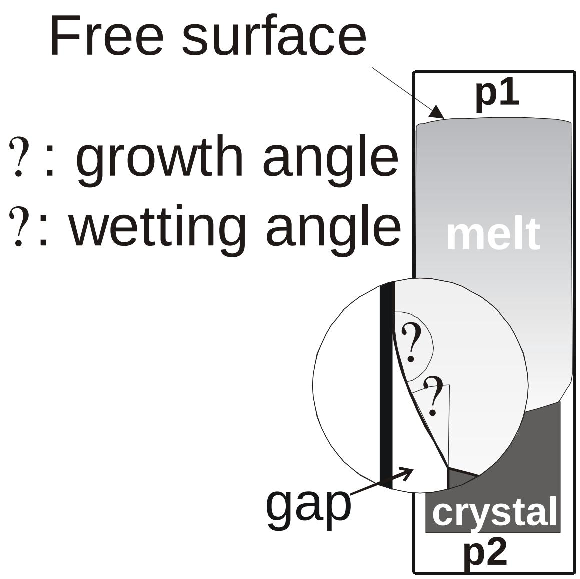

Figure 1. Detached Bridgman growth.

Advantages and Limitations

Compared to float-zone (FZ) growth, Bridgman growth has the advantage that sample materials with high vapor pressures can be grown. On Earth, it has the further advantage over FZ growth that there is no size limitation except that placed by the size of the furnace and available power. Two disadvantages of normal (attached) Bridgman growth include contact of the melt with the container, which causes contamination if the container material is soluble in the melt, and contact of the solidified crystal with the container, which causes dislocations in the crystal if the thermal expansion coefficients of the container and sample are different—the usual case. Samples that are grown detached are not in contact with the container in the solid form and thus have much lower dislocation densities. The typical ratio in etch-pit densities for samples grown under identical conditions except for attachment or detachment is about 100:1[10]. Furthermore, the free melt surface is limited to the small annular meniscus area, which does not exceed some tens or hundreds of micrometers. This is consistent with the fact that time-dependent surface tension driven convection, observed frequently during float zone growth, has not been detected so far in detached grown crystals.[6]

Stability of Detached Bridgman Growth

As noted previously, detachment during microgravity Bridgman experiments has been observed in a relatively large percentage of those experiments compared to experience on the Earth. To be sure, these include distinct types of ‘detachment’ such as pinch off and bubbles as well as the type of detachment depicted in figure 1, which is the phenomenon of interest here. In this type of detached growth, the separation between the outer surface of the solid and the container wall is fairly uniform (under uniform growth conditions) and ranges usually from micrometers to hundreds of micrometers.

This type of detachment can be stable, in which case extended lengths or complete samples can be grown detached, or it can be unstable, in which case the detachment may occur as a bubble or as a ring. In its unstable form, this type of detachment has been observed in several diverse materials including not only Ge and GeSi, but also HgCdTe[11] and HgZnSe[12]. Clearly an understanding of the stability of this type of detachment is necessary for determining the growth conditions that promote its occurrence such that complete crystals can be grown detached.

One of the authors (SM), in conjunction with L. Vujisic, has investigated this stability and has established some of the important parameters. This analysis has been used to calculate the width of the gap between solid and container with substantial agreement to the experimental results. More importantly, this analysis shows that the detachment stability is improved by increasing the pressure difference between the melt free surface and the gap. In normal Earth-based growth (see figure 1), the analysis shows that the pressure difference required to achieve the desirable level of stability cannot be obtained in most cases because it far exceeds the point at which bubbling takes place. This shows why detachment has been observed primarily in microgravity (until the past few years when detachment has been systematically studied). Only when the contact angle between sample and container is very large and a pressure near the bubbling pressure is maintained, can detachment be stabilized in unit gravity to the point of enabling the growth of substantial lengths of detached material.

The evidence for detachment is obtained by examination of the surface characteristics of the grown crystals with optical and electron microscopy and a profilometer. Details of this methodology have been presented elsewhere[6,13].

How Microgravity Will Help

Although we have determined the terrestrial conditions that will allow us repeatedly to grow detached Ge and GeSi in pyrolitic boron nitride (pBN) containers (contact angle 173° for Ge[14] and 168° for Ge-7.1at%Si[15]), we have also demonstrated that detachment is much less stable in quartz containers, even though the contact angle is still large (117°)[14,15] compared to the angles for many semiconductor-container pairs. The theory of detachment that we have developed suggests that application of a larger pressure difference across the melt would stabilize the detachment in quartz containers. As suggested in the preceding section on stability of detachment, however, these pressures lead immediately to bubbling of gas upward through the melt until the pressure difference is released to the point where the detachment is only marginally stable. In contrast to the results we have achieved in pBN containers, numerous samples have been grown in quartz in which bubbles and rings of detachment have occurred but none in which detachment has continued for more than several millimeters. Conducting these experiments in microgravity will allow the application of larger pressure differences and thus enable us to test the theory we have developed.

Planned Bridgman Flight Experiments

To completely satisfy the investigation objectives, a series of ten growth experiments is planned. These would include experiments that would determine the influence of Si concentration, ampoule material, as well as pressure differential between the gap and the free surface of the melt. Other factors that will be investigated but which are not discussed in this paper include the atmosphere inside the growth container and the effect of an applied rotating magnetic field.

In addition to confirming or refining our theory of detachment stability, we also plan to use these experiments to determine what caused the gas pressure difference in previous flight experiments where detachment was observed[7]. Specifically, we expect to be able to determine if the evolution of dissolved gas into the gap through the small liquid meniscus between the growing crystal and the container wall[16,17,18,19,20] plays a role in detachment. With an empirically confirmed theory of detachment stability and an understanding of the importance of evolved gas in achieving and maintaining detachment, the probability of developing the parameters for terrestrial detached growth techniques for numerous technologically important crystalline materials will be greatly enhanced.

FLOAT-ZONE GROWTH

Advantages and Limitations

Float-zone processing is truly containerless, that is, the melt is not in contact with a container, which means there is no contamination from that source, and the solid crystal is not in contact with a container so it shares this advantage with detached Bridgman growth. Figure 2 exhibits shapes of radiation heated float zones, the one on the left hand side under the influence of hydrostatic pressure under Earth conditions, the right hand one under microgravity. Whereas the depicted one for the 1g case is already close to the stability limit, results in the µg zone a certain deviation from a cylindrical shape only if the density of melt and solid differ (as it is the case for semiconductor crystals).

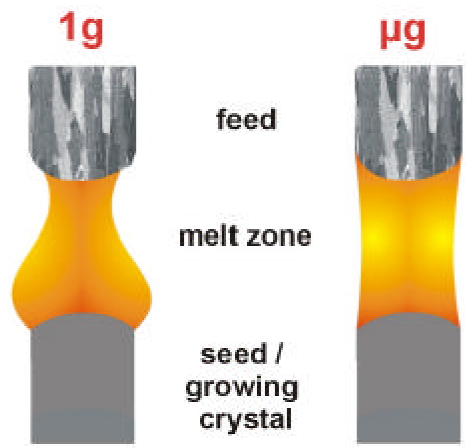

Figure 2. Radiation heated float zones, with (left) and without (right) the action of hydrostatic pressure.

The main restriction of float-zone processing is the size limitation of the zones due to the hydrostatic pressure under gravity. The possibility to overcome the size limitation by processing under microgravity has been demonstrated in recent years with experiments on the Space Shuttle: Single crystals of GaAs with 20mm diameter and of GaSb with 16mm diameter, approximately three times the size of earth-grown float-zone crystals, have been successfully grown during the missions STS 55/D2 in 1993 and STS 77/Spacehab-4 in 1996, respectively[21,22,23]. Further, a reduction of the etch pit density (EPD) by a factor of 5-8 has been found in microgravity GaAs crystals as compared to the Czochralski-grown starting materials[23].

Types of Convection in FZ Growth

A major issue in float-zone (FZ) growth is segregation of dopants and, for alloy samples, the constituents. Following an initial transient in the segregation, controlled primarily by the characteristics of the molten zone geometry, this segregation is governed by the influence of convective flows on the mass transfer in the zone. In addition to the thermal and solutal buoyancy-driven convection present in Bridgman melts, in all FZ experiments there is additionally the influence of Marangoni (thermocapillary and/or solutocapillary) convection, stemming from the gradients of surface tension, which in turn originate from thermal or compositional gradients. Due to the large ratio of free surface to melt volume as compared to other melt growth processes, surface tension driven convection is dominant in most semiconductor float-zone experiments (excepting radio frequency (RF) heating). For low Prandtl number melts, such as metals and semiconductors, the occurrence of dopant striations not generated by rotation or radio frequency heating, is practically always caused by time-dependent thermocapillary convection[24,25]. The critical Marangoni number Ma_{c2} for the onset of time-dependent convection was determined in several microgravity experiments: it is about 150 for silicon and 375 for GaSb[25,26], whereas typical values present during the crystal growth process can easily reach 10^3 or 10^4.[27]

How Microgravity Will Help

As already suggested, the size of crystals that can be grown on Earth is limited by the strength of the surface tension of the melt compared to its density or weight. For Ge and Ge-rich GeSi alloys, this limit is around 9mm. For samples of this diameter, surface effects such as dopant fluctuations due to surface tension driven flows in the case of float zone growth, or dislocations caused by crystal-container interaction in normal Bridgman growth will dominate the entire sample cross section. Thus, if one intends to make a valid comparison of the three growth methods used in this investigation, larger diameter crystals must be grown. For a realistic comparison of FZ crystals with Bridgman crystals, the FZ crystals must also be grown with a large diameter. This can only be done in reduced gravity. Larger diameter FZ crystals needed to further this investigation require microgravity.

The second reason microgravity is necessary to achieve the objectives of this investigation is related to Marangoni convection. In 1g there are two different sources for convection for Ge samples; that is, thermal buoyancy flow and thermal Marangoni flow. In the alloy samples, there are four sources of convection, the two above as well as solutal buoyancy and solutocapillary flows. In microgravity these will be reduced to pure thermocapillary flow (for Ge) or thermo- and solutocapillary flow for GeSi.[28] Also, under microgravity conditions, the larger zone size enables the variation of Marangoni numbers over a much wider range than on Earth. Microgravity makes it possible to measure critical values of the Marangoni numbers—something that cannot be done on Earth, in most cases. When the sample is retrieved and analyzed by characterizing the microsegregation, we will obtain information about the time-dependence and the frequency behavior of the Marangoni flow, which will allow us to validate numerical simulations and theoretical results.

Solutocapillary convection itself provides the third reason for conducting FZ experiments in microgravity. The investigation of solutocapillary flow effects in semiconductor melts is still at a very early stage of development even though these flows are present in many metallurgical processes with free surfaces and binary melts. The germanium-silicon alloy system has a very large dependence of surface tension on composition and is, therefore, well suited as a model substance for the investigation of solutocapillary flows. With the use of the rotating magnetic field capability in the FMF, large values of the magnetic Taylor number can be reached. This number describes the effect of a rotating magnetic field on the melt.[29] At the moment, no information is available for the interaction of solutocapillary flow with external fields. Because external fields have proven so useful in the investigation of other aspects of crystal growth and are used in some industrial processes, the nature of this interaction is potentially important in understanding solutocapillary flows.

Planned Float Zone Flight Experiments

The main objectives of the float zone experiments can be summarized as follows:

?? Investigate the strength and the characteristics of the thermocapillary and the solutocapillary convection in FZ experiments and determine the influence of solutocapillary convection on the interface morphology and the micro- and macrosegregation.

?? Control time-dependent surface tension driven convection (STDC) by using a rotating magnetic field; examine the influence on the curvature of the solid-liquid interface and the heat/mass transport.

?? Measure the influence of STDC on the microscopic growth rate using an ultrasonic pulse-echo method. Investigate transient growth processes as a function of the process parameters and determine the microscopic growth rate as a function of the convective flow.

It is nearly impossible to directly measure the strength or the contribution of solutocapillary convection during a real growth experiment (i.e. it is not possible to determine the flow velocity as a function of the concentration gradient nor image the concentration field in front of the solid-liquid interface). The same is true for distinguishing between thermocapillary and solutocapillary effects. Therefore, our results must be obtained by comparing crystals or parts of crystals, which have been grown under identical conditions except for the variation of a single parameter. The single parameter, which is varied, will either enhance or weaken the impact of the solutocapillary convection while maintaining the thermocapillary contribution constant (or vice versa, respectively). Then, we can attribute changes in the morphology or the segregation to the specific STDC.

If we can obtain information about the three main objectives called out above, a pioneering paper with respect to the role of STDC in semiconductor growth with free melt surfaces can be published. To reach this aim, a total of six float zone experiments is required. These experiments will be set up in a matrix that will enable us to distinguish between the effects due to thermocapillary convection and the effects due to solutocapillary convection. Growth length, sample diameter, rotating magnetic field, diagnostics etc. all remain constant for all samples.

SUMMARY

An international collaboration expected to serve as a pattern for experimentation aboard the ISS has been described. Results from this experiment are expected to help understand phenomena that will have a substantial impact on the science and technology of terrestrial crystal growth of many semiconductor materials of substantial economic importance. The two phenomena of primary importance that this investigation will enable on Earth are reproducible detached Bridgman growth and accurate modeling of solutocapillary convection during float-zone growth.

ACKNOWLEDGMENTS

The Physical Sciences Division of the National Aeronautics and Space Administration Office of Biological and Physical Research supports the United States portion of this work. Support for the German part of the investigation is provided by the Deutsches Zentrum für Luft- und Raumfahrt and the European Space Agency. More details are given in footnotes to the text.

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