REDUCTION OF DEFECTS IN GERMANIUM-SILICON

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Objectives of the Investigation

Crystals grown without being in contact with a container have superior quality to otherwise similar crystals grown in direct contact with a container, especially with respect to impurity incorporation, formation of dislocations, and residual stress in the crystals. In addition to float-zone processing, detached Bridgman growth, although not a completely crucible-free method, is a promising tool to improve crystal quality. It does not suffer from the size limitations of float zoning and the impact of thermocapillary convection on heat and mass transport is expected to be negligible. Detached growth has been observed frequently during μg experiments [1]. Considerable improvements in crystalline quality have been reported for these cases [2]. However, neither a thorough understanding of the process nor a quantitative assessment of the quality of these improvements exists. This project will determine the means to reproducibly grow GeSi alloys in a detached mode and seeks to compare processing-induced defects in Bridgman, detached-Bridgman, and floating-zone growth configurations in GeSi crystals (Si $\leq$ 10 at%) up to 20mm in diameter.

Specific objectives include:
- measurement of the relevant material parameters such as contact angle, growth angle, surface tension, and wetting behavior of the GeSi-melt on potential crucible materials;
- determination of the mechanism of detached growth including the role of convection;
- quantitative determination of the differences in defects and impurities for crystals grown using normal Bridgman, detached Bridgman, and floating zone (FZ) methods;
- investigation of the influence of a defined flow imposed by a rotating magnetic field on the characteristics of detached growth;
- control of time-dependent Marangoni convection in the case of FZ growth by the use of a rotating magnetic field to examine the influence on the curvature of the solid-liquid interface and the heat and mass transport; and
- growth of benchmark quality GeSi-single crystals.

Microgravity Relevance

Prior to the beginning of this investigation, the most reliable environment for obtaining detached Bridgman growth was reduced gravity. At this time, we and others are repeatedly growing partially detached Bridgman samples in unit gravity. Nonetheless, the reasons for completing the microgravity parts of this investigation still remain viable:

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- The comparison of samples grown by detached growth with float-zone samples of the same diameter is fundamental to this study because the float-zone technique is truly and completely containerless in contrast to detached Bridgman growth. Terrestrial floating zones of this material are limited to diameters of about 8mm. Therefore, these larger diameter floating-zone experiments can only be conducted in a reduced gravity environment.
- The occurrence of detachment during Bridgman growth is postulated to be dependent upon the difference in gas pressures in the crucible above and below the melt and it is further believed that the evolution of gases at the growth interface is required to maintain the necessary pressure difference [3, 4, 5]. Determining whether this pressure difference is essential in all cases is one of the objectives of this investigation. If the growth and contact angles are favorable, detachment will take place without a pressure difference. This will only be possible for very few material-crucible combinations. Gas evolution and the resulting maintenance of the pressure difference will be strongly effected by convection in the melt, which is dominated in the Bridgman configuration by buoyancy-driven flows. Thus, to the extent that this phenomenon is necessary for detachment, the conditions for detached growth will differ significantly between unit gravity and microgravity because of the influence of gravity on convection in the melt.
- The effect of an intentional pressurization of the volume below the meniscus either by using pressurized gas [6] or by changing the temperature profile, as in this project, is limited by the emission of bubbles under gravity once the pressure of the hydrostatic head is attained.
- Segregation effects due to significant differences in density between Ge and Si have to be considered during the growth of GeSi alloys. Experiments have shown that the orientation of the gravity vector is essential in respect to the segregation profile of GeSi Bridgman-grown crystals. In order to avoid gravitational effects it is essential to grow GeSi crystals under microgravity.
- Finally, the FZ growth of GeSi alloys is accompanied by interesting differences in the shape of the growth meniscus (compared to Ge or Si) due to the interaction between thermocapillary and solutocapillary effects. The specifics are discussed later but the full understanding of the interaction of these two effects, which might also influence detached growth, will require comparison between 1g and microgravity results.

Results

During the two years since the previous NASA Microgravity Materials Science Conference, most of the work supported by both the NASA and the DLR (German Space Agency) RDGS investigation has been published and is available for viewing or downloading from the RDGS web site. This includes work carried out in Germany as well as in the United States.

Float zone work supported by the German RDGS is described, for example, in two Journal of Crystal Growth articles, [7] and [8].

The sessile drop measurements were completed and the results were presented at the Thirteenth International Conference on Crystal Growth (ICCG-13) in Kyoto, Japan in 2001 [9], and in two Journal of Crystal Growth articles, (for germanium) [10] and (for germanium-silicon alloys) [11].

Substantial additional progress was made on understanding the detached Bridgman growth process. The experimental part of this work was the subject of two additional presentations at the ICCG-13 on

germanium [12], and germanium-silicon alloys [13]. Both papers were accepted for inclusion in the proceedings issue of the Journal of Crystal Growth, (germanium) [14] and (germanium-silicon).[15]

A detailed, quantitative comparison of the etch pit density in germanium grown detached from the container wall and normally (attached to the container wall) was presented in a paper at the Thirteenth American Conference on Crystal Growth and Epitaxy (ACCGE-13) in Burlington, Vermont in 2001 [16], and a related paper was published in the Journal of Crystal Growth [17].

An overview of the investigation was presented at the Conference on International Space Station Utilization in 2001 [18].

This body of work, along with some yet to be published on the modeling of detached growth and the methods developed for characterizing the as-grown surfaces, enabled the investigation to successfully complete the Science Concept Review in December 2000.

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