REDUCTION OF DEFECTS IN GERMANIUM-SILICON

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Objectives of the Investigation

Crystals grown without contact with a container have far superior quality to otherwise similar crystals grown in direct contact with a container. In addition to float-zone processing, detached-Bridgman growth is a promising tool to improve crystal quality, without the limitations of float zoning. Detached growth has been found to occur frequently during μg experiments 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. This project is determining the means to reproducibly grow Ge-Si alloys in the detached mode.

Microgravity Relevance

At this time, the most reliable environment for obtaining and studying detached growth is reduced gravity. The proposed work seeks to compare processing-induced defects in Bridgman, detached Bridgman, and floating-zone growth configurations in Ge-Si crystals (Si $\leq$ 10 at%) 20mm in diameter. The occurrence of detachment during growth is widely thought to be related to gas pressures in the crucible and the evolution of gases at the growth interface. Gas evolution will be strongly effected by convection in the melt, which is dominated in the Bridgman configuration by buoyancy-driven flows. Thus, terrestrial detached growth (even when reproducible) will differ significantly from microgravity detached growth and the comparison of the two will provide vastly more insight than either alone. There is also a high potential for gaining new understanding of the role of convection in defect generation. Finally, 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 floating-zone experiments can only be conducted in a reduced gravity environment.

Results

Sessile drop measurements of Ge (36 experiments) and $Ge_{1-x}Si_x$ ($x \leq 12$ at.%) (23 experiments) on different substrate materials (fused silica, sapphire, AlN, Si_3N_4, pBN, SiC, glassy carbon coated graphite) in active vacuum, slight overpressure of Argon and forming gas (2% Hydrogen in 5N Argon) have shown that pyrolitic boron nitride (pBN) has the highest contact angle and is therefore most likely to promote detachment during Bridgman growth. Surface tension including both temperature and compositional dependences were also determined from these measurements. These parameters are required to model the float-zone growth of $Ge_{1-x}Si_x$.

Partially detached Bridgman growth of $Ge_{1-x}Si_x$ ($x \leq 2$ at.%) has been achieved repeatedly in both Freiburg and Huntsville for samples up to 15mm in diameter. The best results, as suggested by the sessile drop results, have been obtained in pBN but detachment has occurred in a fused silica ampoule. There is no single typical characterization of the detachment. Some ingots have been detached over 90% of the circumference for axial length ~2cm while others have been completely or nearly completely detached around the circumference for lesser axial lengths. Detachment near the initial growth interface, reattachment for a short distance (~1-3 mm) and a second detachment followed by a final reattachment near the last-to-freeze part of the ingot has been repeated numerous times. Detachment is detectable by changes in the surface features of the ingot including the appearance of growth facets and by a reduction in the diameter of up to 50 μm where detachment occurs.

So far these experiments have been done in open-ended tubes (inside a sealed ampoule) so that it is not certain if gas can be trapped in the annular space below the solid-liquid interface, which accompanies detachment. To help address this important question, experiments are being done in tubes closed on the bottom and a theoretical analysis is well advanced. The theoretical analysis is based on the hypothesis that the pressure in the trapped gas volume must support the sum of hydrostatic head of the melt column, the gas pressure at the top free surface of the melt, and the capillary pressure drop across the meniscus. A thermal model of the growth system including the furnace, ampoule and the charge has been developed to track the solidification process and calculate the temperature distribution in the lower gas cavity and in the gas volume above the melt. The pressure in the gas volumes is calculated based on the initial mass of gas in the cavities using the perfect gas law and the instantaneous temperature distribution in the cavities. The pressure in the lower gas volume does not include any contributions from the possible evaporation of dissolved gases from the melt into the gas volume, and thus represents a conservative estimate of the pressure in that cavity. The analysis using the experimental conditions has shown that for *at least* upto about 2.5 cm of growth the pressure in the lower gas volume can be kept sufficiently high to permit detached growth.

$Ge_{1-x}Si_x$ ($x \leq 10$ at.%) single crystals have been grown by the float-zone technique applied within a radiation heated monoellipsoid mirror furnace. The boron-doped ($\approx 1\text{-}2 \cdot 10^{17}$ at/cm^3) feed crystal consisted of synthesized $Ge_{0.95}Si_{0.05}$ polycrystalline material. All crystals were grown using a <100> Ge seed. The etch pit density is about one order of magnitude lower than the EPD of Bridgman grown crystals. Compositional axial and radial profiles have been determined. The maximum silicon concentration was 10 at.%. All crystals show a characteristic distortion of the interface morphology near the crystal edge, a disturbance which was not observed in silicon-free Ge:Ga-doped ($\approx 10^{18}$ at/cm^3) reference crystals. This distortion in the interface morphology is considered to be caused by solutal Marangoni convection due to the concentration dependence of surface tension and a segregation coefficient larger than one. The effect of solutocapillary convection is also evident in corresponding numerical simulations of the melt zone. Using a static axial magnetic field ($B \leq 400$mT), this radial distortion can be reduced and the irregular bending of the interface curvature is shifted toward the crystal edge.

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