# REDUCTION OF DEFECTS IN GERMANIUM-SILICON

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## 1 Objectives of the Investigation

It is well established that 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 often cited as a promising tool to improve crystal quality, without the limitations of float zoning. Detached growth has been found to occur quite often 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 will determine the means to reproducibly grow Ge-Si alloys in the detached mode.

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 of defects and impurities among normal Bridgman, detached Bridgman, and floating zone (FZ) growth;
- investigation of the influence of defined azimuthal or meridional flow due to rotating magnetic fields on the characteristics of detached growth;
- control 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
- grow high quality GeSi-single crystals with Si-concentration up to 10 at% and diameters up to 20 mm.

## 2 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%) 20 mm 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 8 mm. Therefore, these floating-zone experiments can only be conducted in a reduced gravity environment.

## 3 Experimental set-up

### 3.1 Ampoule preparation and growth facility

Growth was performed in double-wall quartz-glass ampoules. The diameter of the seed and the growing crystal was 9 mm, the length of the seed 35 mm, and the length of the grown crystal was 41 mm. Before the starting material was filled into the ampoule, the quartz was cleaned with MUCASOL™ and $H_2O$ (18 MΩ) and baked out under vacuum ($10^{-6}$ mbar) at 1100°C for 2 hours. Undoped germanium (<111>-oriented) served as the seed, the feed was pill-doped with gallium with an averaged concentration of $C_0=8.2\cdot10^{18}$ at/cm$^3$. First, the germanium was rinsed with $H_2O$ (18 MΩ) followed by acetone. Then it was etched for about 3 minutes with the 18:8:5 polishing etch ($HNO_3$ : $CH_3COOH$ : HF).[1] After this treatment, the germanium shows a smooth and shiny surface. Then the material was put into the ampoule and baked out at 900°C for 2 hours under an alternating atmosphere of $H_2$ (normal pressure) and vacuum ($10^{-6}$ mbar). Finally, the ampoule was sealed under an Argon pressure of 600 mbar (pressure at room temperature).

The growth experiment took place in a monoellipsoid mirror furnace.[2] To obtain a temperature profile suited for Bridgman growth, the lamp was moved 2 mm out of focus toward the center of the furnace.[2] The solid-liquid interface was observed by a borescope and a CCD-camera connected to a video tape recorder. With this set-up it is possible to observe and record the position of the growing interface, however, the length is restricted to ~40 to 45 mm and the temperature gradient is about 100 K/cm at the interface, increasing the development of stress and dislocations.

For growth, the ampoule was heated up within 15 minutes and kept at a constant temperature for 45 minutes to guarantee a homogeneous distribution of the dopant in the melt. The ampoule was pulled down with a constant velocity of 0.5 mm/min. No ampoule rotation was applied.

### 3.2 Crystal preparation and characterization

The surface of the grown crystal was analyzed by scanning electron microscopy (SEM). The sample was first cut axially (parallel to the 110-plane) for segregation measurements (4-point measurements and analysis by Nomarski Differential Interference Contrast Microscopy-NDIC). The axial slab was polished with 9 μm and 1 μm diamond paste and SYTON™ and etched with the 1:1:1 etch ($H_2O_2$ : $CH_3COOH$ : HF) for 30 seconds. From the remaining part of a half cylinder, radial wafers have been cut (orientation: <111>, thickness: 3 mm), polished and etched by the Billig etch[3] (12g KOH, 8g $K_3[Fe(CN)_6]$, dissolved in 100 ml $H_2O$) for 8 minutes at ≈80°C.

## 4 Results

After growing ≈7 mm by the normal Bridgman mode with wall-contact, detachment started and continued for 27 mm. The wall-free growth took place over the whole circumference of the crystal except for some small ridges. (This topic will be discussed in more detail.) In the detached grown part, the three <111>-related growth lines (or micro-facets) showed up; one of them can be seen in figure 1 on the upper-left hand side. The remaining 7 mm of the crystal grew again with wall-contact. The transition from de-wetting to wetting behavior of the melt was visible before the solid-liquid interface reached that point. This suggests that the detachment is mainly influenced by the surface condition of the container wall. This transition did not take place across a line but over a band about 1 mm wide as seen in figure 1.

With the transition from detached to attached growth, there is an increase of the crystal diameter, as seen in figure 1. From this diameter enlargement, the dimension of the gap between detached grown crystal and container wall can be determined; at the given location it was measured to be 30 μm (see figure 1, right hand side). Therefore it can be concluded that the size of the meniscus has not exceeded some tens of micrometers, and the thermocapillary convection which can arise from such a small free surface area can be neglected or is at least not in the time-dependent state. This is in coincidence with the literature.[4] The absence of time-dependent convection has been proven by the absence of dopant striations in the detached grown part. Due to the absence of dopant striations, the interface curvature can be determined only at the transition from undoped seed to doped crystal: The phase boundary is slightly convex with a deflection toward the melt of approximately 250 μm.

The axial macrosegregation was estimated by 4-probe measurements. The dopant distribution (figure 2) falls between the theoretical curves for complete mixing and purely diffusive mass transport. For the calculation, $k_0$=0.087 and D=$1.9 \cdot 10^{-4}$ $cm^2/s$ was used.[5] The reduced mixing indicates low radial temperature gradients and a rather flat solid-liquid interface. At the transition from attached to detached (x=7 mm) as well as at the reverse transition (x=34 mm), no influence of the melt-ampoule interaction on the macrosegregation (i.e. on the mixing state of the melt) is seen.

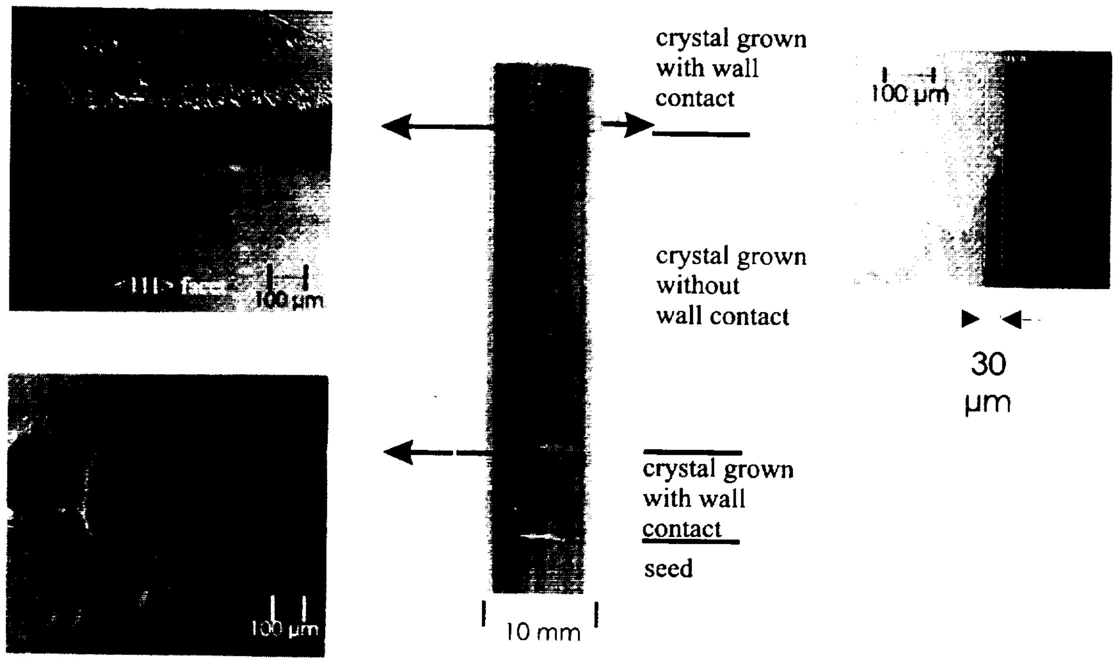


**Figure 1. Photograph of the complete crystal (middle part) and SEM-images of the surface, showing the transition from detached to attached growth. Front view is on the left; side view is on the right hand side. Photos show surface as it grew, i.e. before etching.**

As mentioned above, the crystal grew detached except for several small ridges, where the melt was wetting the ampoule wall. The dimension of these ridges is several tens of micrometers in width and some hundreds of micrometers in length. A similar observation was made by Witt et al.[6, 7] (and described as "Chinese wall"). This implies that the surface layer which prevented wetting of the quartz wall by the melt was not coating the ampoule entirely but was disconnected at some points. The radial EPD-distribution shows that these ridges are related to a strong increase of the defect structure. Due to the high temperature gradient during the growth process and a substantial EPD in the seed material, the overall EPD in the grown crystal is high. Nonetheless, the EPD is significantly lower in the part grown without attachment to the wall. Quantitative measurements are in progress.

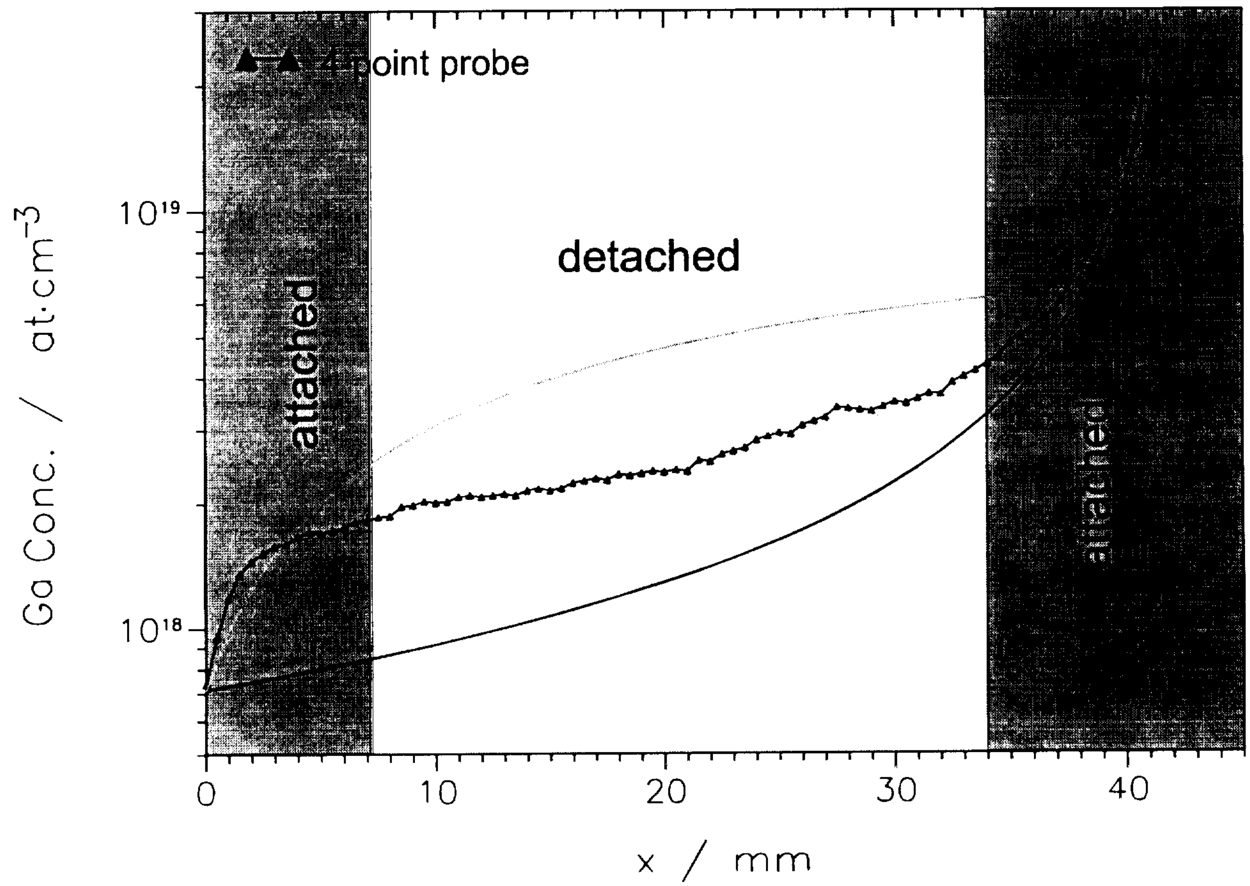


**Figure 2. Axial dopant distribution, measured by 4-point probe. The detachment does not influence the macrosegregation.**

## 5 Discussion

Without taking into account the hydrostatic pressure, the sum of the growth angle of the crystal and the contact angle of the melt (with respect to the container wall) has to be larger than or equal to 180° to realize detachment.[8] The values of these angles given in literature[8,4] suggest that this will not normally be the case. Either the surface treatment (or the coating or the status of oxidation) of the container[8] or the gas pressure at the triple point melt-crystal-container[9] can produce detached growth even if this condition is not met. Duffar et al.[8] have introduced a relationship for the gap-width between crystal and ampoule wall, the radius of the crystal, the growth angle, and the contact angle. Using this relationship, a contact angle of 174±4° (cf. 106° reported[4] for Ge on silica) is needed to obtain a gap width of about 30 μm. This relation does not consider a difference in gas pressure at the meniscus compared to the top of the melt. This condition existed in our configuration because there was gas exchange between the location of the meniscus and the top of the ampoule. The transition from attached to detached growth and vice versa, as well as the irregular transition (i.e. the simultaneous appearance of attached and detached growth at different positions of the interface), suggest that the surface condition of the quartz glass ampoule was the main source for the detachment in this case. The exact mechanism of the different wetting behavior can not be explained yet and will be the subject of systematic investigations (e.g. measurement of the contact angle with respect to surface treatment of the quartz glass). An important point is that the detached growth is possible even under normal gravity conditions, where the hydrostatic pressure assures that the melt touches the container wall.

## 6 Summary

For the first time, detached Bridgman growth was observed in-situ. The main results can be summarized as following:

- The gap between the detached-grown crystal and the wall of the quartz-glass ampoule was measured to be about 30 μm.
- Detached growth occurred over the whole circumference of the crystal; the crystal was in contact to the ampoule only along some small ridges.
- The transition from attached to detached and vice versa did not take place across a line but over a band about 1 mm wide.
- No dopant striations are seen in NDIC-images, indicating that the free surface of the melt meniscus does not cause time-dependent thermocapillary convection.
- No influence of the detachment is seen on the macrosegregation. The axial dopant distribution falls between the theoretical curves for complete mixing and diffusive mass transport.
- The EPD is noticeably reduced in the detached grown part (quantitative measurements in progress).

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