Influence of Containment on the Growth of Germanium-Silicon in Microgravity

M. P. Volz\textsuperscript{1}, K. Mazuruk\textsuperscript{2}, A. Cröll\textsuperscript{2,3} T. Sorgenfrei\textsuperscript{3}

\textsuperscript{1}NASA, Marshall Space Flight Center, EM31, Huntsville, Alabama, USA
\textsuperscript{2}University of Alabama in Huntsville, Huntsville, Alabama, USA
\textsuperscript{3}Kristallographie, University of Freiburg, Germany
This investigation involves the comparison of results achieved from three types of crystal growth of germanium and germanium-silicon alloys:

- Float zone growth
- Bridgman growth
- Detached Bridgman growth

The fundamental goal of the proposed research is to determine the influence of containment on the processing-induced defects and impurity incorporation in germanium-silicon (GeSi) crystals (silicon concentration in the solid up to 5 at%) for three different growth configurations in order to quantitatively assess the improvements of crystal quality possible by detached growth.
What is Detached Bridgman Growth?

Sufficient condition for detachment$^{1,2}$:

$$(\alpha + \theta \geq 180^\circ)$$

Advantages

- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination


What are the conditions for detachment in microgravity and how do they depend on the governing parameters?
- Growth angle
- Contact angle
- Pressure differential
- Bond number (ratio of gravity to capillarity)

Which detached growth solutions are dynamically stable?

How does an initial crystal radius evolve to one of the following states?
- Stable detached gap
- Attachment to the crucible wall
- Meniscus collapse

What are the effects of angular dependence on the crystal shape (faceting effects)?
Detached Crystal Growth
Etch Pit Densities in Detached/Attached Crystals

Completely detached grown crystal UMC7

EPD $\approx 200 \text{cm}^{-2}$

Attached grown crystal UMC6

EPD $\approx 2 \cdot 10^4 \text{cm}^{-2}$

Schematic Diagram of Detached Solidification

α: growth angle
θ: contact or wetting angle

Calculation of Meniscus Shapes

Young-Laplace Equation

\[ \frac{d^2 z}{dr^2} + \frac{dz}{dr} \left( 1 + \left( \frac{dz}{dr} \right)^2 \right)^{3/2} = \Delta P - Bz(r) \]

\[ \Delta P = \frac{\Delta P_m r_0}{\sigma}, \quad \Delta P_m = P_H - P_C + \rho gh + 2 \frac{\sigma}{r_H} \]

\[ B = \frac{\rho g_0 r_0^2}{\sigma} \]

\( B = 3.248; \) Ge, \( r_0 = 6 \text{ mm} \)

\( B = 4.651; \) InSb, \( r_0 = 5.5 \text{ mm} \)

\[ \frac{\partial r}{\partial s} = \cos \beta, \quad \frac{\partial z}{\partial s} = \sin \beta, \quad \frac{\partial \beta}{\partial s} = -\frac{\sin \beta}{r} + \Delta P - Bz \]

Boundary Conditions

\( z(0) = 0; \quad \beta(0) = 90^\circ - \alpha; \)

\( \beta(1) = \theta - 90^\circ; \quad r(1) = 1 \)

\( \Delta P: \) Dimensionless pressure differential across the meniscus

\( B: \) Bond number; ratio of gravity force to surface tension force

Set of 3 coupled differential equations

\( \alpha: \) growth angle

\( \theta: \) contact or wetting angle
Gap Width vs. Pressure Differential (Ge at 1g)

\[ \theta + \alpha < 180^\circ \]

\[ \theta + \alpha > 180^\circ \]

\( \theta = 140^\circ \)
\( \theta = 152^\circ \)
\( \theta = 164^\circ \)
\( \theta = 172^\circ \)

\( \alpha = 14.3^\circ \)

\( B = 3.248 \)
Gap Width vs. Pressure Differential (Ge at $10^{-6} \times g_0$)

$\theta + \alpha < 180^\circ$

$\theta + \alpha > 180^\circ$

$\alpha = 14.3^\circ$

$B = 3.248 \times 10^{-6}$
“Influence of Containment on the Growth of Silicon-Germanium” (ICESAGE) is a collaborative investigation between NASA and the European Space Agency (ESA).

The ICESAGE experiments will be conducted in the Low Gradient Furnace (LGF) in the Materials Science Laboratory on the International Space Station (ISS).

Processing parameters will be varied to assess their affect on detachment:

- Sample Material (GeSi, Ge:Ga)
  - Affects the growth angle
  - Comparison of semiconductor alloy and doped element
- Inner Ampoule surface material (SiO₂, boron nitride)
  - Affects the contact angle
- Pressure: positive, negative, or zero (vacuum) gas pressure below the meniscus
Microgravity Effects

- Microgravity reduces the pressure head ($\rho gh$) resulting from the weight of the melt.
  - Detached growth requires that capillary forces dominate over gravitational forces.
  - On Earth, gravity complicates a comparison of detached growth theory and experiment: the pressure head continuously decreases as the melt solidifies and the pressure varies along the height of the meniscus.

- Microgravity allows a larger value of the gap width.
  - On Earth, when the gap width becomes too large, gravity overcomes surface tension, a stable meniscus cannot be maintained, and the melt will flow down between the crystal and ampoule wall.
  - A large initial gap width will allow measurement of anisotropy in the growth angle.

- Microgravity enables a study of the dynamic stability of crystallization independent of thermal effects.
A Ge$_{1-x}$Si$_x$ ingot is placed inside a pyrolitic boron nitride (pBN) tube and sealed in a SiO$_2$ ampoule.

The ampoule is placed inside a cartridge which is inserted into the furnace.

Thermocouples in the cartridge provide for real-time monitoring of the thermal profile.
When the top of the ingot melts, different pressure volumes are created.
As the ingot is inserted into the furnace, the pressure above the meniscus increases faster than below the meniscus.
**Negative Pressure Configuration**

- When the top of the ingot melts, different pressure volumes are created.
- As the ingot is inserted into the furnace, the pressure below the meniscus increases faster than above the meniscus.
Summary

- Crystals grown by the detached Bridgman method have greatly increased crystalline perfection, motivating a systematic study of the phenomenon.
- A theory describing the conditions for detachment has been developed.
- Only crystals where $\alpha + \theta > 180^\circ$ are expected to achieve stable detached growth in microgravity.
- Reproducible detached growth has been achieved in the laboratory under limited conditions.
- Microgravity will allow the study of detachment over a range of parameters not possible to achieve on Earth.
- A series of Ge and GeSi crystal growth experiments are being developed for processing on the ISS.