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Influence of Containment on the Growth of Silicon-Germanium: A Materials Science Flight Project

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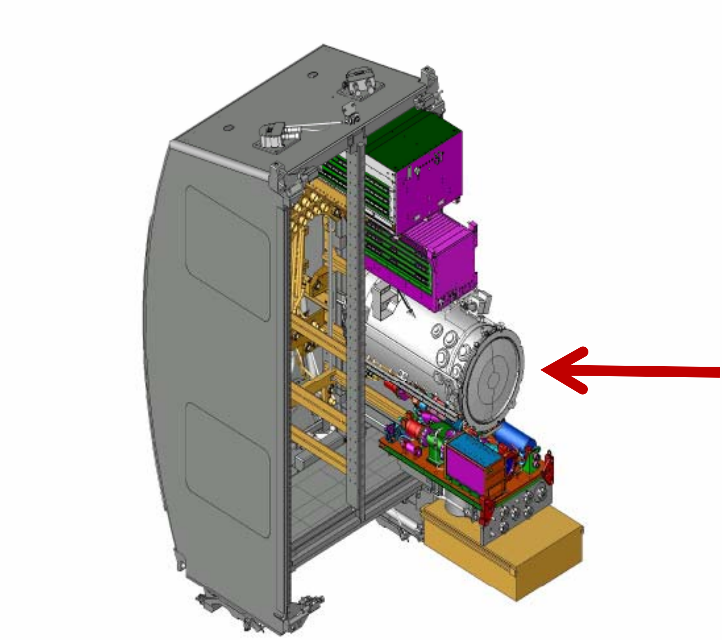
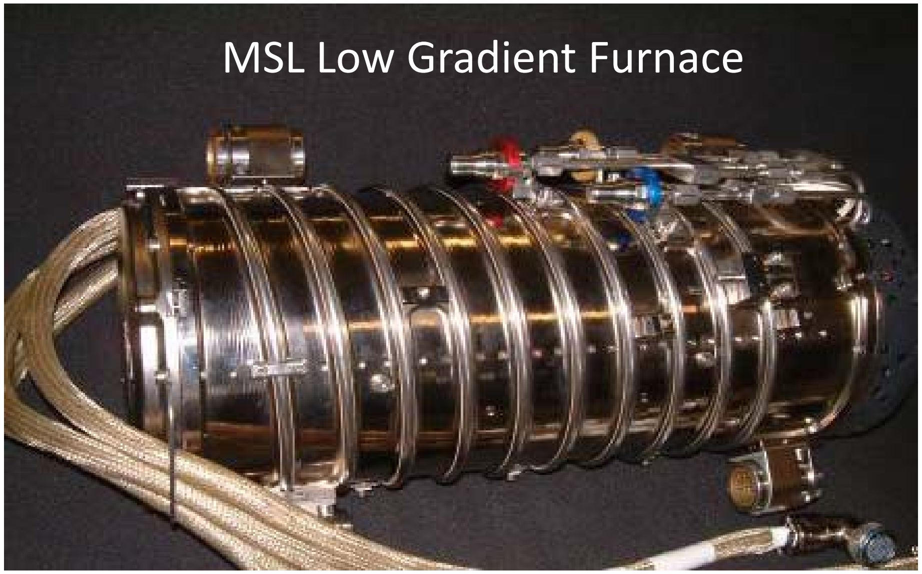
ICESAGE Flight Investigation

- “Influence of Containment on the Growth of Silicon-Germanium” (ICESAGE) is a NASA Materials Science Flight Investigation
- 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)



Materials Science Laboratory

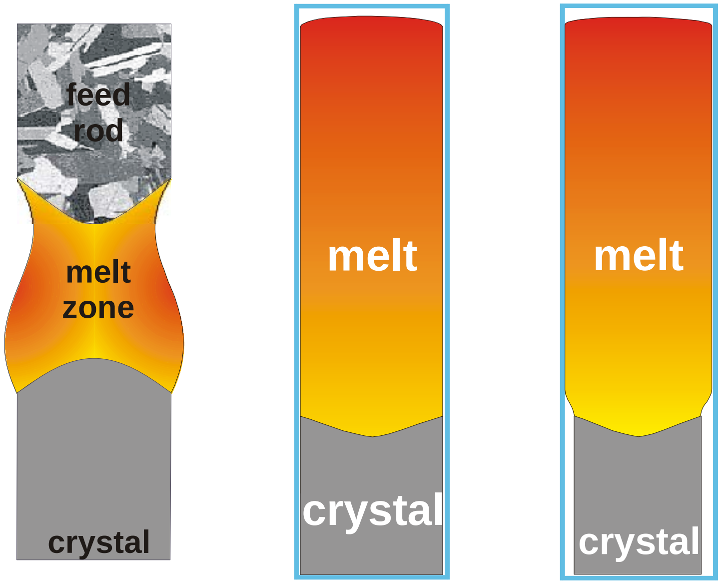


MSL Low Gradient Furnace

Overview of the Investigation

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



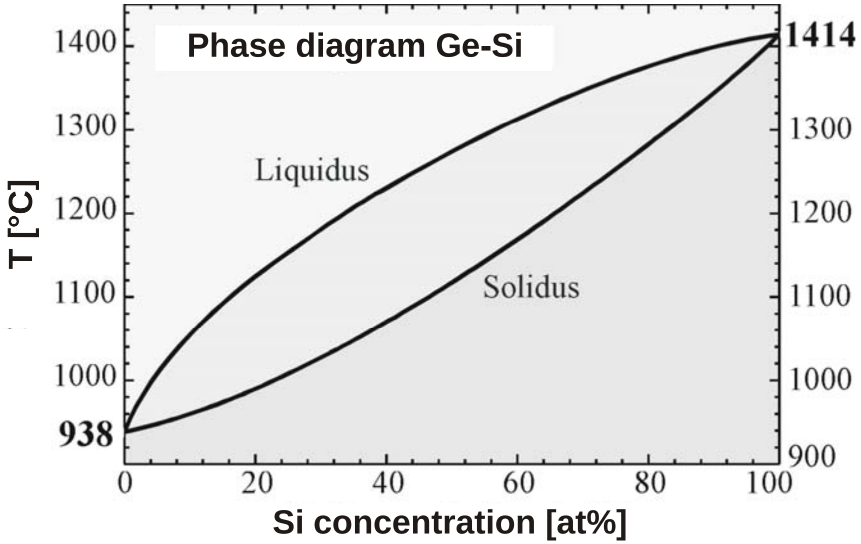
The fundamental goal of the proposed research is to determine the influence of containment on the processing-induced defects and impurity incorporation in germanium-silicon (GeSi) crystals (silicon concentration in the solid up to 5 at%) for three different growth configurations in order to quantitatively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

Why Study Germanium-Silicon Alloys?

- Technological applications
  - X-ray and neutron optics (gradient crystals)
  - High-efficiency solar cell material
  - Thermoelectric converters
  - Increased carrier mobility compared to silicon, but can still be integrated into Si technology
- Characterization methods for silicon and germanium are well-established and are applicable to the alloy crystals.
- Relatively well known material properties and material parameters
- The vapor pressure of silicon and germanium melts can be neglected; they are non-toxic materials.

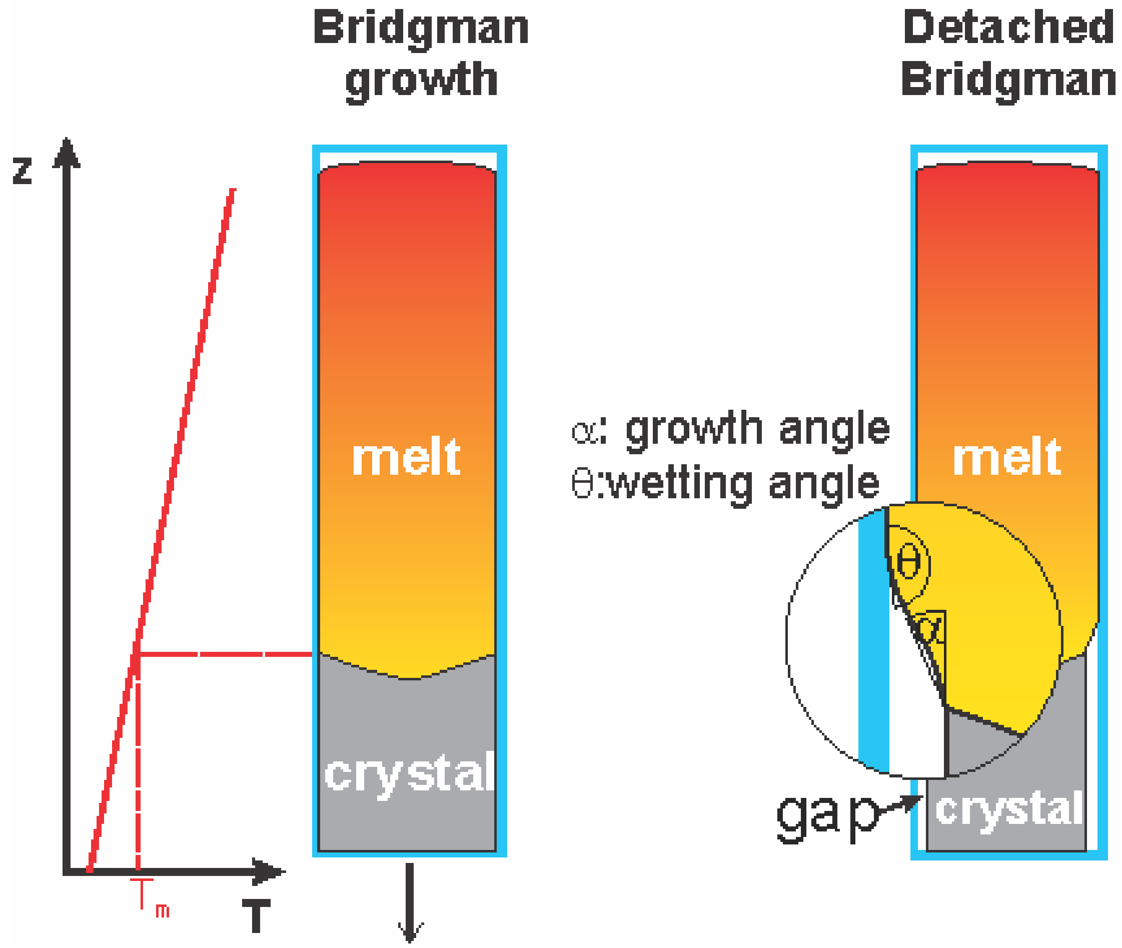
Technological Challenges of $Ge_{1-x}Si_x$

- Large separation of solidus and liquidus curves leads to strong segregation
- Lattice mismatch (4%) leads to increased stress, cracks, high dislocation densities, polycrystalline growth
- The reactivity of liquid silicon leads to a reaction with crucible materials (sticking) as well as contamination of the melt and the crystals



Principles of 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

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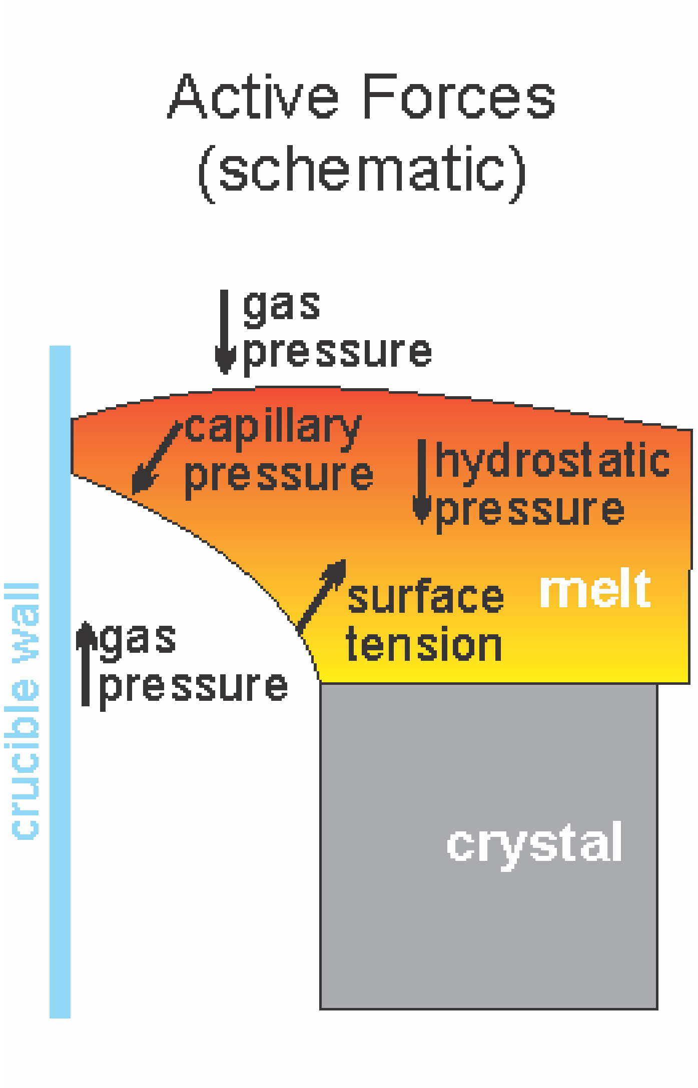
[1] V. S. Zemskov: Fiz. Khim. Obrab. Mater. 17 (1983) 56

[2] T.Duffar, I Paret-Harter, P.Dusserre: J.Crystal Growth 100 (1990) 171.

Pressures in Detached Bridgman Growth



$$\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\Delta P$$ Young-Laplace Equation

where

γ: surface tension

R_1, R_2: radii of curvature of the meniscus

ΔP: pressure differential across the meniscus

$$\Delta P=\Delta P_{external}+\rho gh+2\frac{\gamma}{r_{tm}}$$

where

$\Delta P_{external}$: external gas pressure differential

ρgh : weight of melt (pressure head)

$2\frac{\gamma}{r_{tm}}$: capillary pressure from top meniscus

Calculation of Meniscus Shapes

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

Young-Laplace Equation

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

ΔP : Dimensionless pressure differential across the meniscus

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

B = 3.248; Ge, r_0 = 6 mm
B = 4.651; InSb, r_0 = 5.5 mm

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

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

Set of 3 coupled differential equations

Boundary Conditions

$z(0) = 0$; $\beta(0) = 90° - \alpha$;

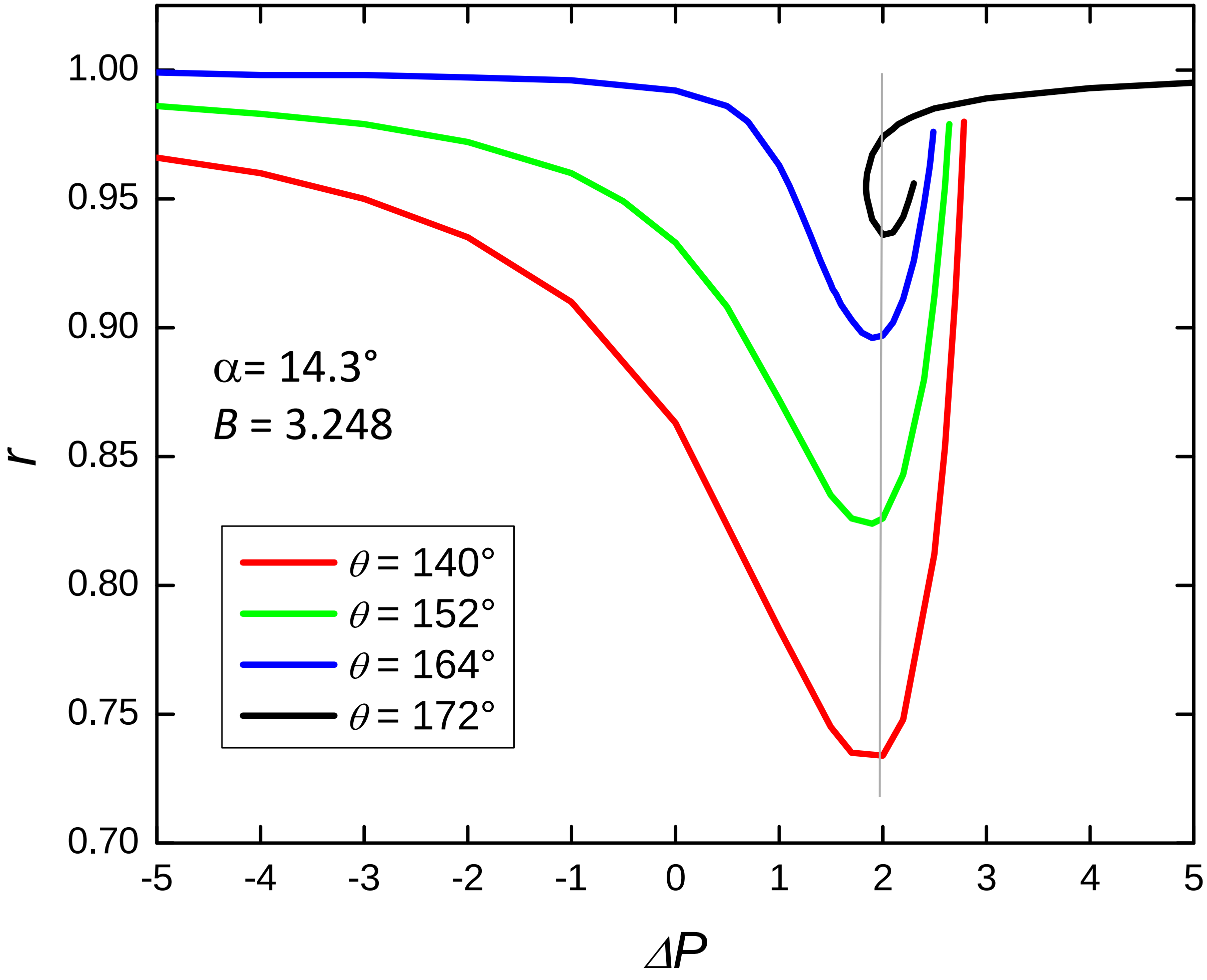
$\beta(1) = \theta - 90°$; $r(1) = 1$

α: growth angle
θ: contact or wetting angle

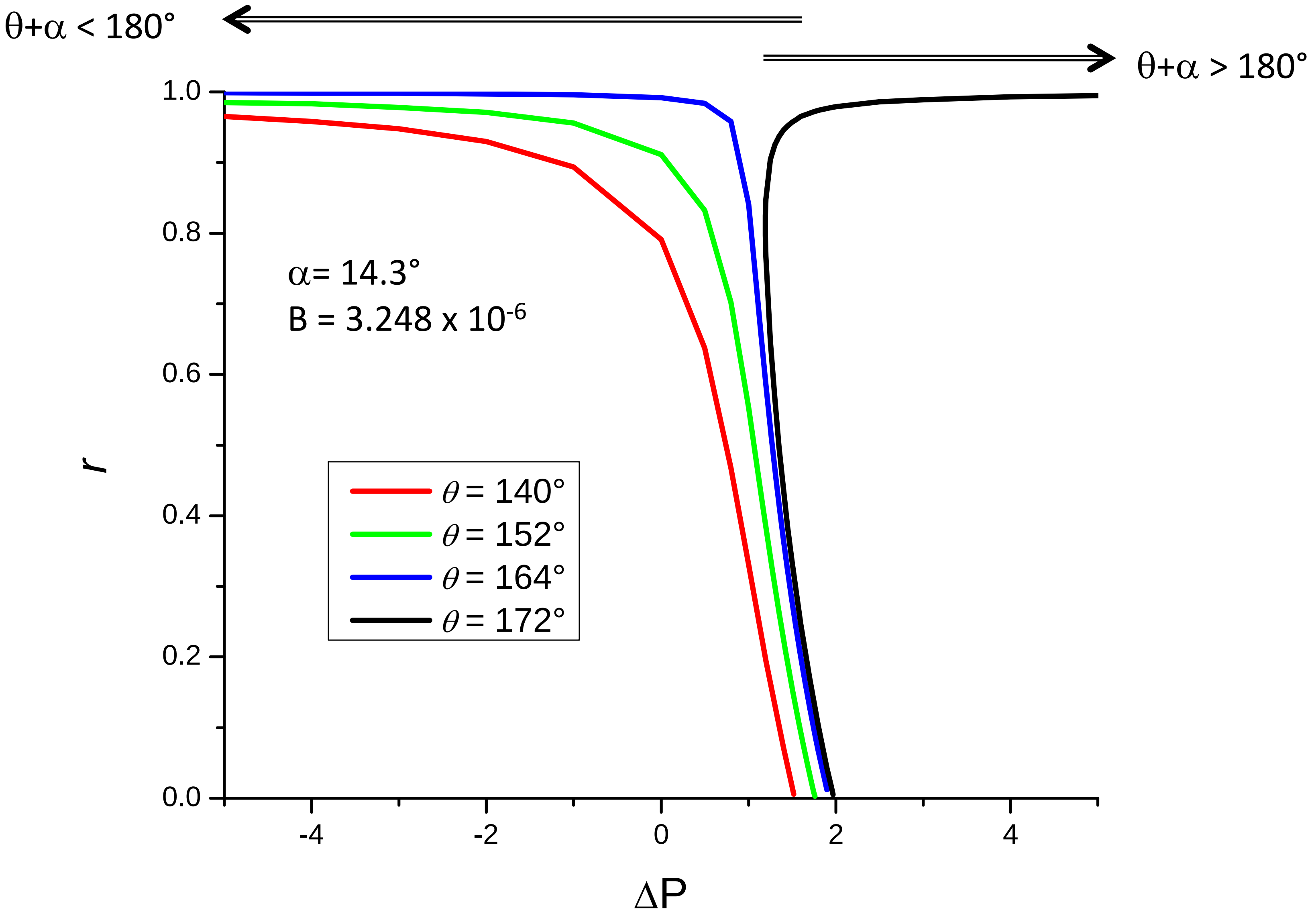
Gap Width vs. Pressure Differential (Ge at 1g)

$\theta+\alpha < 180°$ ←

→ $\theta+\alpha > 180°$

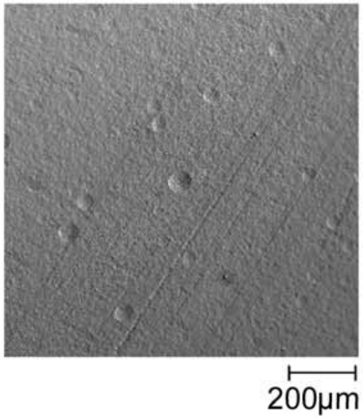


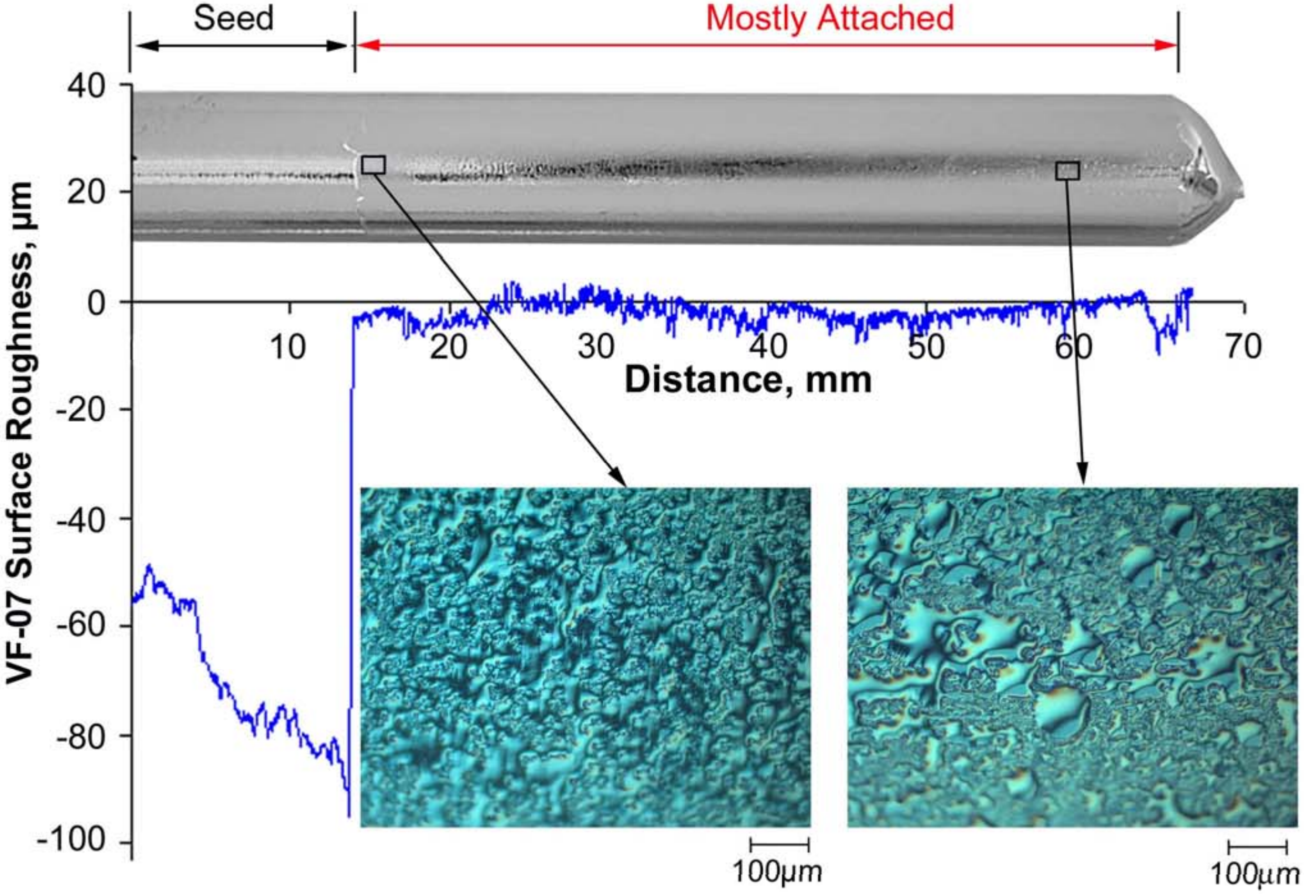
Gap Width vs. Pressure Differential (Ge at $g = 10^{-6}\ g_0$)



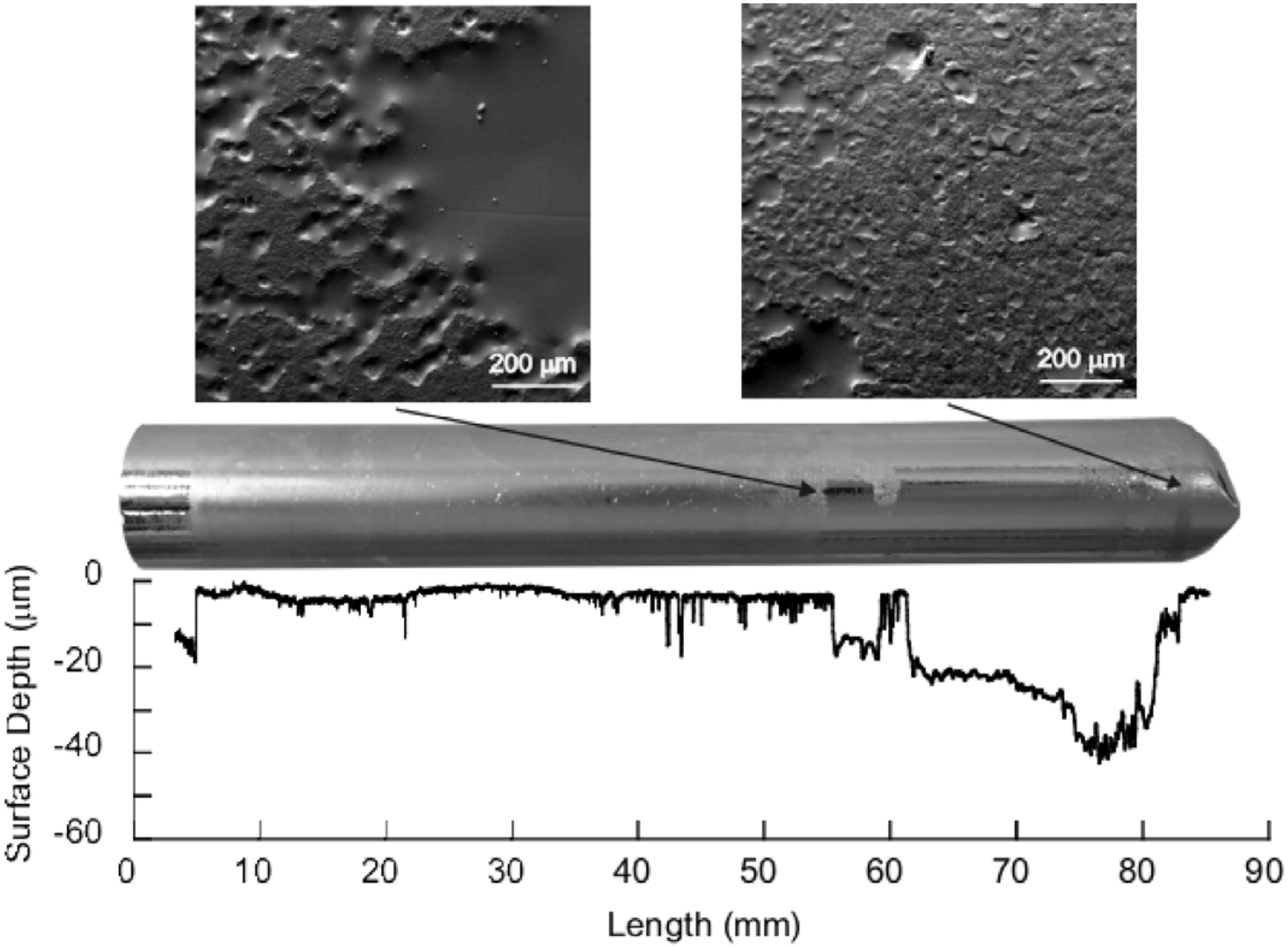
“Attached” Germanium

pBN Ampoule Surface



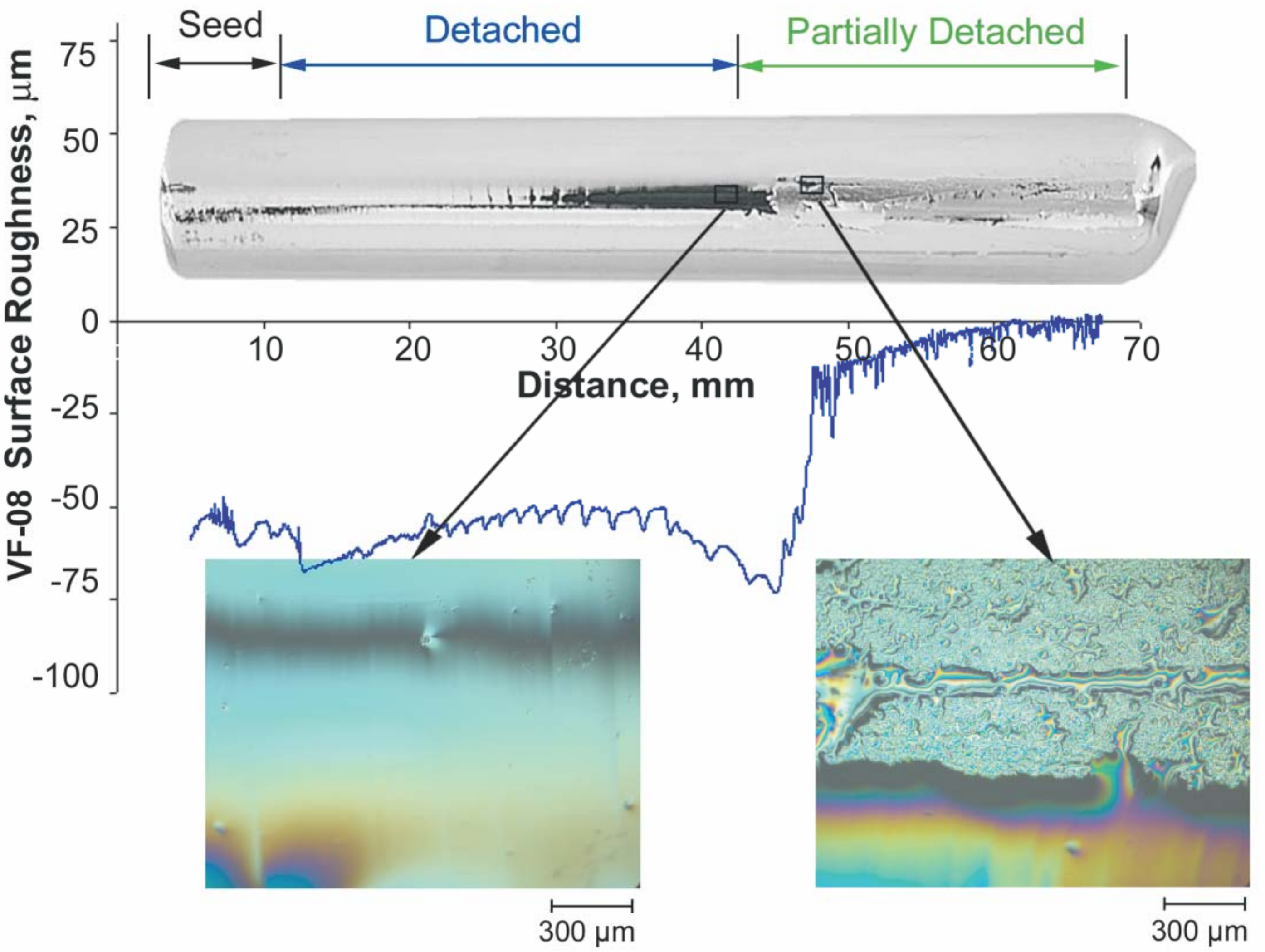


Partially Attached GeSi



M. P. Volz, M. Schweizer, N. Kaiser, S. D. Cobb, L. Vujisic, S. Motakef, F. R. Szofran, *JCG* 237-239 (2002) 1844-1848

Detached Ge in pBN Ampoule



Etch Pit Densities in Detached/Attached Crystals

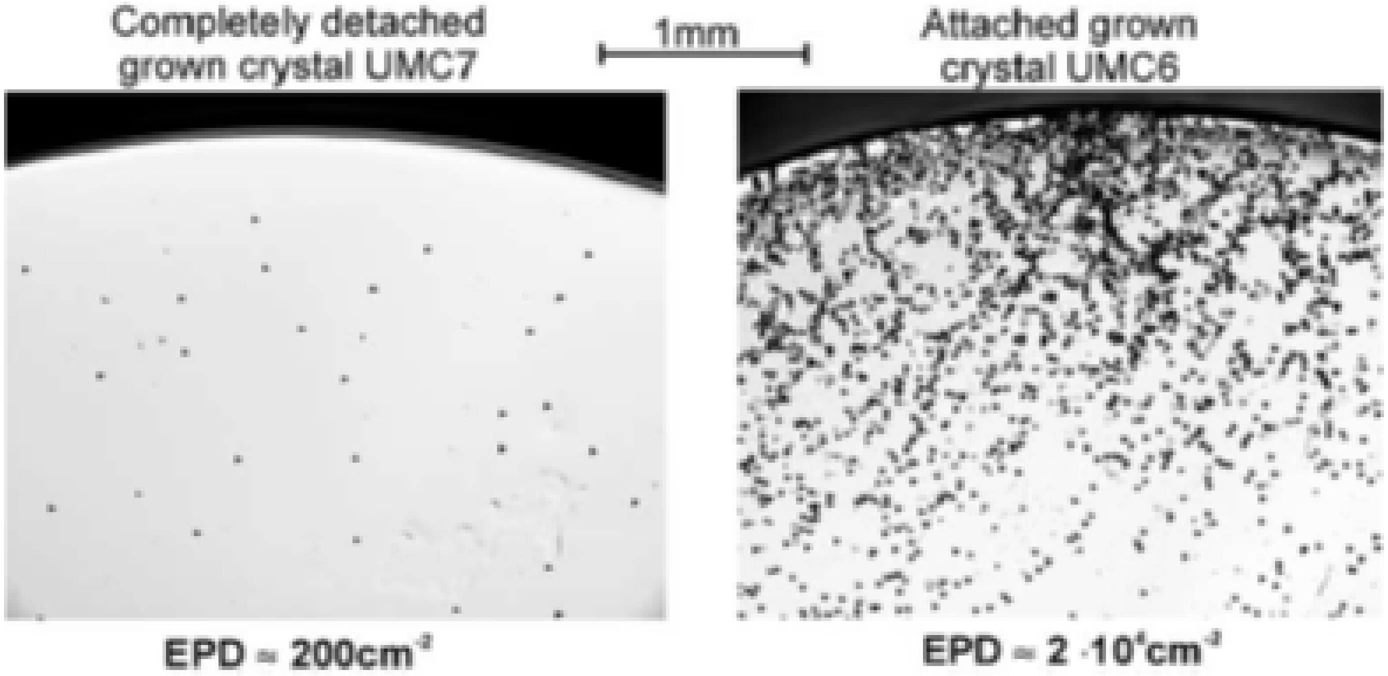


Fig. 5. Micrograph from the detached-grown sample UMC7 and from the attached-grown sample UMC6.

M. Schweizer, S. D. Cobb, M. P. Volz, J. Szoke, F. R. Szofran,
JCG 235 (2002) 161-166

Etch Pit Density Variation With Attachment

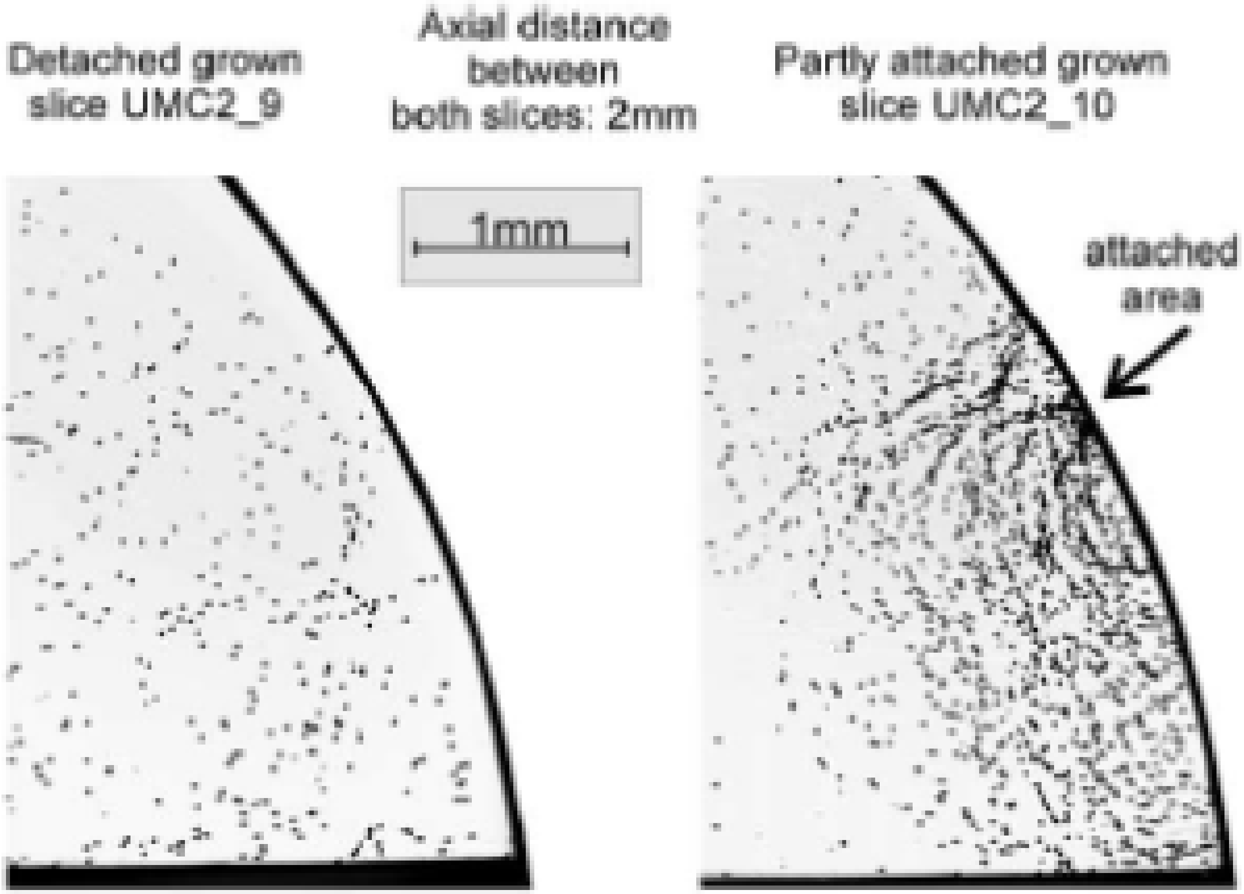


Fig. 6. Localized increased EPD after the crystal attaches partially to the wall.

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Microgravity Effects

- Microgravity reduces the pressure head (ρgh) 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.

Flight Investigation Objectives

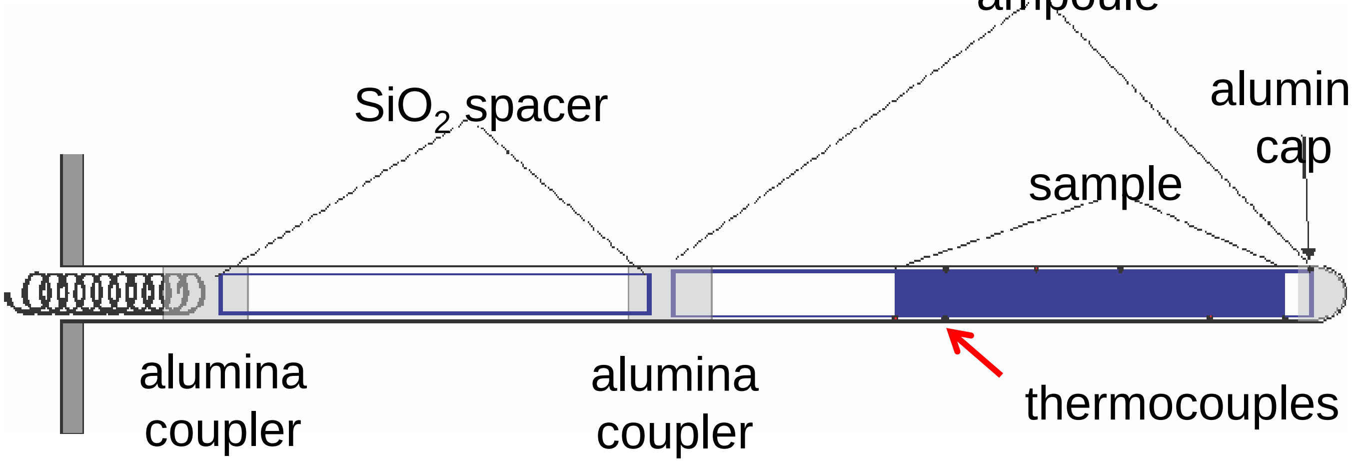
Ten flight experiments have been selected to address the flight objectives of the Bridgman component of the ICESAGE investigation.

1) **Test the following detached growth hypotheses:**
   a. **For a given set of growth and contact angles, there exists a range of pressure differential between the upper surface of the melt and the meniscus at the detachment gap such that detachment occurs.**
   b. **Larger gap widths are possible in microgravity than in unit gravity.**
   c. **Dynamic stability of detached growth in microgravity does not depend on thermal effects.**
   d. **Measurement of the growth angle anisotropy can be made in detached growth in microgravity.**

2) **Quantitatively compare the defect structure and impurity levels of microgravity-grown normal and detached Bridgman and float-zone crystals to determine the optimum growth process.**

Ampoule and Cartridge Layout

- 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



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