

ACCGE-17 ABSTRACT

Influence of containment on defects in GeSi crystals

M. P. Volz^a, A. Cröll^b, K. Mazuruk^c

^aNASA, Marshall Space Flight Center, EM30, Huntsville, AL 35812, USA

^bKristallographisches Institut, University of Freiburg, Hebelstr. 25, D-79104, Freiburg, Germany

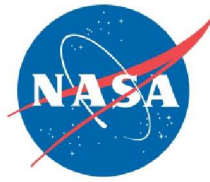
^cUniversity of Alabama in Huntsville, Huntsville, AL 35762, USA

Abstract

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 crystals. “Detached” or “dewetted” Bridgman growth is similar to regular Bridgman growth in that most of the melt is in contact with the crucible wall, but the crystal is separated from the wall by a small gap, typically of the order of 10^{-5} m. A small meniscus bridges the gap between the top of the crystal and the wall. Key parameters involved in achieving detached growth are the contact angle between the melt and crucible and the pressure differential across the meniscus. Sessile drop measurements were used to determine the wetting angles of $\text{Ge}_{1-x}\text{Si}_x$ melts on a variety of substrates and found that the highest wetting angles were achieved with pyrolytic boron nitride (pBN). GeSi crystals have been repeatedly grown detached in pBN crucibles but only occasionally in crucibles with lower wetting angles. Experiments have been conducted to assess the effect of pressure differential across the meniscus in sealed crucibles. This was done by adjusting the temperature profile after partial melting of the starting material. In a separate set of experiments, the pressure was controlled by connecting the volume below the meniscus to a regulated gas supply. The experiments were in agreement with calculations which predicted that stable detachment will only occur in crucibles with a low wetting angle over a relatively narrow range of pressure differential. Detached-grown crystals exhibited superior structural quality as evidenced by measurements of etch pit density, synchrotron white beam X-ray topography and double axis X-ray diffraction.



17th American Conference on Crystal Growth and Epitaxy
Lake Geneva, Wisconsin
August 9-14, 2009



Influence of Containment on Defects in GeSi Crystals

M. P. Volz^a, A. Cröll^b, K. Mazuruk^c

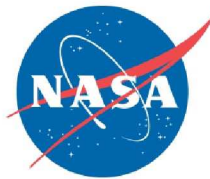
^aNASA, Marshall Space Flight Center, EM30, Huntsville, AL 35812, USA

^bKristallographisches Institut, University of Freiburg, Hebelstr. 25, D-79104, Freiburg, Germany

^cUniversity of Alabama in Huntsville, Huntsville, AL 35762, USA



U. S. RDGS Personnel



MSFC/Contractor Scientists

Dr. Martin Volz (current NASA PI)
Dr. Frank Szofran (original PI),
Dr. Sharon Cobb
Dr. Shari Feth
Dr. Witold Palosz
Ms. Penny Pettigrew

Cape Simulations

Dr. Shariar Motakef
Dr. Ljubomir Vujisic

University of Illinois

Dr. John Walker

University of Alabama Huntsville

Dr. Consty Mazuruk

Visiting Scientists (Germany)

Dr. Arne Cröll (current ESA PI),
Dr. Natalie Kaiser (Salk)
Dr. Peter Dold
Dr. Markus Schweizer

Visiting Scientists (Hungary)

Dr. Janos Szoke

Technical Support

C. Bahr/D. Lovell/J. Quick,
Morgan Research/MSFC
P. Carpenter/C. Cochran, USRA/MSFC
S. Gallop, Tec-Masters/MSFC

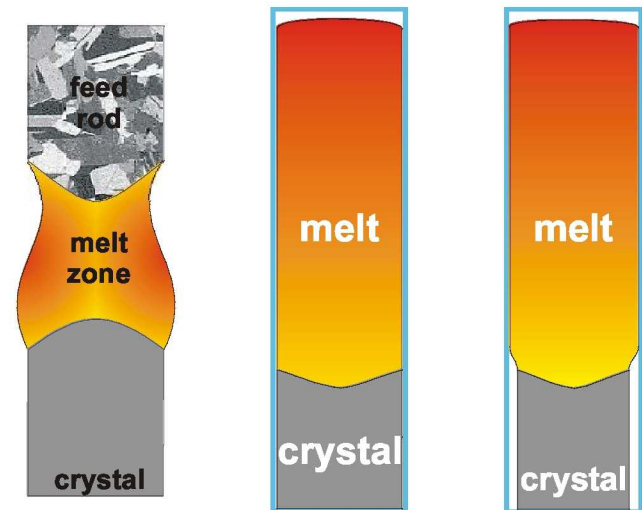


Overview of Investigation



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



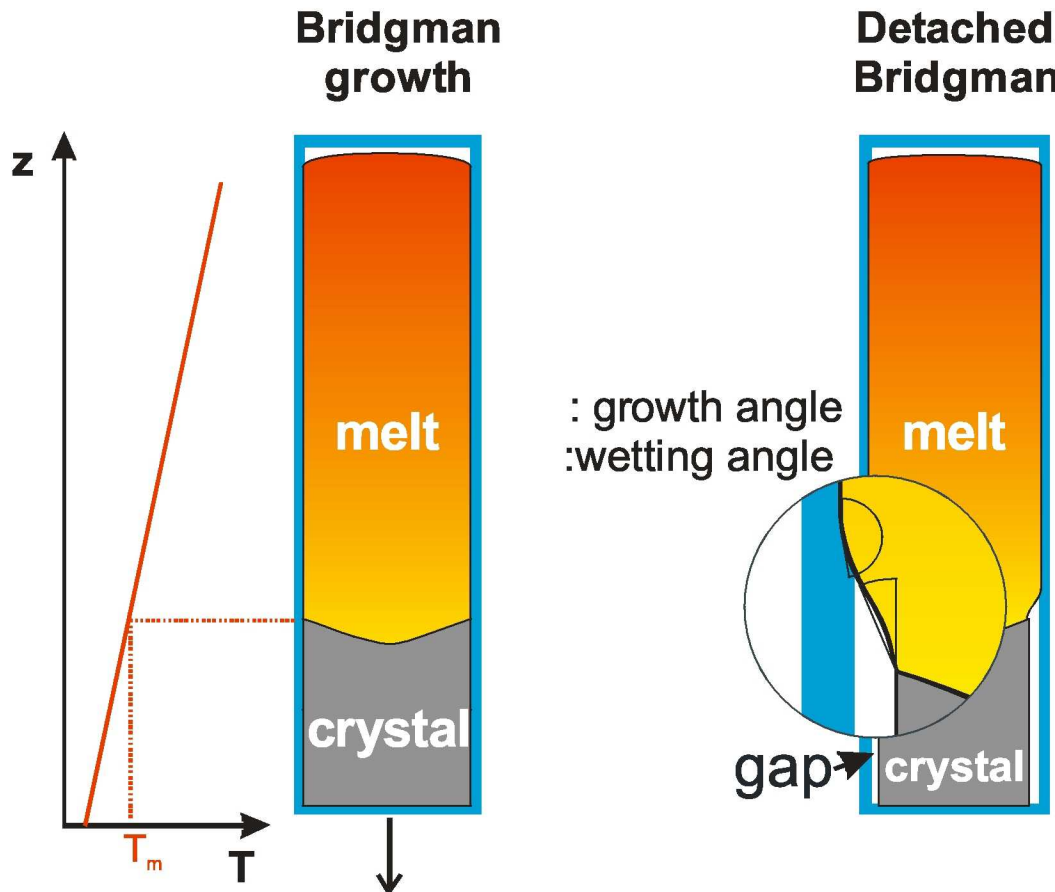
An understanding of the de-wetting process that enables detached Bridgman growth and of the roles of thermo- and solutocapillary convection in determining the characteristics of float zone Ge-Si crystals are the prerequisite objectives of this investigation. The fundamental objective is a quantitative comparison of the defects induced by various growth factors among the three types of growth methods.



Principles of Detached Bridgman Growth



Sufficient condition for detachment^{1,2}:
 $(\alpha + \theta \geq 180^\circ)$



Advantages

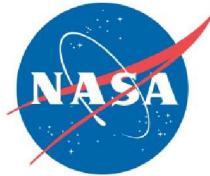
- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination

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

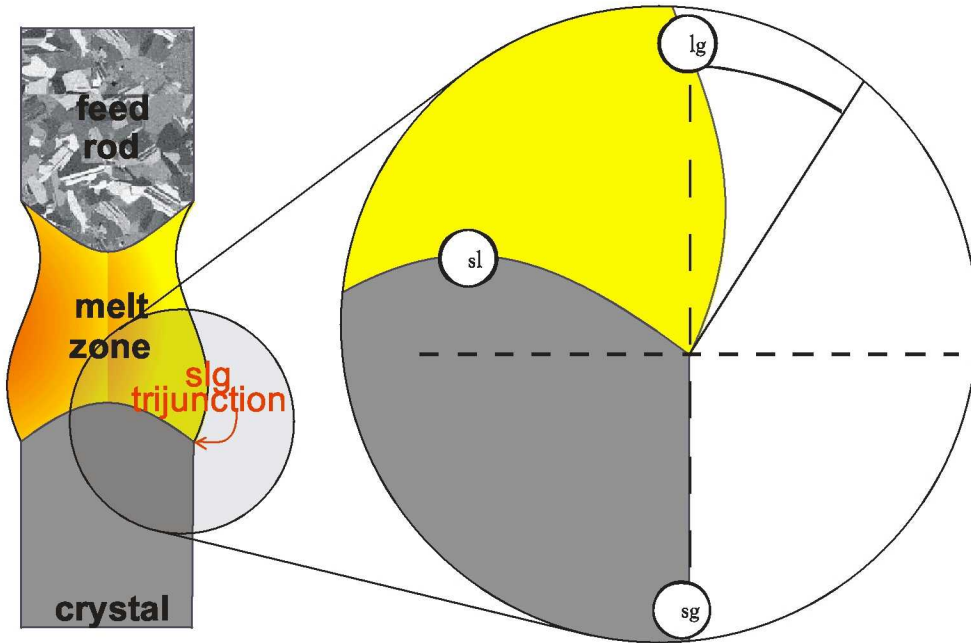
²T. Duffar, I. Paret-Harter, P. Dusserre:
J. Crystal Growth 100 (1990) 171.



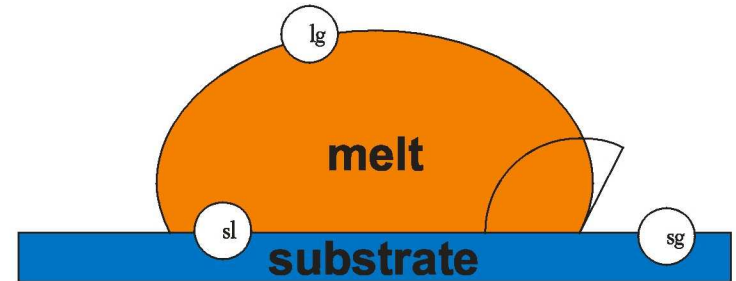
Growth Angle and Wetting Angle



Growth angle :



Wetting angle :



$$\theta = \arccos \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

(Young equation)

$$\alpha = \arccos \left(\frac{\gamma_{sg}^2 + \gamma_{lg}^2 - \gamma_{sl}^2}{2 \cdot \gamma_{sg} \cdot \gamma_{lg}} \right)$$

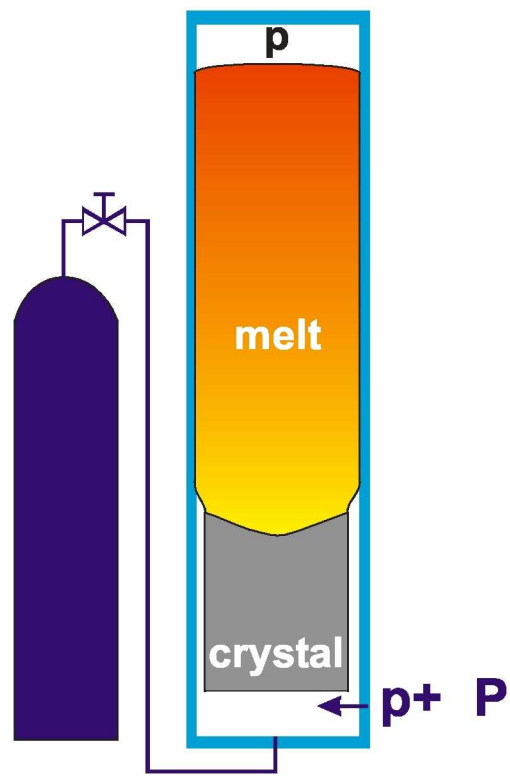
W.Bardsley, F.C. Frank, G.W. Green, D.T.J. Hurle:
J. Crystal Growth 23 (1974), 341

lg: surface energy liquid-gas
sl: surface energy solid-liquid
sg: surface energy solid-gas



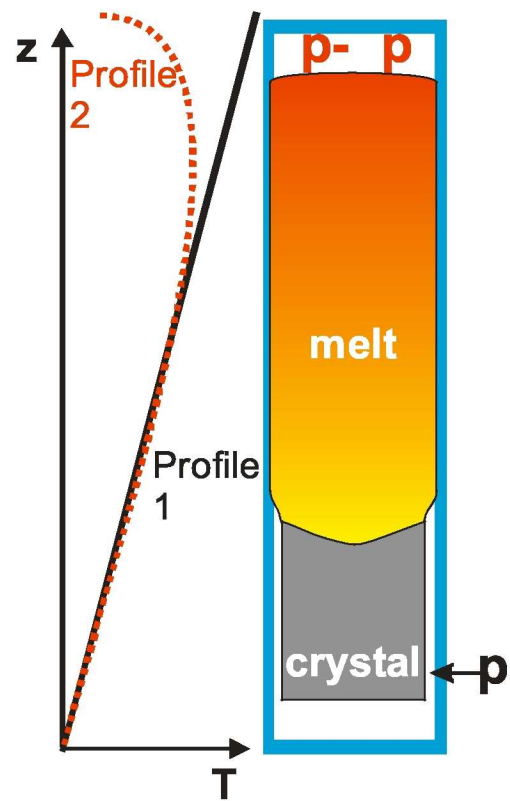
Gas Pressure Below Meniscus

Higher pressure below the meniscus by active pressurization

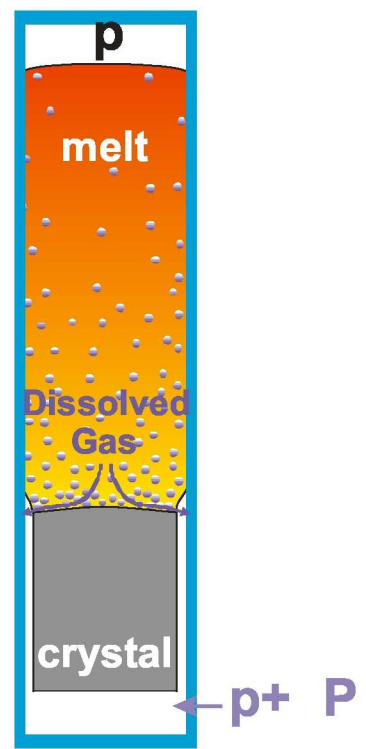


T. Duffar, P. Dusserre, F. Picca, S. Lacroix, N. Giacometti: J. Crystal Growth 311 (2000), 434

Higher pressure below the meniscus by temperature reduction above the melt



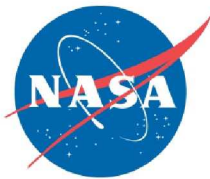
Higher pressure below the meniscus due to segregation at the interface



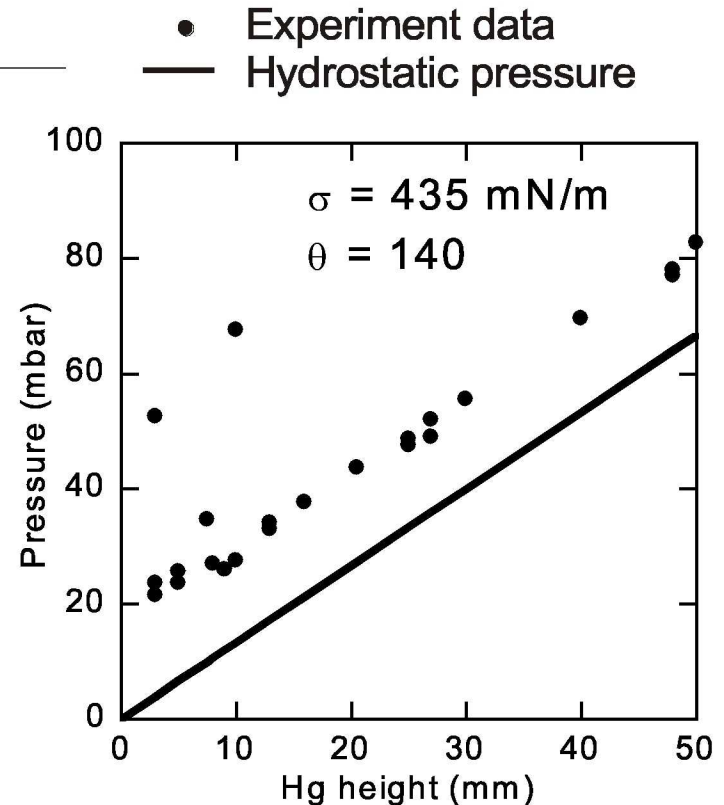
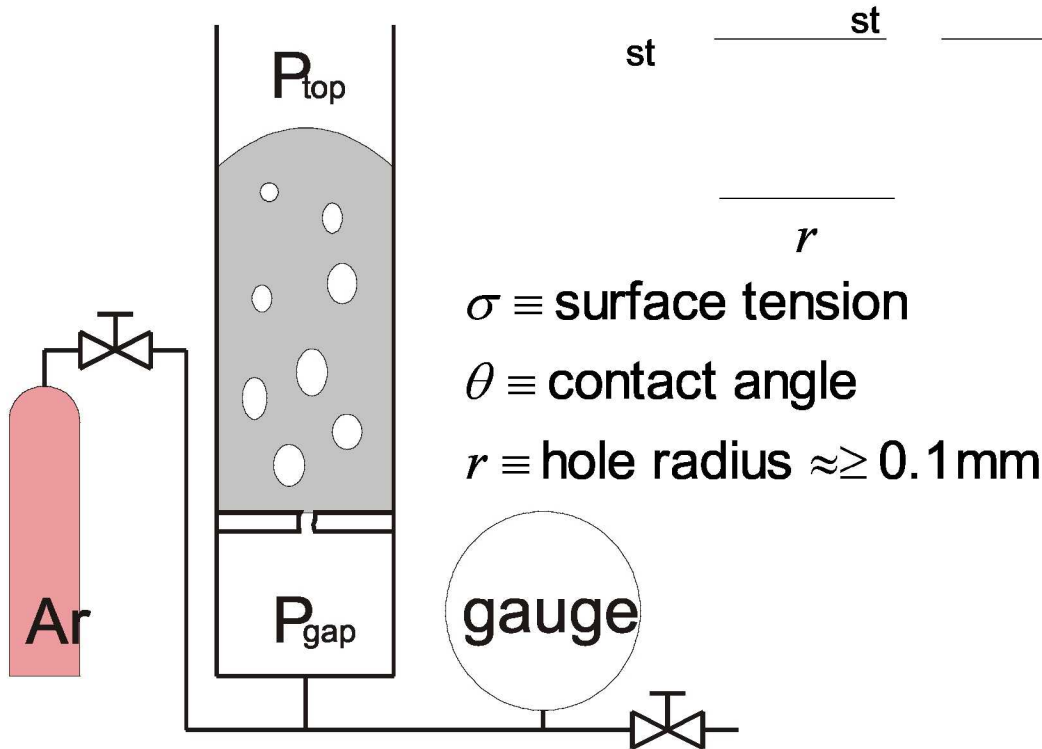
W.R. Wilcox, L. Regel: Microgravity Sci. Technol. VIII (1995), 56



Bubble Formation Limits ΔP on Earth

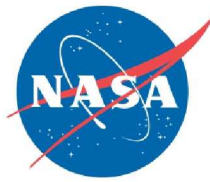


On earth, when the pressure difference $P_{\text{gap}} - P_{\text{top}}$ increases beyond the hydrostatic head of the liquid column and overcomes the surface tension, bubbles will form and rise. In space, larger pressure differences, leading to better stability of detachment can be used.





Selected Ampoule/Liner Materials for $\text{Ge}_{1-x}\text{Si}_x$ Growth



pBN

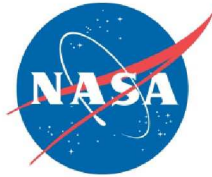
- + High wetting angle (160° - 170°)
- + No significant decrease of wetting angle over time
- + Large areas grow detached in closed bottom containers even without temperature inversion
- + No sticking of the sample, even of attached parts
- + Lower dislocation density than fused quartz
- *Tendency for polycrystalline growth*
- *Boron contamination (10^{17} - 10^{18}cm^{-3}) leads to p-type material*

Fused quartz

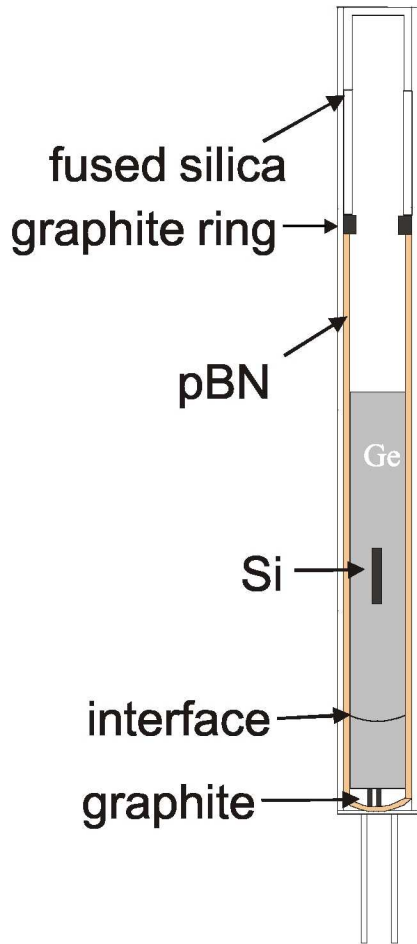
- *Low wetting angle (100° - 130°)*
- *Reduction of wetting angle with time*
- + Partial detached growth has been achieved in a few cases
- *Crystal parts grown attached initially stick to ampoule, ampoule cracks*
- *High dislocation density in attached parts*
- + Usually single crystalline growth
- + No electrically active doping by contamination from the crucible



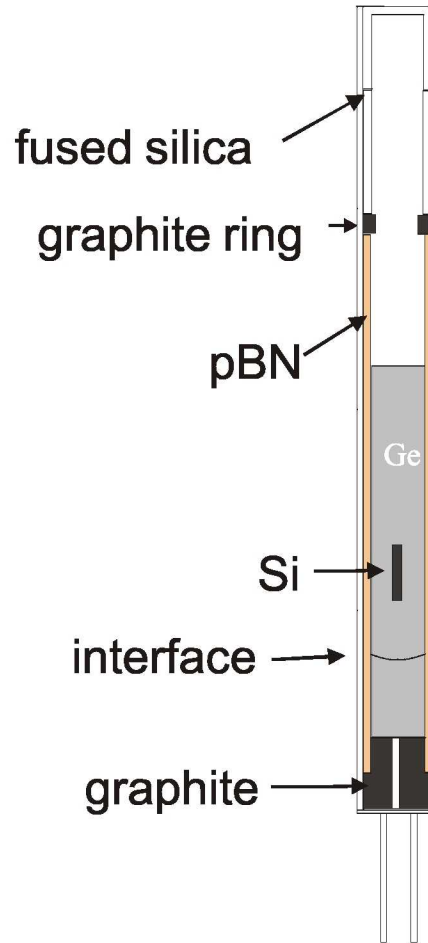
Bridgman Growth Ampoule Configurations



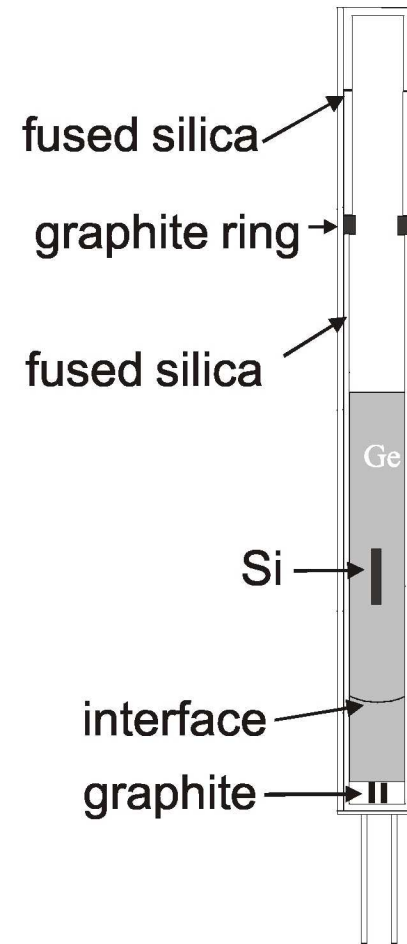
Closed pBN



Open pBN

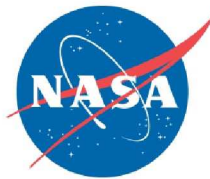


Closed fused silica





Ampoule Preparation and Growth Procedures



- Heat pBN or fused silica ampoule, graphite pieces and SiO₂ pieces in outer ampoule to about 1000°C at 10⁻⁶ torr.
- Etch Ge and Si and assemble ampoule
- Evacuate ampoule and flush with Ar/2% H₂
- Seal-off ampoule under 600 mbar or 10⁻⁶ torr vacuum
- Install ampoule in furnace
- Lower heated furnace over sample until about 2 cm of Ge seed remains unmelted
- Homogenize (if GeSi alloy) and then translate furnace

Growth Parameters

\$PSRXOH □ □³RSHQ' □ S%1 □ □³FORVHG' □ S%1 □ □RU □³FORVHG' □ IXVHG

Sample diameter: 9, 12, & 15 mm

Ge seed orientation: (100), (110), or (111)

Translation velocity: 0.2 - 0.3 μm/s for GeSi; 1.38 μm/s for Ge



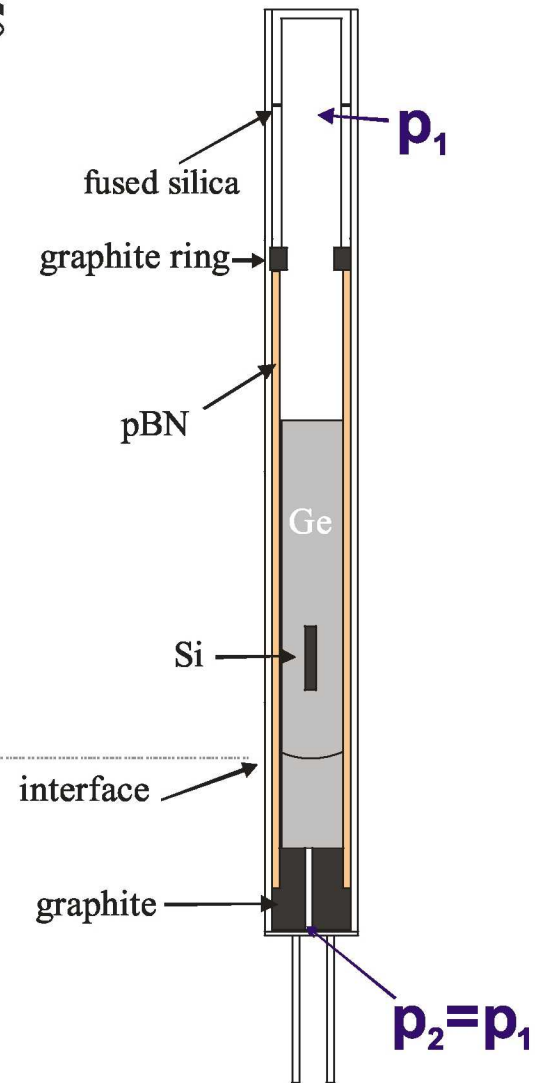
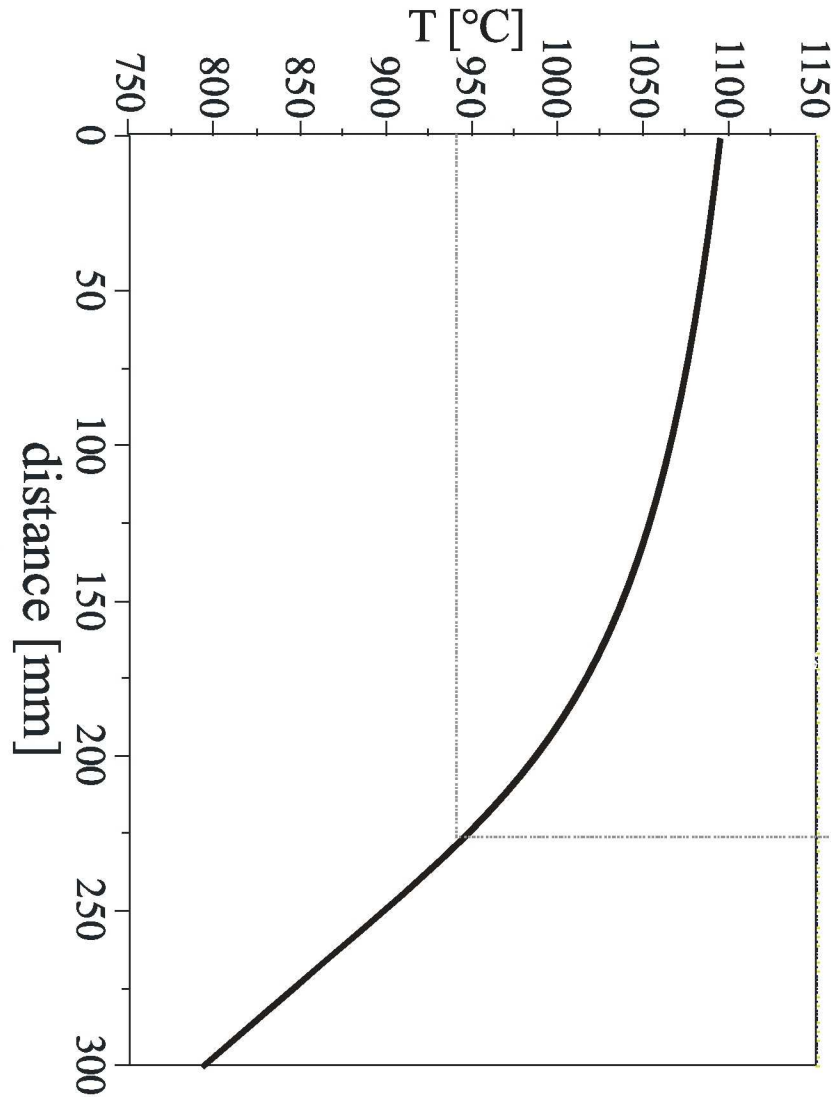
Detached Growth without Pressure Difference



The gas volumes above the melt and below the meniscus are connected

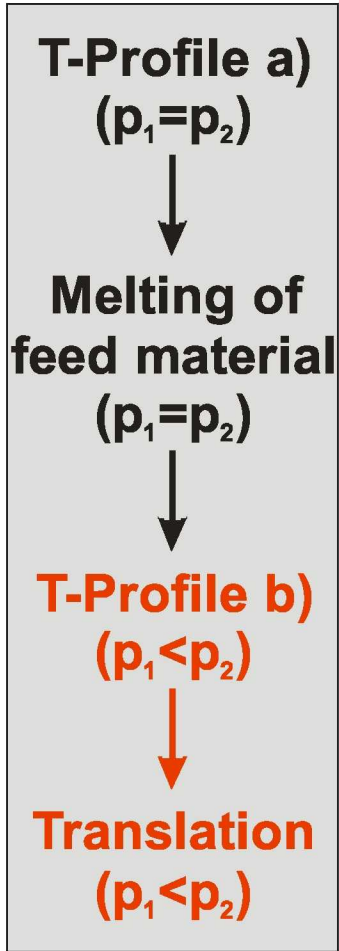
$$\Rightarrow p_2 = p_1$$

no pressure difference possible

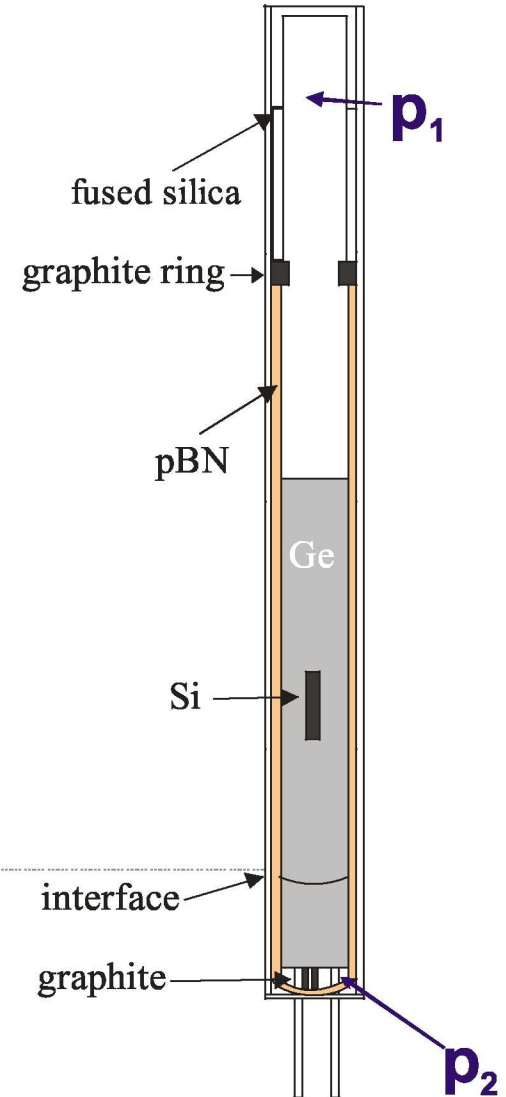
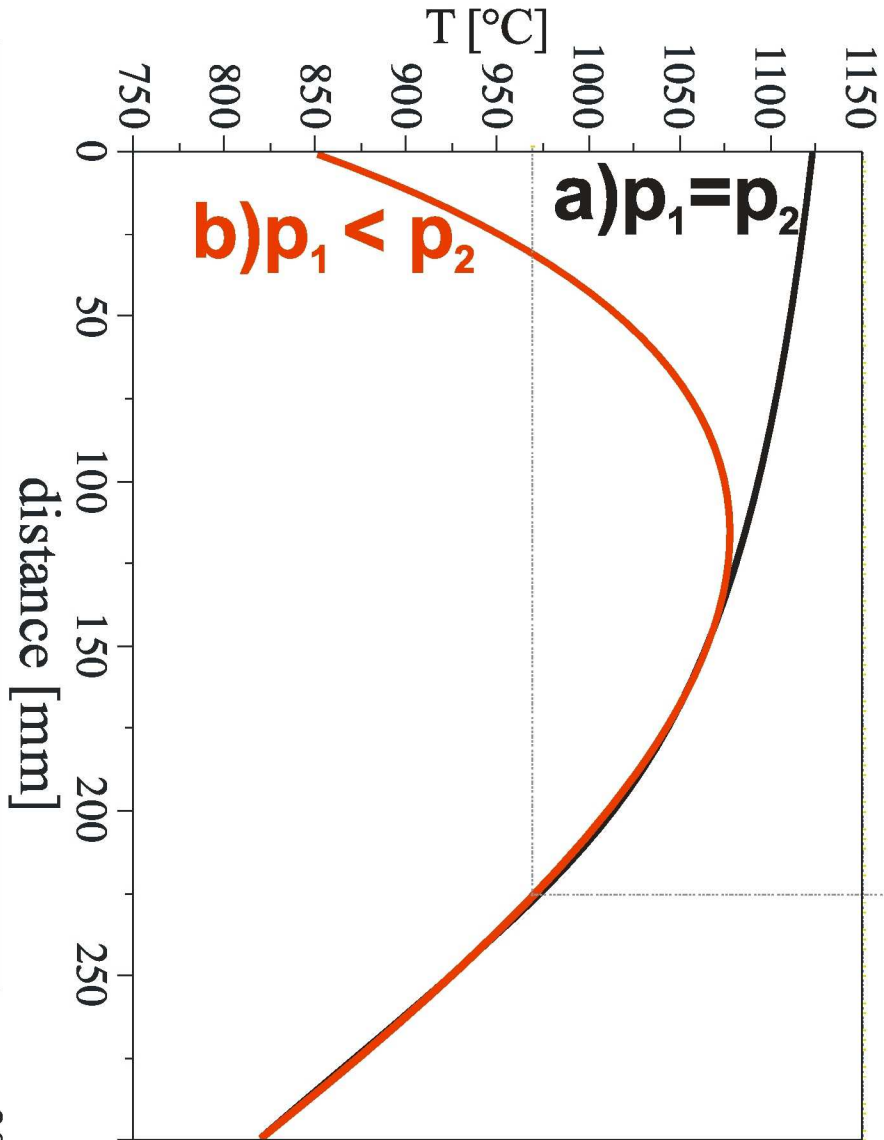




Growth with Forced Pressure Difference

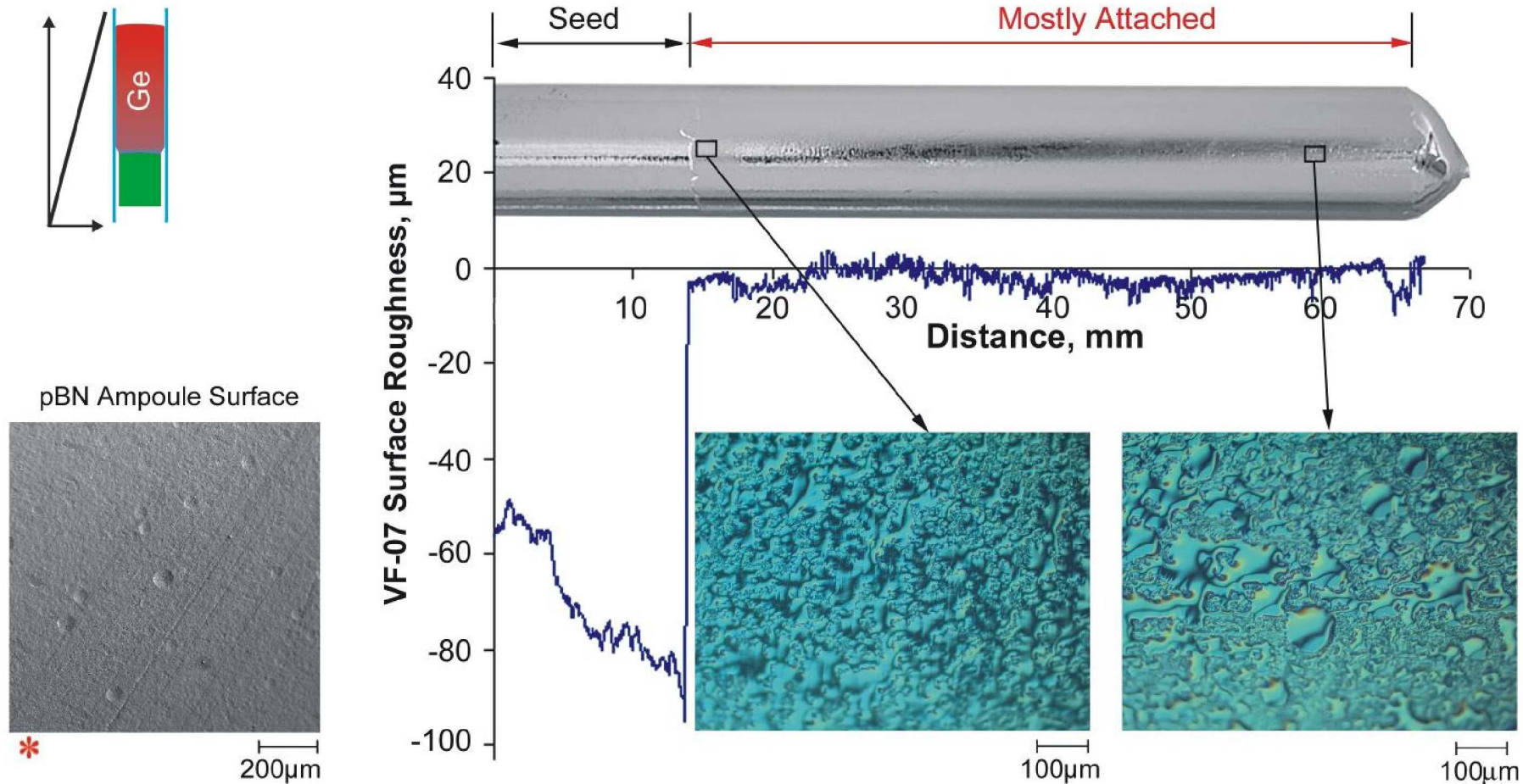


300





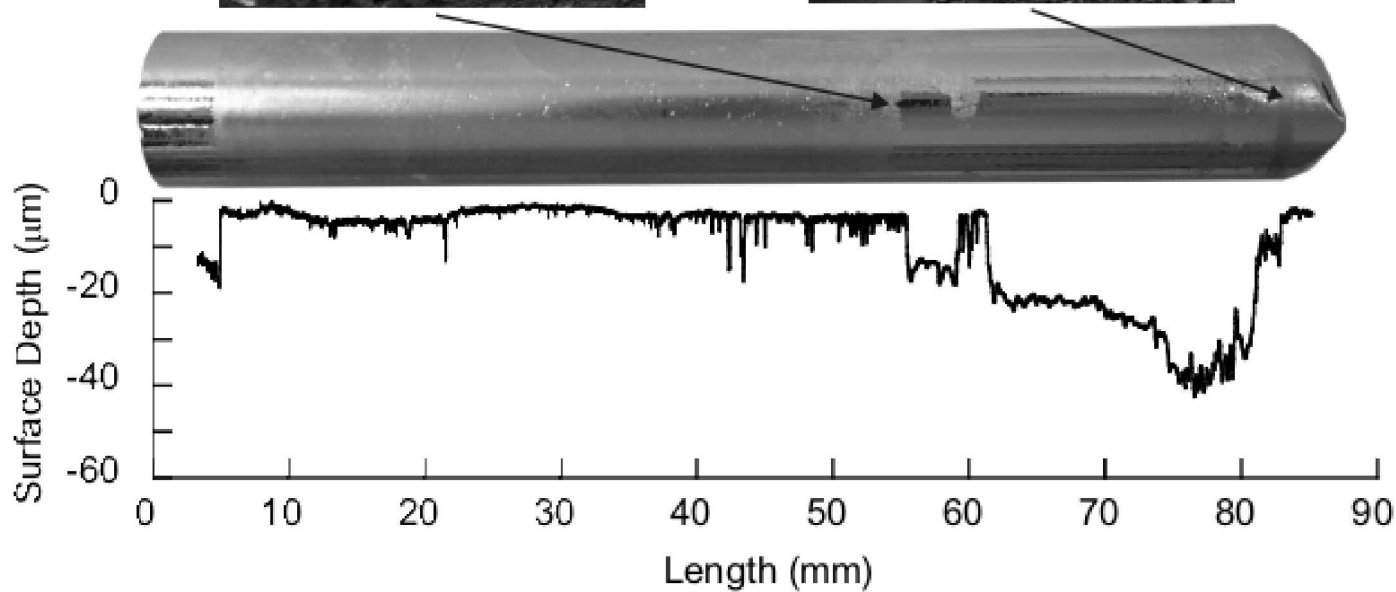
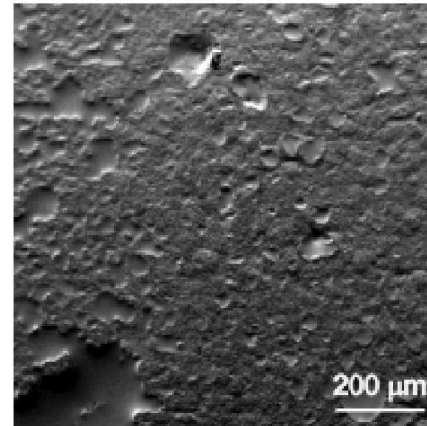
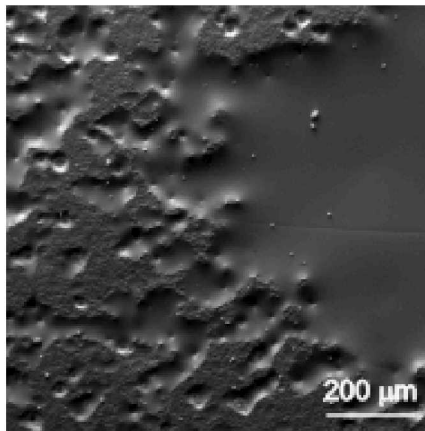
Effect of Open Bottom pBN Ampoule (Ge)



➤ For Ge in an open pBN ampoule, a pressure difference sufficient for detachment cannot develop.



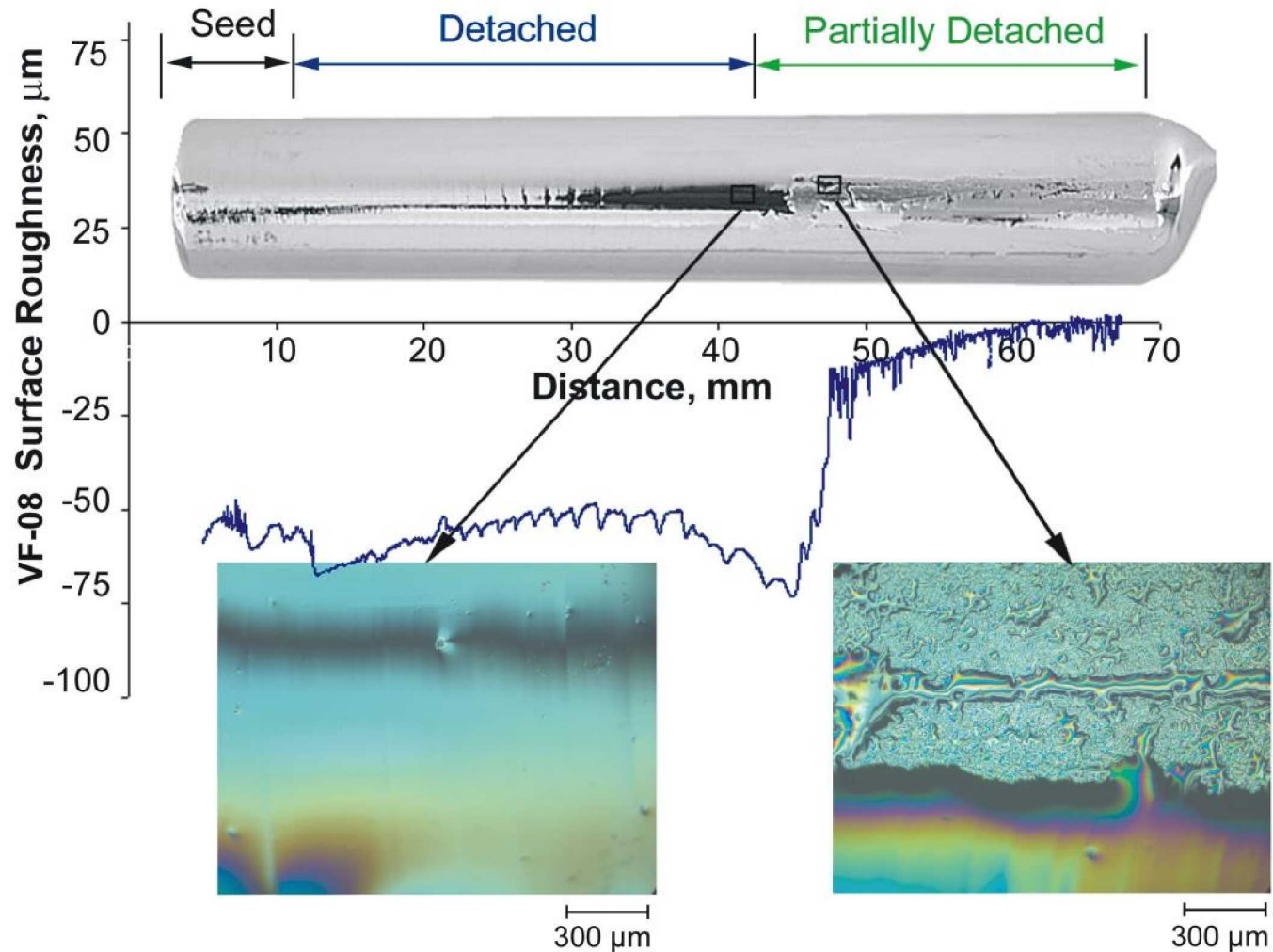
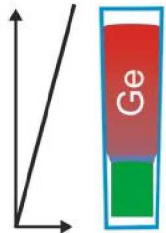
Effect of Open Bottom pBN Ampoule (GeSi)



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



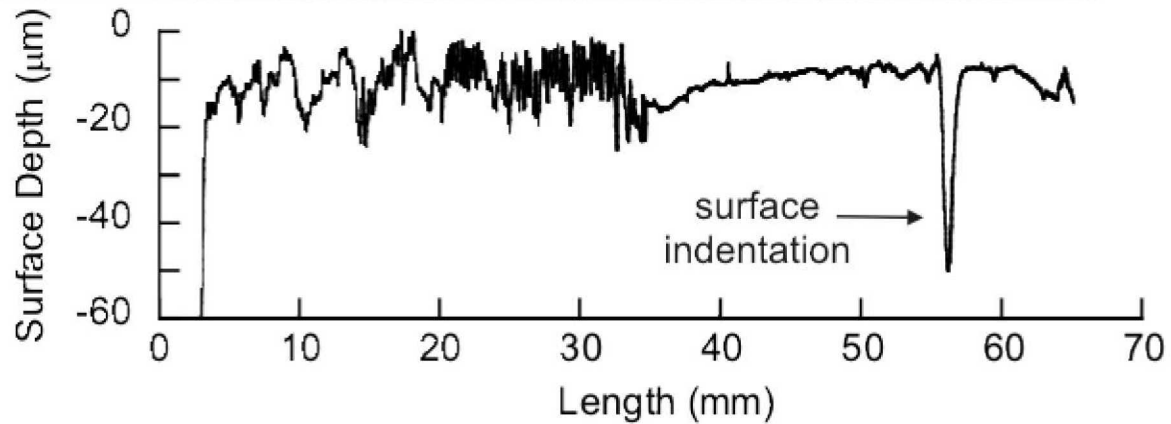
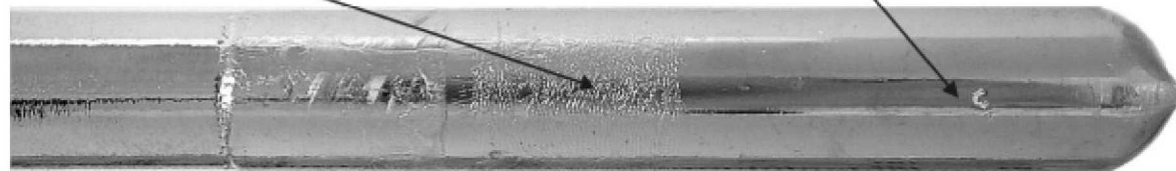
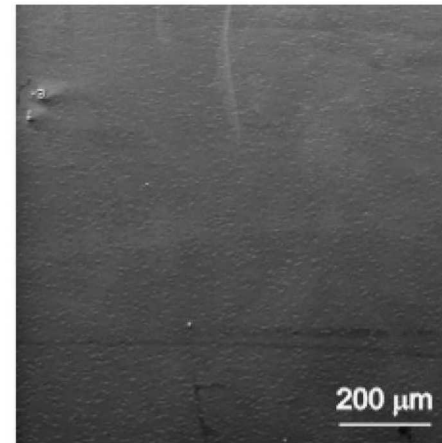
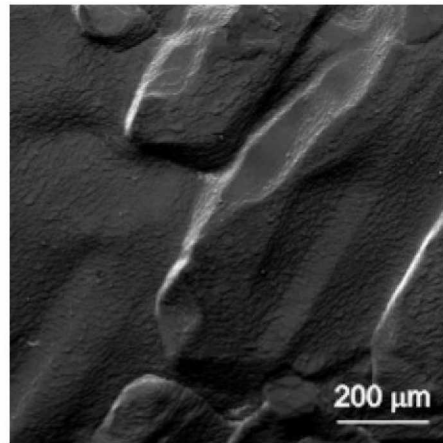
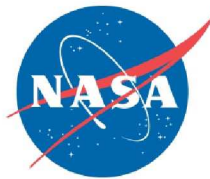
Effect of Closed Bottom pBN Ampoule (Ge)



➤ For Ge in a closed pBN ampoule, enough pressure develops in the gap to produce detachment.



Effect of Closed Bottom pBN Ampoule (GeSi)





In-situ Pressure Control Setup

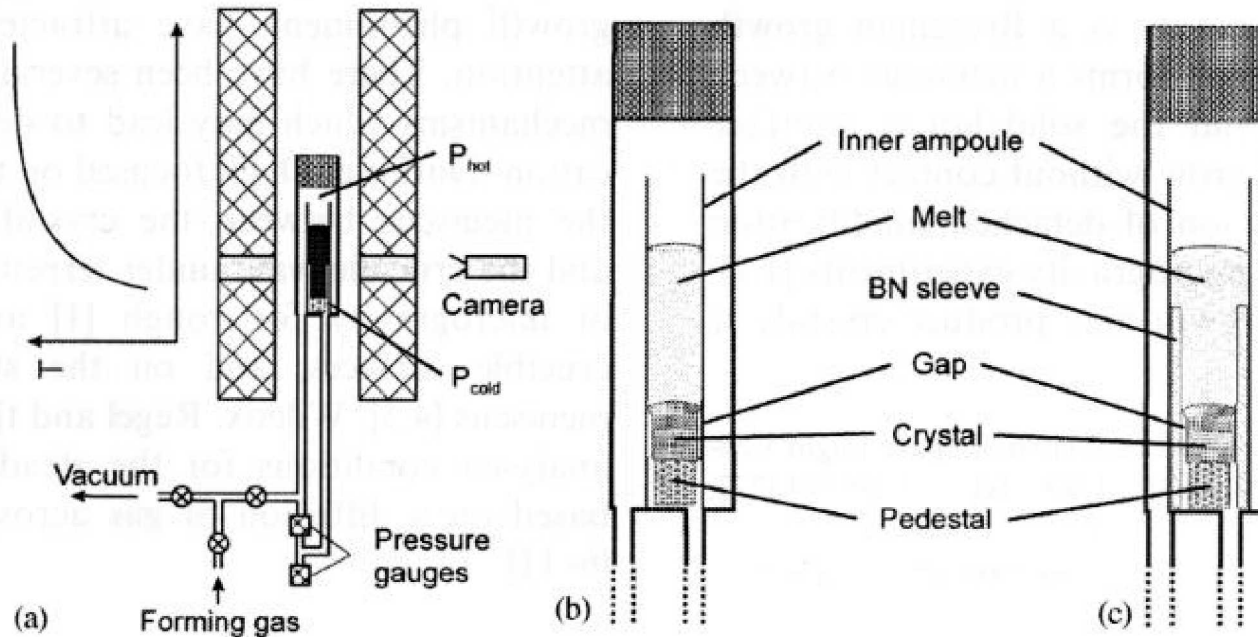


Fig. 1. Experimental system: (a) growth configuration; (b) ampoule with silica crucible; (c) ampoule with pBN insert.



Schematic Diagram of Detached Solidification

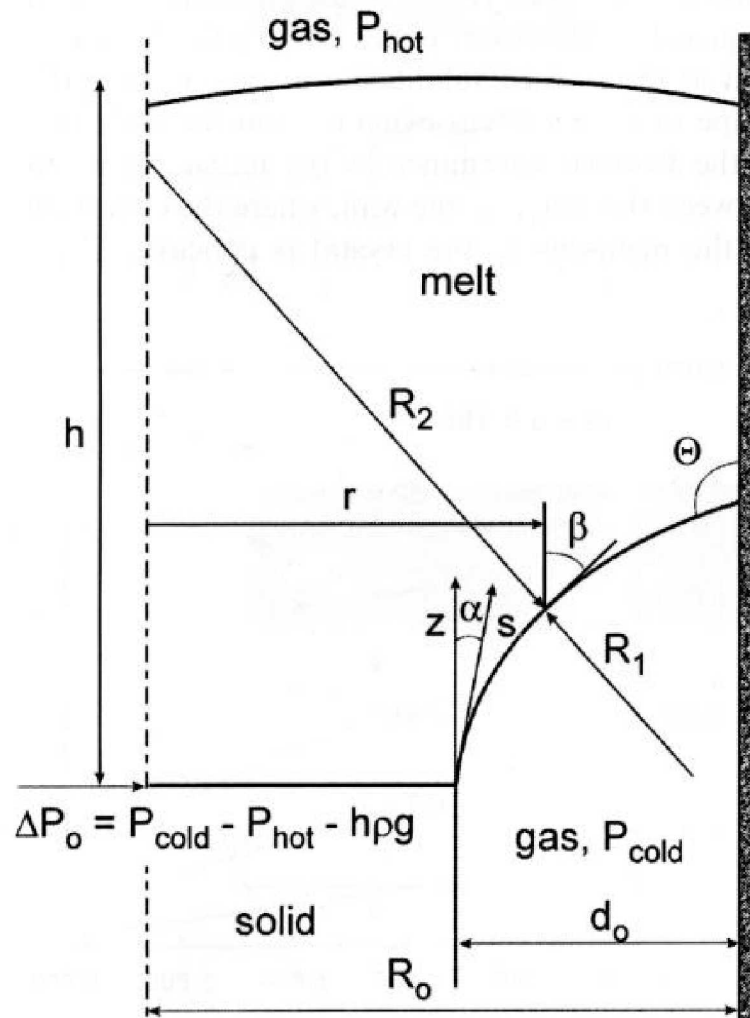


Fig. 2. Schematic diagram of detached solidification.

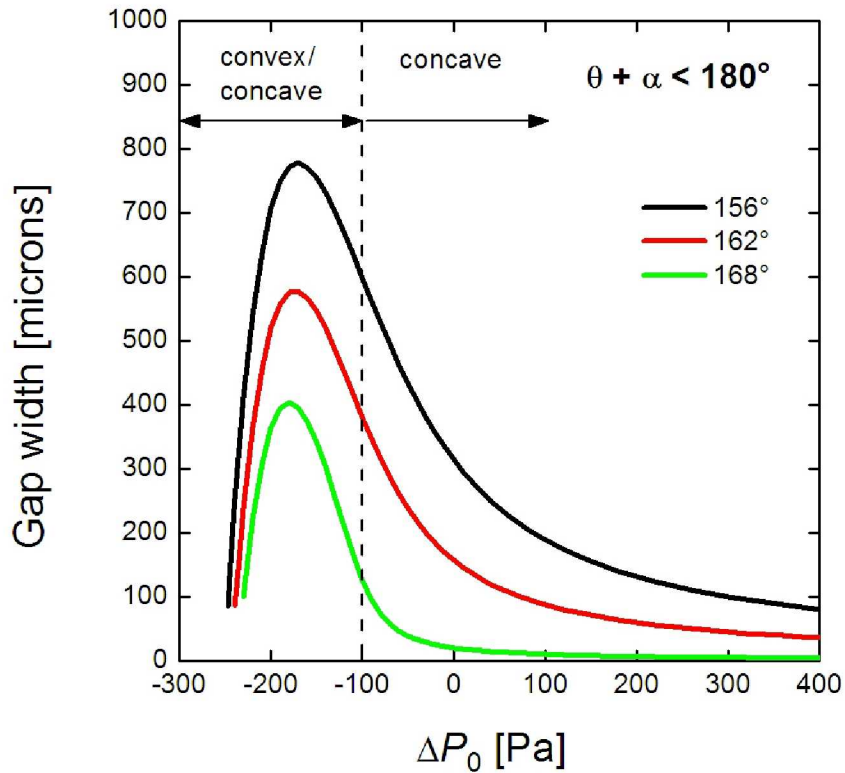
W. Palosz, M. P. Volz, S. Cobb, S. Motakef,
F. R. Szofran, JCG 277 (2005) 124-132



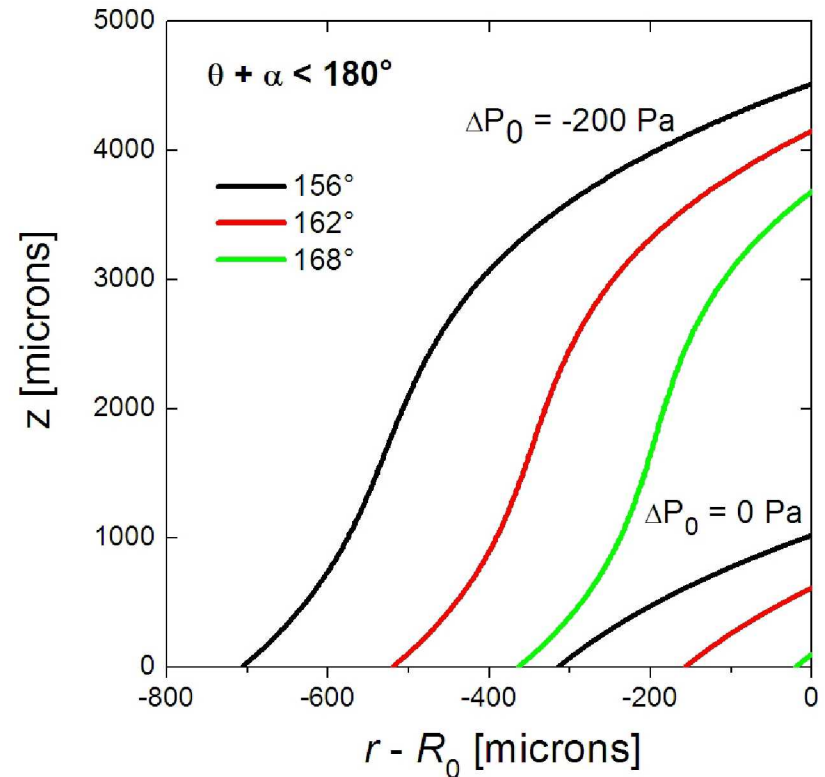
Gap Widths and Meniscus Shapes vs. Pressure for $(\theta + \alpha) < 180$



Gap widths



Meniscus shapes

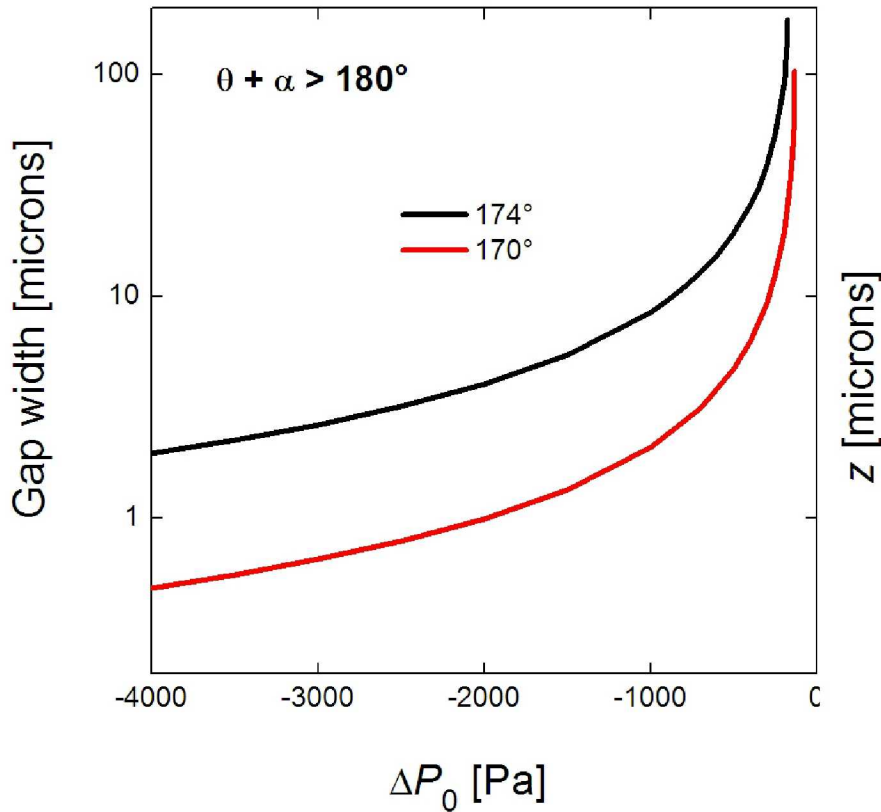




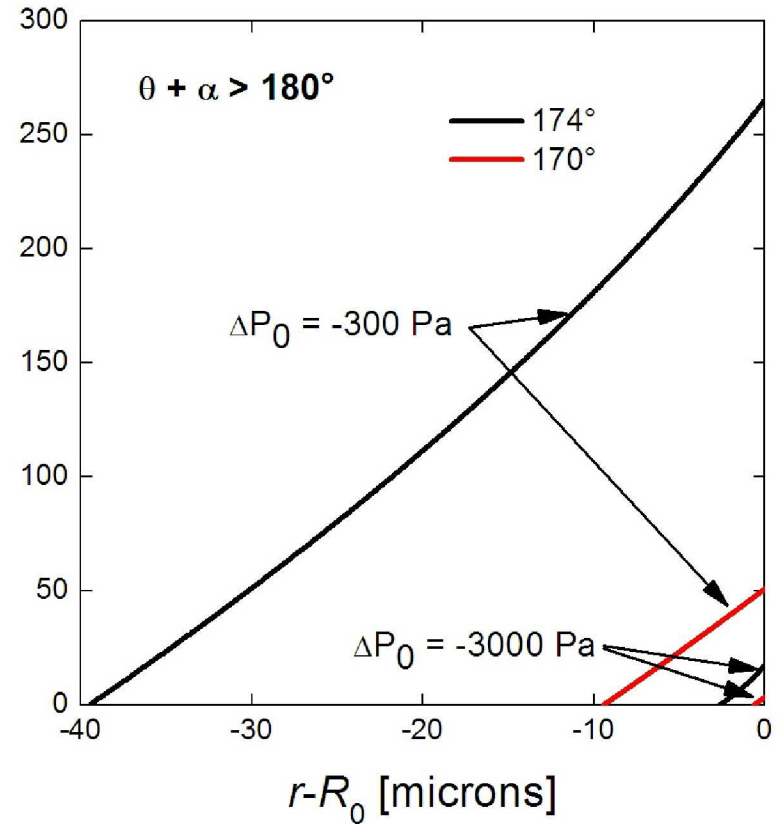
Gap Widths and Meniscus Shapes vs. Pressure for $(\theta + \alpha) > 180$



Gap widths

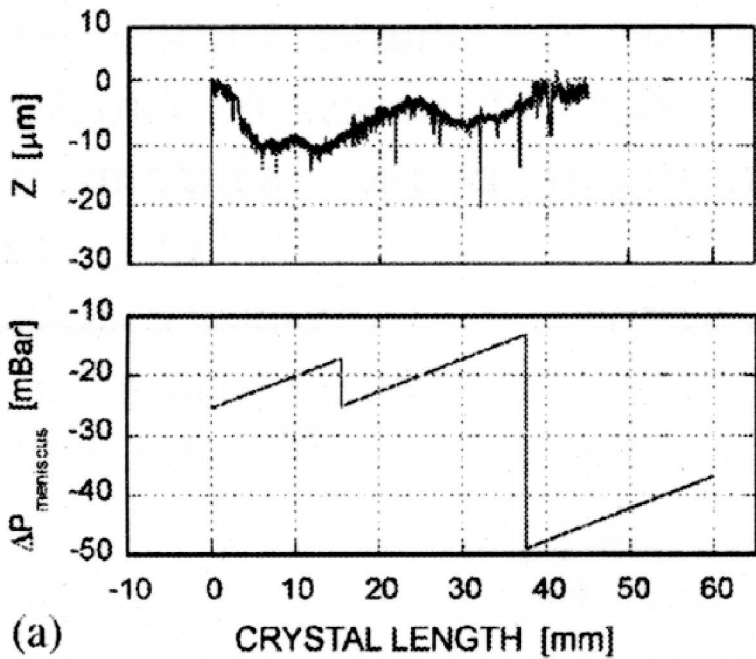
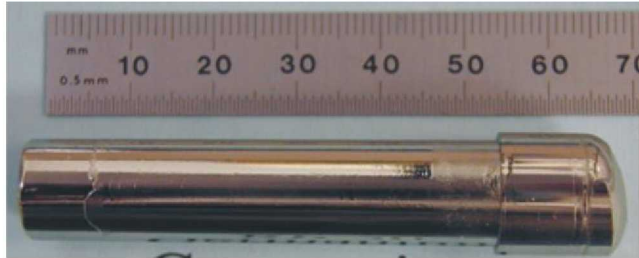
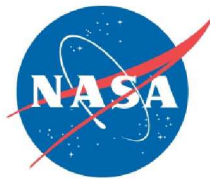


Meniscus shapes

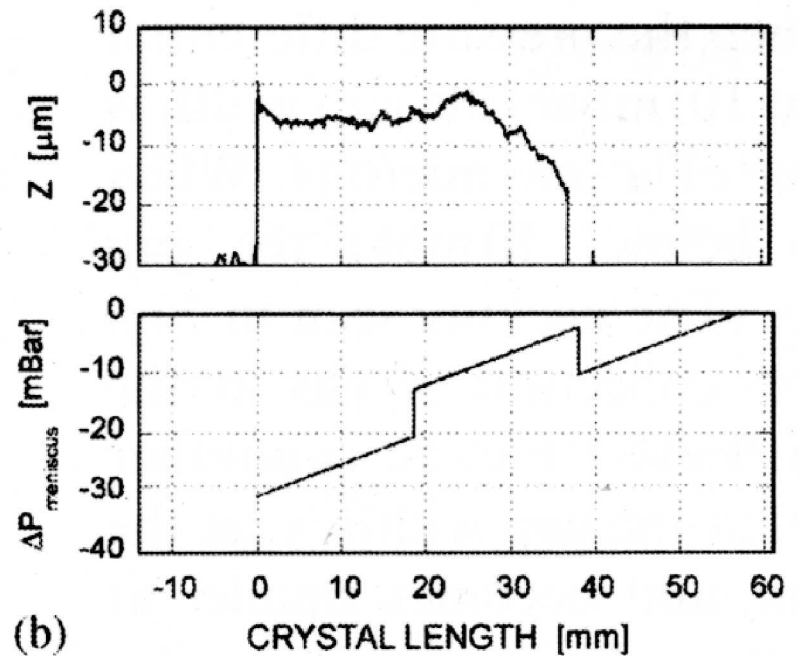
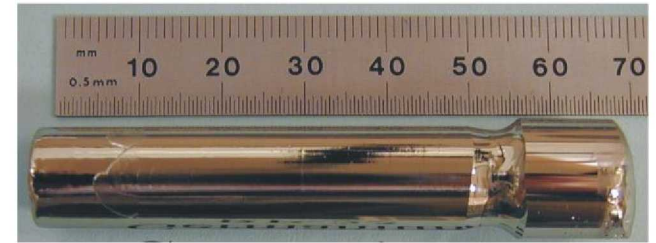




Ge Grown in pBN ampoules



(a)



(b)



Propagation of Defects in Detached/Attached Crystals

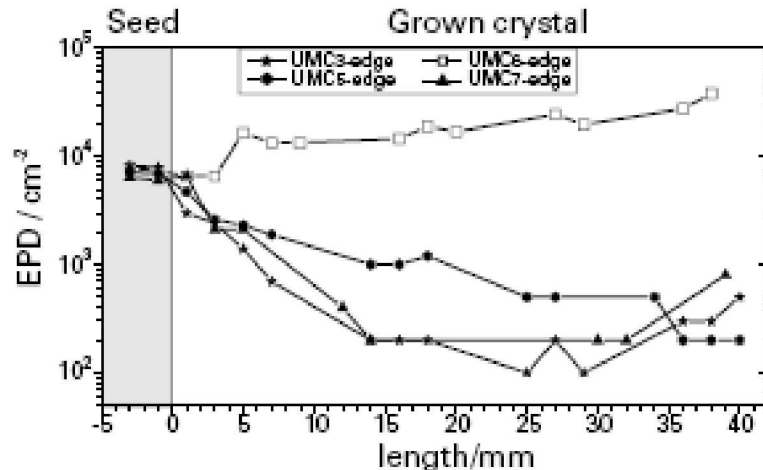
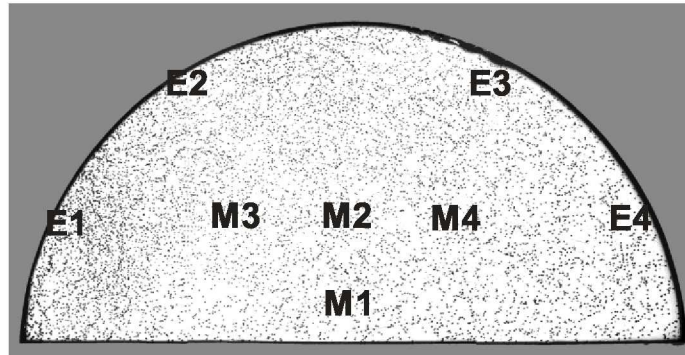


Fig. 3. Axial EPD variation along the edge in detached- (closed symbols) and attached-grown (open symbols) crystals. In the detached-grown crystals the EPD is reduced more than two orders of magnitude compared to the attached-grown crystal UMC6.

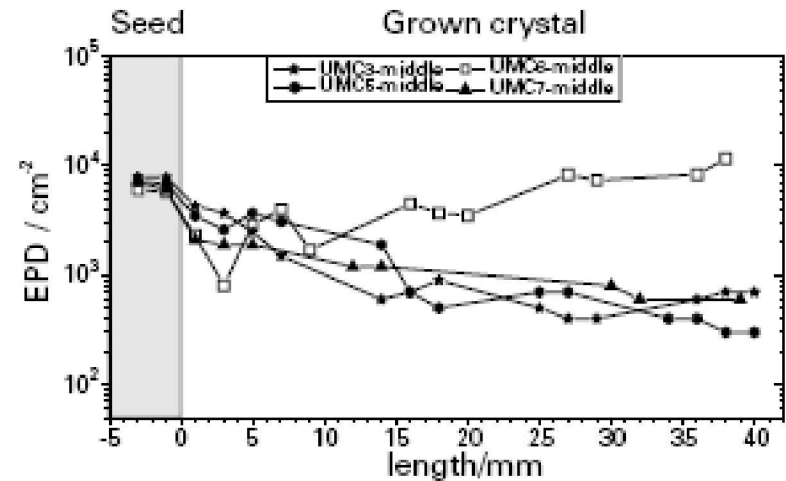


Fig. 4. Axial EPD variation in the middle in detached- (closed symbols) and attached-grown (open symbols) crystals.



Etch Pit Densities in Detached/Attached Crystals

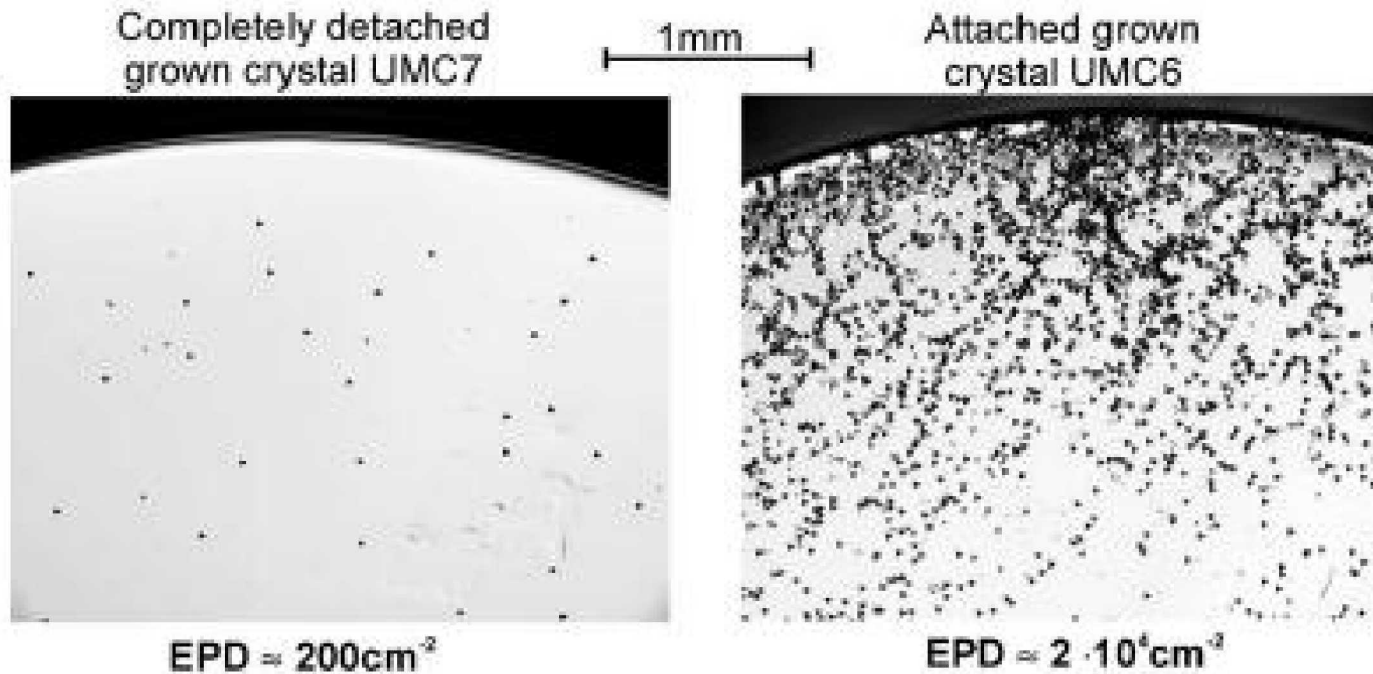


Fig. 5. Micrograph from the detached-grown sample UMC7 and from the attached-grown sample UMC6.



Etch Pit Density Variation With Attachment

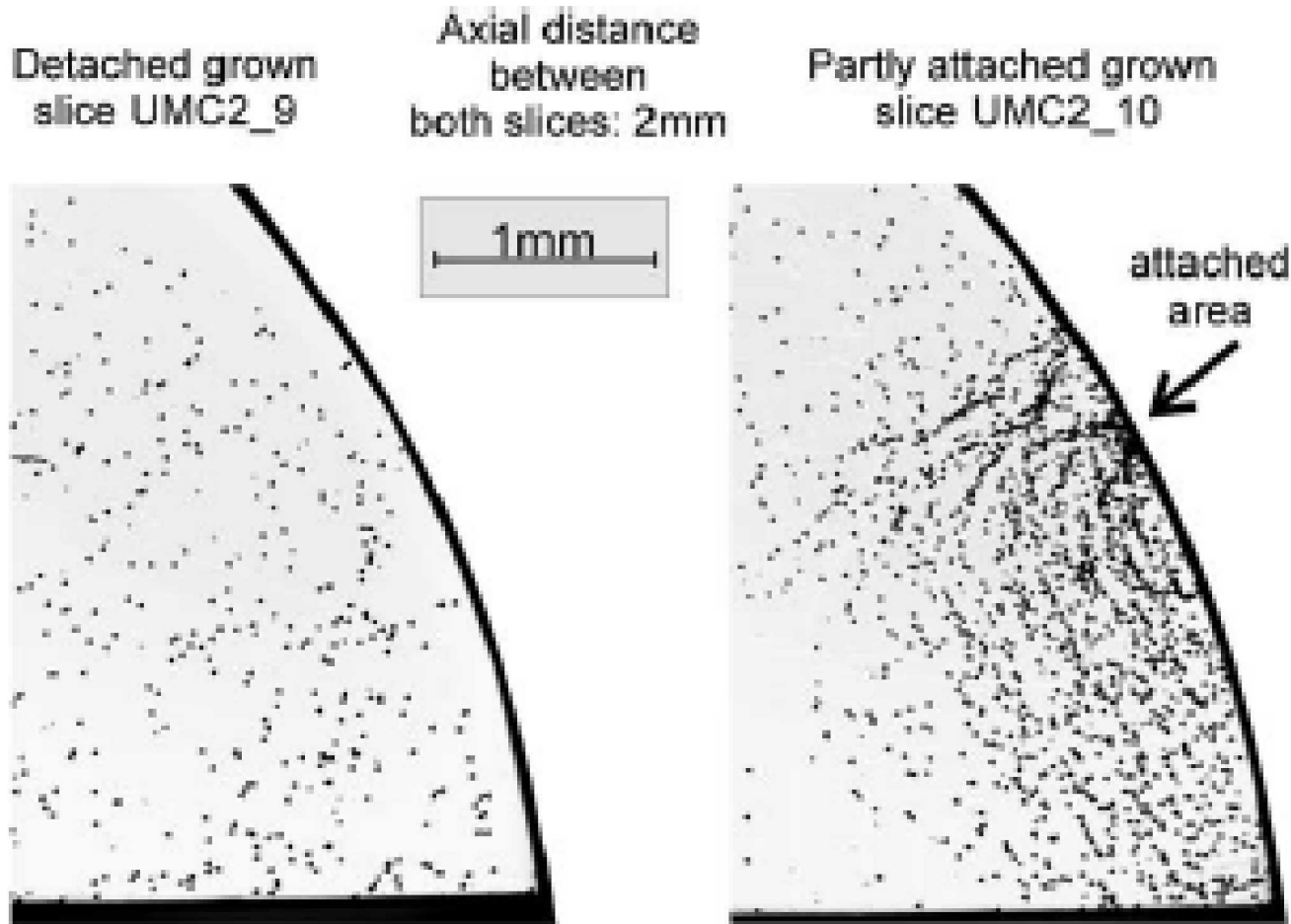
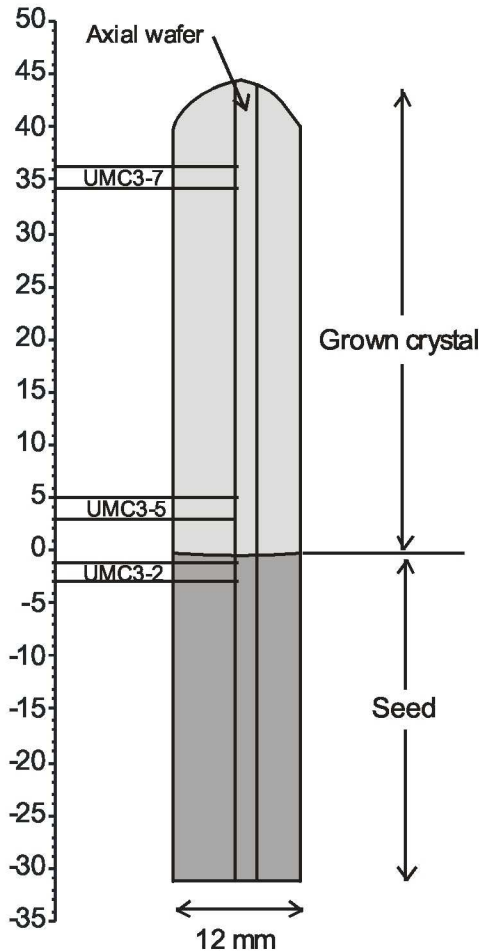


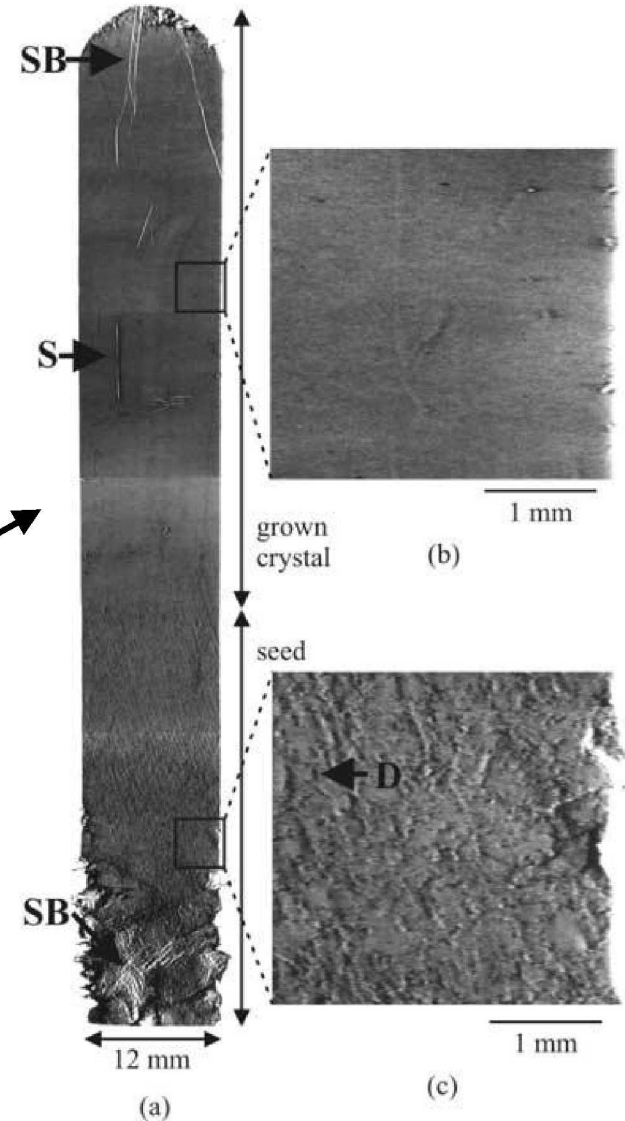
Fig. 6. Localized increased EPD after the crystal attaches partially to the wall.



X-Ray Synchrotron Topography of Detached Ge

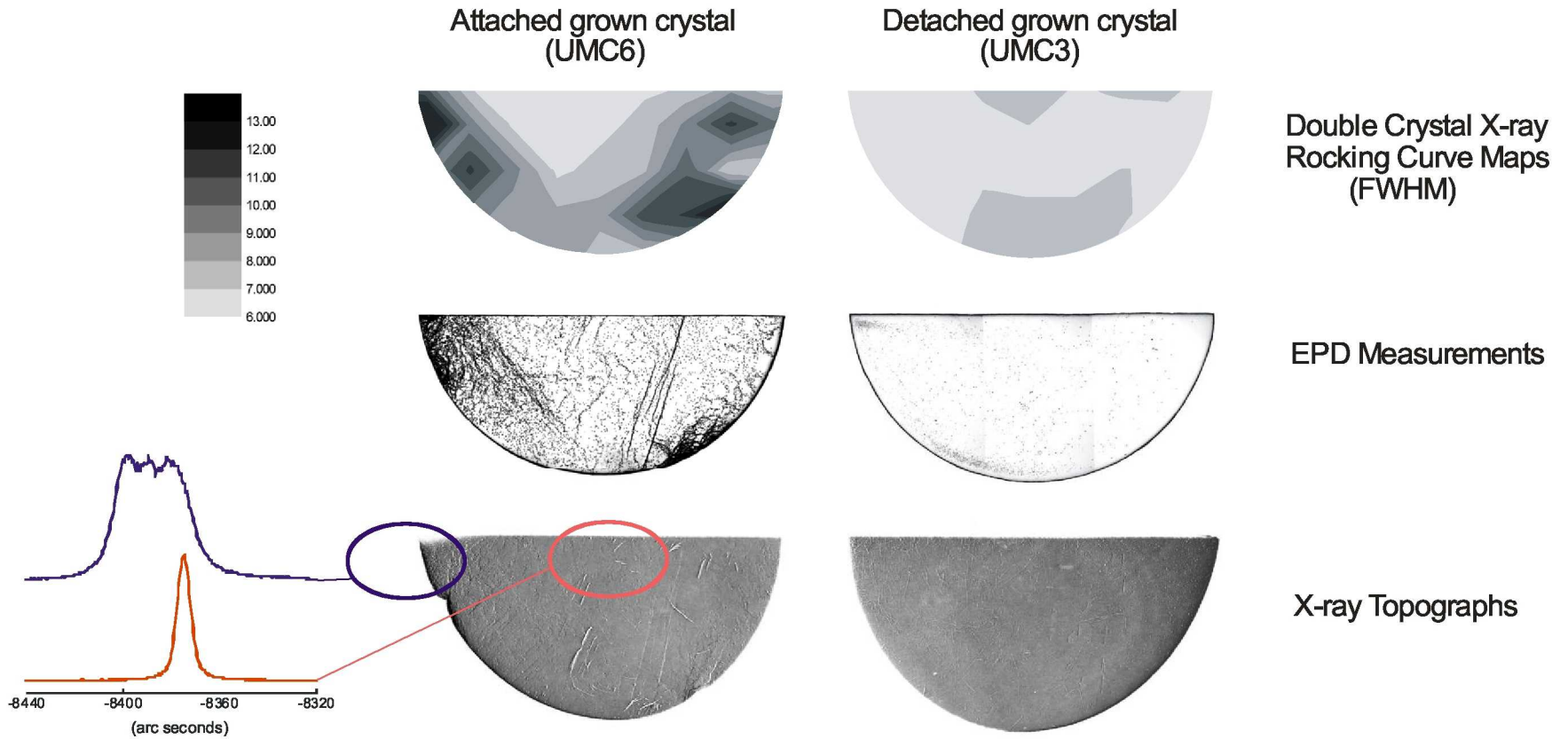


220 reflection topograph ($\lambda = 0.69 \text{ \AA}$) recorded from a detached-grown UMC3 crystal wafer cut parallel to the growth axis (S \pm scratch, SB \pm subgrain boundary, D \pm dislocation).



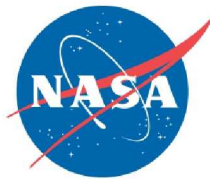


Double Crystal Rocking Curve Maps of Detached Ge





Conclusions



- Detachment can be achieved reproducibly in systems where the sum of the growth and wetting angle is close to 180 degrees
- Pressure differentials across the meniscus can be used to enhance detachment
- Pressure control has been achieved using both temperature inversion and with an external gas source
- Detached crystals clearly show superior quality; fewer defects and stresses result from an absence of contact with the container wall
- A basic understanding of the mechanical stability of detachment has been achieved