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SPACE- AND GROUND-BASED CRYSTAL GROWTH USING A BAFFLE (CGB)

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INTRODUCTION

The composition of semiconductor crystals produced in space by conventional melt-growth processes (directional solidification and zone melting) is affected by minute levels of residual micro-acceleration, which causes natural convection. The residual acceleration has random magnitude, direction and frequency. Therefore, the velocity field in the melt is apriori unpredictable. As a result, the composition of the crystals grown in space can not be predicted and reproduced.

The method for directional solidification with a submerged heater or a baffle was developed under NASA sponsorship [1-3]. The disk-shaped baffle acts as a partition, creating a small melt zone at the solid-liquid interface. As a result, in ground based experiment the level of buoyancy-driven convection at the interface is significantly reduced. In several experiments with Te-doped GaSb, nearly diffusion controlled segregation was achieved.

The investigation "Space- and Ground-Based Crystal Growth with a baffle (CGB)" is funded under NRA-94-OLMSA-06. The key goal of this investigation is to explore the use of the baffle in microgravity conditions. We anticipate that in space experiments, the baffle will reduce the level of natural convection in the melt driven by residual acceleration. The combined effect of microgravity (reduction of gravitational acceleration g by a factor of 10^6) and small zone melt (reduction of L and ΔT by a factor of 10^3) will generate the effective conditions of "nano-gravity" (the Rayleigh number is reduced by a factor of 10^9).

The investigation "Space- and Ground-Based Crystal Growth with a Baffle (CGB)" is funded under NRA-94-OLMSA-06. The investigation passed the Science Concept Review (SCR) on October 8, 1998. The main objective of the present investigation is to develop a method of directional solidification (Bridgman with baffle) which is less sensitive to residual acceleration than the conventional methods. The following systems will be studied:

a) GaSb doped with Te; the equilibrium segregation coefficient k = 0.35.
b) Ga-doped Ge; k = 0.087.
c) Pseudo-binary $(GaSb)_{1-x}(InSb)_x$ doped with Te; $0.001<x<0.01$; k = 0.1
d) Quasi binary $(GaSb)_{0.97}(InAs)_{0.03}$ doped with Te; k = 1.07 to 1.5.

The key goals of CGB are to:

1. Demonstrate a method of directional solidification (submerged baffle) which, in microgravity, yields crystals with *predictable* and *reproducible composition*.
2. Measure the exact shape of the initial transient in composition; the shape will provide the value of the diffusion coefficient of the dopant at the growth interface, D_i.
3. Test the Segregation number [4]
4. Determine if the ground-based experiments with the baffle and magnetic fields are nearly diffusion-controlled.

CGB is a parent investigation to the Materials Science Glovebox (MSG) investigation "Solidification Using the Baffle in Sealed Ampoules"(SUBSA). SUBSA is manifested for the First Utilization Flight 1 (UF1), August 2001, as one of the two first materials science experiments to be conducted at the International Space Station (ISS).

I. Ampoule Design

In the past two years, the ground-based research was focused on the Materials Science Glovebox (MSG) investigation. The flight hardware - furnace for directional solidification - was designed and built by Tech-Masters Inc.

In contrast to terrestrial experiments, space growth has to be conducted in sealed ampoules. Therefore, a key objective of this flight definition research is to design and test a simple and reliable baffle that can be used to grow the semiconductor crystals in sealed silica ampoules. We are currently developing and testing the ampoules with "Automatically Moving Baffles" for SUBSA. The schematic diagram of the ampoule is shown in Figure 1. The baffle is attached to a shaft and a

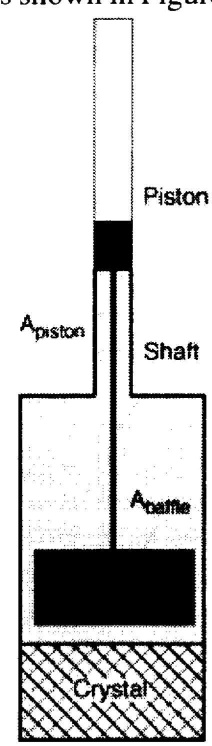


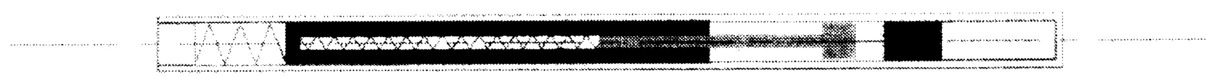
Figure 1. Schematic diagram of "automatic baffle."

piston covering the top surface of the melt. Due to the volumetric expansion during freezing, the melt is pushing on the piston which controls the axial position of the baffle. The ratio between the cross-sectional area of the piston and the cross-sectional area of the baffle is set equal to the coefficient of volumetric expansion during freezing,

$$\frac{A_{\text{piston}}}{A_{\text{baffle}}} = \beta = \frac{\rho_l - \rho_s}{\rho_s} \tag{1}$$

where ρ_l is density of the melt and ρ_s is density of solid at the melting point. During growth, the distance between the baffle and the crystal remains constant regardless of the growth rate or temperature distribution. There is no moving parts outside the ampoule. For MSG investigations we have chosen doped InSb and $InSb_{1-x}CdTe_x$ quasi-binary alloy because of the low melting point (512°C), and high coefficient of volumetric expansion during freezing (β=12.5 %). The design of the ampoule with the automatic baffle, the parts and the motion of the baffle during a growth cycle is shown in Figure 2.

a) Beginning of Melting: The first spring extends until the piston touches the shoulder in the ampoule. Subsequently, the second spring will start extending.



b) End of Melting: The diameter of the baffle shaft is dimensioned to compensate for the reduction in volume during melting. Thus, the solid/liquid interface always stays 10 mm away from the baffle.

c) Growth: During freezing, because of the volumetric expansion, the baffle slowly returns in its original position, remaining always 10 mm from the interface.

d) End of Growth: The baffle is frozen in the crystal.

Figure 2. Motion of the automatic baffle during directional solidification.

Figure 3 shows a photograph of the ampoule with the automatic baffle developed at the Center for Microgravity and Materials Research, (CMMR). Figure 4 shows a photographs of the furnace for the Materials Science Glovebox investigation SUBSA developed by Tech-Masters Inc. Tech-Masters Inc. is testing and calibrating this furnace using ampoules with the baffle (such as the one in Figure 3).

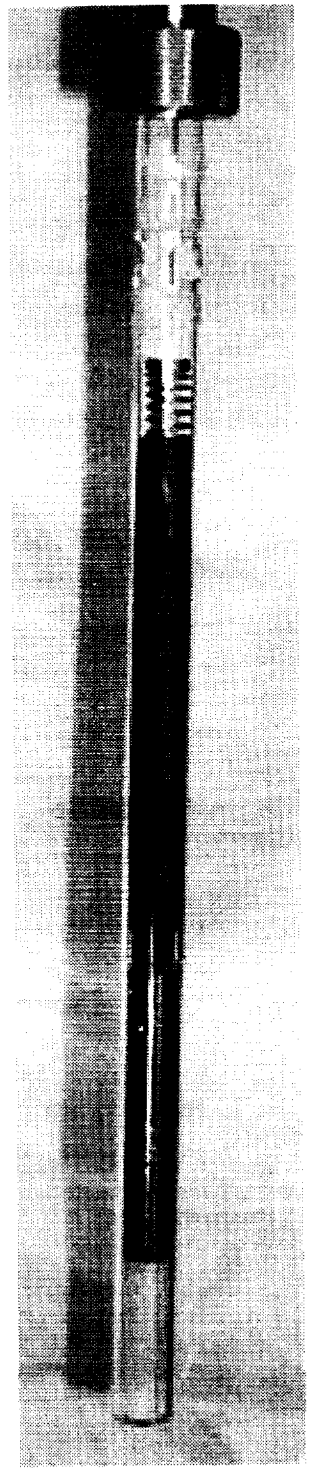


Figure 3. Sealed ampoule for SUBSA.

II. Ground Crystal Growth Experiments

Directional solidification as conducted in a low pressure Electro Dynamic Gradient (EDG) "Mellen" furnace with 18-heating elements (zones). The temperature of each control thermocouple was controlled by a computer, with 14 ½ bit resolution (corresponding to 0.03 °C resolution).

Numerous experiments were conducted with doped InSb. We focused on dopants having equilibrium segregation coefficient $k > 1$, *e.g.*, Ca, Zn and Ga. Two growth experiments were conducted

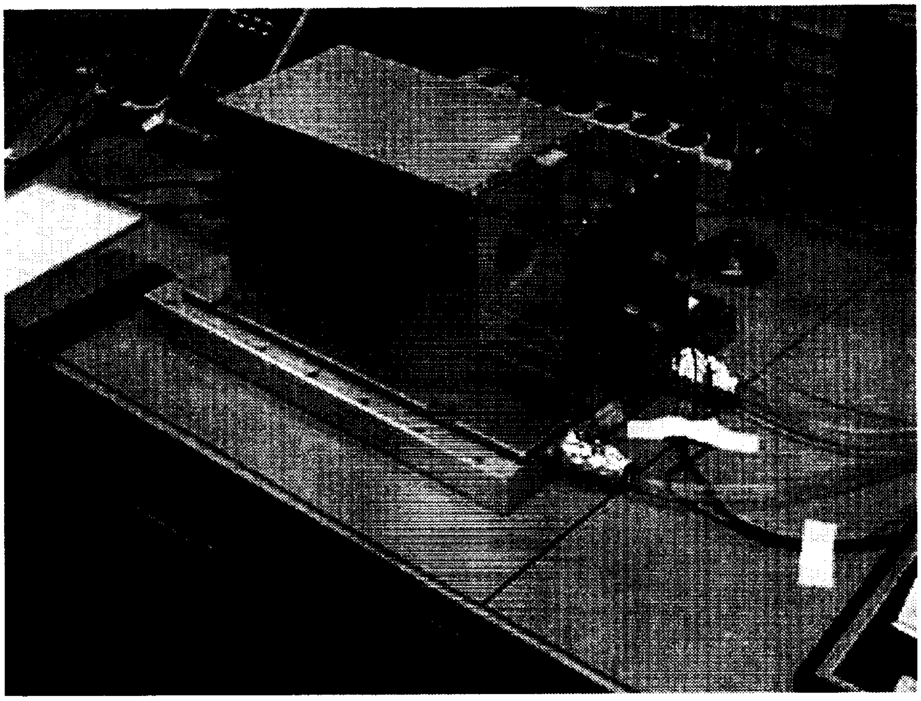


Figure 4. Furnace for MSG investigation developed by Tech-Masters Inc.

by melting together pre-synthesized InSb and CdTe, to form a melts having a composition $(InSb)_{1-x}(CdTe)_x$ [6]. Our goal was to determine whether in the grown crystals the concentration of Cd will remain equal to the concentration of Te. Note that the segregation coefficients of Cd and Te in InSb are different: $k_{Cd}= 0.25$ and $k_{Te} = 0.6$ respectively.

The charge was etched and rinsed. The 8 mm ID, sphere-shaped bottom, silica ampoule, was etched with HF, rinsed in DI water and methanol. The charge was kept at 250°C under vacuum for 15 hours and subsequently sealed in argon pressurized slightly below one atm. The temperature in the Mellen furnace was kept at 540°C for 25 hours, to allow dissolution of CdTe in InSb. Mechanical vibrations were imposed on the ampoule at irregular intervals (every 2-3 hours) to enhance the dissolution of CdTe and homogenize the melt. The melt was solidified by lowering the ampoule at 3.23 mm/h through the temperature gradient.

Figure 5 shows typical tip-nucleated crystals grown in the 8 mm ID silica ampoules. The grown crystals were free of cracks, which can be explained by the exceptionally low lattice mismatch.

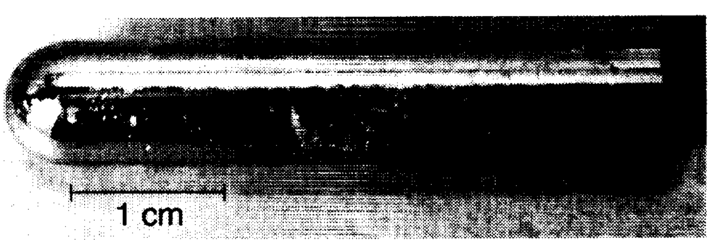


Figure 5. Tip-nucleated specimen *InSbCdTe#2*

Figure 6 shows the axial composition in the specimen *InSbCdTe#2* determined using the Electron Probe Micro-Analysis (EPMA). The concentration of Cd remained equal to the concentration of Te throughout the specimen. Since the equilibrium segregation coefficient of Cd (k=0.25) and Te (k=0.5 to 1) in InSb are notably different [7] our experiments seem to indicate that: (i) Cd and Te

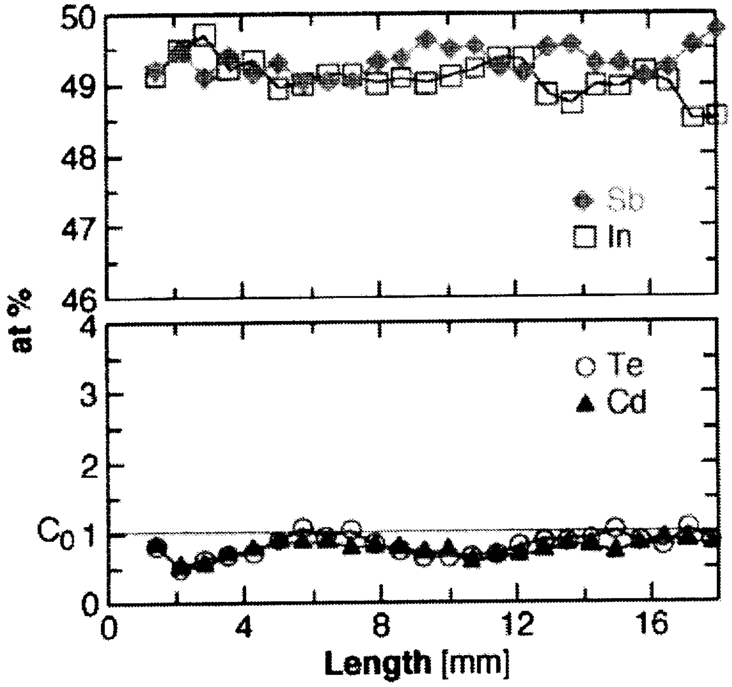


Figure 6. Axial composition of *InSbCdTe#2*; initial melt composition C_0 = 2% of CdTe, i.e., 1% Cd and 1% Te. Note k_{Cd} = 0.25 and k_{Te} = 0.6

remain associated in the InSb melt, and (ii) CdTe molecules are absorbed at the phase boundary. Therefore, the composition of these crystals is quasi-binary $(AB)_{1-x}(CD)_x$, not quaternary $A_xC_{1-x}B_yD_{1-y}$. The constraint x=y is held. Since the initial melt coposition is known) (2 % of CdTe, *i.e.*, 1% Cd and 1% Te), the effective segregation coefficient $k_{effective}$ of CdTe in InSb can estimated to be ~1. This favorable segregation coefficient may be related to the negligible lattice mismatch (0.0027 %).

III. Numerical Modeling

Numerical modeling is an integral part of our research in preparation for CBG and SUBSA. For modeling, we are using the finite code NEKTON [8], which is based on "macro" (spectral) finite elements. The numerical simulations are used:

- as a design tool, to optimize the geometry and the temperature field in the furnaces;
- as a research tool, to study the transport processes in different melt-dopant systems.

IV. Value to Scientific Field

If SUBSA and CGB yield the expected results, directional solidification with the baffle may become a preferred technique for directional solidification in space. The experiments will demonstrate that the baffle, without additional expense and drawbacks, will reduce the natural (*i.e.* free buoyancy-driven) convection in the melt to the point that it will not affect segregation. Furthermore, for the first time, we will measure precisely the diffusion coefficient at the growth interface, which is needed for interpretation of space experiments and modeling.

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