Crystal Growth of II-VI Semiconducting Alloys by Directional Solidification

Dr. Sandor L. Lehoczky, Principal Investigator
NASA Marshall Space Flight Center
Mail Code ES75
Marshall Space Flight Center, AL 35812
Phone: (256) 544-7758
Fax: (256) 544-8762
E-mail: sandor.lehoczky@msfc.nasa.gov

Co-Investigators:
Dr. Frank R. Szofran, NASA Marshall Space Flight Center
Dr. Ching-Hua Su, NASA Marshall Space Flight Center
Dr. Sharon D. Cobb, NASA Marshall Space Flight Center
Dr. Rosalia A. Scripa, University of Alabama at Birmingham
Dr. Yi-Gao Sha, University Space Research Association

This research study is investigating the effects of a microgravity environment during the crystal growth of selected II-VI semiconducting alloys on their compositional, metallurgical, electrical and optical properties. The on-going work includes both Bridgman-Stockbarger and solvent growth methods, as well as growth in a magnetic field. The materials investigated are II-VI, Hg$_{1-x}$Zn$_x$Te, and Hg$_{1-x}$Zn$_x$Se (0<x<1), with particular emphasis on x-values appropriate for infrared detection and imaging in the 5 to 30 μm wavelength region. Wide separation between the liquidus and solidus of the phase diagrams with consequent segregation during solidification and problems associated with the high volatility of one of the components (Hg), make the preparation of homogeneous, high-quality, bulk crystals of the alloys an extremely difficult nearly an impossible task in a gravitational environment.

The three-fold objectives of the on-going investigation are as follows:

1. To determine the relative contributions of gravitationally-driven fluid flows to the compositional redistribution observed during the unidirectional crystal growth of selected semiconducting solid solution alloys having large separation between the liquidus and solidus of the constitutional phase diagram;

2. To ascertain the potential role of irregular fluid flows and hydrostatic pressure effects in generation of extended crystal defects and second-phase inclusions in the crystals; and,

3. To obtain a limited amount of "high quality" materials needed for bulk crystal property characterizations and for the fabrication of various device structures needed to establish ultimate material performance limits.

The flight portion of the study was to be accomplished by performing growth experiments using the Crystal Growth Furnace (CGF) manifested to fly on various Spacelab missions. The
investigation complements the experiments being done on the crystal growth of Hg$_{1-x}$Cd$_x$Te using the Advanced Automatic Directional Solidification Furnace (AADSF) flight instrument. The investigation consists of an extensive ground-based study followed by flight experimentation and involves both experimental and theoretical work. Just as for the AADSF-related studies. Both melt and solvent growth methods are being pursued, with the melt growth being the primary emphasis of the initial flight experiments. The combination of the two studies provides the basis for the evaluation of the influence of alloy property variations on the relative importance of various gravity- and non-gravity-related effects. Several alloy properties including the effective diffusion coefficient, segregation coefficient, thermal conductivity, microhardness, etc. are known to vary substantially with composition and from alloy system to alloy system. For example, the “effective” mass diffusion coefficients deduced from directional solidification compositional redistribution data differ by about a factor of 10, with that of Hg$_{1-x}$Cd$_x$Te being the largest and Hg$_{1-x}$Zn$_x$Te being the smallest. These variations will cause non-gravity-related effects to be more significant in some cases than in others.

A series of HgZnTe crystal ingots has been grown from pseudobinary melts by Bridgman-Stockbarger type directional solidification using the CGF Ground Control Experiment Laboratory (GCEL) furnace, as well as MSFC heat pipe furnaces. Several ZnTe crystals were also grown using a Te-solvent zone growth method. Various thermal boundary conditions and growth rates were employed and several of the ingots were rapidly quenched during the steady-state portion of growth to establish correlation between thermal conditions and melt/solid interface shapes. These experiments also indicated that the ingots can be successfully quenched and back melted to allow a rapid return to steady-state growth. The fitting of the measured crystal compositional distributions to appropriate theoretical models was used to obtain an estimate of the effective HgTe-ZnTe “liquid diffusion coefficient.” To assist the modeling of the pertinent heat and mass transport processes, selected portions of the pseudobinary phase diagram, thermal diffusivity, melt viscosity and melt density have been measured.

A ground pre-processed and quenched sample was successfully back-melted and partially regrown in the CGF instrument during the First United States Microgravity Laboratory (USML-1) mission. The meltback interface was within 0.5 mm of the desired value. Because of the loss of power to the CGF, the experiment was prematurely terminated after approximately 39 hours into the planned 150 hour growth period. About 5.7 mm of sample had been grown at that point. Surface photomicrographs of the sample clearly showed significant topographical differences between the space- and ground-grown portions. Compositional measurements along the sample axis indicated that the desired steady-state growth for the axial composition was reached at about 3 mm into the growth because of the quenched in melt composition for steady state growth. An x-ray diffraction and SEM survey of the sample showed that both the ground and flight portions of the ingot contained only a few grains (i.e., were nearly single crystals) and the crystallographic orientation was maintained following back-melting and space growth. The interface shape, radial compositional variations, and the quenched-in dendritic structures of the flight sample all have shown an asymmetric behavior. The compositional data strongly suggest that the most likely cause was unanticipated transverse residual accelerations.

A new seeded method has been developed for the growth of HgZnTe crystal ingots from pseudobinary melt by the Bridgman-Stockbarger type directional solidification for the Second
United States Microgravity Laboratory (USML-2) mission. A vapor transport method developed by us was used to grow 2 cm ZnTe seed crystals in the fused silica ampoules. Then a stack of precast pseudobinary alloys of varying compositions were loaded in the remaining ampoules. The alloy compositional variation in the stack was chosen to correspond to the expected melt composition variation along the growth axis for steady-state diffusion-controlled growth conditions. A series of Hg$_{0.84}$Zn$_{0.16}$Te and Hg$_{0.88}$Zn$_{0.12}$Te crystals were then grown using the CGF Ground Control Experiment Laboratory (GCEL) furnace, as well as in heat-pipe furnaces. Several crystals were also grown under the influence of a 5T axial magnetic field. Detailed compositional and microstructural characterization of the samples indicated that the alloy stacks could be successfully back-melted within 0.5 mm of the seed interface to assure that growth begins under nearly steady-state growth conditions. The applied magnetic fields had a significant influence on radial alloy segregation and interface constitutional supercooling breakdown demonstrating the importance of gravity-induced fluid-flow effects.

Two Hg$_{0.88}$Zn$_{0.12}$Te seeded ampoules were chosen for processing in the CGF during the Second United States Microgravity Laboratory (USML-2) mission. The results from a similar experiment that was inadvertently terminated during the previous USML-1 mission strongly indicated that residual accelerations transverse to the growth axis are detrimental for achieving the primary experiment objectives. Thus a Shuttle flight attitude that minimizes such accelerations was requested for the USML-2 mission. Just prior to launch the attitude was disallowed because of programmatic constraints and a decision was made not to perform the flight portion of the experiment under unfavorable growth conditions.

Several Hg$_{0.9}$Zn$_{0.1}$Se crystals were grown by the Bridgman-Stockbarger method with and without the presence of axial magnetic fields. The measured dislocation densities were more than an order of inaptitude lower than typically observed for other II-VI alloys. This has been attributed to highly favorable growth conditions.