

Topical: Inorganic Crystal Growth in a Reduced Gravity Environment

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1. Introduction

Inorganic crystals are essential to almost all of today's high technology industries. As described in the NASA MaterialsLab Workshop report from 2014 [1], they are required for "key components in microelectronics, energy generation (i.e. photovoltaics), and detector and sensor systems. Specific applications are numerous and include radiofrequency and terahertz detector systems, gamma-ray, X-ray, and neutron detectors, UV and IR lasers, electro-optics, and hyper-spectral imaging systems. Because semiconductor materials are used extensively in so many industries, even slight improvements in material quality or production yield can have a large economic impact." Although crystalline materials are important to many of the new technologies at the core of U. S. economic growth, there has been a marked decrease in the U. S. over the past 20 years in the capability to pursue those opportunities involving the discovery of new crystalline materials and the science and art of crystal growth [2]. The National Academy of Sciences report "Frontiers in Crystalline Matter: From Discovery to Technology" describes the importance of the discovery and growth of crystalline materials (DGCM), and the challenges and opportunities in DGCM [2]. The report also provides specific recommendations on enhancing opportunities in the field, which include focused, multiagency initiatives.

Experiments on the ISS, or on other reduced gravity platforms, can play a significant role in elucidating important effects that occur during the growth and processing of single crystals. Bulk single crystals are typically grown from the melt or by vapor transport and processes that occur in the melt or vapor phase can have an effect on the resultant crystalline properties. "On Earth, gravity interacts with thermal and solutal gradients to cause convection, and sedimentation and buoyancy can also occur. Crystal imperfections and inhomogeneities resulting from gravitationally driven processes degrade the performance of semiconductor devices." [1] Gravitationally induced effects can also mask other potentially important effects such as Soret diffusion. Finally, microgravity experimentation can provide thermophysical property data in selected systems which are required for computational materials modeling.

2. Previous Studies

The potential of reduced-gravity experimentation to elucidate processes of inorganic crystal growth and to produce higher quality crystals has long been recognized. Crystal growth experiments have been conducted on Skylab, Apollo-Soyuz, Spacelab, MIR, ISS, and suborbital rocket flights. There is no known comprehensive review of all of these experiments but a listing of many of those conducted prior to 1998 is given by Regel and Wilcox [3]. The majority of these experiments were one-shot tests done under a single set of conditions, making it sometimes difficult to be confident in cause and effect relationships. Also, melt growth processes typically require many hours or days, and vapor growth can take weeks. Early microgravity experimentation time was quite limited, and often only partial crystals could be grown. The ISS does provide the opportunity to conduct series of crystal growth experiments, with careful selection of experiment parameters, closer akin to what is done in Earth laboratories. However, crystal growth on the ISS has been limited by agency priorities and resource limitations.

3. Recommended Areas of Research

In the 1990's, the NASA Materials Science Discipline Working Group developed a recommended set of areas for research which are described in the NASA Research Announcement "Microgravity Materials Science: Research and Flight Experiment Opportunities, NRA-98-HEDS-05" [4]. These scientific areas have largely retained their relevance and many of the open questions can be addressed through experimentation related to inorganic crystal growth. Some of the important areas are given below.

A. Phase Separation and Interfacial Phenomena

Surface tension driven convection (Marangoni convection) is driven by a temperature or composition variation along a free surface. As described in reference [4],

"Limited experience during space experiments indicates that above a critical Marangoni number (ratio of surface tension force to viscous force), the flow becomes unsteady and temperature fluctuations in the melt are observed. In addition, a detailed series of ground and low-gravity experiments have demonstrated that striations due to Marangoni convection are produced in float-zone grown silicon. Magnetic fields are used in crystal growth to reduce bulk fluid motion, but these fields cannot completely compensate for surface tension driven flow, which is confined to a thin boundary layer near the surface of the growing crystal. A microgravity environment is very effective for studying these surface tension driven flows because other, buoyancy driven, phenomena are suppressed.

Additional interfacial energy effects are the determining factors in other forms of microgravity materials processing. One example is the formation of potentially unique composite materials by the directional solidification of an alloy melt that initially contains a uniform dispersion of fine solid particles. In this case, the interplay between solidification velocity and particle/liquid interfacial energy is crucial in determining the distribution of the strengthening particles. Some combinations of these processing variables result in the particles being entrapped at the solidification front to give a uniform microstructure, while others result in particles being repelled from the solidification front, producing segregation of the particles and poor properties."

B. Transport Phenomena

The properties that result from crystal growth depend on heat and mass transport. This transport is a combination of convection and diffusion. On Earth, gravitationally driven convection resulting from chemical or thermal gradients is nearly unavoidable and microgravity allows the researcher to obtain conditions where transport is dominated by diffusion. Where free surfaces can be avoided, microgravity thus provides an environment to study diffusive processes, both to make experimental measurements of diffusion coefficients and to compare resultant material properties with or without convective influence. Experimental data can also be obtained to quantify the effect of the magnitude, direction and frequency of gravity on transport to compare

with expectations from computational models. For example, model experiments can be used to quantify the effects of g-jitter. Through scaling laws, the measured effects can be used to determine the parameter space where diffusive transport is dominant for future experiments.

C. Thermophysical Properties

Computational materials models cannot be more accurate than the thermophysical properties on which they are based. Microgravity provides an ideal environment for the experimental measurement of selected properties. For semiconductor crystal growth, diffusion is one such important thermophysical parameter. Present estimates of diffusivity in molten semiconductors can typically provide an order of magnitude estimate only, without any information on their dependency on dopant type or temperature. The fundamental mechanisms of mass diffusion in the liquid state are not understood well enough to allow for the prediction of diffusion of one species into another or even within itself. This observation is especially true with respect to the dependence of diffusion mechanisms on temperature as well as on the dopant type. Experiments are required to provide quantitative data on Fickian (mass) and Soret (thermal) diffusion as a function of dopant and temperature. Diffusion data near the melt point may provide insight into potential clustering of molecular species in the liquid state prior to solidification.

D. Defect Generation and Control

As described in reference [4],

“Temperature gradients in the melt are unavoidable during directional solidification of materials such as semiconductors. Furthermore, in growth from solutions, segregation of primary constituents, and to a lesser extent impurities, produce compositional variations in the melt. Under most processing conditions on Earth, the resulting density gradients yield significant buoyancy-induced convection that gives rise to property variations on both macroscopic (e.g., axial and radial segregation) and microscopic scales (e.g., point defect density fluctuations). These gravity-induced flows can produce local thermal and compositional variations at the growth surface, which in turn introduce defects into the solid with variable pattern, type, and number density. Another source of defects is the container wall, which can introduce strain and impurities into the crystal. The number and distribution of these defects, superimposed on macroscopic variations, then influence, often strongly, the performance of devices manufactured on or in these crystals. Indeed, the inability to control the defect structure of bulk crystals has led, for example, to the need for epitaxial thin films to improve the quality of semiconductor devices. It is clear that a better understanding of the mechanisms of defect generation would help in devising processes to control them. The space laboratory with variable acceleration vector has proven useful to improving our understanding of the crystal growth process.”

There is ample evidence from reduced-gravity flight experiments that fluid flow can affect the generation of defects. An early example is the growth of Te-doped InSb on Skylab [5]. It was shown unambiguously the origin of segregation discontinuities associated with facet growth, the mode of nucleation and propagation of rotational twin boundaries, and the specific effect of

mechanical-shock perturbations on segregation. Another interesting result is from the Bridgman growth of $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ grown on the USML-1 spacelab mission [6]. There, the space grown crystal showed a thousand-fold reduction in the (111) dislocation density and the complete elimination of the cellular (mosaic) structure typical of terrestrial material. The difference was attributed to a separation between the melt and container that occurred in microgravity without the pressure head effect that occurs on Earth.

E. Magnetic Field Effects

On the ISS as well as other orbiting platforms, the gravity level is not zero. Rather, the level of gravity can vary between $O(10^{-6})$ to $O(10^{-3})$, depending on the frequency. Also, generally there is no way to control the alignment of a growth crucible, and thermal gradients, with respect to the residual gravity vector. Depending on the thermophysical properties, there are systems in which the gravitational environment of the ISS is not good enough to result in diffusion-controlled growth. A static magnetic field can be used to further reduce flow velocities in melt growth systems. A static magnetic field interacts with an electrically conducting melt and acts as a brake on fluid motion driven by buoyancy. So-called magnetic damping can also reduce the influence of surface tension driven convection and transients in melt flow velocities associated with g-jitter. Static magnetic fields are used to help control fluid flow and the dispersion of dopants in crystal growth systems on Earth [7]. The idea of combining microgravity and static magnetic fields has been around for decades, but not put into practice. This combination would increase the types of systems amenable to microgravity research and provide a rich field for experimentation.

Another approach to the control of fluid motion is through the use of alternating magnetic fields, such as travelling magnetic fields and rotating magnetic fields (RMF)s. Potential benefits of alternating magnetic fields include homogenization of the melt temperature and concentration distribution, control of the melt-crystal interface shape, and reduction in growth-related defects [8]. The MSRR has a RMF with a magnetic flux density of up to 3.5 mT and frequencies between 5-400 Hz. However, this author is unaware of any NASA funded investigation that has used this capability as a means to control fluid flow during crystal growth.

4. Research Priorities

At the MaterialsLab workshop, scientists from industry, academia, and government developed a set of four research priority areas in the area of semiconductor crystal growth [1]. These priorities remain valid and there has not yet been any significant implementation of these recommendations.

The first priority was the “Bulk Growth of Semiconductor Compounds for High Value Sensors and Detectors”. The object was to both understand fundamental aspects of the growth process (segregation, growth kinetics, liquid structure, diffusion, particle engulfment, thermal and solutal capillary flows, etc.) and to grow benchmark materials. In addition to sensors and detectors, more recent applications may also include crystals for quantum information systems. Execution

of well-defined series of experiments in microgravity can provide the necessary data for predictive computational models and potentially novel benchmark materials.

The second priority was “Meniscus-Defined and Semicontainerless Semiconductor Processing”. Containerless processing provides for a reduction in thermal and mechanical stresses that are otherwise caused by contact between the crystal and the crucible wall and eliminates potential contamination from the crucible. Crystalline quality has been shown to be significantly improved by containerless processing [9]. Microgravity enables the study of the fundamental aspects of semicontainerless processing without the complications of gravitational effects such as the weight from the hydrostatic head and buoyancy effects.

“High Temperature Processing of Industrially Relevant Semiconductors” is the third priority listed. Current ISS furnaces do not provide temperatures much above 1200 °C and many industrially relevant materials require processing above 1400 °C. These include Si, BN, Si₃N₄, SiC, AlN, GaN and ZnO. Processing of such materials will require a new furnace. It is important that materials be processed with non-contact techniques such as physical vapor transport or float-zone to insure little or no contact between the crucible and melt. The microgravity environment will expand the number of high melting-point systems that can be grown with limited contact.

The fourth priority was “Thermophysical Property Measurements”. Under terrestrial conditions, thermophysical property measurements in melts can be mitigated by gravitationally driven flows. A diffusion-controlled flow regime in microgravity enables the attainment of more accurate data. Essentially all semiconductor processing is coupled to modelling efforts, and accurate thermophysical property data are certain to be used by industry, academia, and government agencies.

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