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Heat Flow Control and Segregation in Directional Solidification: Development of an Experimental and Theoretical Basis for Bridgman-Type Growth Experiments in a Microgravity Environment

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Abstract

Within the framework of the proposed research, emphasis was placed on application of magnetic fields to semiconductor growth systems. Through complementary support by the Air Force and DARPA, we were able to acquire a superconducting magnet which can provide axial magnetic fields of up to 30 kGauss for melt stabilization in the NASA facility for heat pipe based vertical Bridgman-Stockbarger growth. It was found that axial fields up to 3 kGauss do not affect the growth behavior nor the macro-segregation behavior in the system Ge(Ga). Applied fields are found to significantly alter the radial dopant distribution, which is attributed to alterations in the spatial orientation of convective cells. Increasing the applied magnet field to 30 kGauss is found to have a fundamental effect on dopant segregation. The initial transient segregation behavior is identical with that predicted by Tiller et al. for diffusion controlled plane front solidification. Within the transient region, the dopant concentration increased by in excess of 600%, a concentration increase which in the magnitude has thus far only been observed in the ASTP experiment conducted in the reduced gravity environment of space. While the apparent achievement of diffusion controlled growth, as indicated by theory, is contingent on the validity of the available database, the experimental results demonstrate that magnetic melt stabilization can be valuable in emulating a limited spectrum of reduced gravity conditions. The experiments also point to the need, in space, for extended equilibration of melts prior to solidification, and alternatively, at the need for force convective mixing in a microgravity environment.

Emphasis was also place on the exploration of the potential of KC-135 flights for preliminary studies of the effects of reduced gravity environment on the wetting behavior of semiconductor systems in growth configuration. The experiments indicated different solidification characteristics; however, it was not possible to obtain quantitative data on wetting. The primary problem consisted of deficiencies of the available hardware. The limited number of experiments conducted does not permit any conclusions on the merits of KC-135 flights for semiconductor processing research. It is established, however, that the effective use of this facility will require acquisition of appropriate hardware.

At professional meetings, presentations were made on the potential of reduced gravity environment of R&D in materials processing.

Dopant Segregation During Vertical Bridgman-Stockbarger Growth with Melt Stabilization by Strong Axial Magnetic Fields

The effects of axial magnetic fields on dopant segregation during crystal growth in a seeded vertical Bridgman-Stockbarger configuration (Fig. 1) were investigated with gallium-doped germanium. The growth system consisted of vertically aligned resistance heated high and low temperature zones which were separated by a 6 cm long diabatic gradient control region;[1] this system provided quantifiable and controllable thermal boundary conditions for the growth cavity (20 mm diameter). For melt stabilization, a superconducting magnet capable of generating vertical magnetic fields of up to 30 kGauss was installed coaxially about the growth system. The charges, polycrystalline ingots and seeds of [100] orientation, were contained in quartz ampoules of 15 mm ID (17 mm OD).

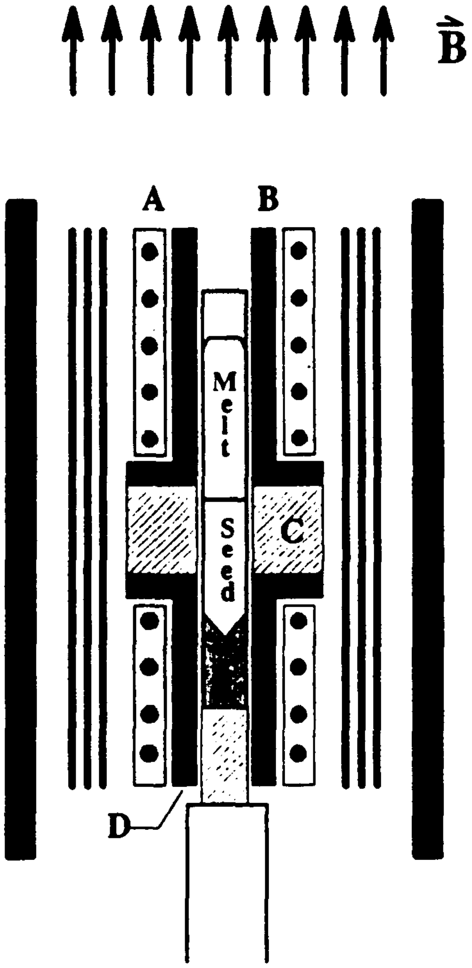


Figure 1. Schematic representation of vertical magnetic Bridgman-Stockbarger growth system: A. heaters, B. heat leveler, C. diabatic gradient control region, D. sodium heat pipe (inconel).

The growth procedure was as follows: the ampoules were inserted to a predetermined position within the growth cavity and the system was purged with argon and maintained at a dynamic overpressure of about 10 torr; after activating the magnet, power was set at 980 and 750°C, respectively achieving seed meltback of about 1 cm with the growth interface being located at 0.5 cm below the heat leveler. Following equilibration of 30 min, growth was initiated by lowering the charge at a constant rate (10μm/s in the reported experiments). After the charge was solidified, the magnetic field was ramped down and the heater power was reduced to zero over a period of 10 hrs. The grown single crystals were removed, appropriately cut, polished, and subjected to differential chemical etching.[2] Macro-segregation profiles were determined through spreading resistance measurements (ASR-100) on longitudinal crystal segments which contained on their surface the geometric crystal axis. The crystal slices, mounted with In-Sn solder on brass disks, were measured in single point mode at spacings of 10 and 100 µm for micro and macro-segregation analyses respectively. The reported data (Fig. 2) are based on average values of three parallel axial scans (center; left and right periphery, 2 mm form the crystal edge) at common longitudinal positions. To ascertain the degree of radial uniformity of dopant distribution, assumed in the macrosegregation analyses, a limited number of radial scans were made on the longitudinal slices. Analyses of multiple radial scans on wafers (from other crystals grown in this system) confirmed radial symmetry of dopant distribution.

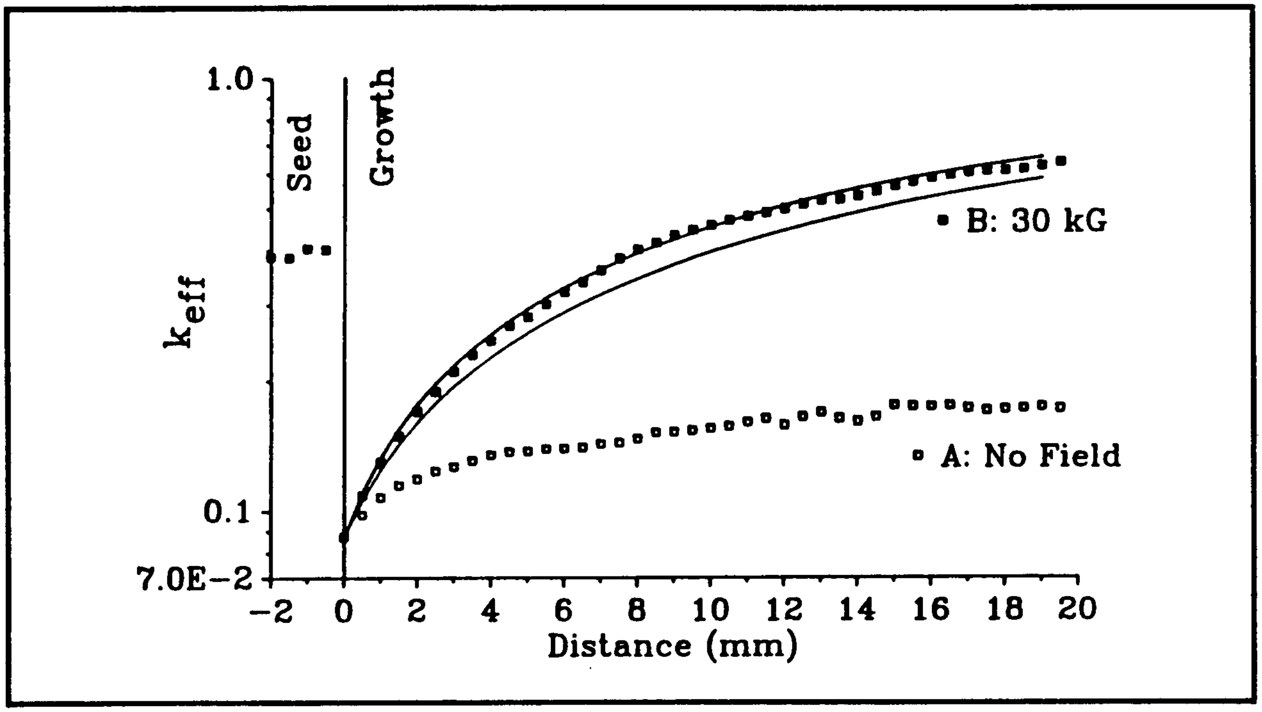


Figure 2. Macrosegregation analysis for growth of Ga-doped germanium. (a) Segregation for growth in the absence of a magnetic field; (b) segregation with an applied axial magnetic field of 30 kGauss. the solid curves about the data for growth at 30 kGauss correspond to theoretical predictions of segregation according to Tiller[4] using D values of 1.7 (upper curve) and 2.1×10^{-4} cm^2/s (lower curve.

Differential etching analyses on all crystals grown in this system revealed rotational and non-rotational dopant striations in the (Czochralski grown) seed portion and the original melt-crystal interface; no striations were observed in any of the crystal portions grown in the Bridgman-Stockbarger system. The curvature of the growth interface in the crystal grown with high magnetic field stabilization (30 kGauss) resulted in a concave (into the solid) morphology with a maximum central deviation from planarity of 20 µm. This interface deflection is almost an order of magnitude less than that observed without stabilization in this thermal configuration.[1]

Figure 2 shows axial composition profiles for the initial 2 cm of crystal growth; curve A was obtained for growth without magnetic field stabilization and curve B for growth with melt stabilization by high axial magnetic field (30 kGauss). In this figure the dopant concentrations, C_s are normalized with $k_0/C_s(0)$ to permit a convenient comparative analysis [$k_0 = 0.087$, the equilibrium distribution coefficient for Ga in Ge, and $C_s(0)$ is the Ga concentration in the crystal portion that was first solidified ($x = 0$)]. Normalization thus yields the effective distribution coefficient [$k_{eff} = C_s \cdot k_0/C_s(0)$] for conditions under which the bulk melt concentration remains constant during solidification. Curve A in Fig. 2 indicates that during conventional , nonstabilized solidification at a rate of 10 μm/s the dopant concentration in the growing crystal increases by a factor of 2 during the first 2.0 cm of growth. The major fraction of the concentration increase occurs within approximately 1 mm of the initial growth interface which reflects the initial build-up of a solute boundary layer. The subsequent segregation behavior is indicative of pronounced thermal convection effects (driven by unavoidable radial thermal gradients in the melt). Thus the observed gradual increase in dopant concentration does not reflect a further increase in the thickness of the solute boundary layer; i.e., it does not reflect an increase in k_{eff}. In the present context it is important to note that the average longitudinal composition profiles obtained for growth without magnetic melt stabilization are virtually indistinguishable from those obtained during growth with melt stabilization by axial and transverse magnetic fields of up to 3 kGauss.[3] Melt stabilization by low fields did not reveal any decrease in macrosegregation. However, it revealed significant changes in radial segregation[3] considered indicative of pronounced magnetic field induced alterations in the patterns of convective melt flows. This phenomenon is currently the subject of further investigations.

Curve B is the normalized initial axial macrosegregation profile for a germanium crystal grown at a rate of 10μm/s in the presence of an axial magnetic field of 30 kGauss. It is observed that the radially averaged dopant concentration under these conditions increased over the first 20 mm of growth by more than a factor of 6 which strongly suggests that the melt stabilization by high magnetic fields led to a reduction or absence of convective interference with segregation. The effectiveness of the magnetic melt stabilization can be assessed through computation of the "approximate critical transient growth distance" (x_{cr}) according to the theory of diffusion controlled plane front solidification by Tiller et al. (4). This theory predicts for diffusion controlled growth the axial dopant concentration, C_s, with growth distance (x):

$$C_S(x) = C_0[1-k_0)e^{-k_0Rx/D}] \qquad (1)$$

where C_0 is the initial dopant concentration in the melt given by $C_s(0)/k_0$, D is the diffusion coefficient of Ga in the Ge melt (2.1×10^{-4} cm^2/s), and R is the growth rate (10 μm/s). Assuming applicability of eq. [1] to solidification of the magnetically stabilized Ga doped Ge melt, the dopant concentration (Cs) in the crystal is expected to have increased from $C_0 \cdot k_0$ to $C_0 \cdot (1-1/e) = C_0 \times 0.63$ after a critical growth length, x_{cr}, given by $D/(k_0R)$. (This approximation is justifiable since k_0 is $<< 1$.) Using a recent publication by Bourret et al. as database,[5] x_{cr}, the critial growth distance, is computed to be 2.4 cm. The experimental segregation data, on the other hand, indicate (Fig. 2) that $C_s = C_0 \times 0.63$ is achieved at $x_{cr} = 1.9$ cm, less than theoretically predicted for diffusion controlled segregation. Since any convective interference with segregation will increase rather than decrease the critical length (xcr), the experimental data appear to conform with diffusion controlled segregation; the discrepancy between theory and experiment is taken to reflect limitations of the database. For the readers' convenience, graphic presentations of eq. [1] are superimposed on the experimental data in Fig. 2. (The two curves correspond to D values of 1.7 and 2.1×10^{-4} cm^2/s.)

The presently reported preliminary results on the effects of melt stabilization by high axial magnetic fields were obtained within the framework of ongoing research on heat and mass transport control directional solidification. Assuming applicability of the theory of plane front solidification and validity of the database, the results of the transient segregation analysis suggest that diffusion controlled solidification has been achieved in vertical Bridgman-Stockbarger growth through melt stabilization by an axial magnetic field of 30 kGauss. This finding appears to confirm theoretical predictions by Oreper et al.,[6] Kim et al.,[7] and Motakef.[8] A detailed study of segregation beyond the initial transient is currently in progress.

Electronic Materials Processing and The Microgravity Environment

Introduction

Progress in solid state technology during the past two decades was dominated by innovative device design and engineering. Projected further advances, according to steadily mounting evidence, are contingent on the availability of electronic materials with a degree of crystalline and chemical perfection which exceeds significantly the capabilities of established processing technology. When considering the background and nature of the existing technological deficiencies, the exploration of the potential of reduced gravity environment of electronic materials processing and for related R&D appears not only attractive, but also logical. Manufacturing technology centers undergo global redistribution and trends indicate clearly that developing countries assume at a steadily increasing rate a primary supplier position in the advanced materials sector. While this shift in manufacturing activities is proceeding, the related R&D activities are almost exclusively conducted in the traditional centers of high technology. By definition, the developing countries become developed countries and are as such expected to also provide for timely advances of their adopted technologies. The broad-based involvement of developing countries in the exploration and anticipated exploitation of microgravity environment for electronic materials processing must thus not only be considered as desirable, but rather as mandatory.

Status

The fundamental semiconductor property requirements dictated by device technology are matrices with controllable, uniformly distributed charge carriers of maximized mobility and lifetime. This requirement translates into the need for semiconductor single crystals of uniform composition and a maximized degree of crystalline perfection. The complexity and changing nature of property requirements, dictated by device engineering, is reflected in some of the emerging GaAs device technology where a primary property requirement extends to the controlled introduction of uniformly distributed interactive point type defects.

Semiconductors of primary industrial concern, Si and Ge originally, now include in addition GaAs, GaP, InP, CdTe, and related ternary and quarternary compounds. All of these materials in bulk form are used either directly or indirectly (as substrates) for device fabrication.

The fundamental electrical properties are conventionally achieved through the incorporation of appropriate electrically active dopant elements into the single crystal semiconductor matrix while simultaneously keeping any contamination by impurities at an absolute minimum.

In excess of 90% of the semiconductor crystals used for device fabrication are produced by the Czochralski process: A single crystal seed of a particular orientation attached to a pulling rod is contacted with the semiconductor melt which is maintained in an inert atmosphere at a temperature somewhat above its melting point. After thermal equilibration, the seed is pulled (at a rate ranging from 0.1 to about 5"/hr) under simultaneous seed and crucible rotation (Fig. 3). Through appropriate temperature adjustments of the melt, the diameter of the growing crystal (ranging in weight from 3 to in excess of 50 kg) can be increased or decreased as desired. Inherent to this crystal growth configuration is radial heat input to the melt and the withdrawal of the crystal along the rotational axis of the system. Accordingly, the melt experiences radial and vertical thermal field distribution thus gives rise to convective melt flows which affect the growth behavior[9-12] as well as the incorporation of the dopant elements (Fig. 4). The driving force for convection in commercial-scale systems is of a magnitude which renders the resulting melt flows turbulent; they are characterized by significant time dependent velocity as well as temperature fluctuations.

These gravity induced melt flows affect the heat and mass transport in the bulk melt, control the nature of all associated boundary layers, and thus by-and-large dictate the crystalline and chemical

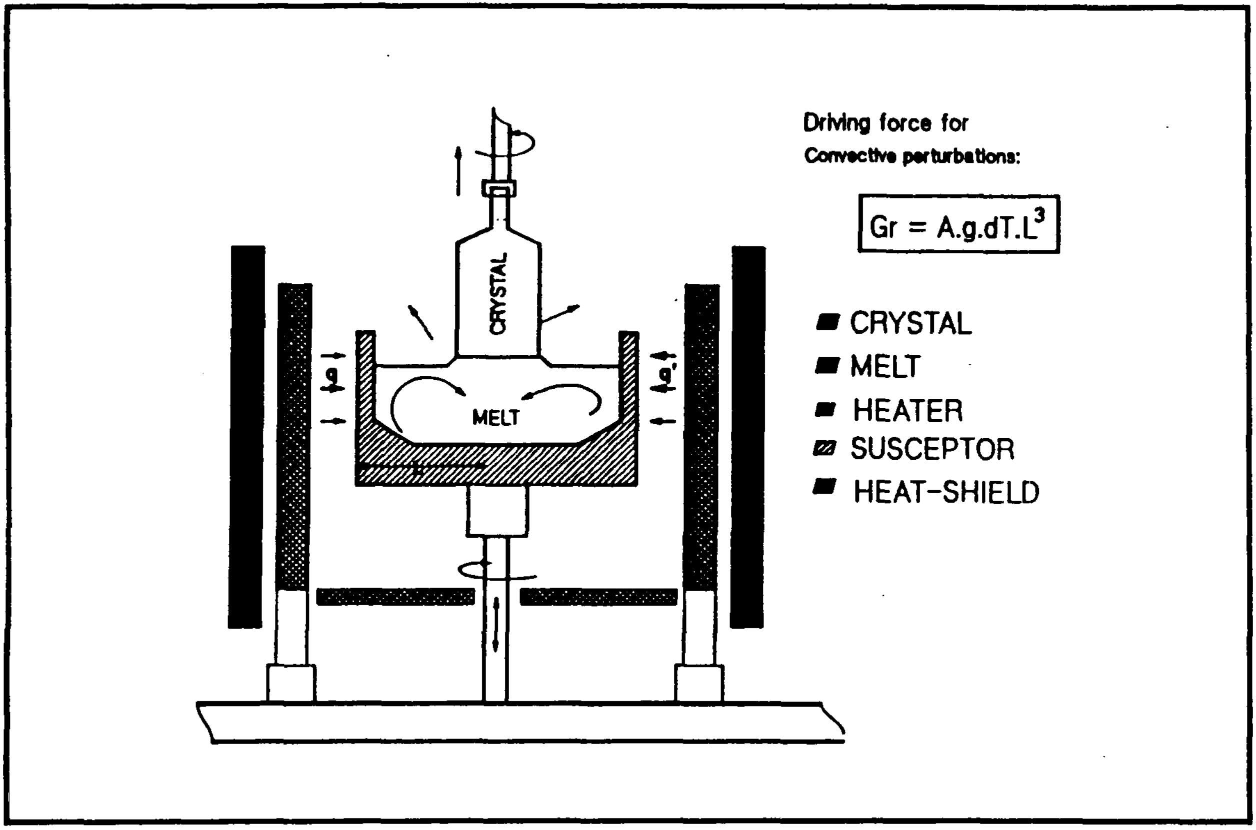


Figure 3. Conventional Czochralski configuration used for pulling of semiconductor single crystals from the melt. Notice the lateral, asymmetric heat input (q) giving rise to three-dimensional turbulent convective melt flows which adversely affect the crystal properties.

perfection of the forming crystal. Effects of concern that can be directly related to convection are summarized in Fig. 5. It should be noted also that inherent to processing on earth is the need for charge confinement and related to it, the potential of melt contamination. Gravity induced melt flows accelerate mass transport and for that reason are also responsible for increased impurity levels in crystals grown from or in containers. Containers, moreover, modify the thermal field distribution in growth systems and adversely affect heat transport control, a critical element in efforts to optimize crystal properties for particular device applications.

Semiconductors for advanced device applications, produced by the established growth technology, fail at a steadily increasing rate to meet property requirements and it si acknowledged that property requirements for projected device technology will likely not be met by presently practiced procedures.

Research aimed at the development of novel approaches to semiconductor growth are severely impeded by the fact that the theoretical framework for solidification and segregation is not quantitatively applicable to crystal growth systems, primarily because of convective interference and the existence of nonquantifiable boundary conditions.

Gravitational effects are clearly recognized as the primary cause of our inability to bridge the existing gap between theory and practice of crystal growth and are therefore the direct cause for our failure to achieve theoretical property limits in materials, the prerequisite for optimization of device performance. They are thus also responsible for industry's heavy reliance on proprietary empiricism in processing technology.

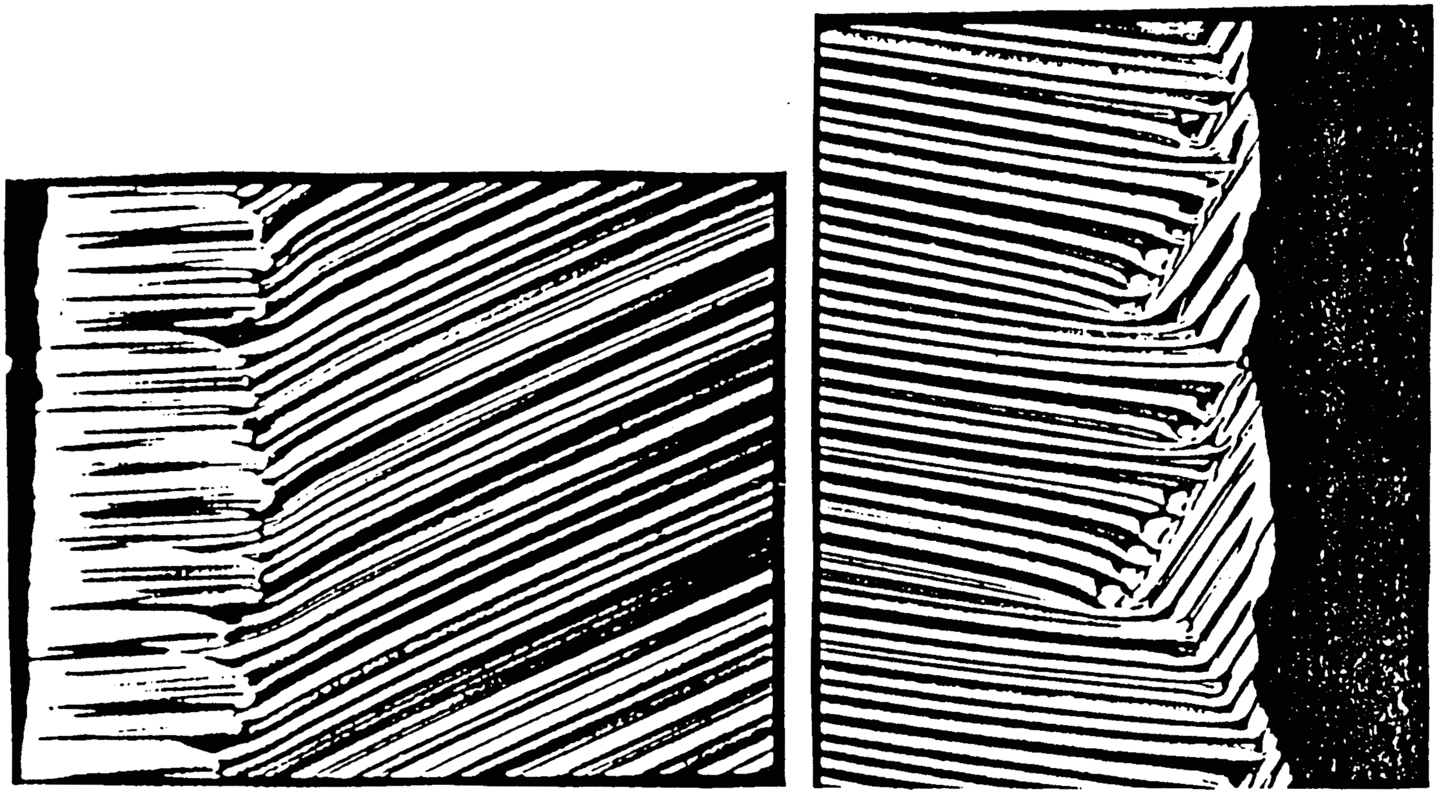


Figure 4. Interface contrast micrography (X600) of etched longitudinal section of doped silicon. The distinct intensity patterns reflect charge carrier fluctuations in the matrix caused by nonuniform dopant incorporation due to gravity induced convection.

Crystal Growth in a Reduced Gravity Environment

The driving force for convective melt flows in semiconductor growth systems is primarily controlled by the magnitude of the gravitational constant. Accordingly, thermal convection can be expected to be virtually absent in a microgravity environment where the g value is reduced by four to five orders of magnitude. This effect provided the primary motivation for the first semiconductor growth experiments in space.[13, 14] These early space activities, conducted in relatively unsophisticated hardware, provided more question marks than answers to existing issues (Fig. 6). Most of all they exposed serious deficiencies in the database of these materials and processes. They also demonstrated that attempts to apply theory to growth experiments are severely limited by the nonquantifiable nature of prevailing boundary conditions.

Shortcomings in the design and execution of the space experiments notwithstanding, their impact on growth technology on earth and their stimulation of growth related R&D is conspicuous. A direct outgrowth of efforts aimed at emulating, to the extent possible, conditions prevailing in reduced gravity environment led to the evolution of magnetic melt stabilization and to the development of magnetic Czochralski growth as practiced in growth technology (Fig. 7). Heat transfer control, virtually neglected prior to these experiments, emerged as a primary issue and resulted in

Macrosegregation of dopants and impurities

Microsegregation of dopants and impurities

Deviations from stoichiometry

Formation and distribution of nonequilibrium point-defects

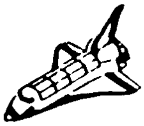
Formation of dislocations and other extended crystal-defects

Constitutional supercooling effects

Growth interface morphology controlled by convective heat-transport

Deterioration of radial vertical thermal gradients in the melt

Figure 5. Summary of the most conspicuous property deficiencies in melt-grown semiconductors that can be attributed to gravity-induced convective melt flows prevailing during their formation.



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RESULTS:

- Diffusion controlled growth and segregation: ?
- Theory of thermo-capillarity: ?
- Theory of radial segregation: ?
- Wetting behaviour of the melt: ?
- Dopant effects on wetting behaviour: ?

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Impact on technology:

- magnetic melt stabilization (MCZ)
- heat transport control by heatpipes
- development of confinement materials
- focus on modified Bridgman growth
- electro-epitaxy

Impact on R/D and science:

- Interface demarcation
- Magneto hydro-dynamics
- Thermo-capillarity
- Expert systems in growth control

Figure 6. Summary of results obtained from semiconductor growth experiments conducted in space and their impact on technology development.

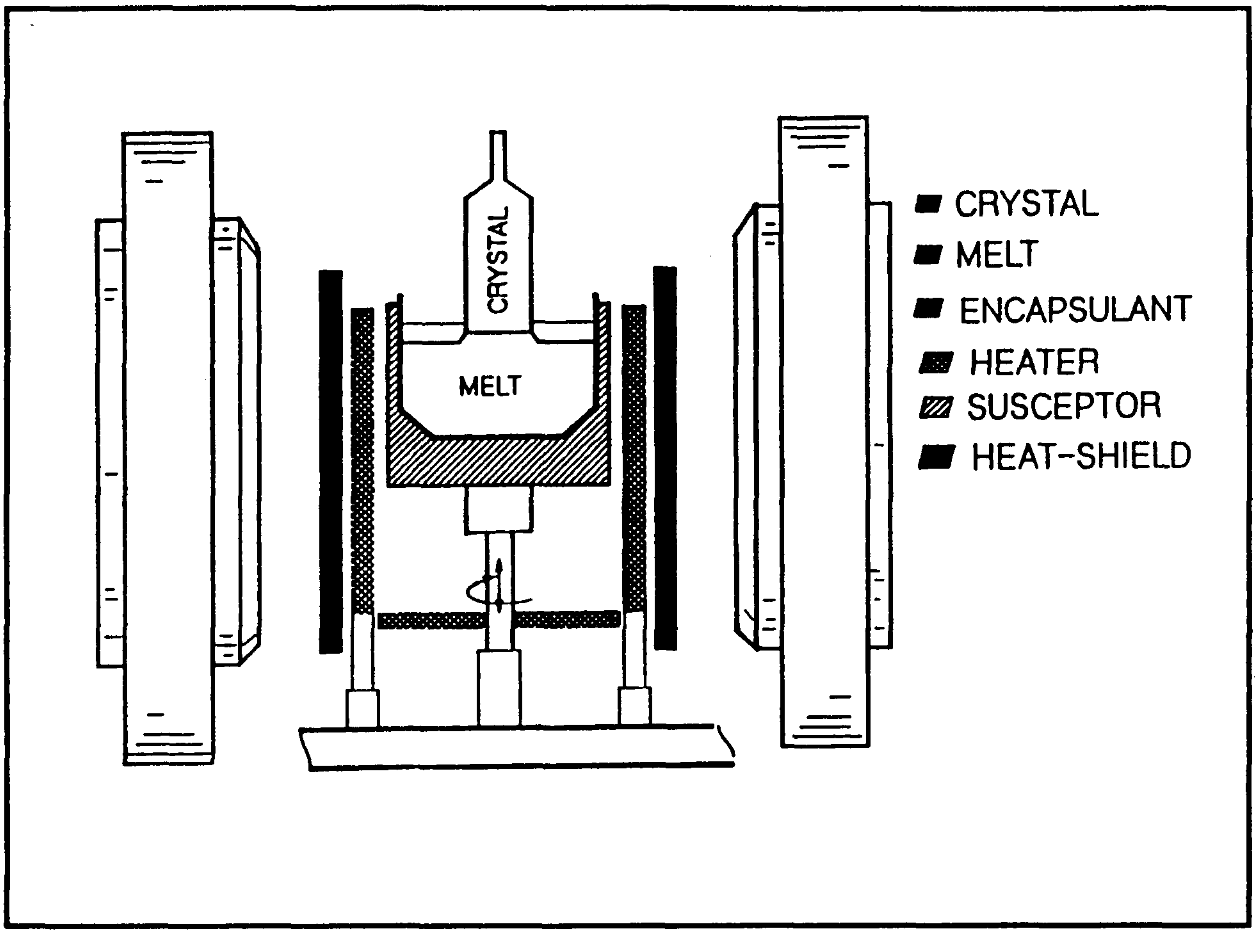

Figure 7. Modified Czochralski configuration for advanced semiconducotr growth. The modifications (magnetic melt stabilization, coaxial heat pipe between heater and crucible) constitute significant advances, which are based on results from experiments conducted in reduced gravity environments.

major efforts aimed at the development of high temperature heat pipes, now considered essential for the establishment of quantifiable boundary conditions are realized as the fundamental prerequisites for meaningful mathematical modeling activities of growth processes and ultimately for efforts aimed at model-based growth control schemes.

Outlook

Experiments in reduced gravity environment have focused attention on Bridgman type growth geometries, primarily because of the fundamental incompatibility of the conventional Czochralski geometry with space environment. These studies stimulated the application of heat pipes for heat transport control (Fig. 8) and resulted in the first applied modeling approach in which the theoretically predicted thermal field distribution was quantitatively confirmed by the experiment.[15,16] More recently this growth geometry (in gradient freeze configuration) has been shown to permit single crystal growth of InP and GaAs with unprecedented low dislocation density.[17] Of interest in context is the finding that vertical Bridgman growth, although characterized by stable axial thermal gradients, does exhibit pronounced thermally driven convective melt flows because of unavoidable radial temperature gradients. These convective melt flows which, as in Czochralski growth, adversely influence the growth and segregation behavior, remain virtually unaffected by axial or transverse magnetic fields of up to 0.3 T (Fig. 9). Increasing the strength of the applied magnetic field by one order of magnitude to 3 T, it is most recently found that convective melt flows in doped germanium are reduced to a point where they no longer interfere with dopant incorporation (Fig. 10); the

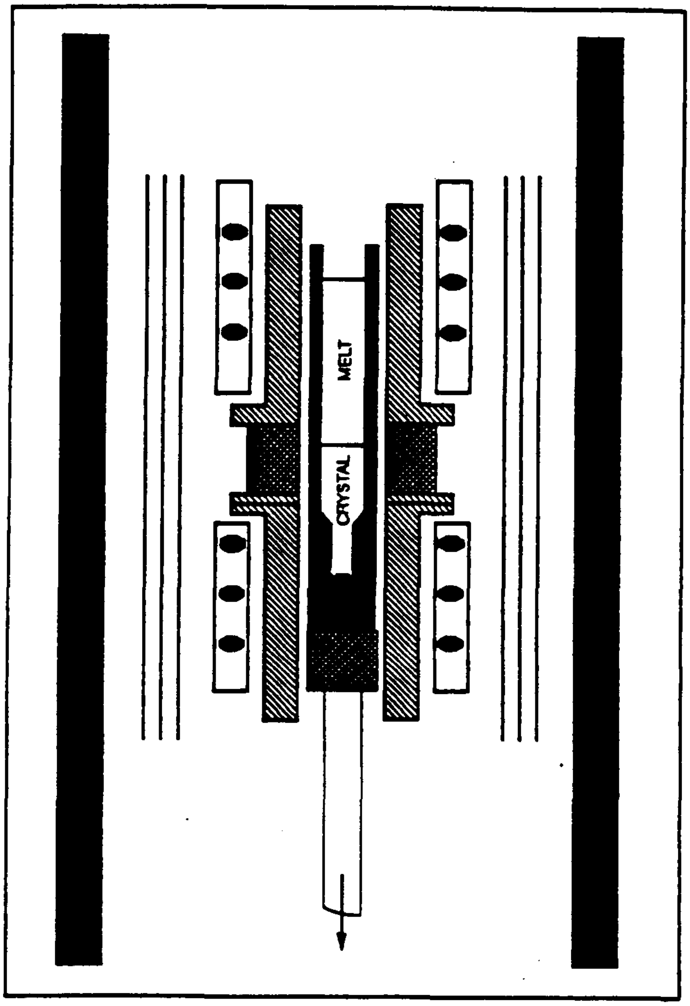

Figure 8. Modified vertical Bridgman-Stockbarger configuration for growth of semiconductor single crystals. This heat pipe based system provides for unprecedented heat transfer control and permits meaningful mathematical modeling.

segregation behavior exhibits characteristics which are very similar to those observed during crystal growth in a reduced gravity environment.

The results of growth experiments with magnetic melt stabilization are of technological interest, primarily because they indicate that convective flows in stabilized melts are laminar and the melt temperature is no longer subject to uncontrollable fluctuations. Such experiments, however, are still subject to other gravity induced side effects, such as melt contamination through interaction with the confinement materials and thermal field distortion due to heat conduction along the crucible walls. Finally, it must be realized that melt stabilization through magnetic fields is only possible in highly conductive melts which severely limits the range of its applicability.

Melt stabilization of growth systems by magnetic fields, in spite of shortcomings, clearly demonstrates elements of the potential of reduced gravity environment for electronic materials processing. The results suggest that growth of crystals (in space) with compositional homogeneity on both a micro- and macro-scale appears achievable. Also achievable appears to be the suppression of constitutional supercooling effects and heat transport control to a point where thermal stresses can be

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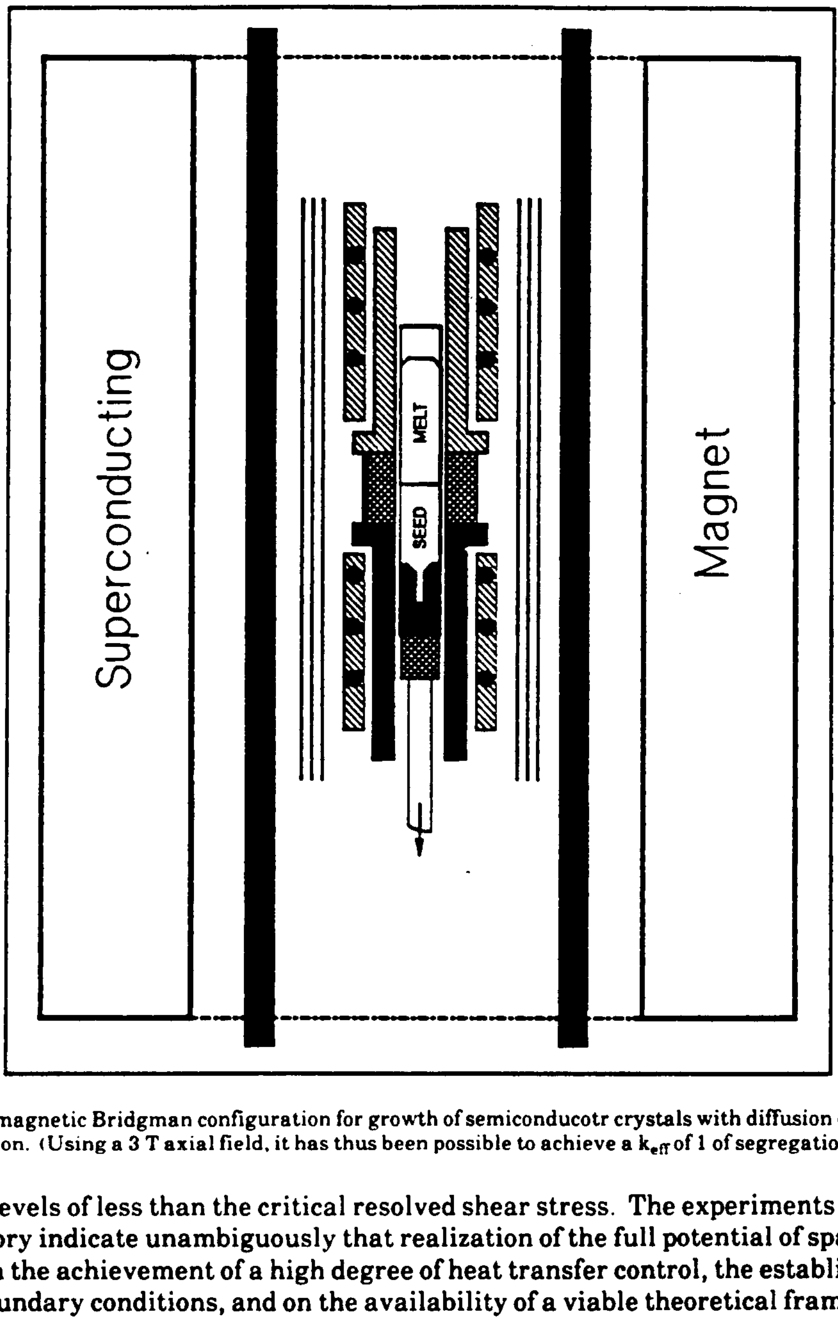

Figure 9. Vertical magnetic Bridgman configuration for growth of semiconducotr crystals with diffusion controlled dopant segregation. (Using a 3 T axial field, it has thus been possible to achieve a k_{eff} of 1 of segregation of Ga in Ge.)

maintained at levels of less than the critical resolved shear stress. The experiments as well as the underlying theory indicate unambiguously that realization of the full potential of space environment is contingent on the achievement of a high degree of heat transfer control, the establishment of quantifiable boundary conditions, and on the availability of a viable theoretical framework for solidification.

Considering the advances of processing technology on earth which resulted from the rather limited number space experiments, it is apparent that direct science and technology transfer from space experiments is an important element. Equally important for significant improvements of ground based operations is the broadening of the database which is expected to accompany experimentation in space.

The fundamental drawbacks of space experimentation relate to costs, limitations in access to space, and uncertainties in man-experiment interaction. Although costs for experiments in space will always be high, the costs for exploring the potential of reduced gravity environment, an element of

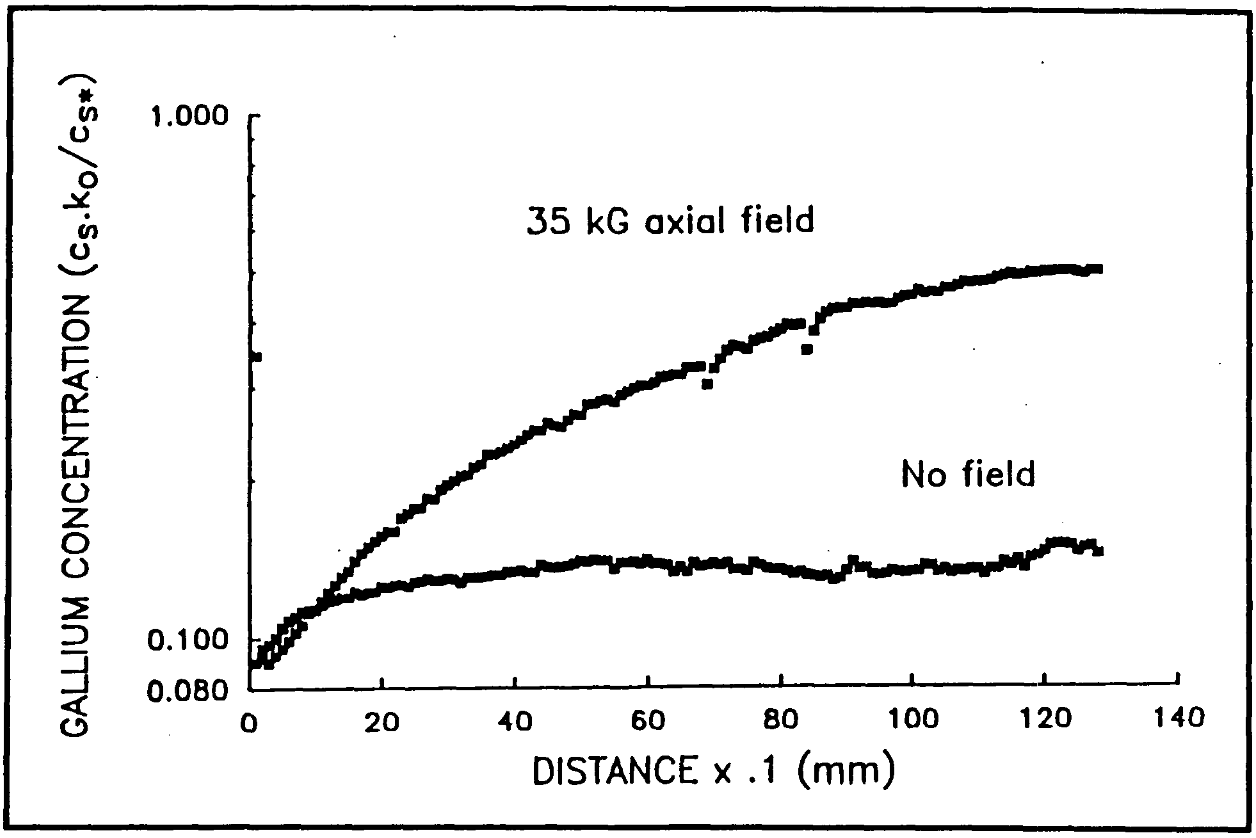

Figure 10. Macrosegregation behavior (of Ga in Ge) in a heat pipe based vertical Bridgman system with and without magnetic field stabilization. The transient segregation in the presence of the magnetic field indicates the absence of convective interference with dopant accumulation at the growth interface.

concern for developing nations, will become less as the scientific framework for processing activities is complemented by results obtained in space. A further cost reduction can be expected from process automation which will make it possible to reduce man-tended experiments to a minimum and allow experiment monitoring and control from the ground.

Conclusions

The capabilities of established semiconductor growth technology are considered inadequate to meet property requirements for projected advances of device technology. Encountered materials deficiencies, inadequate crystalline and chemical perfection, can primarily be related to gravitational interference with the melt growth process. It has been shown that semiconductors grown in a reduced gravity environment do not exhibit these deficiencies and that results of growth experiments in space can provide substantive input to the advancement of processing technology on earth.

Considering the fact that semiconductor manufacturing technology is at a steadily increasing rate being relocated to developing nations, their participation in the exploration and possible exploitation of the potential of space environment for semiconductor growth appears not only desirable but mandatory.

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