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Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport

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I. Introduction

The materials to be studied in this project are ZnSe and the related ternary compound semiconductors such as ZnSeTe, ZnSeS and ZnCdSe. With an energy gap of 2.7 eV at room temperature and an efficient band-to-band transition, ZnSe has been studied extensively as the primary candidate for a blue light emitting diode and laser for optical displays, high density recording, and military communications. However, developments in the bulk crystal growth has not advanced far enough to provide the low price, high quality substrates needed for the thin film growth technology. The realization of routine production of high-quality single crystals of these semiconductors requires a fundamental, systematic and in-depth study on the physical vapor transport (PVT) growth process and crystal growth by vapor transport in low gravity offers a set of unique conditions for this study.

The previous results from vapor phase crystal growth of semiconductors showed improvements in surface morphology, crystalline quality, electrical properties and dopant distribution of the crystals grown in reduced gravity as compared to the crystals grown on Earth. Previously, two reasons have been put forward to account for this. The first is weight-related reductions in crystal strain and defects. These are thought to be caused by the weight of the crystals during processing at elevated temperatures and retained on cooling, particularly for materials with a low yield strength. The second, and more general, reason is related to the reduction in density-gradient driven convection. However, the detailed mechanisms responsible for the improvements and the gravitational effects on the complicated and coupled processes of vapor mass transport and growth kinetics are not well understood.

The PVT crystal growth process consists of essentially three processes; sublimation of the source material, transport of the vapor species and condensation of the vapor species to form the crystal. The latter two processes can be affected by the convection caused by gravitational accelerations on Earth. The results of some fluid dynamic analyses stated that the effects of gravity on heat transfer and mass transport in most of the PVT systems were insignificant. However, the convective flows caused by the buoyancy-driven perturbation in the transport flow field in the vicinity of the growing surface will affect the growth kinetics on the growing surface. This results in phenomena such as interface fluctuation, non-uniform step bunching, etc. which will cause non-uniformity in the incorporation of impurities and defects as well as in the deviation from stoichiometry in the grown crystal. This, in turn, will further modify the local mass transport characteristics and result in irregular flows at the vicinity of the growing surface. It is expected that the reduction in convective contamination by performing flight experiments in a reduced gravity environment will help to simplify the complexity of the coupled mass transport and growth kinetics problem. An improved comparison between the experimental results and theoretical simulations will be beneficial to any growth process involving vapor mass transport or vapor-crystal interface growth kinetics.

II. Scientific Objectives

The scientific objectives and priorities of this investigation are:

1. Grow ZnSe crystals in reduced gravity using Physical Vapor Transport (PVT) processes:

- to establish the relative contributions of gravity-driven fluid flows to (i) the non-uniform incorporation of impurities and defects and (ii) the deviation from stoichiometry observed in the grown crystals as a result of buoyancy-driven convection, irregular fluid-flows and growth interface fluctuations.
- to assess the amount of strain developed during processing at elevated temperatures and retained on cooling caused by the weight of the crystals.
- to obtain a limited amount of high quality space-grown materials for various thermophysical and electrical properties measurements and as substrates for device fabrication and thus assess device performance as influenced by a substantial reduction in gravity-related effects.

2. Perform *in-situ* and real-time optical measurements during growth to independently determine:

- the vapor concentration distribution by partial pressure measurements using optical absorption.
- the evolution of growth interface morphology and instantaneous growth velocity by optical interferometry.
- and thus help to simplify the complexity of the coupled mass transport and growth kinetics problem.

3. Evaluate the additional effects of gravity on the PVT process in the future flight experiments by examining:

- The growth kinetics on various seed orientations.
- the dopant segregation and distribution in the Cr doped ZnSe.
- the compositional segregation and distribution in the ternary compounds grown by PVT.

III. Investigation Approach

1. Mass Flux:

The main disadvantage of PVT growth technique is that the growth rate is usually low and inconsistent. Therefore, a systematic and complete study was performed to optimize the mass flux in the ZnSe PVT system.

(1) One-dimensional diffusion model:

From the results of a one-dimensional diffusion analysis, four experimentally adjustable parameters, the source temperature, the deposition temperature, the partial pressure ratio over the source (vapor phase stoichiometry) and the residual gas (CO, CO_2 and H_2O) pressure, determine the diffusive mass flux in a PVT system. However, two of these four parameters, the partial pressure ratio over the source and the residual gas pressure, are more critical than the others. These two parameters are critically dependent on the proper heat treatments of the starting materials for optimum mass flux.

(2) Thermodynamic properties:

The pertinent thermodynamic properties were determined. The partial pressures of Zn and Se_2 over ZnSe(s) were measured for several samples by the optical absorption technique and the standard Gibbs energy of formation of ZnSe(s) from Zn(g) and $0.5Se_2$(g) was found to be independent of the sample stoichiometry. The Zn-Se phase diagram was described using an associated solution model for the liquid phase and the behavior of the thermodynamic properties of the system pertinent to the PVT process, such as the partial pressures of Zn and Se_2 along the entire three-phase curve, was calculated. The associated solution model was then extended to the Zn-Se-Te system and the thermodynamic properties, such as the partial pressures of Zn, Se_2 and Te_2 along the three-phase curve for various $ZnSe_{1-x}Te_x$ ($0 < x < 1$) pseudobinary systems were established.

(3) Mass flux measurements:

An *in-situ* dynamic technique was set up for the mass flux measurements which has the following advantages over the previous techniques; (i) the instantaneous flux (instead of an average value) was measured and (ii) multiple data points were determined from one ampoule. The mass fluxes in the ZnSe PVT system were measured on the source materials provided by various vendors and treated with different heat treatment procedures.

(4) Residual gas measurements:

The residual gas pressures and compositions in the processed ampoules were measured and it was found that (i) carbon and oxygen in the residual gas originated mainly from the ZnSe source materials and (ii) the oxygen content can be significantly reduced by hydrogen reduction treatment.

(5) Heat treatment of starting materials:

Various heat treatments were conducted to control the partial pressure ratio over the source and the effectiveness of the treatments was evaluated by partial pressure measurements. The optimum hydrogen reduction and vacuum heat treatment procedures were established for the source to maximize the mass flux in the ZnSe PVT process.

2. Crystal Growth and Characterization:

The crystal growth activities were concentrated on a novel three thermal-zone translational growth in a closed system. In order to study the effects of gravity on the various properties of the grown crystals the growth experiments were performed with the growth direction at an angle of 0° (vertical destabilized configuration), 90° (horizontal configuration) and 180° (vertical stabilized configuration) to the gravity vector direction. Self-seeded and seeded growths of ZnSe as well as the self-seeded growth of ZnSeTe and Cr doped ZnSe were conducted. The grown crystals were characterized by various techniques; including spectroscopy (atomic absorption, spark source mass spectroscopy and secondary ion mass spectroscopy), X-ray diffraction (Laue reflection, rocking curve and reciprocal lattice mapping), synchrotron radiation images from a white X-ray beam (reflection and transmission), microscopy (optical, electron, and atomic force), sample polishing and etching and optical transmission. The electrical and optical characterization was performed by optical transmission and photoluminescence measurements.

3. Effects of Gravity Vector Orientation:

The effects of gravity orientation were studied by comparing the following characteristics of the vertically and horizontally grown ZnSe crystals.

(1) Grown crystal morphology:

The morphology of the as-grown, self-seeded ZnSe crystals grown in the horizontal configuration grew away from the ampoule wall and exhibited large (110) facets which tended to align parallel to the gravitational direction. Crystals grown in the vertical configuration grew in contact with the ampoule wall over the full diameter and when the furnace translation rate was too high for the mass flux, the growing crystal surface became morphologically unstable with voids and pipes embedded in the crystal. The as-grown seeded ZnSe crystals in both the horizontal and vertical configurations showed similar characteristics in the morphology as described above for the self-seeded growth.

(2) Surface morphology:

The as-grown surfaces of the horizontally grown ZnSe and Cr doped ZnSe crystals were dominated by (110) terraces and steps. On the other hand, the as-grown surface of the vertically grown ZnSe crystals showed granular structure with tubular features (200nm OD, 75nm ID and 25nm in height) on the top. The as-grown surface of the vertically grown Cr doped ZnSe crystals showed a network of high plateaus with each island 30-70μm in diameter and 3.5μm in height. Numerous nuclei with diameters around 20-50nm and heights of 1-7nm were observed on top of these islands.

(3) Segregation and distribution of defects and impurities:

From the secondary ion mass spectroscopy mappings, for the horizontally grown self-seeded ZnSe crystal, [Si] and [Fe] showed clear segregation toward the bottom of the wafer cut axially along the growth axis. For the vertically grown seeded ZnSe crystal, [Si] and [Cu] showed segregation toward the peripheral edge of the wafer cut perpendicular to the growth axis. From the photoluminescence mappings of near band edge intensity ratios, it was determined that all of the horizontally grown crystals showed the following trends in the radial and axial segregation of [Al] and [V_{Zn}] due to the buoyancy driving force and diffusion boundary layer: [Al] segregates radially toward the top and axially toward the first grown region and [V_{Zn}] segregates radially toward the bottom and axially toward the first grown region. The as-grown surface of the seeded vertically stabilized grown crystal showed [Al], [Li and/or Na] and [V_{Zn}] segregate radially toward the center. Finally, the as-grown surface of the self-seeded vertically destabilized grown crystal showed [Al] and [V_{Zn}] segregate radially without an apparent pattern.

(4) Axial compositional variation in ZnSeTe:

The mole fraction of ZnTe in the grown $ZnSe_{1-x}Te_x$ crystals, x, was determined from precision density measurements on slices cut perpendicular to the growth axis. The vertically (stabilized) grown crystals showed less axial variations and better agreement with the source compositions than the horizontally grown crystals. The composition of the initial grown crystals and the compositional variations in the horizontally grown samples were not consistent with the one-dimensional diffusion model.

The experimental results clearly showed that the convective flows caused by the buoyancy-driven perturbation in the flow field in the vicinity of the growing surface resulted in non-uniformity in the axial and radial incorporation of impurities and defects as well as in the deviation from stoichiometry.

4. *In-situ* monitoring during growth:

In-situ and real-time measurements of (1) partial pressure using optical absorption and (2) the growth interface morphological evolution and instantaneous growth velocity using optical interferometry during growth were performed to study the coupled mass transport and growth kinetics problem. The growth furnace, optical monitoring set-up and growth ampoule design for *in-situ* optical monitoring during the PVT growth of ZnSe were constructed and optimized. Michelson and Fabry Perot optical interferometers were set up for *in-situ* monitoring of the growing surface of the crystal. The Michelson setup was flexible, i.e. the optics were easily adjusted both before and during growth, however the fringe patterns were not stable due to the thermal convection of the surrounding air. It was shown that a modification of the ampoule significantly suppressed this noise. Also, this effect is not expected to be of significant consequence in the reduced gravity environment. The Fabry-Perot interferometer provides good quality fringe patterns, but the optics is rigid and difficult to adjust during the crystal growth run. Using the interferometric techniques, the thermal expansion coefficient of ZnSe was measured between 25°C and 1080°C. Phase maps of the growing crystal surface were constructed in real-time using fringe data from both interferometric set-ups. A visual observation of the growing crystal was performed and the results can be correlated with the phase map results.

5. Transport processes modeling:

Besides the one-dimensional diffusion model, the transport process modeling also included:

(1) Two-dimensional analytical calculation:

Two-dimensional description of fluid flow using thermal conditions (no solutal effects) for a typical growth experiment was studied to estimate the maximum flow velocities for the vertical and horizontal configurations. The calculated maximum shear (perpendicular to growth direction) flow velocity was 5.2μm/s for the horizontal configuration and

0.22µm/s for the vertical configuration under $1g_o$ condition (where g_o is the gravity level on Earth).

(2) Two and three-dimensional numerical modeling:

Two and three-dimensional numerical simulations physical vapor transport process using finite element technique to treat both thermal and solutal induced buoyancy forces were performed. Both compressible and Boussinesq fluids were assumed for a system of multiple transport species with residual gas. The results of the two and three-dimensional calculation agreed well with the benchmark studies. The effects of gravity on the flow field were examined by plotting the differences between the calculated flow velocities for various gravity levels and that for zero gravity. The calculated maximum shear flow velocity difference under $1g_o$ condition was 50µm/s for the horizontal configuration and 9.4µm/s for the vertical configuration. The maximum allowable acceleration level during the flight experiments was established by taking the criterion that the maximum shear velocity should be equal to or less than 10% of the crystal growth rate. This resulted in the requirement of a maximum residual longitudinal acceleration level of 2.7×10^{-3} g_o and a transverse level of 1.0×10^{-4} g_o for the flight experiments with a growth rate of 3mm/day or 0.035µm/s.

IV. Summary

Complete and systematic ground-based experimental and theoretical analyses on the PVT of ZnSe and related ternary compound semiconductors have been performed. The analyses included thermodynamics, mass flux, heat treatment of starting material, crystal growth, partial pressure measurements, optical interferometry, chemical analyses, photoluminescence, microscopy, x-ray diffraction and topography as well as theoretical, analytical and numerical analyses. The experimental results showed the influence of gravity orientation on the characteristics of (1) the morphology of the as-grown crystals as well as the as-grown surface morphology of ZnSe and Cr doped ZnSe crystals (2) the distribution of impurities and defects in ZnSe grown crystals and (3) the axial segregation in ZnSeTe grown crystals.