Crystal Growth of Ternary Compound Semiconductors in Low Gravity Environment

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A low gravity material science experiment has been prepared to be performed in the Low Gradient Furnace (LGF) in the Material Science Research Rack (MSRR) on International Space Station (ISS).

There are two sections of the flight experiment:

(I) Investigation toward crystal growth by physical vapor transport (PVT): the growth of ZnSe and related ternary compounds, such as ZnSeS, ZnCdSe, and ZnSeTe,

(II) Investigation on the melt growth of CdTe and CdZnTe by directional solidification.
Technological significance:
Growth (melt and vapor) and characterization of II-VI and IV-VI compounds semiconducting materials, such as HgCdTe, HgZnTe (for IR detectors), CdS and ZnO (for UV detector), ZnSe, ZnSeTe (for green/blue laser), CdTe and CdZnTe (for x-ray, gamma ray detectors), PbTe, PbTeSe, and PbSnTe (thermoelectrics).

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<table>
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<tr>
<th>Compounds</th>
<th>HgTe</th>
<th>HgCdTe</th>
<th>CdTe</th>
<th>CdZnTe</th>
<th>ZnTe</th>
<th>CdS</th>
<th>ZnSe</th>
<th>ZnS</th>
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<td>Melting points (°C)</td>
<td>670</td>
<td>700</td>
<td>1092</td>
<td>1130</td>
<td>1292</td>
<td>1397</td>
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<td>PVT growth temperature (°C)</td>
<td>850</td>
<td>1000</td>
<td>985</td>
<td>1120</td>
<td>1150</td>
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1. To establish the relative contributions of gravity-driven fluid flows, both in liquid and vapor, to (1) the non-uniform incorporation of impurities and defects and (2) the deviation from stoichiometry and (3) the compositional variation observed in the grown crystals.

2. To assess the self-induced strain developed during processing at elevated temperatures and retained on cooling caused by the weight of the crystals.

3. The relation between fluid phase processes and the generation of defects in a grown crystal is an outstanding problem in materials growth. Studies in microgravity will be compared with modeling and will lead to a greater understanding of the processes involved.
Phase Diagram of Zn-Se
Partial pressures along the three-phase curve for ZnSe(s)

At 1156 °C, $P_{Zn}$ varies from 8.4 to $1.3 \times 10^{-4}$ atm, $P_{Se_2}$ varies from 20 to $5 \times 10^{-9}$ atm and $\alpha = P_{Zn}/P_{Se_2}$ varies from $1.7 \times 10^9$ to $6.5 \times 10^{-6}$
Calculated mass flux of ZnSe as a function of $\Delta T$ and different values of $\alpha(L)$. The source temperature was 1080 °C. Solid lines are for $\alpha(L) > 2$ and dashed lines are for $\alpha(L) < 2$. 

Calculated mass flux of ZnSe as a function of $\Delta T$ under the same conditions except a residual gas pressure of 0.008 atm is present in the system.

Calculated mass flux of ZnSe as a function of residual gas pressure for source temperature at 1080 °C and different values of $\alpha(L)$. 

Su, et al. (1998); Sha et al. (1995)
Simultaneous measurements of mass flux and partial pressure
Simultaneous measurements of mass flux and partial pressure
Simultaneous measurements of mass flux and partial pressure

- $P_{Zn}$ measured over the deposit; $\alpha_{\text{deposits}} = 17$.
- The measured $P_Z$ value was used in the calculation.

![Graph showing mass transported vs. time and pressure](image)
Calculated partial pressure profiles for ZSTO-3 run 2

- \( P_z = 17 \)
- \( P_{Zn} = 6.4 \)

\( \alpha = 17 \)

\( \alpha = 6.4 \)

ZSTO-3, run 2
- \( T_s = 1160^\circ C \)
- \( T_d = 1130^\circ C \)
Summary of one dimensional diffusion analysis

- Four experimentally adjustable parameters, the source temperature, the deposition temperature, the partial pressure ratio over source and the residual gas pressure, determine the diffusive mass flux of a PVT system.

- However, two of these four parameters, the partial pressure ratio over source and the residual gas pressure, are more critical than the others. As will be shown, these two parameters are critically dependent on the proper heat treatments of the starting materials for optimum mass flux.
Optimum Heat Treatments of Starting Materials

$P_{Se_2}$ in equilibrium with ZnSe for various optical cells

H$_2$ reduction and vacuum treatments for ZnSe(O)-3 established to be the optimum procedure

Su et al. (1998)
Crystal Growth by Physical Vapor Transport: temperature profile and initial ampoule positions

- The growth ampoules can be equipped with optical windows to confirm the stoichiometry of the starting material before growth.
- The thermal profile, with a maximum in the middle, was provided by a three-zone furnace with an adiabatic zone between central and cold zones.
- Growth was initiated by translating furnace to the right.

Su (1995)
1. Self-seeded growth of ZnSe in vertical (stabilized and destabilized) and horizontal configurations
2. Seeded growth of ZnSe in vertical and horizontal configurations
3. Self-seeded growth of Cr-doped ZnSe in vertical and horizontal configurations
4. Self-seeded growth of ZnSeTe in vertical and horizontal configurations
5. *In-situ* and real-time optical monitoring of seeded growth in a horizontal configuration
Flow chart of sample characterization plan

- residual gas pressure measurements
- crystal growth by PVT
- open ampoule
- examine interface by SEM, AFM and optical microscope
- growth orientation by X-ray (Laue)
- slice crystal by wire saw
- polishing
- SIMS
- etch pit density by SEM & optical microscope
- TEM
- GDMS & SSMS on crystal & source
- triple crystal rocking curve
- synchrotron radiation imaging
- optical absorption measurements
- WDS & EDS measurements
- photoluminescence
- precision density measurements
- Hall measurements
- TCT for mobility and lifetime
- thin film epitaxy
Effects were studied by comparing the following characteristics of horizontally and vertically grown ZnSe crystals in:

- Grown crystal morphology: contactless growth for the horizontal configuration.
- Surface morphology of the grown crystals was examined by SEM and AFM. (growth was terminated by stopping furnace translation, lowering the source temperature by 10 °C and then cooling the thermal profile at the same rate)
- Segregation and distribution of defects and impurities in the grown crystals was determined by photoluminescence, SIMS and precision density measurements.
Gravity Effects on the Grown Crystals

Morphology of the as-grown crystals:

I. Self-seeded ZnSe: Crystals grown in the horizontal configuration grew away from the ampoule wall with large (110) facets tend to align parallel to the gravitational direction. Crystals grown in the vertical configuration grew in contact with the wall to the full diameter.

II. Seeded ZnSe: the as-grown seeded crystals for the horizontal and vertical configurations showed similar characteristics in the morphology as described above for the self-seeded growth.

As-grown surface morphology:

I. As-grown surface of horizontally grown crystals was dominated by (110) terraces and steps (identified to be (221) in one case).

II. As-grown surface of the vertically grown
(a) Crystals showed granular structure with nanotubes (200nm OD, 75nm ID, 25nm in height for one case on ZnSe) on the top.
(b) Some crystals showed a network of high plateau with each island 30 – 70mm in diameter and 3.5mm in height. Numerous nuclei were observed with diameter 20 - 50nm and height of 1 - 7nm on top of these islands.
Morphologies of Self-seeded Vertically Grown ZnSe Crystals

ZnSe-25: vertically stabilized
ampoule ID: 15mm

ZnSe-31: vertically destabilized
Morphologies of Self-seeded Horizontally Grown ZnSe Crystals

ZnSe-44

ZnSe-43
Gravity Effects on As-grown crystal morphology

• For furnace translation rates higher than the mass flux:
  – In the horizontal configuration the crystal maintained the growth surface morphological stability by (1) self-adjusting the degree of supersaturation to increase the mass flux or/and (2) by reducing the cross section area of the grown crystal.
  – In the vertical configuration the crystal growth surface became morphologically unstable with voids and pipes embedded.

ZnSe-47H 7.5 mm/day  ZnSe-35V 11.4 mm/day
Morphologies of Seeded Vertically Grown ZnSe Crystals

ZnSe(S)-9V → g → ZnSe(S)-12V
Morphologies of the Seeded Horizontally Grown ZnSe crystals

ZnSe(S)-11H

ZnSe(S)-13H

ZnSe(S)-8H
I. Results from SIMS mappings:

For the horizontally grown self-seeded ZnSe crystal [Si] and [Fe] showed clear segregation toward the bottom on the wafer cut axially along the growth axis.

For the vertically grown seeded ZnSe crystal [Si] and [Cu] showed segregation toward the edge of the wafer cut perpendicular to the growth axis.

II. Mappings of PL near band edge intensity ratios indicated:

(1) All the horizontally-grown crystals showed the following trends in the radial and axial segregation of [Al] and [V$_{Zn}$]: [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 last grown region.

(2) The as-grown surface of the seeded vertically stabilized grown crystal showed [Al], [Li or/and Na] and [V$_{Zn}$] segregate radially toward the center.

(3) The as-grown surface of the self-seeded vertically destabilized grown crystal showed [Al] and [V$_{Zn}$] segregate radially without an apparent pattern.

Su et al (1999)
Impurities Distribution by SIMS (horizontally grown)
Impurities Distribution by SIMS (vertically grown)
**Summary on the Photoluminescence $I_2$ and $I_1^{\text{deep}}$ emissions**

**$I_2$ emission:**
- $I_2$, the exciton bound to substitutional donor, emission in our ZnSe samples can be attributed mainly to Al impurity, with $A(I_2)/A(F_x) = 4.88$ corresponding to 1700 ppb, atomic, or $7.46 \times 10^{16} \text{ cm}^{-3}$.
- Isshiki et al. (1991) gave the expression between intensity ratio $(I_2)/(I_{Fx})$ and $N_D$:
  \[
  \log_{10}(I_2/I_{Fx}) = -22.0775 + 1.46268 \log_{10}N_D(\text{cm}^{-3})
  \]
- Therefore, $\left(\frac{I_2}{I_{Fx}}\right) = 82 \left[\frac{A(I_2)}{A(F_x)}\right]$.

**$I_1^{\text{deep}}$ emission:**
- $I_1^{\text{deep}}$ is related to exciton bound to $V_{Zn}$ deep acceptor and $[V_{Zn}]$ is proportional to $A(I_1^{\text{deep}})/A(F_x)$.
- The reaction during Zn vapor annealing:
  \[
  \text{Zn}(\text{g}) + V_{Zn} \rightarrow \text{ZnSe}
  \]
  \[
  K = [V_{Zn}] \times P_{Zn} = K_1 \frac{A(I_1^{\text{deep}})}{A(F_x)} \times P_{Zn}
  \]
- The ZnSe samples were annealed at 1104 °C:
  1. $A(I_1^{\text{deep}})/A(F_x) = 7.52$ when sample is in equilibrium with $P_{Zn} = 6.1 \times 10^{-3} \text{ atm}$ ($\alpha = 6.05$) $A(I_1^{\text{deep}})/A(F_x) \times P_{Zn} = 0.0459 \text{ atm}$.
  2. $A(I_1^{\text{deep}})/A(F_x) = 5.18$ when sample is in equilibrium with $P_{Zn} = 9.0 \times 10^{-3} \text{ atm}$ ($\alpha = 19.43$) $A(I_1^{\text{deep}})/A(F_x) \times P_{Zn} = 0.0466 \text{ atm}$.
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (horizontally grown)
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (horizontally grown)
Distribution of \([V_{\text{Zn}}]\) and \([\text{Al}]\) in ZnSe (vertically grown)

Vertical stabilized configuration
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (vertically grown)

Vertical destabilized configuration
Thin twin lamellae (TL) and three sets of (111) slip bands (S) originating from the lateral twin boundaries.

Synchrotron X-ray Transmission Topography of ZnSe wafer

(a) $g = (133)$

(b) $g = (313)$

(c) $g = (331)$

ampoule wall

$\times$ gravity

(diffraction vector)
Reflection SWBXT image on the as-grown facet of ZnSe-43H showed areas of twins. The crystalline quality is generally good except that the upper region, where the crystal started to grow into full diameter and away from the ampoule wall, showed lattice strain.
In-situ optical monitoring during crystal growth

- Optical absorption for partial pressure measurements along the length of the growth ampoule to measure vapor phase transport species distribution

- Optical interferometry to measure seed thermal etching, instantaneous growth rate and the evolution of surface topography

- Visual observation of the growth evolution
Measured Partial Pressure as a Function of Time
Interferometry Results from Seed Crystal Surface
(Room Temperature)

Fringes from Fabry-Perot Interferometer

Fast/Vai Phase Map of Crystal Surface, (from Fringes)

2.8 (±.5) mm

3.7 (±.5) mm
Interferometry Results from Seed Crystal Surface (at 1120°C)

Fringes from Fabry-Perot Interferometer

Fast/Vai Phase Map of Crystal Surface, (from Fringes)
Synchronized plots of sample temperature and the measured thermal expansion
Thermal Expansion Coefficient of ZnSe from Interferometry

Expansion $\Delta L = n(\lambda/2)$  \[ \lambda = 632.8\text{nm} \quad L_0 = 4.5\text{mm} \]

\[ \frac{\Delta L}{L_0} / \Delta T = 4.95 \times 10^{-6} \text{°C}^{-1} \]

- $4.52 \times 10^{-6} \text{°C}^{-1}$
- $5.23 \times 10^{-6} \text{°C}^{-1}$
- $4.56 \times 10^{-6} \text{°C}^{-1}$
Numerical Modeling of Physical Vapor Transport

- Two dimensional and three dimensional calculations
- Finite element technique - Fidap code
- Thermal and Species induced buoyancy forces
- Compressible or Boussinesq model
- Benchmark - 2D (H$_2$-I$_2$ system - PVT growth)
- ZnSe calculations with residual gas
- Benchmark - 3D (Natural convection in a cylinder)
- 3-D ZnSe calculations with residual gas
- Ongoing and future work

Ramachandran et al. (2000)
The Physical Model

species A (& B) in carrier C

\[ \frac{\partial c}{\partial y} = 0 \]

Dimensionless wall temperature distribution - PVT

\[ 0 = 1 - 3X - 0.0675X^2 \]

Dimensionless distance (X)

Dimensionless temperature (θ)
Benchmark → the H₂-I₂ System

- benchmark calculations by Rosenberger et al. (J. Crystal Growth 51 426 1981; 67 241 1984; 118 49 1992)
- source temperature Ts=370.5 K
- crystal temperature Tc=358.1 K
- ampoule pressure : 100 torr
- I₂ (M=254) is the deposited species and H₂ (M=2.016) is inert
- 2-d Cartesian system
- linear wall temperature
- quasi-compressible and Boussinesq calculations
- Peclet number analysis, Pe ~ 1 for diffusive flow
- growth rate results
3-D Computational Grid and Code Validation Results

* Schiroky and Rosenberger (1984)
Parameters of ZnSe System with Residual Gas

\[ \alpha = 2.9 \]

- density, 1.2x10^{-5} g/cm^3
- dynamic viscosity, 4.3x10^{-5} Pa-s
- kinematic viscosity, 36 cm^2/s
- diffusivity, Zn in N_2, 64.59 cm^2/s
- diffusivity, Se_2 in N_2, 71.46 cm^2/s
- thermal expansion coefficient, 7.1x10^{-4} K^{-1}
- Prandtl number, 0.439
- Schmidt number, Sc_{zn} = 0.557
- Schmidt number, Sc_{se} = 0.503
Velocity Difference Plots - procedure

- calculations for pure diffusion limited conditions, 0g
- calculations for other g conditions, a conditions, etc.
- calculate differences in axial (u) and transverse (v) velocities at all identical grid locations between previous steps; e.g. U(0g) - U(1g) and V(0g)-V(1g)
- contour the velocity differences and plot
- determine g-sensitivity
- Note: all calculations were using the Boussinesq approx.

conventions:

source
y,V

Ts
x,U
crystal
Tc ; [T=T(y)]

θ=0; horizontal
θ=90; vertical stabilized
θ=270; vertical destabilized
Gravity Effect on Velocity Difference (horizontal case)

- g-effects with constant crystal temperature, \( T_c \).
  \[ \Delta U \approx 0.3 \text{ mm/s}; \Delta V \approx 50 \text{ \( \mu \)m/s} \]

- g-effects with crystal temperature variation, \( T_c = T_c(y) \).
  \[ \Delta U \approx 0.3 \text{ mm/s}; \Delta V \approx 43.75 \text{ \( \mu \)m/s} \]

- g-sensitivity (horizontal case) based on max. buoyancy driven flow normal to growth direction is 10% of crystal growth rate (3mm/day or 0.035 \( \mu \)m/s)

\[ \text{transverse acceleration requirement: } \sim 1 \times 10^{-4} g_0 \]
Gravity Effect on Velocity Difference (vertical case)

- g-effects with crystal temperature variation, $T_c = T_c(y)$.
  Stabilized orientation: $\Delta U \sim 23.1 \, \mu m/s; \Delta V \sim 9.4 \, \mu m/s$

- g-effects with crystal temperature variation, $T_c = T_c(y)$.
  Destabilized orientation: $\Delta U \sim 18.1 \, \mu m/s; \Delta V \sim 9.4 \, \mu m/s$

As far as transverse velocity difference is concerned both vertically stabilized and destabilized orientations have similar effects

- g-sensitivity (vertical case) based on max. buoyancy driven flow normal to growth direction is 10% of crystal growth rate (3mm/day or 0.035 \, \mu m/s)

longitudinal acceleration requirement: $\sim 2.7 \times 10^{-3} \, g_o$
• significant flow observed along the ampoule axis (z-direction) indicative of more deposition in the central area than near the walls
• velocity contours in the cross planes (x-y) show appreciable variation only near the end walls (source and crystal)
• species (Zn and Se$_2$) show fairly uniform distributions in the cross planes
• predicted crystal growth rate from 2-D and 3-D calculations are in fair agreement
• 2D and 3D calculations performed for ZnSe system
• Residual gas effects considered
• Calculations show that shear flow velocities of 10 to 50 microns/s are induced by buoyancy effects (290 to 1400 times growth rate)
• $g$-level requirements established based on time scale analysis
  required transverse $g$ level: $< 1.2 \times 10^{-4} g_0$
  required longitudinal $g$ level $< 8.5 \times 10^{-3} g_0$
• It is noted that the Boussinesq model used in the calculations tend to underpredict velocities
Flight Experiments on International Space Station

- The flight experiments will be conducted in the Low Gradient Furnace (LGF) in the Microgravity Science Research Rack (MSRR) on International Space Station (ISS).

- Nine different growth runs will be performed for ZnSe, Cr-doped ZnSe, ZnSeTe, ZnSeS and ZnCdSe materials with different growth parameters.

- The flight experiments are scheduled to commence in late 2015.


Refereed Publications on Vapor Growth


Refereed Publications on Vapor Growth


Refereed Publications on Vapor Growth


“Beer Law Constants and Vapor Pressures of HgI₂ over HgI₂(s,l)”, J. Crystal Growth 235 313-319 (2002).


“Partial Pressures of In-Se from Optical Absorbance of the Vapor”, J. Phase Equilibria 23 397-408 (2002).
