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

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Scientific Objectives

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.
Crystal Growth Activities at MSFC

Technological significance:
Growth (melt and vapor) and characterization of II-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).

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### II-VI semiconducting compounds grown at MSFC

<table>
<thead>
<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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<tbody>
<tr>
<td>Melting points (°C)</td>
<td>670</td>
<td>700</td>
<td>1092</td>
<td>1130</td>
<td>1292</td>
<td>1397</td>
<td>1526</td>
<td>1718</td>
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<tr>
<td>Melt growth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>PVT growth</td>
<td>850</td>
<td>1000</td>
<td>985</td>
<td>1120</td>
<td>1150</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>temperature (°C)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
Results of Cl doped CdTe crystal grown by PVT in microgravity on the EUREKA-1 mission. The plots are two dimensional resistivity distributions mapped across the axial direction of two crystal wafers. The wafer on the left was grown in the microgravity environment, while the wafer on the right was grown on Earth. (Benz, et al. 1997)
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)
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.
Heat Treatment of CdTe Starting Materials

Table 2. Amounts of CdTe loaded, heat treatment conditions, the measured partial pressure of Te$_2$, $P_{Te_2}$, and the calculated pressure ratio, $P_{Cd}/P_{Te_2}$, at 870 °C for as-synthesized and heat treated batches.

<table>
<thead>
<tr>
<th>cell</th>
<th>amount of CdTe (g)</th>
<th>heat-treated temperature (°C)</th>
<th>heat-treated duration (min)</th>
<th>$P_{Te_2} \text{ (atm) at 870 °C}$</th>
<th>$P_{Cd}/P_{Te_2}$ at 870 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td>4.06x10$^{-3}$</td>
<td>1.92</td>
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<tr>
<td>7</td>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td>1.65x10$^{-1}$</td>
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<td>7A</td>
<td>13.0</td>
<td>870</td>
<td>8</td>
<td>3.44x10$^{-3}$</td>
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<td>9</td>
<td>12.4</td>
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<td>-</td>
<td>8.90x10$^{-2}$</td>
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<td>10</td>
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<td>4.95x10$^{-3}$</td>
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<td>870</td>
<td>8</td>
<td>2.74x10$^{-3}$</td>
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<tr>
<td>11</td>
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<tr>
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<td>860</td>
<td>8</td>
<td>2.96x10$^{-3}$</td>
<td>3.11</td>
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<td>13A</td>
<td>17.9</td>
<td>800</td>
<td>8</td>
<td>4.18x10$^{-3}$</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Su et al. (1998)
Optimum Heat Treatments of Starting Materials

$P_{\text{Se}_2}$ in equilibrium with ZnSe for various optical cells

$H_2$ reduction and vacuum treatments for ZnSe(O)-3 established to be the optimum procedure

$$\alpha = \frac{P_{\text{Zn}}}{P_{\text{Se}_2}}$$

Su et al. (1998)
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)
Steps of PVT Seeded Growth of CdTeS-14

1. ampoule as loaded

2. ampoule after soaking at saturated position for 12 hours

3. reinsert ampoule and process PVT growth

The initial position of the growth ampoule needs to be carefully located so that (1) to avoid spontaneous nucleation (2) to sublime part of the single crystal seed but (3) not completely dissolve the seed.
PVT Growth of Various Semiconductors

unseeded growth of CdS

seeded growth of CdS

unseeded growth of PbSe

unseeded growth of ZnTe
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

1. residual gas pressure measurements
2. crystal growth by PVT
3. open ampoule
4. examine interface by SEM, AFM and optical microscope
5. photo documentation
6. slice crystal by wire saw
7. polishing
8. SIMS
9. etch pit density by SEM & optical microscope
10. growth orientation by X-ray (Laue)
11. GDMS & SSMS on crystal & source
12. triple crystal rocking curve
13. synchrotron radiation imaging
14. optical absorption measurements
15. WDS & EDS measurements
16. photoluminescence
17. precision density measurements
18. Hall measurements
19. TCT for mobility and lifetime
20. thin film epitaxy
21. TEM
Gravity Effects on the Grown Crystals

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

ZnSe-31: vertically destabilized

ampoule ID: 15mm
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
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\text{Zn}]:
[Al] segregates radially toward the top and axially toward the first grown region and [V\text{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\text{Zn}] segregate radially toward the center.

(3) The as-grown surface of the self-seeded vertically destabilized grown crystal showed [Al] and [V\text{Zn}] segregate radially without an apparent pattern.
Impurities Distribution by SIMS (horizontally grown)
Impurities Distribution by SIMS (vertically grown)

X gravity and growth direction
**Summary on the I_2 and I_1^{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 7.46x10^{16} cm^{-3}.
- Isshiki et al. (1991) gave the expression between intensity ratio (I_2)/(I_{F_x}) and N_D:
  \[
  \log_{10}(I_2/I_{F_x}) = -22.0775 + 1.46268 \log_{10}N_D(\text{cm}^{-3})
  \]
  Therefore, \( I_2/I_{F_x} = 82 \) [A(I_2)/A(F_x)]

**I_1^{deep} emission:**
- I_1^{deep} is related to exciton bound to V_{Zn} deep acceptor and [V_{Zn}] is proportional to A(I_1^{deep})/A(F_x).
- The reaction during Zn vapor annealing:
  \[
  Zn_{Zn} + V_{Zn} + Zn(g) \rightarrow K = [V_{Zn}] \times P_{Zn} = K_1 A(I_1^{deep})/A(F_x) \times P_{Zn}
  \]
- The ZnSe samples were annealed at 1104 °C:
  1. A(I_1^{deep})/A(F_x) = 7.52 when sample is in equilibrium with P_{Zn} = 6.1x10^{-3} atm (\( \alpha = 6.05 \))
     \( A(I_1^{deep})/A(F_x) \times P_{Zn} = 0.0459 \) atm.
  2. A(I_1^{deep})/A(F_x) = 5.18 when sample is in equilibrium with P_{Zn} = 9.0x10^{-3} atm (\( \alpha = 19.43 \))
     \( A(I_1^{deep})/A(F_x) \times P_{Zn} = 0.0466 \) atm.
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (horizontally grown)
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (horizontally grown)
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (vertically grown)

Vertical stabilized configuration

$A(I_{1^0})/A(F_{1^0})$
Distribution of $[V_{Zn}]$ and $[Al]$ in ZnSe (vertically grown)

Vertical destabilized configuration
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 (H₂-I₂ 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

wall

gravity

Tc

C_{AC}

C_{AS}

Ts

source

wall temperature

wall

\frac{\partial C}{\partial y} = 0

\frac{\partial C}{\partial y} = 0
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 \( T_s = 370.5 \) K
- Crystal temperature \( T_c = 358.1 \) K
- Ampoule pressure : 100 torr
- \( \text{I}_2 \) (M=254) is the deposited species and \( \text{H}_2 \) (M=2.016) is inert
- 2-d Cartesian system
- Linear wall temperature
- Quasi-compressible and Boussinesq calculations
- Peclet number analysis, \( \text{Pe} \sim 1 \) for diffusive flow
- Growth rate results
Parameters of ZnSe System with Residual Gas

\[ \alpha = 2.9 \]

- density, \( 1.2 \times 10^{-5} \) g/cm\(^3\)
- dynamic viscosity, \( 4.3 \times 10^{-5} \) 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, \( 7.1 \times 10^{-4} \) 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:
- Ts
- crystalline
- source: y,V
- 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, $T_c$.  
  $\Delta U \sim 0.3 \text{ mm/s}; \Delta V \sim 50 \mu\text{m/s}$

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

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

  **transverse acceleration requirement:** $\sim 1 \times 10^{-4} g_o$
Gravity Effect on Velocity Difference (vertical case)

- g-effects with crystal temperature variation, Tc = Tc(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, Tc = Tc(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: $\sim 2.7x10^{-3} \, g_0$
3-D Computational Grid and Code Validation Results

* Schiroky and Rosenberger (1984)
ZnSe with Residual Gas - 3D Calculation Results

- 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 Se₂) show fairly uniform distributions in the cross planes
- predicted crystal growth rate from 2-D and 3-D calculations are in fair agreement
Summary of Theoretical Calculation

- 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


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).
Refereed Publications on Vapor Growth
