Bridgman Growth of Germanium and Germanium-Silicon Crystals under Microgravity

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OVERVIEW

• Introduction and FOTON M4 flight

• Sample Setup and Growth Parameters
  • Bridgman growth of Ge:Ga with RMF
  • Bridgman growth of Ge:Ga with Vibration
  • Detached Bridgman growth of Ge-Si
  • Simulations

• Flight and Reference Crystal Analysis
  • Ge:Ga with RMF
  • Ge:Ga with Vibration
  • Detached growth

• Future ISS experiments

• Conclusions
INTRODUCTION

• 3 Bridgman experiments on Ge:Ga and 1 Bridgman experiment on Ge-Si were performed on the unmanned mission FOTON M4 in 2014.
• The experiments were part of the RDGS/ICESAGE projects of ESA/NASA/DLR
• Original objectives:
  • Analyzing segregation transitions (diffusive - laminar flow, laminar - time-dependent flow) in Ge:Ga Bridgman crystals by means of a rotating magnetic field (Exps. “K1”, “K2”)
  • Influencing segregation and interface curvature in Ge:Ga Bridgman crystals by means of axial vibrations (Exp. “K3”)
  • Detached Bridgman growth of Ge-Si (Exp. “K4”)

28.07.2016
POLIZON-Experiments on FOTON-M4
FOTON M4 LAUNCH

Launch: July 18, 2014
Rocket: Soyuz 2-1a

Source: www.federalspace.ru
**FOTON M4 FLIGHT PARAMETERS**

- Launch: July 18, 2014
- Perigee: 258.4 km
- Orbital period: 92.56 min
- Landed: Sept. 1, 2014
- Apogee: 568.7 km
- Orbit inclination: 64.89°

**Typical μg levels**
POLIZON M2 FURNACE

4(+1) Heating Zones
Vacuum furnace
Cartridge diameter 42mm
Max. ampoule diameter 36mm
Automated cartridge exchange
Rotating Magnetic Field
4 TC‘s on the ampoule (flight)

Technical performance:

Long inductor:
induction from 0.1 to 1.0 mT;
frequency from 25 to 200 Hz

Short inductor:
induction from 1 to 4 mT;
frequency from 25 to 200 Hz
## EXPERIMENT TIMELINE

<table>
<thead>
<tr>
<th>Experiment, sample</th>
<th>Date, hh:min (MDT)</th>
<th>Planned duration, hh:min</th>
<th>Real duration, hh:min</th>
</tr>
</thead>
<tbody>
<tr>
<td>K4 GeSi</td>
<td>29.07.2014 10:00 – 01.08.2014 00:09</td>
<td>61:30</td>
<td>62:09</td>
</tr>
<tr>
<td>K1 Ge:Ga</td>
<td>01.08.2014 17:00 – 01.08.2014 07:09</td>
<td>13:30</td>
<td>14:09</td>
</tr>
<tr>
<td>F1 CdZnTe:In</td>
<td>02.08.2014 02:00 – 08.08.2014 20:07</td>
<td>200:00 (100 h. by the contract)</td>
<td>162:07</td>
</tr>
</tbody>
</table>
K1/K2 SAMPLE SETUP

• Gallium-doped Germanium crystals
• {100}-oriented seeds
• Sample divided into two parts: single crystalline doped \((1 \cdot 10^{17} \text{cm}^{-3} \text{Ga})\) lower half, undoped polycrystalline upper half
• pBN crucible, Ta fixation pins for the seed
• Graphite plug with CFC spring to avoid free melt surface
• No inert gas - vacuum

• K1: Transition from diffusive to laminar convection regime (RMF)
• K2: Transition from laminar to time-dependent convection regime and back (RMF)
RMF TESTS

measured induction, mT

specified induction, mT

- 25 Hz (1000 C)
- 50 Hz (1000 C)
- 100 Hz (1000 C)
- 25 Hz (RT)
- 50 Hz (RT)
- 75 Hz (RT)
- 100 Hz (RT)
RMF – INDUCTION DISTRIBUTION

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K1 GROWTH PARAMETERS

Timeline K1

- H1 (1025 °C)
- H2 (1015 °C)
- H3 (1020 °C)
- H4 (982 °C)
- Translation
- RMF

temperature [°C]

time [h]

RMF 0.2 mT; 25 Hz
Translation 12 mm/h
RMF 0.2 mT; 25 Hz
K1 PARAMETERS - MEASURED
K1 TEMPERATURE PROFILES

TC positions

Temperature, °C

0 200 400 600 800 1000 1200

Time, date hh:mm

01/08/14 6:00 01/08/14 9:30 01/08/14 13:00 01/08/14 16:30 01/08/14 20:00 01/08/14 23:30

T1
T2
T3
T4
K1 TEMPERATURE PROFILES

Temperature, °C

Length, mm

- Preflight 11.2013
- Flight translation_start
- Flight RMF_switch-on
- Flight translation_end
K2: CRITICAL TAYLOR NUMBER

Unsteady flow

Steady flow

Length of melt, mm

Taylor number

1.E+07

1.E+06

1.E+05

1.E+04

1.E+03

0 10 20 30 40 50 60 70 80 90

28.07.2016

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K2 PARAMETERS - MEASURED

Temperature, °C

Time, date hh:mm

Induction, mT

Temperature, °C

Induction, mT

Time, date hh:mm

Temperature, °C

Induction, mT

Time, date hh:mm

Temperature, °C

Induction, mT

Time, date hh:mm

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Temperature, °C

Induction, mT

Time, date hh:mm

Temperature, °C

Induction, mT

Time, date hh:mm
K2 TEMPERATURE PROFILES

POLIZON-Experiments on FOTON-M4
K2 TEMPERATURE PROFILES

![Graph showing temperature profiles over length, with labels for different conditions: K1_0h translation, K2_0h translation, K1_3h translation, K2_3h translation, K1_end translation, K2_end translation. Temperature is measured in °C, and length is measured in mm.]
K3 SAMPLE SETUP

- Gallium doped Germanium crystals, \{100\}-oriented seed
- Sample divided into a single crystalline doped \((1 \cdot 10^{17} \text{cm}^{-3} \text{Ga})\) lower half and undoped poly-crystalline upper half
- pBN crucible and seed are connected to the vibration motor by a Ti tube
- Graphite plug with CFC spring to avoid free melt surface
- No inert gas - vacuum

28.07.2016 POLIZON - Experiments on FOTON - M4
K3 VIBRATION CALIBRATION

Driving Coil Characteristics - Comparison with Russia

- Idr. at 200Hz [mA]
- Idr. at 100Hz [mA]
- Idr. at 50Hz [mA]
- 50 Hz No Load
- 50 Hz 400 g Load
- 50 Hz 800 g Load
- 100 Hz No Load
- 100 Hz 400 g Load
- 100 Hz 800 g Load
K3 VIBRATION CALIBRATION
K3 VIBRATION CALIBRATION

Sample Displacement

Amplitude [µm]

Driving Coil Voltage [V]

- 50 Hz No Load
- 50 Hz 400 g Load
- 50 Hz 800 g Load
- 100 Hz No Load
- 100 Hz 400 g Load
- 100 Hz 800 g Load

Growth experiment
**K3 VIBRATION CALIBRATION**

1g growth experiment

![Graph showing current strength and amplitude over time](#)
K3 PARAMETERS - MEASURED

[Graph showing temperature and current over time with specific intervals for vibrations and translation speed.]
K3 TEMPERATURE PROFILES

TC positions

Temperature, °C

Time, date hh:mm

28/07/14 13:00 28/07/14 16:00 28/07/14 19:00 28/07/14 22:00 29/07/14 1:00 29/07/14 4:00 29/07/14 7:00

POLIZON-Experiments on FOTON-M4
K3 VIBRATION AMPLITUDES

POLIZON - Experiments on FOTON-M4
**Sufficient condition for detachment**\(^{1,2}\):
\[ (\alpha + \theta \geq 180^\circ) \]

**Advantages**
- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination

**K4 BACKGROUND**

FOTON M3 (2007) detached µg Bridgman experiment on Ge-Si (2%Si):

- Initial growth w/o pulling for a few mm - „normal“ detachment
- Formation of a large free melt zone when pulling
- → Unstable detachment
- → strong thermocapillary convection
- → change of interface curvature 24.7 mm 4.5 mm 19.0 mm 50.0 mm
K4 Sample Setup

- $\text{Ge}_{1-x}\text{Si}_x$ crystals ($x \approx 0.03$ in the melt)
- (100)-oriented undoped Ge as seed
- Sample divided into 3 parts: single crystalline undoped lower part, undoped Si wafer, single crystalline undoped upper Ge part
- pBN crucible, Ta fixation pins for the seed
- Quartz glass plug to avoid SiC formation
- No inert gas - vacuum
- No pressure difference between top and bottom volumes (vacuum, holes for seed fixation)
K4 PARAMETERS - MEASURED

Graph showing temperature over time with different rates:
- 0.5 mm/h
- 1.0 mm/h
- 5 mm/h

Legend:
- H1
- H2
- H3
- H4
- Scheduled
K4 TEMPERATURE PROFILES
SIMULATIONS

- **Geometry based on FM/RM ampoules**
  (only melt and crystal/seed)

- **Defined heat flux**
  (crucible bottom, mounting holes)

- **Time dependent temperature profiles**
  \( T(t, y) \)
  (melt/crucible, UDF/C++)

- **Low resolution / high resolution grid**
  ~200,000 cells / ~400,000 cells
SIMULATIONS K1/K2

temperature distribution $T(t,y)$

divergence from measured data
SIMULATIONS K1/K2

- 1g along $\vec{y}$ (UDF/C++)
  K1-009-RM, K2-007-RM
- Rotating $\mu g$-vector (UDF/C++)
  based on flight data
- Ga Doping (Ansys Fluent species module)
- RMF (Ansys Fluent MHD module)
1g along \(-\ddot{y}\) (UDF/C++)
K3-006-RM

- Rotating \(\mu g\)-vector (UDF/C++)
  based on flight data
K3-004-FM

- Ga Doping
  (Ansys Fluent species module)

- Vibration (UDF/C++)

\[ \nu(t) = A 2\pi f \cos(2\pi f t) \]
SIMULATIONS K3

Velocity Vectors Colored By Velocity Magnitude (m/s) (Time=1.0822e+04)

ANSYS Fluent Release 16.1 (3d, dp, pbns, lam, transient)
CRYSTAL PREPARATION

- Visual Inspection of the ampoule after the experiment
- Disassembly of all ampoule parts
- Visual Inspection of the crystal
- Axial section by inner diameter saw (IKZ Berlin)
- Grinding and polishing
- Etching (striations)
- Analysis (Profilometer, NDIC microscopy, 4-point-probe, EDX, X-ray topography, …)
K1 - RESULTS

- Detachment of the flight crystal despite the CFC spring
- Both μg and 1g samples are single crystals
- No dopant striations visible in the grown crystals
**K1: AXIAL SEGREGATION**

- **µg crystal** shows mostly diffusive behaviour in the detached region and a decrease in Ga concentration at the beginning of the rotating magnetic field phase.
- The curvature changes from mostly diffusive behaviour (Tiller) to complete mixing (Scheil).
- Reference crystals show the typical distribution for complete mixing, no visible change at the switching point of the rotating magnetic field.

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**µg: K1-004-FM**

- Detached region
- 0.2 mT, 25Hz

**1g: K1-009-RM**

- K1-009-RM axial
- Scheil
- Tiller
- C(0)
LAUE X-RAY TOPOGRAPHY

X-ray camera
back reflection

white beam

crystal

goangiometer

double slit

white beam

X-ray camera
transmission

h₁k₁l₁

Pb - absorber

h₂k₂l₂
X-RAY TOPOGRAPHY AT ANKA, KIT

1. Be-window
2. Fast shutter
3. Double slit
4. Back reflection film camera
5. Sample on two-circle goniometer
6. Transmission film camera

X-RAY TOPOGRAPHY AT ANKA, KIT

POLIZON-Experiments on FOTON-M4

28.07.2016
**K1: DISLOCATIONS**

Synchrotron topography image $\mu$g

NDIC image $\mu$g

Dislocation density $\mu$g: $3 \cdot 10^2 - 5 \cdot 10^3$ cm$^{-2}$

Synchrotron topography image 1g

Dislocation density 1g: $\approx 5 \cdot 10^4$ cm$^{-2}$
• Detachment of the flight crystal despite the CFC spring
• Both µg and 1g samples are single crystals
• No striations visible in the grown crystals
**K2: AXIAL SEGREGATION**

- Both µg and 1g crystals show similar overall behavior
- A small deviation during the first growth stage in the µg-crystal
- Drop at switching point of the rotating magnetic field in both cases
K2: DISLOCATIONS

Synchrotron topography image µg

NDIC image µg

Dislocation density µg: $3 \cdot 10^3 - 8 \cdot 10^3$ cm$^{-2}$
Flight sample starts to become polycrystalline from one side, reference sample is single crystalline

No striations visible in the grown crystals
The µg crystal shows a constant concentration during the 1st vibration stage and a decrease in Ga concentration at the beginning of the 2nd, but with disturbances.

Vibration shows an effect on segregation - the resulting profile is neither Scheil or Tiller-like.

The reference crystal shows the typical distribution for complete mixing. No visible change during vibration → buoyancy convection is stronger.
SIMULATIONS K3 – 1g – no vibration
SIMULATIONS K3 – 1g
SIMULATIONS K3 – 1g cont’d
SIMULATIONS K3 – 1g cont’d
SIMULATIONS K3 – $\mu g$
SIMULATIONS K3-μg-Ga concentration
**K4 - RESULTS**

- Successful detachment over 21.4mm → wetting angle is sufficient for detachment w/o pressure difference
- Polycrystalline growth after 3 mm (µg) and 7 mm (1g) due to constitutional supercooling
- Both samples show strong striations, more visible in the flight sample
- Striations are also visible in the attached area (!)

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**µg: K4-004-FM**

**1g: K4-005-RM**

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28.07.2016
POLIZON-Experiments on FOTON-M4
- Profiler measurements on 10 different radial positions (only one example shown)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean Max. Detachment [µm]</th>
<th>Max. Length [mm]</th>
<th>Min. Length [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1-004-FM</td>
<td>450</td>
<td>14.5</td>
<td>13.3</td>
</tr>
<tr>
<td>K2-Flight</td>
<td>500 (strong variation)</td>
<td>12.1</td>
<td>1.3</td>
</tr>
<tr>
<td>K4-004-FM</td>
<td>500</td>
<td>21.4</td>
<td>21.0</td>
</tr>
</tbody>
</table>
K4: AXIAL AND RADIAL SEGREGATION

μg: K4-004-FM

• Only ~3 mm of single crystal region due to constitutional supercooling
• Higher increase of Si content compared to previous experiments due to use of rotating magnetic field + detachment (solutocapillary flow), also increased max. value
• Increase over the whole detachment region
• Radial distribution follows the visible striations
• Only ~7 mm of single crystal region, also constitutional supercooling visible
• Higher increase of Si content compared to test experiments due to use of a rotating magnetic field, but lower than μg sample, also increased max. value
• Increase only until switching point, 2nd switching point more noticeable here
• Radial distribution follows the visible striations
K4: DISLOCATIONS $\mu g$

Synchrotron topography image $\mu g$

NDIC image $\mu g$

Dislocation densities $\mu g$ and $1g$:
$3 \cdot 10^5$ cm$^{-2}$
K4: DISLOCATIONS 1g

Dislocation densities $\mu g$ and 1g:
$3 \times 10^5$ cm$^{-2}$
A series of 10 Ge$_{1-x}$Si$_x$ (x: 0-0.02) samples will be processed in the Low Gradient Furnace (LGF) in the Materials Science Research Rack (MSRR) on the ISS. The samples are currently scheduled to be launched to the ISS in 2017.

The experiments will vary parameters that are key to a better understanding of the theory of detached growth: pressure differential across the meniscus, contact angle, growth angle, and Bond number (ratio of capillary and gravitational forces).
CONCLUSIONS

• All experiments on FOTON M4 were successful and yielded crystals for analysis

• Both the K1 and K2 crystals grew partially detached

• The K4 µg crystal is symmetrically detached over the whole circumference and over 21.4 mm length, whereas the 1g reference crystal is attached

• The K3 vibration experiment crystals show a visible effect on the segregation in the µg crystal, not visible in the 1g crystal

• An experimental parametric study of detachment (“ICESAGE“) is planned for 2017/18 on the ISS
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