Synthesis and Crystal Growth in the US

Presented by:
David Bliss, President
American Association for Crystal Growth
US Crystal Growth Research

For Inorganic Materials

- Industrial - 30% of members
  - Small-business SBIRs
  - Systems houses IR&D
  - Equipment suppliers
- Academic Institutions - 35% of members
  - Contractual with government or industry
- Government Laboratories - 35% of members
  - Focused on mission applications
Crystal growth personnel

US Employment of R&D Scientists and Engineers

- **Bulk crystal growth** – 25% (200-300)
  - Melt growth
  - Solution growth
  - Hydrothermal growth
  - Physical vapor transport

- **Epitaxial crystal growth** – 75% (600-1000)
  - Molecular beam epitaxy (MBE)
  - Organometallic vapor phase (OMVPE)
  - Hydride vapor phase (HVPE)
Bulk Crystal Markets

US Suppliers of Single Crystals

- **Czochralski growth**
  - Silicon – other than MEMC, entirely foreign owned
  - Oxides - many small business suppliers
  - Compound Semiconductors – weak US presence

- **Solution Growth**
  - Optical crystals – Corporate and Gov’t Laboratories
  - Gemstones – Commercial companies

- **Zone melting**
  - Specialty oxides - Academic sources
20th Century Success Stories

Technologies dependent on and driven by Crystal Growth

- Computers - Silicon
- Global Positioning - Quartz
- Cellular Phones - Gallium arsenide
- Lasers - Ruby, YAG, oxides
21st Century Challenges

Next Generation Technologies Requiring Crystal Growth

- Green Energy Lighting - Gallium Nitride
- Detectors for WMD - Scintillators
- InfraRed Optics - Semiconductors
- Space Communications - Antimonides
- High Q Timing Devices - Langasite

Who is paying the bill?
White Light Crystals

Solid-State Replacements for Light Bulbs

- Gallium Nitride-based LEDs
  - No commercially available substrate GaN crystal
  - Research using high pressure autoclaves
    - Gov’t Labs in Poland and US
  - No National Program for GaN crystal development
    - Sporadic funding through SBIRs
    - Japanese Industry/Gov’t funding Polish and UCSB effort
Infrared Detectors

For IR Focal Plane Arrays

- HgCdTe-based detector arrays
  - No US vendor of Substrate Crystals
  - DoD relies on foreign sources

- Indium Antimonide Focal Plane Arrays
  - Present day: 2-inch diameter growth technology
  - Mandate for scale-up to 6-inch diameter wafers
    - Funded by SBIRs
Next-generation Piezoelectrics

Crystals for Timing and Sonar

- After quartz, what crystals will operate at higher frequency?
  - Langasite Crystals of high quality
  - Cannot be grown by conventional means
    - Solution growth - academic effort at UCF

- After Lead Zirconate, what crystals will give higher power?
  - Relaxor ferroelectrics – PMN alloy crystals
    - Mainly funded through SBIRs
What future course of action?

- **What are US future needs?**
  - Is there a market?

- **What is the state of existing US technology?**
  - Corporate, Academic, and Government Labs

- **What are the obstacles to crystal growth?**
  - Technical challenges
Crystal Growth Operations

- Over 100 US companies
  - List of crystal suppliers
  - Updated by AACG
  - Small businesses
    - Commercial vendors
  - Systems houses
    - Captive suppliers

Factory floor at CC Tech
State of Existing US Technology
Where the jobs are

1. **Conservative methods**
   - Batch processes – conservation of mass
     - Czochralski method (Cz, LEC, MLEC)
     - Bridgman method (VB, HB)

2. **Non-Conservative methods**
   - Continuous processes – melt replenishment
     - Zone Melting
     - Traveling heater method
     - Continuous feeding methods
Obstacles to Growth

New crystals require advanced crystal growth methods

- Non-congruently melting crystals
  - Stoichiometry is difficult to achieve
- Alloy segregation during growth
  - Non-Uniform composition of crystal
- Metastable phase formation
  - Cannot grow at melting temperature
- Miscibility Gaps
  - Phase separation occurs
Non-congruent crystals

- Congruent melting point

*Differs from*

- Crystal Stoichiometry
  - Examples:
    - Lithium Niobate
    - Langasite
    - Bismuth Titanate

AB Compound

Lithium Tantalate Crystals
Congruent vs. Stoichiometric

- **Lithium Niobate Growth**
  - Congruent crystals
    - Periodically poled LN
    - (PPLN)
    - Poor properties in green
  - Stoichiometric Crystals
    - Difficult to grow
    - Efficient PPLN in green

Lithium Niobate Crystals
Efforts to Control Segregation

- Major cause of non-uniformity in crystals
  - Solution A: reduce melt convection
    - Diffusion controlled regime
    - Similar to microgravity conditions
  - Solution B: increase stirring
    - Reduce boundary layer thickness
    - Melt replenishment needed
Model for Magnetic Stabilization

One recent example

- High pressure chamber
  - Synthesize volatile melts

- Strong Magnetic Field
  - Control turbulence

- 6-inch diameter crystal
  - Control shape
  - Maintain crystal structure
Magnetic LEC Crystal Puller

For Synthesis and Growth of Indium or Gallium Phosphide

- High pressure chamber
- 2kG Helmholtz Coil
- Multi-zone heaters
- 50kW power supply
Magnetic Stirring

Another approach:

- To induce melt stirring:
  - Rotating field
  - Alternating field
  - Traveling field
- For uniform composition
  - Alloy crystals
Crystal Growth under Applied Fields

- Magnetic
- Electric
- Gravitational
- Vibration frequency

The state-of-the-art in bulk crystal growth

Ongoing research efforts in:
- Germany
- France
- Japan
Metastable Phase Growth

- Wrong Crystal Structure at Melting point
  - Equilibrium phase is not desired
  - Cooling through phase change
    - Results in cracking
  - Examples:
    - Barium borate - $\beta$ phase
    - Quartz - $\alpha$ phase

$\beta$ – Barium Borate
Crystals with Miscibility Gaps

- **Alloy composition is limited under equilibrium growth conditions**
  - Examples:
    - InGaSb - IR detectors, mid IR lasers
    - InGaN - Green and Blue Lasers, LEDs

- **Require non-standard growth methods**
  - High pressure
  - Low temperature

Lattice matching
Crystal growth funding in the US

- Corporate
  - High market volume crystals: silicon, quartz
    - Ownership is now offshore
  - Military market: defense contractors
    - No requirement for US materials
  - Telecom market: lasers and microwave devices
    - Fragmented post dot-com boom
  - Niche markets: medical, spectroscopy, space, etc.
    - Over 100 small companies, many SBIRs
US Funding for Crystal Growth

- **Academic**
  - Focus has turned to nano-technology
  - NASA’s microgravity program terminated 2004
  - Many groups have disintegrated
    - Renewed funding at NSF may help reverse this

- **Government Laboratories**
  - DoD, DOE are highly focused on applied research
  - NIST, NREL have primary missions
    - If budget is passed, the ACI initiative will help
Where is the potential support for crystal growth?

- **US Basic research budget**
  - 6.1 DoD basic research
  - DOE basic energy science program
  - NSF, NIST American Competitiveness Initiative

- **SBIR Program – 2% of gov’t procurement**
  - Heavily competitive with device applications

*Can these funds be directed toward crystal growth?*
Where do we go from here?

- The US crystal growth community is ready for change
  - Dispersed and diffuse, there is no single concentration of talent
  - To the question; “Is there a market?”
    - We need to establish small “markets”
    - Sponsor advanced topics for crystal growth research
- Need a forum where Academic, Government, and Corporate participants can interact
“Who dominates materials dominates technology”

Prophetic saying of Dr. Tadahiro Sekimoto, Japanese businessman and scientist who rose to be the chairman of NEC
List of Companies doing Crystal Growth in the US

Advanced Photonic Crystals—Hydrothermal KTP, vanadates and other oxides
Alfalight—Diode laser materials
Amberwave—Strained silicon and compound semiconductors
Apollo Diamonds—Gem quality diamonds
ASE Americas (now owned by Schott Solar)—Solar silicon
AXT, Inc.—GaAs, InP, Ge
BP Solar—Solar silicon
Ceres Crystal Industries—Skull melting of cubic zirconia
Ceramare Corporation—Crystal growth and fabrication
Cermet—Zinc oxide
Chatham Created Gems—Artificial gems
Cleveland Crystals—Nonlinear optical materials
Coherent Advanced Crystal Group—Nonlinear optical materials
Commercial Crystal Laboratories—Potassium tantalate and other oxides
Corning—Basic research in a variety of crystal growth areas, including III-V laser materials
Cree Research—Silicon carbide
Crystacomm Inc.—InP
Crystagon Inc.—Magnesium fluoride
Crystal Genesis—Top seeded solution growth of oxides
Crystal IS, Inc.—AlN
Crystal Photonics—Crystals for scintillators
US Crystal Growth Companies (2)

Crystal Specialties—GaAs
Crystal Systems, Inc.—Sapphire, silicon
Crystal Technology, Inc.—Lithium niobate, lithium tantalate, tellurium oxide
CTI PET Systems (Knoxville, TN) —Scintillator crystals
Deltronic/Isowave—Lithium Niobate, yttrium iron garnet
Diamond Innovations—Industrial and colored diamonds
Dow Corning Compound SemiconductorSolutions—Silicon Carbide
Emcore—Photovoltaics
Evident Technologies—Quantum dots
Evergreen Solar—Solar silicon
Galaxy Semiconductor—InSb and GaSb
General Electric—Industrial diamond, single crystal superalloys
Honeywell—Sapphire
Howmet (division of Alcoa)—Single crystal nickel-based superalloys for gas turbine blades
HRL Laboratories—Lasers, nonlinear optics II-VI sensor materials
IBM—Basic research in a variety of crystal growth areas, including Si, SiGe, nanocrystallization
II-VI, Inc.—II-VI compounds and wide bandgap semiconductors
VLOC (a subsidiary of II-VI) —YAG, fluoride laser hosts
eV Products, Inc. (a subsidiary of II-VI)—CdTe, CdZnTe
US Crystal Growth Companies (3)

Inrad—Nonlinear optical crystals
Integrated Photonics, Inc.—Garnets (mostly magnetooptic), perovskites, other oxide materials
Intrinsic—SiC
IQE—Semiconductor wafer products
Isomet Corporation—Acousto-optic materials
ITT Night Vision—Epitaxial GaAs for image intensifiers
Keystone Crystal Corporation—CdTe
Kopin—Epitaxial GaAs for transistor applications
Laser Crystal Corp—Ruby
Laser Materials Corp—Nd:YAG
M/A-COM (Tyco Electronics)—GaAs and InP
MEMC—IC grade silicon
Microlink Devices—MOCVD of III-V materials
Northrop Grumman Space Technology—GaAs
Synoptics—Laser host crystals
Novalux—Display materials
Ocean Nanotech—Quantum dots
Philips-Lumileds—All sorts of LEDs
Princeton Lightwave—Epitaxial III-V films
US Crystal Growth Companies (4)
Quantum Dot Corporation—Quantum dots
Radiation Monitoring Devices—Radiation detection materials
Rubicon Technology, Inc.—Kyropoulos Sapphire
Saint Gobain
Formerly Saphikon—Sapphire
Formerly Bicron and Harshaw—Scintillation products
Photonic crystal products (Washougal, WA, formerly owned by Union Carbide)—Sapphire, ruby, Ti:sapphire, doped YAG
Sarnoff Laboratories—Basic research in a variety of crystal growth areas, including lasers and detectors
Sawyer Research Products, Inc.—Hydrothermal quartz
Scientific Materials (Bozeman, MT)—Electro-optic crystals
Semiconductor Technology Research—Epitaxial semiconductors
Sensors Unlimited (now owned by Goodrich Corporation)—InGaAs devices
Solaicx—Solar silicon
Spectrolab—Compound semiconductor and lighting products
Spire Bandwidth Semiconductor—Custom compound semiconductor epitaxy
Technologies and Devices International, Inc. (TDI, Inc.)—GaN
Triquint Semiconductor—Epitaxial GaAs
Trumpt Photonics—Diode laser materials
Uniroyal Optoelectronics—LED materials
Zia Laser—Quantum dots