GERMANY,
JUNE 15 - 19

BERLIN 2014

6th International Workshop on Crystal Growth Technology

IWCGT-6

THE FUTURE OF CRYSTAL GROWTH TECHNOLOGY – BRINGING NEW TECHNOLOGIES TO INDUSTRIAL GROWTH APPLICATION

Advances in bulk crystal growth of semiconductor & photovoltaic materials

Optical and laser crystals

Scintillators, piezo- and magnetoelectrics

Substrates for wide band-gap and oxide semiconductors

Growth control, quality assurance, and management of resources

Crystal shaping and layer transfer technologies

Frontiers in crystal growth technology

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Leibniz Institute for Crystal Growth (IKZ)

International Organization for Crystal Growth

The Organizing Committee would like to acknowledge support provided by

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6th International Workshop on Crystal Growth Technology

Berlin, Germany June 15 - 19, 2014

Welcome message

Dear participants of the IWCGT-6,

a warm welcome to you, and sincere thanks that you take part in this exciting event, the 6th International Workshop on Crystal Growth Technology (IWCGT-6) held at June 15-19, 2014 at the Novotel Am Tiergarten, Berlin, Germany. The workshop is organized by the Leibniz Institute for Crystal Growth (IKZ) Berlin, Germany, under the auspices of the International Organization for Crystal Growth (IOCG).

This workshop has already a long-standing history. Initiated by Hans Scheel in 1998 and held four times in Beatenberg, Switzerland, the workshop was originally intended to be a familiar meeting „by invitation only“ of experts in crystal growth technology, with a focus lying on the preparation of bulk and substrate crystals. The idea at that time was to gather those crystal growers who were active in the field of tension between R&D and the actual production, to discuss issues which go beyond academic treatment as presented e.g. in the existing series of crystal growth conferences. Clearly, this mission has not changed over time.

As the interest in this workshop kept on growing, the steering committee decided to switch to a more open format, between school and lecture. At the same time, the workshop re-located to Berlin, Germany. At the IWCGT-5 held in 2011, only keynote lectures were presented orally, were while the contributed papers were discussed in two lively poster sessions. This meeting was a great success with over 170 attendees from all over the world. Especially the idea of long coffee breaks and an extended boat tour with dinner to stimulate discussions and provided networking opportunities proved extremely fruitful. So we have adopted this format for the current IWCGT-6 and hope you‘ll experience this collaborative workshop flair.

Crystal growth technologists provide the backbone of today‘s technology and thus clearly contribute to solving the grand challenges of mankind. To produce crystals of higher perfection and at lower cost is a prerequisite for their application in new and efficient devices and functionalities in a rapidly changing world. In this workshop, we intend to discuss the latest developments in crystal preparation, industrial production, machining, and equipment. The workshop is grouped into sessions highlighting different categories of materials. The broad spectrum will allow for a good overview on the very different growth technologies that have been developed to provide the most useful crystals for different materials and applications. This will enable opportunities for sharing ideas and cross-fertilizing existing technologies. Additional sessions are concerned with important crystal growth technology related processes such as growth control, management of resources, layer transfer technologies, and emerging growth technologies. Finally, the start of the workshop is provided by a panel discussion on one of the most critical points in crystal growth technology development: How to bring new technologies to industrial growth application?

The IWCGT-6 would like to provide a forum where science meets practice, i.e., where industry and academia can establish a profitable dialog. We hope that this workshop is most productive and efficient to you in terms of establishing new collaborations, partnerships, and generating new ideas.

Finally, we would like to thank all the members of the steering committee, the session chairs, the invited speakers, our exhibitors and sponsors, and—last but not least—the IKZ local organization team for their most valuable contributions.

Enjoy the IWCGT-6!

Matthias Bickermann, Chung-Wen Lan, Peter G. Schunemann

IWCGT-6 chairpersons

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Local Organization

The IWCGT-6 is organized by members of the Leibniz-Institute for Crystal Growth (IKZ).

- Sabine Bergmann (website, flyer, abstract book)
- Matthias Bickermann (chair)
- Christiane Frank-Rotsch (program)
- Steffen Ganschow (program)
- Christo Guguschev (program, gala dinner)
- Andrea Lepper (organization, gala dinner)
- Robert Menzel (organization)
- Uwe Rehse (registration, organization)
- Maike Schröder (organization, sponsoring)
- Dietmar Siche (program)

Workshop Program - Sunday, June 15

16:10	Registration
18:00	Dinner
Panel	**The future of crystal growth technology – bringing new technologies to industrial growth application** Chairs: Peter Rudolph (Crystal Technology Consulting, Germany), Jochen Friedrich (Fraunhofer IISB, Germany)
19:15	**Norbert Thiel (PVA Tepla, Germany)** **Alexander Gektin (Institute for Single Crystals, Kharkov, Ukraine)** **Dirk Ehrentraut (Soraa, USA)** **Edith Bourret-Courchesne (Lawrence Berkeley National Laboratory, USA)** **Xingming Huang (JA Solar, China)** **Koichi Kakimoto (Kyushu University, Japan)**
21:45	End

Workshop Program - Monday, June 16

Session 1		**Advances in bulk crystal growth of semiconductor & photovoltaic materials** Chair(s): Nathan Stoddard (SolarWorld USA), Maria Porrini (SunEdison, Italy)
08:30	S1 / oral 1	Steven Kimbel (MEMC Electronic Materials, USA) **Development of 450 mm Semiconductor Silicon Crystal Process**
09:20	S1 / oral 2	Wilfried von Ammon (Von Ammon Consulting, Germany) **FZ and CZ Silicon Crystal Growth: Cost Driving Factors and New Perspectives**
10:10		Coffee
10:30	S1 / oral 3	Koichi Kakimoto (Kyushu University, Japan) **Understanding and Control of Silicon Crystal Growth for LSIs and PVs**
11:20	S1 / oral 4	Etienne Pihan (CEA-INES, France) **Status and industrial future of DW wafered mono-like silicon crystals grown by directional solidification for high efficiency solar cells**
12:10		Break
12:30		Lunch
Session 2		**Optical and laser crystals** Chair: Reinhard Uecker (IKZ Berlin, Germany)
14:00	S2 / oral 1	Xutang Tao (State Key Lab of Crystal Materials, Shandong University, China) **Crystal growth of nonlinear optical properties of $BaTeMo_2O_9$**
14:50	S2 / oral 2	Christian Kraenkel (University of Hamburg, Germany) **Growth by the Heat Exchanger Method and Llaser Operation of Rare-earth Doped Sesquioxides**
15:40		Coffee
16:10	S2 / oral 3	Ludmilla Isaenko (Russian Academy of Sciences, Novosibirsk, Russia) **Growth of bulk nonlinear crystals $LiBC_2$**
17:00	S2 / oral 4	Joseph Kolis (Clemson University, USA) **The Hydrothermal Method of Single Crystal Growth**
17:50		Break
18:00		Dinner
19:10		Industrial Session
19:15		Industry 1
20:00		Poster 1
21:45		End

Poster Presentation - Monday, June 16

	Advances in bulk crystal growth of semiconductor & photovoltaic materials
P1.01	Michael Gonik (University of Freiburg, Germany) **Segregation control in crystal growth of SiGe alloys from a thin melt layer**
P1.02	Ellen Hedegaard (Aarhus University, Denmark) **Functionally Graded Thermoelectrics by Bulk Crystal Growth**
P1.03	Roland Kunert (Fraunhofer CSP, Germany) **Silicon Float-Zone Crystals from low-cost Feed-Material**
P1.04	Chung-Wen Lan (National Taiwan University) **Grain Structures of Multi-crystalline Silicon Grown By Using Patterned Crucibles**
P1.05	Zaoyang Li (Xi‘an Jiaotong University, China) **Evaluation of seed crystal reuse for cast quasi-single crystalline silicon ingots**
P1.06	Satoshi Nakano (Kyushu University, Japan) **Effect of top and side heaters during two growth process on oxygen concentration, dislocation density and residual stress in a multicrystalline silicon for solar cells**
P1.07	Xiaofang Qi (Xi‘an Jiaotong University, China) **Modeling of three-dimensional heaters in numerical simulation of an industrial directional solidification furnace**
P1.08	Kirils Surovovs (University of Latvia) **Modelling of dopant transport during floating zone growth of silicon**
P1.09	Amina Tandjaoui (CNRS-SIMAP, EPM, France) **Grain Structure of Multi-Crystalline Silicon: X-ray Synchrotron Imaging Characterisation**
P1.10	Yutao Tao (University of Minnesota, USA) **Modeling of Particle Engulfment during the Growth of Multicrystalline Silicon for Solar Cells**
P1.11	Satoshi Watauchi (University of Yamanashi, Japan) **Feed size dependence of suitable mirror position for silicon crystal growth by infrared convergent heating floating zone method**

Poster Presentation - Monday, June 16

	Optical and laser crystals
P2.01	Derradji Bahloul (Université El-Hadj-Lakhdar de Batna, Algeria) **The crystal growth process of titanium doped sapphire fibers by the micro-pulling down technique**
P2.02	Omar Benamara (Claude Bernard University Lyon1, France) **Bubbles defects observation during shaped sapphire crystal grown by the micro-pulling down techniques**
P2.03	Aleksey Brykovskiy (Lomonosov Moscow University, Russia) **Nonstoichiometry and defect formation in scheelite-like double tungstates grown by the Czochralsky technique**
P2.04	Joseph Daniel (SSN College of Engineering, Kalavakkam, India) **Growth and thermoluminescence studies on rare earth orthogallate ($NdGaO_3$) single crystal by Floating zone technique**
P2.05	Jindřich Houžvička (CRYTUR, Czech Republic) **Growth of very large, stress-free YAG crystals with a new method**
P2.06	Liudmila Ivleva (A.M.Prokchorov General Physics Institute RAS, Russia) **Investigation of Second Harmonic Generation in SBN Crystals**
P2.07	Zhitai Jia (Shandong University, China) **Growth of Nd:GGG crystals with the diameter up to 190 mm by Czochralski method**
P2.08	Tetsuo Kudo (Tohoku University, Japan) **Growth of $Ca_3Ta(Ga_{1-x}Al_x)_3Si_2O_{14}$ piezoelectric single crystals by Czochralski method and their piezoelectric properties**
P2.09	SP. Prabhakaran (Bharathidasan University, Tamil Nadu, India) **Growth and optical studies of bulk 4-Aminobenzophenone single crystal by modified vertical dynamic gradient freeze technique**
P2.10	Mitsuyoshi Sakairi (OXIDE Corporation, Japan) **Czochralski growth of ferroelectric $LaBGeO_5$ single crystals for UV-generation**
P2.11	Masahiro Sasaura (OXIDE Corporation, Japan) **Single crystal growth of $KTa_xNb_{1-x}O_3$ by the Bridgman method**
P2.12	Ekaterina A. Simonova (Institute of Geology and Mineralogy SB RAS, Russia) **Investigation of phase equilibria and growth of BBO (β-BaB_2O_4) crystals in BaB_2O_4–LiF system**
P2.13	Abdallah Laidoune (Université El-Hadj-Lakhdar de Batna, Algeria), **Optimization of the growth of titanium doped sapphire fibers by the micropulling down technique**
P2.14	Bing Teng (Qingdao University, China), **The Synthesis, Crystal Growth, and Properties of Organic 4-N,N-diethylamino-4‘-N‘-methyl-stilbazolium tosylate (DAST)**
	Frontiers in crystal growth technology
P7.01	Hyunchul Jang (Yonsei University, Korea) **Comparison of the influences of in-situ doping using B_2H_6 and PH_3 on polycrystalline Ge layers**
P7.02	Byongju Kim (Yonsei University, Korea) **Effect of phosphorus on epitaxial growth of Ge layers on Si(111) substrates**
P7.03	Lu Shi (INP Grenoble, France) **High temperature solution growth and characterization of V_2AlC single crystals**
P7.04	Amina Tandjaoui (CNRS-SIMAP, EPM, France) **Characterization of Liquid Oxide by Sessile Drop Method on Refractory Substrates**

Workshop Program - Tuesday, June 17

Session 3		**Scintillators, piezo- and magnetoelectrics** Chair(s): Alexander Gektin (Institute for Single Crystals, Kharkov, Ukraine), Edith Bourret-Courchesne (Lawrence Berkeley National Laboratory, USA)
08:30	S3 / oral 1	Merry Koschan (University of Tennessee, Knoxville, USA) **A retrospective on the development of lutetium oxyorthosilicate (LSO)**
09:20	S3/ oral 2	Edith Bourret-Courchesne (Lawrence Berkeley National Laboratory, USA) **Crystal Growth of Alkali Earth Halides**
10:10		Coffee
10:30	S3 / oral 3	Akira Yoshikawa (Tohoku University, Japan) **Material Design and Crystal Growth of High Performance Scintillators**
11:20	S3 / oral 4	Jun Luo (TRS Technologies, USA) **Recent development on piezoelectric crystals for transducer and sensor applications - Understanding and overcoming the technical barriers to commercialization**
12:10		Break
12:30		Lunch
Session 4		**Substrates for wide band-gap and oxide semiconductors** Chair(s): Matthias Bickermann (IKZ Berlin, Germany)
14:00	S4 / oral 1	Tania Paskova (North Carolina State University, USA) **Status of HVPE grown GaN and AlGaN templates and bulk substrates: electrical and thermal conductivity**
14:50	S4 / oral 2	Dirk Ehrentraut (Soraa, USA) **SCoRA – New Technology for Scalable, High Rate Growth of Bulk Gallium Nitride**
15:40		Coffee
16:10	S4 / oral 3	Zbigniev Galazka (IKZ Berlin, Germany) **Bulk Single Crystals of Transparent Semiconducting Oxides: Growth and Properties**
17:00		Break
18:00		Gala Dinner
23:00		End

Workshop Program - Wednesday, June 18

Session 6		**Crystal shaping and layer transfer technologies** Chair: Albrecht Seidl (Schott, Germany)
08:30	S6 / oral 1	Irina Shikunova (Russian Academy of Sciences, Chernogolovka, Russia) **Sapphire Shaped Crystals for Medicine**
Session 4		**Substrates for wide band-gap and oxide semiconductors** Chair: Matthias Bickermann (IKZ Berlin, Germany)
09:20	S4/ oral 5	Noboru Ohtani (Kwansei Gakuin University, Japan) **SiC epitaxial wafers for power device applications: present status and prospect**
10:10		Coffee
Session 5		**Growth control, quality assurance, and management of resources** Chair: Michael Neubert (IKZ Berlin, Germany)
10:30	S5 / oral 1	Patrick Berwian (Fraunhofer IISB, Germany) **Quality Assurance in the Epitaxy of SiC and its Relevance for Device Reliability**
11:20	S5 / oral 2	Jan-Freerks Rieken (ppm Pure Metals, Germany) **Origin and Supply Security of Minor Metals**
12:10		Break
12:30		Lunch
14:00	S5 / oral 3	Benno Orschel (MEMC Electronic Materials, USA) **Requirements for Model Predictive Control in Industrial Crystal Production by Czochralski Process**
Session 7		**Frontiers in crystal growth technology** Chair: Chung-Wen Lan (National Taiwan University, Taiwan)
14:50	S7 / oral 1	Andrea Ferrari (Cambridge University, Great Britain) **Graphene Future Emerging Technology**
15:40		Coffee
16:10	S7 / oral 2	Lain Jong Li (Academia Sinica, Taiwan) **Growth of Transition Metal Dichalcogenide Monolayers with Chemical Vapor Deposition**
17:00	S7 / oral 3	Mikael Syväjärvi (Linköping University, Sweden) **The cubic sublimation method: prospects for bulk 3C-SiC growth and photovoltaic applications**
17:50		Break
18:00		Dinner
19:15		Industry 2
20:00		Poster 2
21:45		End

Poster Presentation - Wednesday, June 18

	Scintillators, piezo- and magnetoelectrics
P3.01	Sara Faraj (Claude Bernard University Lyon1, France) **Growth and characterization of cerium doped LuAG fibers grown by µ-Pulling down for medical imaging devices and scintillators**
P3.02	Md Anwar Hossain (University of Yamanashi, Japan) **Floating zone growth and characterization of $SrFeO_{3-d}$ and $CaFeO_{3-d}$ single crystals**
P3.03	Kei Kamada (Tohoku University, Japan) **Growth of N-benzyl-2-methyl-4-nitroaniline (BNA) single crystal fibers by micro pulling down method**
P3.04	Jan Pejchal (Tohoku University, Japan) **Crystal growth, scintillation and luminescence properties of Li_4SiO_4 single crystals for neutron detection**
P3.05	Guohao Ren (Shanghai Institute of Ceramics CAS, China) **Growth of bulk CsI(Tl) crystal and its light output uniformity**
P3.06	Yasuhiro Shoji (C&A Corporation, Japan) **Czochralski Growth of 2inch $(Gd_{1-x-y}La_xCe_y)_2Si_2O_7$ (Ce:La-GPS) single crystal and its scintillation properties**
P3.07	P. Vijayakumar (SSN College of Engineering, Kalavakkam, India) **Growth and characterization of $AgGa_{0.5}In_{0.5}Se_2$ single crystal by vertical Bridgman method for IR applications**
P3.08	Jiayue Xu (Shanghai Institute of Technology, China) **Bridgman growth and scintillation properties of rare-earth doped $Bi_4Si_3O_{12}$ crystals**
P3.09	Akhiro Yamaji (Tohoku University, Japan) **Crystal growth and luminescence properties of $Cr{:}Gd_3Ga_{5-x}Al_xO_{12}$ crystals for IR scintillator**
P3.10	Yuui Yokota (Tohoku University, Japan) **Growth and Scintillation Properties of 1 inch $Eu{:}SrI_2$ Bulk Crystals Grown by the Bridgeman Method Using High-Frequency Induction Heating**
P3.11	Weiguo Zhang (Aalto University, USA) **Large Size Single Crystal Growth, and Multifunctional Properties of Materials $LiMP_2O_7$ (M = Fe, Cr)**
	Substrates for wide band-gap and oxide semiconductors
P4.01	Seido Araki (Kyushu University, Japan) **Unsteady thermodynamical analysis of the polytype stability in PVT growth of SiC using 2D nucleation theory**
P4.02	Michal Fijalkowski (Institute of High Pressure Physisc PAS, Poland) **Free-standing HVPE-GaN crystals obtained from ammonothermal GaN substrates as seeds for the HVPE growth**
P4.03	Boleslaw Lucznik (Institute of High Pressure Physics PAS, Poland) **HVPE-GaN growth on non-polar and semi-polar seeds**
P4.04	Yun Ji Shin (INP Grenoble, France) **The effect of rotation on the macro-steps formation during 4H-SiC solution growth**
P4.05	Tomasz Sochacki (Institute of High Pressure Physics PAS, Poland) **Examination of growth rate during Hydride Vapor Phase Epitaxy of GaN on ammonothermal GaN seeds**
P4.06	Peng Su (Xi'an Jiaotong University, China) **Combined computational fluid dynamics and quantum chemistry calculations for the gas phase nucleation of GaN**

Poster Presentation - Wednesday, June 18

	Growth control, quality assurance, and management of resources
P5.01	Jeffrey J. Derby (University of Minnesota, USA) **A perspective on the history and future of Bridgman crystal growth**
P5.02	Evgeny Galenin (Institute for Scintillation Materials NAS, Ukraine) **Optimized Algoritms of Atomated Bulk Crystal Growth**
P5.03	Fadila Haddad (Université Houari Boumediene, Algeria) **Forced Convection Effect on Heat Exchanger Crystal Growth**
P5.04	Robert Král (Institute of Physics AS CR, Czech Republic) **Growth and luminescence properties of pure and RE-doped $RbPb_2Cl_5$ crystals prepared by vertical Bridgman method**
P5.05	Abdelkrim Merah (Université de M'hamed Boumerdes, Algeria) **Numerical Investigation of Hydrodynamic Stability in CZ Process**
P5.06	Faiza Mokhtari (University Mouloud Mammeri de TiziOuzou, Algeria) **Free Surface Study in Silicon Czochralski Melt**
P5.07	Jeffrey Peterson (University of Minnesota, USA) **A Comprehensive Model of the Growth of Cadmium Zinc Telluride (CZT) by the Traveling Heater Method (THM)**
P5.08	Andrey Sadovskiy (D. Mendeleyev University of Chemical Technology, Russia) **Verification of numerical model of AVC technique for crystal growth from melt**
	Crystal shaping and layer transfer technologies
P6.01	Martin Klejch (CRYTUR, Czech Republic) **Growth of sapphire capillaries for X-ray studies under supercritical conditions**

Workshop Program - Thursday, June 19

Session 4		**Substrates for wide band-gap and oxide semiconductors** Chair: Matthias Bickermann (IKZ Berlin, Germany)
08:30	S4 / oral 4	Zlatko Sitar (North Carolina State University, USA) **Growth of AlN crystals and AlGaN epitaxy on AlN wafers**
Session 6		**Crystal shaping and layer transfer technologies** Chair: Albrecht Seidl (Schott, Germany)
09:20	S6/ oral 2	Shinichi Shikata (Diamond Research Labs, AIST, Japan) **Diamond Wafer Prospect for the Power Device Application**
10:10		Coffee
10:30	S6 / oral 3	Noah Smick (GT Advanced Technologies, USA) **Using Proton-Induced Exfoliation to Manufacture Low-Cost, Device-Quality Single Crystal Substrates**
11:20	S6 / oral 4	Sarah Kajari-Schröder (Institute for Solar Energy Research IFSH, Germany) **Kerfless Wafering for Photovoltaics**
Session 1		**Advances in bulk crystal growth of semiconductor & photovoltaic materials** Chair: Michael Neubert (IKZ Berlin, Germany)
12:10	S1 / oral 5	Xingming Huang (JA Solar, China) **Development of High-quality Multi-crystalline Silicon Ingots**
13:00		Closing
13:10		Lunch

EFG Berlin - 50 years of X-ray technique

The EFG company started 1961 with the development of high stabilized X-ray generators. The next step was the designing and construction of customer required units mainly in the X-ray diffraction field. The largest one was a stress analysis machine for air craft turbines.

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In the last years the production of exact oriented wafers of different materials, Sapphire, SiC and others, became important. Exact orientation is impossible without X-ray diffraction. EFG developed a set of machines applicable for the various production steps.

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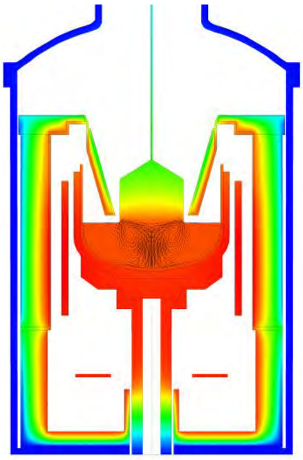

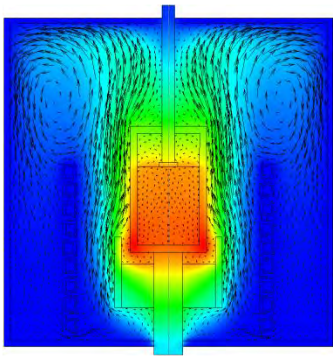

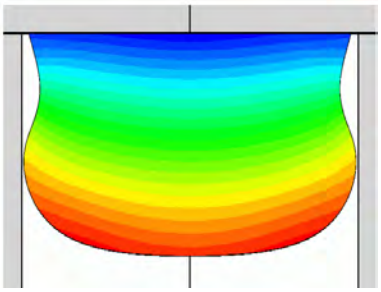

TECHNOLOGIES SHAPING OUR TOMORROW'S WORLD

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CRYSTAL GROWING –

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Sunday, June 15

16:10		Registration
18:00		Dinner
Panel		**The future of crystal growth technology – bringing new technologies to industrial growth application** Chairs: Peter Rudolph (Crystal Technology Consulting, Germany), Jochen Friedrich (Fraunhofer IISB, Germany)
19:15		**Norbert Thiel (PVA Tepla, Germany)** **Alexander Gektin (Institute for Single Crystals, Kharkov, Ukraine)** **Dirk Ehrentraut (Soraa, USA)** **Edith Bourret-Courchesne (Lawrence Berkeley National Laboratory, USA)** **Xingming Huang (JA Solar, China)** **Koichi Kakimoto (Kyushu University, Japan)**
21:45		End

Monday, June 16

Session 1		**Advances in bulk crystal growth of semiconductor & photovoltaic materials** Chair(s): Nathan Stoddard (SolarWorld USA), Maria Porrini (SunEdison, Italy)
08:30	S1 / oral 1	Steven Kimbel (MEMC Electronic Materials, USA) **Development of a 450 mm Semiconductor Silicon Crystal Process**
09:20	S! / oral 2	Wilfried von Ammon (Von Ammon Consulting, Germany) **FZ and CZ Silicon Crystal Growth: Cost Driving Factors and New Perspectives**
10:10		Coffee
10:30	S1 / oral 3	Koichi Kakimoto (Kyushu University, Japan) **Understanding and Control of Silicon Crystal Growth for LSIs and PVs**
11:20	S1 / oral 4	Etienne Pihan (CEA-INES, France) **Status and industrial future of DW wafered mono-like silicon crystals grown by directional solidification for high efficiency solar cells**
12:10		Break
12:30		Lunch
Session 2		**Optical and laser crystals** Chair: Reinhard Uecker (IKZ Berlin, Germany)
14:00	S2 / oral 1	Xutang Tao (State Key Lab of Crystal Materials, Shandong University, China) **Crystal growth and nonlinear optical properties of $BaTeMo_2O_9$**
14:50	S2 / oral 2	Christian Kraenkel (University of Hamburg, Germany) **Growth by the Heat Exchanger Method and Llaser Operation of Rare-earth Doped Sesquioxides**
15:40		Coffee
16:10	S2 / oral 3	Ludmilla Isaenko (Russian Academy of Sciences, Novosibirsk, Russia) **Growth of bulk nonlinear crystals $LiBC_2$**
17:00	S2 / oral 4	Joseph Kolis (Clemson University, USA) **The Hydrothermal Method of Single Crystal Growth**
17:50		Break
18:00		Dinner
19:10		Industrial Session
19:15		Industry 1
20:00		Poster 1
21:45		End

Development of 450mm Semiconductor Silicon Crystal Process

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The design of any new crystal process is a multifaceted and multidisciplinary challenge. When embarking on a new larger platform of products like the 450mm platform, one must consider the at least the following.

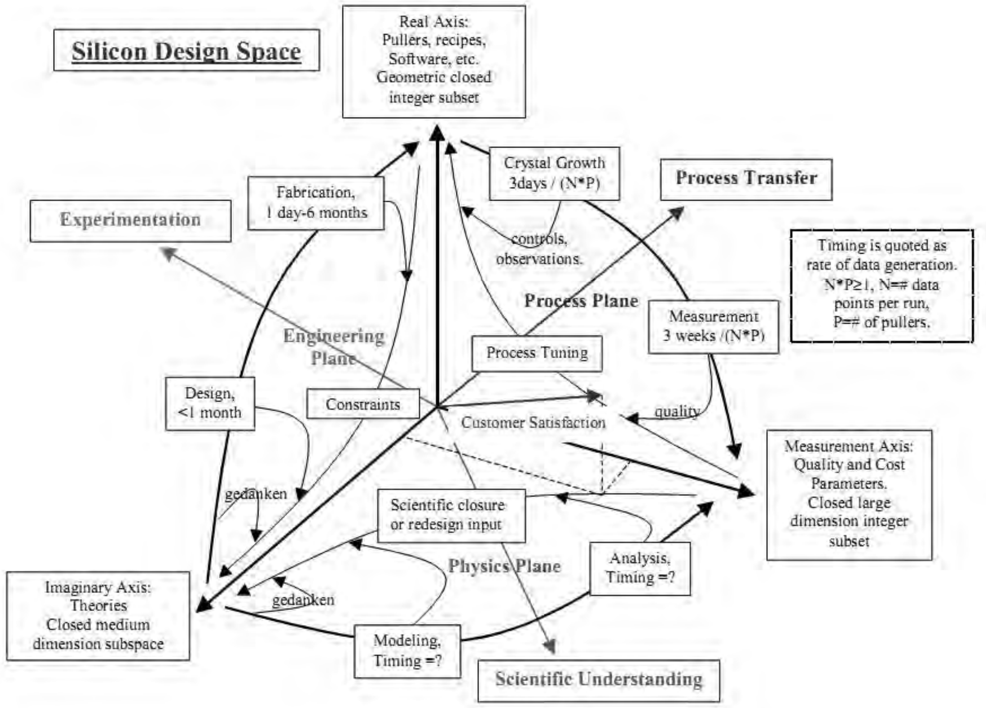
Product
- Customer needs and desires that drive the ultimate equipment and process design.

Physics and Modeling
- Precipitated defect type and size vs. crystal thermal field and crystal process parameters (e.g. growth rate, rotations, radiative power inputs, and magnetic field strength)
- In-situ dimensional metrology and control.

Physical / Dimensional
- Necessary neck strength or other means to support the heavy ingot.
- Hotzone and ingot body target dimensions, plus ultimate migration path of the equipment to larger ingots.
- Equipment design for medium vacuum plus automated control of flow, rotations, lifts, heater(s) and magnet(s) to achieve target diameter and quality control.

Materials
- Selection, specification and development of hotzone graphite, feedstock and crucible materials.

Observation and Measurement
- Identification of and elimination of sources of structure loss.
- Available and required process and product metrology



Silicon Design Space, from "*An Estimation Method for Czochralski Silicon Diameter Measurement*", S. L. Kimbel thesis, May 2000, Sever Institute of Washington University, © S.L. Kimbel

Above is a 3D function representation of a new product development, where after the customer request occurs along the imaginary axis, modeling of the product quality is made on the Physics Plane, providing product measurement expectations. Once predicted quality is acceptable compared with the customer specifications, constrained design and fabrication of the necessary hardware, recipes software, etc, to generate a viable process for making the desired product can proceed on the Engineering Plane. The developed equipment and process, verified by experimentation may then be used to generate a series of in-situ and ex-situ observations during and after crystal growth on the Process Plane and a set of final product quality measurements. Comparison of the product measurement expectation with quality measurements provides further Scientific Understanding. The Customer Satisfaction vector drawn represents the strong dependence on product quality and cost measurements, with dependence also on equipment design and process physics understanding.

One presentation finding planned for review is that of sources of structure loss in silicon crystal growth development, with example illustrations.

FZ and CZ silicon crystal growth: Cost driving factors and new perspectives

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In the field of dislocation free silicon crystal growth, the Czochralski (CZ) as well as the floating zone (FZ) method have grown to a mature technology over the last 60 years. During this period of time, the costs have been continuously reduced. For both methods, the cost for the feedstock material has remained as the dominant cost driver until today, despite the dramatic erosion of the poly silicon price over the last years. This is particularly true for FZ where notably more than 50% of the cost of ownership are related to the polysilicon feed rods which are much more expensive as compared to the chunk polysilicon as used for CZ. As a consequence, the FZ method is economically less attractive as compared to CZ and, therefore, FZ grown crystals are not considered for solar cell production, although the very low oxygen content of FZ crystals allows for higher cell efficiencies and avoids light induced degradation. In addition, the FZ process development always lagged at least one diameter generation behind the actual largest standard diameter of the semiconductor industry and the current 200 mm FZ process will most likely be the ultimate diameter limit for this technology. Up to now, the FZ method is only used for niche applications like the fabrication of high power devices where silicon material with very low oxygen concentration is mandatory.

Due to the strong influence of the feedstock material on cost, the main focus of the development work for both methods has been on the increase of crystal yield and the identification of factors impacting the yield. However, for most electronic and, in particular, for solar application, the crystal yield has reached a level where significant improvements cannot be expected anymore. In case of CZ, this is also true for cost reductions of consumables like the silica crucible which is the second largest contribution to the CZ cost of ownership. As a bad crucible quality can severly affect the crystal yield, the options for cost savings in the production of crucibles are limited. On the contrary, it is usually more economical to pay a higher price for a good quality crucible if the crucible increases the crystal yield. With respect to cycle time reduction, a further increase of the pull rate would be wishful, but the built up of thermal stress beyond a critical value and the deformation of the cylindrical shape of the growing crystal sets a clear limit for the pull rate which has meanwhile been reached with water cooled heat shields. With the potential change from p- to n-type silicon in the solar industry, previously developed techniques, like continuously recharged CZ, which were finally stopped for electronic applications, are reconsidered and will be discussed with respect to their future potential.

Special attention will be given to the advantages and disadvantages of the FZ method. It will be shown that the economical drawback of FZ can be remedied by a new technique which avoids the use of expensive polysilicon feed rods and enables the FZ method to grow dislocation free crystals with inexpensive silicon granules [1]. The silicon granules are supplied through a funnel onto the surface of a rotating silicon plate, where they are continuously molten by an upper HF coil (Figure). The melt flows through a tubular opening in the center of the silicon plate whereby a melt neck between the lower end of the tubular opening and the melt bath on top of the growing crystal is formed. Thus, a continuous melt flow from the top of the silicon plate, where the silicon granules are molten, down onto the top of the growing crystal is established. The switch to silicon granules not only significantly lowers the cost for the feedstock material, but also minimizes the feedstock losses in case of structure loss during growth. The granule supply and the process can be stopped at any time without the consequence of downgrading unusable feedstock. If the new method can be successfully applied in high volume production, an almost ideal base material for high efficiency solar cells can be offered at a competitive price. Reference: 1) W.v.Ammon, US patent application US 2003/0145781A1

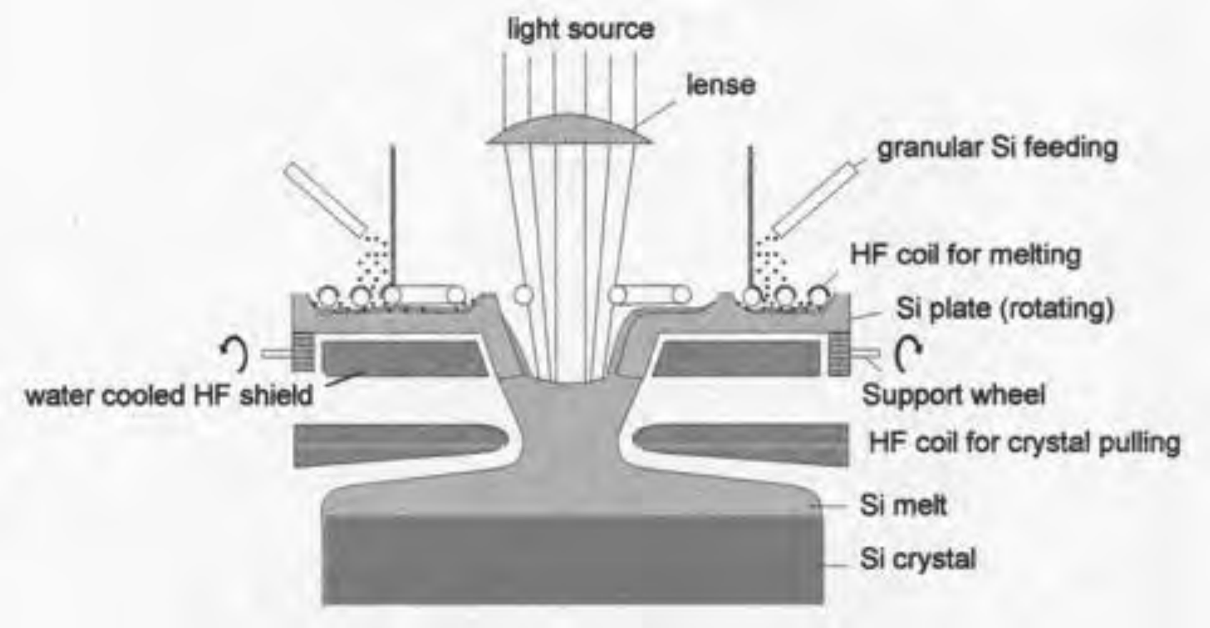

Figure: FZ like growth with continuous charging of silicon granules instead of a poly silicon feed rod as a feedstock material [1].

Understanding and control of silicon crystal growth for LSIs and PVs

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Further developments in devices such as large scale integrated circuits (LSIs), solar cells (PVs) and power devices for electric vehicles are required to improve the quality of our life derived from the information, energy production and energy saving fields. Single and multi-crystals of silicon are one of the key materials to realize the requirements. Silicon single crystals have been widely used in applications such as the internet, solar cells and inverter in power devices. To realize these improvements, we need to grow silicon crystals with low concentrations of impurities such as oxygen and carbon, dislocations and point defects. Growing crystals remain in contact with a quartz crucible in which the melt is set, then it is easy to contaminate the melt by impurities and to introduce defects during whole processes including ramping up the raw materials, crystal growth and cooling from melting point to room temperature. Defect formation occurred until Czochralski developed the novel "Czochralski method", which allows formation with low defects in crystals.

Multicrystalline silicon has now become the main material in the photovoltaic market because of its low production cost. The directional solidification method is a cost-effective technique for large-scale production of multi-crystalline silicon material. Similar to the Czochralski method, the unidirectional solidification is connected with transport of impurities [1]. Carbon is one of the major impurities in multicrystalline silicon. If the carbon concentration exceeds $1x10^{16}$ $atom/cm^3$, it will markedly influence the precipitation of oxygen during thermal annealing of crystals and during device processing of the wafers cut from these crystals [2–6]. Oxygen precipitation is known to act as intrinsic gettering sites for impurities and to affect the mechanical strength of the wafer [7].

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Status and industrial future of DW wafered mono-like silicon crystals grown by directional solidification for high efficiency solar cells

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Crystal growth of nonlinear optical crystal of $BaTeMo_2O_9$

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Abstract

Two new crystals: β-$BaTeMo_2O_9$(β-BTM) and α-$BaTeMo_2O_9$(α-BTM) have been grown by flux method and their linear and nonlinear optical properties have been studied[1-4]. The second order nonlinear optical properties of β-BTM were studied by means of the Marker fringe technology and the phase matching method. The values and relative signs of the second order nonlinear optical coefficients were obtained, with the largest one being $d_{31} = 9.88$ pm/V. At 1064 nm, the crystal can realize both type I and type II phase matching, and the effective nonlinear coefficient is 10.3 pm/V for phase matching II in the xoy plane.

The generations of high energy 1st, 2nd and 3rd-order stimulated Raman scattering (SRS) lasers with both the b-BTM and α-BTM crystals were demonstrated for the first time.

A self-frequency-doubled β-BTM Raman laser at 589 nm is realized in an external resonator. A β-BTM crystal cutting along noncritical phase-matching direction is used to generate Raman laser output at 1178 nm from a 1064 nm pump laser. Self-frequency doubling of the Raman laser is accomplished in the same crystal, and a 589 nm yellow laser is obtained. At a pump pulse energy of 48 mJ, the maximum output pulse energy of 5.6 mJ for the yellow laser is obtained with an optical-to-optical conversion efficiency of 11.7%.

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Growth by the heat exchanger method and laser operation of rare-earth doped sesquioxides

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Cubic sesquioxides with the chemical composition RE_2O_3 (RE = Lu, Y and Sc) are excellent high power laser host materials in the infrared spectral range. They exhibit a high thermal conductivity, low phonon energies and a good mechanical stability as well as a large transparency range covering the spectral region between 0.2 µm and 8 µm. However, the growth of these materials is very challenging due to the extremely high melting point of more than 2400 °C, which is about 500 °C higher than for the common laser host material $Y_3Al_5O_{12}$ (YAG) [1]. In the last years we improved the growth of cubic sesquioxides by the heat exchanger method (HEM, see Fig. 1) and for the first time single crystalline samples with several cm^2 volume and high optical quality were available for high power laser experiments [2].

Among the cubic sesquioxides Lu_2O_3 appears to be the most suitable material to be doped with the heavier rare earth ions such as ytterbium, thulium, erbium and holmium. This is due to the low mass difference between the substituted lutetium-ion and the respective rare earth ion, leading to a very small influence of the dopant ion on the thermal conductivity, which thus remains high even for high doping concentrations [3]. With crystals grown by the heat exchanger method we demonstrated that Lu_2O_3 is an excellent host material for rare-earth-doped high-power diode-pumped solid-state lasers with unprecedented performance in the 1, 2, and 3 µm range.

Around 1 µm, Yb:Lu_2O_3 thin disk lasers delivered several 100 W of output power at optical efficiencies exceeding 70 % [3]. At 2 µm Tm-doped Lu_2O_3 allowed for nearly 100 W of output power and slope efficiencies approaching 60% [4]. Ho:Lu_2O_3 bears the potential for even more efficient lasers in this wavelength range once suitable laser diodes in the 1.9 µm range are available as pump sources [5]. In the 3 µm range, Er:Lu_2O_3 is a highly attractive laser material. It allowed for the highest output power from any room-temperature crystalline Er-laser at 3 µm [6].

Moreover, the strong crystal field of the sesquioxides leads to broad emission bandwidths making these materials highly interesting also for modelocked operation with ultrashort pulses [7, 8].

In this presentation we present the state of the art of the growth of rare earth doped sesquioxides by the heat exchanger method, discuss our latest improvements regarding the growth atmosphere during the cooling down process and review the latest results of diode-pumped high-power lasers based on rare-earth-doped Lu_2O_3 emitting in the 1, 2, and 3 µm wavelength range.

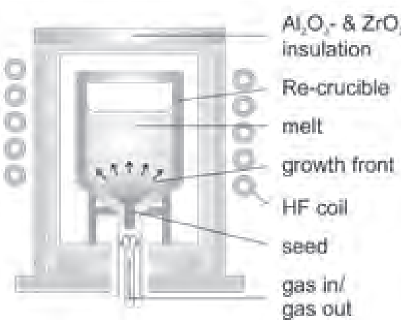

Fig. 1: Setup for the HEM growth

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Growth of bulk nonlinear crystals $LiBC_2$

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A study of linear and nonlinear optical properties for members of the $LiBC_2$ family with B = Ga, In and C = S, Se shows that these compounds are extremely useful for nonlinear optical devices operating in the mid IR. Their orthorhombic structure results in extended phase-matching conditions and low anisotropy of thermal expansion whereas a wide bandgap results in lower two-photon absorption. Small mass of metal ion (Li) is responsible for higher vibrations frequencies and higher thermal conductivity.

Usage of new nonlinear crystals of multicomponent chalcogenides in optoelectronic devices for mid-IR spectral range stimulates additional studies of their chemical, optical and mechanical stability. Combination of a complex of parameters, not only the main ones, brings nonlinear crystal sometimes to the category of the most effective materials for certain application. $LiGaS_2$ is characterized by the modest nonlinear coefficients among the $LiBC_2$ family combining its maximum bandgap (3.76 eV) in the set of the mid-IR crystals and its high optical damage threshold be become suddenly the best material for fsec OPO systems[1]. In is important that LGS exhibits no surface aging effects as the other $LiBC_2$ compounds.

Recently the LGS-based OPO with 1064 nm pumping from 100-Hz/8-ns and 1-kHz/1-ns laser sources. Idler pulses with 134 µJ energy and 5.4 ns duration were generated near 5.46 µm[2]. On the other hand, if one needs high nonlinear susceptibility combined with maximum transparency in the mid-IR $LiInSe_2$ is recommended.

All members of the $LiBC_2$ family were grown by the Bridgman-Stockbarger technique and their optical properties were studied in detail. However, the problem of reproducibility of these properties still remains to be solved. In as-grown samples color varies from colorless to pink, sometimes crystals are milky as a result of submicron inclusions and point defects. This indicates that the melt composition is not always optimal to grow stoichiometric and homogeneous crystals. Any perturbations in the steady state growth condition might be responsible for the phenomenon. First of all, there may be a deviation of the crystal stoichiometry because of nonstoichiometry in presynthesized charge. Secondly, a progressive change in melt composition may occur during the growth run because of incongruent evaporation or two-phase crystallization. In such case the growth of a single crystal is interrupted. To find optimal composition and growth conditions, the binary phase diagram Li_2C-B_2C_3 in the 50 to 100 mol% Li_2C range was studied. The Li_2C-B_2C_3 diagram was found pseudobinary and monotectic in the region studied. $LiBC_2$ compounds melted congruently and homogeneity range on the Li_2C - rich side was < 1 mol %. The monotectic type of the diagram with an extensive field of two immiscible liquids (emulsion separation) explains why it is never possible to grow inclusion-free LiBC2 crystals from the melt strongly enriched in Li_2C. But if melt compositions deviates only slightly from 50%, the main mechanism for non-homogeneity formation is precipitation of the Li_2C inclusions. They are observed in some milky crystals, yellow in color, and are instable on air. On the other hand, following the well-known diagram of the Li_2Se-In_2Se_3 system, one can expect growth of perfect, single-phase crystals from melt compositions ranged from 50 to 52 mol. % of B_2C_3. In this case nonstoichiometric crystals grown from self-solutions demonstrate pink color[3].

To order to improve crystal quality, we paid attention to three essential components of growth process: i) careful preparation of starting reagents; ii) choosing a correct growth composition and iii) using the very stable growth system.

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The Hydrothermal Method of Single Crystal Growth

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The hydrothermal method provides an alternative method of growth of single crystals.[1] The growth reactions are generally performed in superheated aqueous fluids at temperatures between 400-700˚C and pressures of 1-3 kbar. The solutions typically contain a mineralizer such as a small nucleophile like hydroxide, carbonate or halide or an electrophile such as acid. Single crystal growth is usually accomplished across a small thermal gradient (15-30˚) with feedstock in the dissolution zone and seed crystals in the growth zone. Supersaturation in the growth zone leads to deposition on the growing crystal site, followed by circulation of the spend fluid to the dissolution zone where fresh feedstock is dissolved for transport to the growth zone. Since this continuous recirculation normally happens through convection, the growth is a constant process requiring no input. In principle, as long as feedstock remains, crystals can grow as large as large as the reactor vessel.

There are a number of advantages to this growth process. It is a relatively low temperature process and occurs in an isothermal bath, so there are minimal thermal strains or defects. Also the growth occurs in a closed system, so impurities are minimized, and there is good reaction control. In addition the system is amenable to chemical control. Thus oxidation state, stoichiometry, acidity and other chemical factors can be controlled during growth.

This talk will review a number of these factors and describe our recent work on the growth of a series of oxides, borates and fluorides. Several chemical systems will be chosen to illustrate the utility of the method. We will focus on refractory oxides that can serve as laser hosts and other optical applications. Thus we will describe the growth of a number of doped garnets such as YAG [2] and LuAG, as well as lanthanide oxides such as Lu_2O_3.[3,4] A particular emphasis will be on the doping of the oxides, and we will discuss both co-doped materials as well as epitaxial growth to form multifunctional single crystals.

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Segregation control in crystal growth of SiGe alloys from a thin melt layer

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The location of an additional heater in front of a growing crystal makes it possible to drastically change the character of convection [1]. In the thin melt layer between the heater and the melt/crystal interface, natural convection is completely suppressed resulting in a weak laminar one caused by the crystal's withdrawal to the cold zone of a furnace chamber. From another hand, the presence of the heater makes the interface itself flatter due to a considerably less radial temperature gradient in comparison with an axial one. The last allows one to create appropriate thermal conditions for growth of a binary SiGe alloy, whose crystal structure is very sensitive to the level of thermal stress. Moreover, modelling the crystal growth for the method of Axial Heating Process (AHP) revealed thermal conditions [2] providing both the longitudinal and lateral uniform distribution of the second component in the alloy.

Recently [3], the longitudinal segregation in the SiGe crystal (see Fig. 1) grown from a Spark plasma sintered charge rod of the composition 80 at% Si and 20 at% Ge by the modified FZ technique (with use of the AHP heater) was shown to be completely dependent, besides other things, on the melt layer thickness, which changed in the experiment from 4 to 8 mm. The less the height of the melt layer, the more is the Ge concentration C_m in it, and consequently, in the grown crystal. Once the melt layer thickness is kept constant, with the C_m value being in correspondence with that in the charge C_s ($C_m = C_s/k_0$, where k_0 is equilibrium segregation coefficient), the distribution of Ge in the crystal becomes constant.

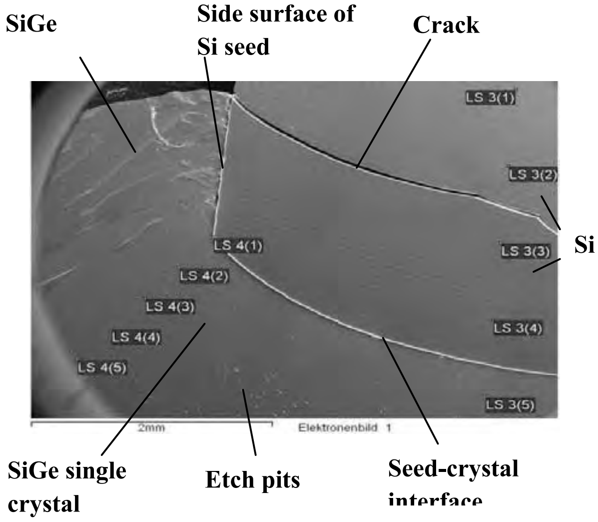

Fig. 1. SE picture of the SiGe crystal area in vicinity of the interface with linescan LS 4 and LS 3; (1-5) – measuring points of the probe.

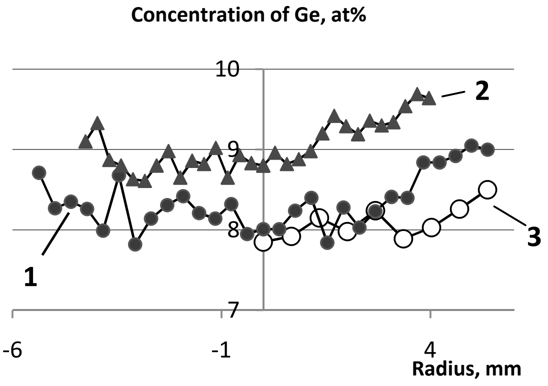

Fig. 2. Lateral Ge distribution: 1 – z=1.5 mm, 2 – z=5 mm, 3 –recalculated data for z=1.5 mm.

In this paper we discuss the lateral distribution, too. The data measured over the radius of the single crystal for one of the half of the ingot showed to be slightly increased (see Fig. 2). Meanwhile, the values measured along the interface differ no more than few hundredths of percent. It means, to provide the radial distribution of Ge in the alloy uniform, one needs to improve the flatness of the interface, which seems quite realistic for crystal growth in the presence of submerged heater. Ways to improve the technique and to obtain homogeneous $Si_{0.9}Ge_{0.1}$ single crystal are under discussion.

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Functionally Graded Thermoelectrics by Bulk Crystal Growth

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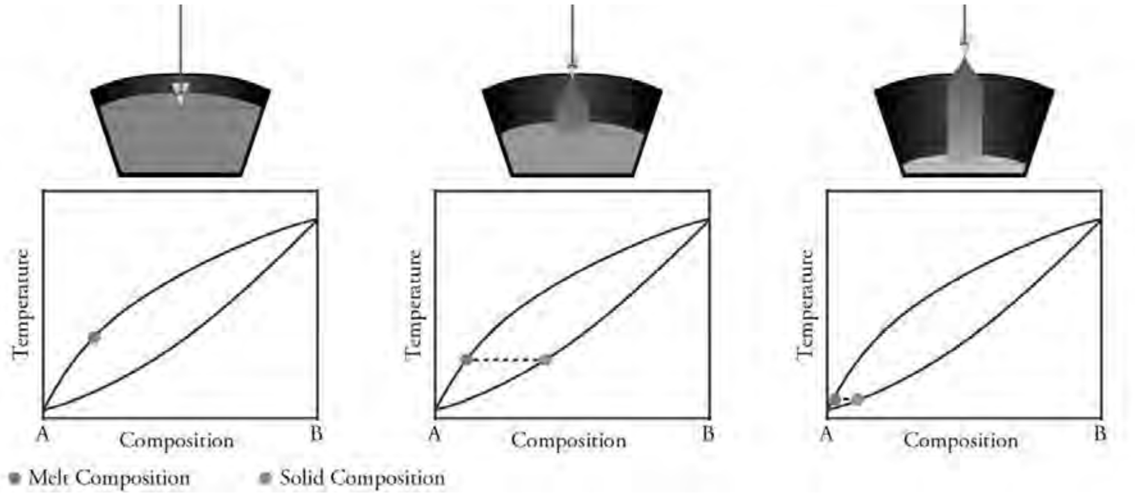
Thermoelectric conversion of waste heat has long been proposed as one of the ways to meet the rising energy demands of the world. However, even the present state of the art thermoelectric materials still need performance improvements to be cost-effective in most applications. Higher efficiency materials could be obtained by optimizing the materials through functionality grading to meet the changing temperature conditions within a thermoelectric module in operation.

Material gradients inherent to directional crystal growth techniques provide a promising one-step route to achieve functionality grading of several state of the art thermoelectric materials. It has previously been shown that thermoelectric materials graded in either composition, and thereby band gap[1], or doping[2] can be prepared in this way, but by combining the two effects through directional solidification a potentially significant improvement in efficiency should be achievable.

This poster presents the idea behind and preliminary results of a study aiming at identifying and testing material systems capable of being graded in both doping and composition through either Czochralski or Bridgman/Stockbarger crystal growth in such a way that these effects enhance each other.

Boron doped $Ge_{1-x}Si_x$ (x= 0 to ~0.25) samples graded in both band gap and carrier concentration have been prepared by the Czochralski method. Along the length of the $Ge_{1-x}Si_x$ samples x changes continuously giving rise to changes in the band gap from 0.87 eV to 0.65 eV. Similarly, gradients in the boron content results in continuous carrier density changes along the sample. This results in samples graded in all material parameters relevant to thermoelectric performance.



The idea behind functionality grading through directional crystallisation. As the crystallisation proceeds from the (pseodu-)binary solid solution the composition changes. By proper control of these mechanisms higher efficiency thermoelectric materials can be made in a one-step synthesis.

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Silicon Float-Zone Crystals from low-cost Feed-Material

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The Float Zone (FZ) method allows the growth of silicon crystals with one to two orders of magnitude lower oxygen concentrations than any other growth method is able to. This makes FZ wafers exceptionally suited for power electronics, where low oxygen is mandatory, but also for high-efficiency solar cells, since no degradation by the formation of boron-oxygen complexes will occur. FZ growth chambers are free of any carbon based parts, reducing the carbon concentration in the grown crystals significantly, compared to e.g. Czochralski crystals. The growth rate itself is about a factor of 2 higher than it is achievable by standard pulling processes. Further, rather uniform axial resistivity profiles can be achieved by doping the ingots during the growth process by the gas phase. The lower energy consumption and the lack of any crucible or hot-zone consumables result in an attractive cost-of-operation profile.

Beside the above listed advantages, certain difficulties have to be mentioned dealing with the FZ process: the specification of the poly-silicon feed rods needed for the FZ process is very tight, the rods have to be crack-free, with a low bow, a smooth morphology, and a diameter in the same range as the anticipated FZ ingot. Only a very limited number of poly-silicon producers are able to fulfill these requirements and to produce FZ-feed rods of satisfactory quality. In any case, the market price for high-quality FZ-feed rods is significantly higher than it is the case for standard poly-silicon chunks or granular material. An additional bottle-neck is the limited amount of automation available for FZ growth processes – success or failure of FZ crystal growth depends a lot on the skills of the operator.

An attractive alternative to poly-silicon feed rods produced by the Siemens-CVD process (the standard method for poly-silicon FZ feed rod material) is the pre-pulling of feed rods from the melt using a modified Czochralski configuration. This approach allows the use of standard solar grade poly-silicon (e.g. broken chunks), nowadays easily available on the market. Since the pre-pulled feed rods do not require dislocation-free growth, or not even a single-crystalline structure, the pulling process can be performed considerably faster than it is the case for conventional Czochralski growth. Pulling several feed rods out of one crucible reduces the cost for the pre-pulling step even further. A great advantage compared to CVD-based poly-silicon feed rods is the fact that any desired diameter can be provided: in the case of the CVD process, the actual limit for the feed rod diameter is in the range of 160 to 180 mm, with 180 mm already stretching the limit of the CVD process. The pre-pulling process has the ability to provide feed rods of 200 mm or more without difficulty. In particular for metallic impurities, the pre-pulling results in a further purification caused by the generally small segregation coefficients of metals in silicon.

During the pre-pulling process, the melt is in contact with a quartz-glass crucible and thus picks-up oxygen. Feed rods produced by the pre-pulling process show oxygen concentrations in the range of $5\text{-}8\cdot10^{17}$ at/cm³, comparable to standard Czochralski in-gots. During the subsequent FZ process, the silicon melt has a relatively large surface to volume ratio and a high convective melt mixing driven by strong temperature gradients, in addition to the inductively induced forced convection. This supports strongly the evaporation of SiO: our FZ-ingots grown from pre-pulled feed rods showed oxygen con-centrations in the range of $1\text{-}2\cdot10^{16}$ at/cm³, which is in the same range as FZ crystals grown from poly-silicon feed rods, but about one and a half order of magnitude lower than the oxygen concentrations in standard Czochralski ingots. The oxygen concentration was measured by FTIR (K. Lauer, Forschungszentrum für Mikrosensorik und Photovoltaik GmbH - CiS, Erfurt, Germany).

The cost structure of our FZ process based on pre-pulled feed rods is favorable compared to a standard process using poly-silicon feed rods from CVD reactors. The additional costs due to the pre-pulling are more than compensated by the use of low cost poly-silicon: we had been able to transform solar-grade silicon chunks or granular material or even wafer scrap into FZ ingots. Thus, Float Zone with pre-pulled feed rods is an interesting alternative for the production of cost competitive wafers with very low oxygen concentrations, as required for power electronics. Furthermore, wafers for photovoltaic applications, in particular in the field of high-end, high-efficiency solar cells, might be produced cost-competitive by this approach.

Grain Structures of Multi-crystalline Silicon Grown By Using Patterned Crucibles

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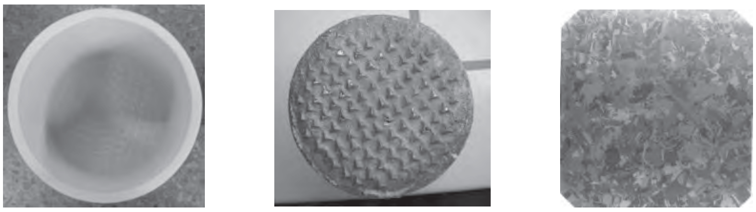
The high performance multi-crystalline silicon (HP mc-Si) has emerged recently by controlling the initial fine grain structure during directional solidification by seeded growth [1]. The average efficiency per ingot based on the normal production line could be easily over 18%. However, the red zone and the back diffusion of the impurities from the seeds significantly reduce the ingot quality and the production yield. The control of seeded growth is also laborious leading to a longer cycle time. By using patterned crucibles, such as the notched one, as shown in Fig. 1, or nucleation agent, we were able to control the fine grain structures through nucleation for growing HP mc-Si. To avoid the stress inside the notches, the thermal expansion coefficient of the crucible material for the notches is adjusted to be about the same as silicon. As shown in Fig. 1(a), the notch size was about 1 cm, and the crystal was grown from the notches without cracks (Fig. 1(b)). As shown in Fig. 1(c), the wafers near the bottom have uniform small grains. The grains were reasonably uniform near the top of the ingot, and the defects were comparable to normal HP-mc in the same ingot height. In this presentation, the grain structures, such as grain orientation and grain boundaries, from the notched crucible will be discussed. The PL mappings will also be used for the defect analysis.



(a) (b) (c)

Fig. 1 (a) Notched crucible (20 cm in diameter); (b) bottom of the grown ingot; (c) grain structure at 5-mm height.

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Evaluation of seed crystal reuse for cast quasi-single crystalline silicon ingots

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Reuse of seed crystals is a hot topic for cast quasi-single crystalline (QSC) silicon ingots, as it is beneficial for reducing production costs. The normal seed crystals are prepared from Czochralski silicon rods, which have no grain boundaries and low dislocation density. After the casting process, the dislocation density in the seed crystals is still low, whereas the impurities, such as oxygen, nitrogen and iron, are enriched in the seed crystals owing to the contact with quartz crucible and silicon melt at high temperature. Therefore, it is necessary to evaluate whether the contaminated seed crystals can be reused.

Iron is an important metallic impurity in crystalline silicon ingots and it has been proved to be an important minority carrier lifetime killer. Recent study has shown that iron transport during casting process can lead to a large region enriched with iron impurity at the bottom of QSC silicon ingots, which corresponds to the large low lifetime region in this location [1]. The seed crystals are highly contaminated during this process. However, it is unkown whether the iron contaminated seed crystals can be reused. One simple method to evaluate the possibility of seed crystal reuse is to compare the iron contaminated regions at the ingot bottom for both normal and reused seed crystals.

Fig.1 shows the distributions of iron impurity and minority carrier lifetime in two QSC silicon ingots with normal and reused seed crystals. Figs.1(a) and 1(b) show the predicted iron distributions in the two ingots after solidification. The initial iron concentrations in the normal and reused seed crystals are zero and 10^{15} atoms/cm^3, respectively [1]. The height of the bottom contaminated region ($>10^{13}$ atoms/cm^3) in Fig.1(b) is larger than that in Fig.1(a), but the difference is very small. Figs.1(c) and 1(d) show the experimental data of minority carrier lifetime distribution for cases using normal and reused seed crystals, respectively. The heights of the bottom low lifetime region (red zone) are similar to each other between the two cases. Therefore, the iron contaminated seed crystals can be reused, as it will not increase the bottom low lifetime region significantly. In the production process, the seed contamination level, the seed preservation time, the purity of silicon feedstock and quartz crucible are always varied. The study will evaluate the possibility of seed crystal reuse under these conditions comprehensively.

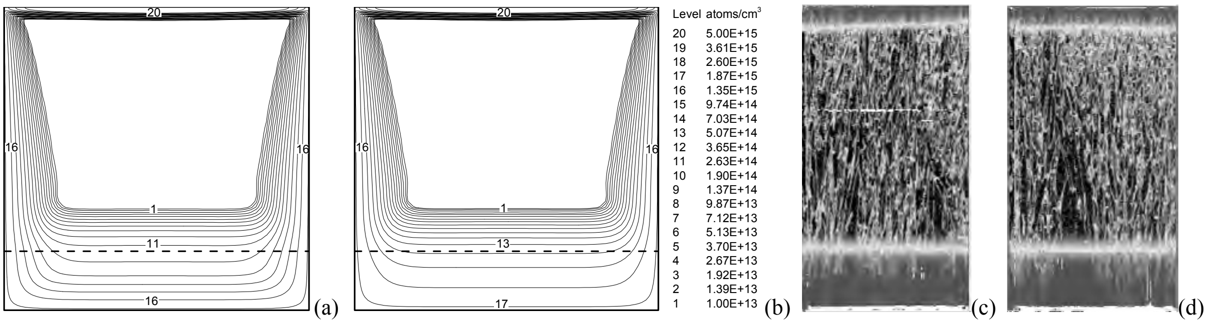

Fig. 1 Numerical and experimental studies on the seed crystal reuse: (a) iron contamination with normal seed; (b) iron contamination with reused seed; (c) lifetime distribution with normal seed; (d) lifetime distribution with reused seed.

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Effect of top and side heaters during two growth process on oxygen concentration, dislocation density and residual stress in a multicrystalline silicon for solar cells

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Multicrystalline silicon is an important material for solar cells because of its cost-effectiveness. However, multicrystalline cells have a problem for the conversion efficiency of solar cells because many impurities incorporate into a silicon ingot during the solidification process. Oxygen is one of the major impurities in multicrystalline silicon. Incorporated oxygen in a silicon ingot causes SiO_2 precipitation [1] and dislocations [2]. These defects reduce the conversion efficiency of solar cells. Dislocation density and residual stress are also serious problems for solar cells because dislocation density causes the reduction of the conversion efficiency of solar cells and residual stress causes the fracture of silicon ingot during the slicing process. It has been reported that dislocation densities rapidly increased during cooling process [3, 4]. Therefore, we have to optimize solidification and cooling process to decrease oxygen concentration, dislocation density and residual stress in a silicon ingot.

We developed a transient global model for the unidirectional solidification process [5]. And we investigated time-dependent dislocation multiplication in a silicon ingot. Thermal stress distribution was solved using temperature distribution in a silicon ingot which we got result from our transient global model. Then, we investigated stress relaxation, creep deformation and dislocation multiplication using Haasen-Alexander-Sumino model [6, 7].

We used a growth system two heaters, top and side heaters and changed heater power ratio. In the first case, heater power ratio of the side heater was high, which is side heating system. In the second case, heater power ratio of the top heater was high, which is top heating system. We investigated that the influence of heating system using top or side heater on oxygen concentration during solidification process and dislocation density, residual stress during cooling process. The results showed that oxygen concentration for the side heating system is lower than that for the top heating system. Therefore, we suggest that it is important to use side heating system during solidification process to decrease oxygen concentration in a silicon ingot. When we used these two heating systems, dislocation density for the top heating system is lower than that for the side heating system. This result causes the difference of outgoing total heat flows from the crystal at high temperature region during cooling process. Therefore, we suggest that it is important to use top heating system during cooling process at high temperature region to decrease rapid change of outgoing total heat flows from the crystal.

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Modeling of three-dimensional heaters in numerical simulation of an industrial directional solidification furnace

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The two-dimensional numerical models are widely used to simulate the heat transfer in industrial directional soldification (DS) furnaces for crystalline silicon ingots. However, the actual configuration of the heaters in the DS furnace is highly three-dimensional asymmetric. Therefore, it is essential to investigate the modeling of the 3D heaters in the 2D numerical simulation of heat transfer in the DS furnace.

The heater providing heating power, is one of the most important components for the industrial DS furnace. The effects of heater position, heating power distribution and heater structure design on the global temperature and flow fields were widely discussed in the 2D numerical simulations based on different models of the 3D heaters. However, little attention was devoted to the fundamental research for the modeling of the 3D heaters. In this research, we carried out 2D and 3D transient global simulations respectively to study the effects of the modeling of 3D heaters in the 2D numerical simulation on the heat transfer in the industrial DS furnace.

Fig.1 shows the schematic diagram of the hot zones in the 3D numerical model. The configuration of the heaters are asymmetric in the 3D model. Fig.2 shows the schematic diagram of the hot zones in the 2D numerical model. In our simulations, heaters are divided into 1, 2, 3, 4 and 5 sections in the 2D models, respectively. The example of 5 sections is shown in Fig.2 (heaters marked with broken line). Fig. 3 shows the comparison of the temperature of TC1 between the simulations and experiment, where the thermocouple (TC1) is used to control the heating power consumption. The temperature TC1 in the 3D simulation agrees very well with the experimental measurements, and the maximal difference of TC1 between the 2D simualtion and that in the experiment is about 25 K. The research provides an important reference for improvement of 2D simulations of DS system with 3D configuration features for growing high quality silicon ingots.

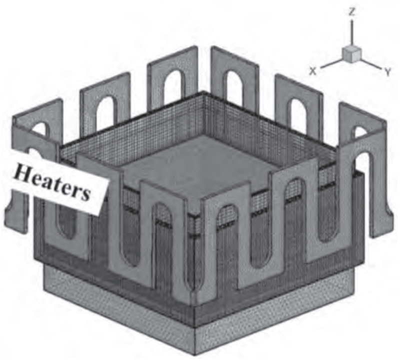

Fig. 1 The hot zone in the 3D model.

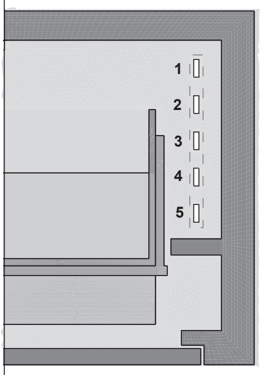

Fig. 2 The hot zone in the 2D model.

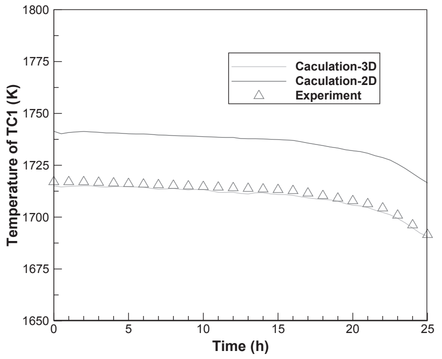

Fig. 3 Evolution of temperature TC1.

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Modelling of dopant transport during floating zone growth of silicon

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Development of software and available computational resources enable the modeling of the floating zone (FZ) process considering coupled electromagnetic (EM), temperature, flow and concentration fields. Due to the high quality requirements it is important to model the dopant transport and its incorporation in the grown crystal as precisely as possible.

Phase boundaries in the FZ crystal growth process are calculated using a 2D axis-symmetric model and a specialized program *FZone* [1]. The calculations of the high-frequency (HF) EM field are done considering the 3D HF inductor.

Axisymmetric calculations of turbulent inert gas flow and dopant transport in a floating zone puller are carried out using an open source software package OpenFOAM. The calculated dopant concentration in the gas is used as a boundary condition for dopant transport in the melt.

The unsteady 3D numerical modeling of the laminar melt flow is performed with the solver FZSiFOAM [2] which is based on the open source software package OpenFOAM. Navier-Stokes equation for incompressible melt flow is solved using the Boussinesq approximation for description of buoyancy. The temperature field is governed by the non-stationary heat transfer equation. For the dopant concentration field the mass transport equation for dopants is solved. From the calculated dopant distribution at the crystallization interface (see Figure 1) the radial resistivity variation profiles are obtained and compared with experimental data for the 4” IKZ Berlin crystal. Boundary conditions with constant concentration and concentration from the dopant transport analysis in the gas are used and the obtained results are compared to each other.

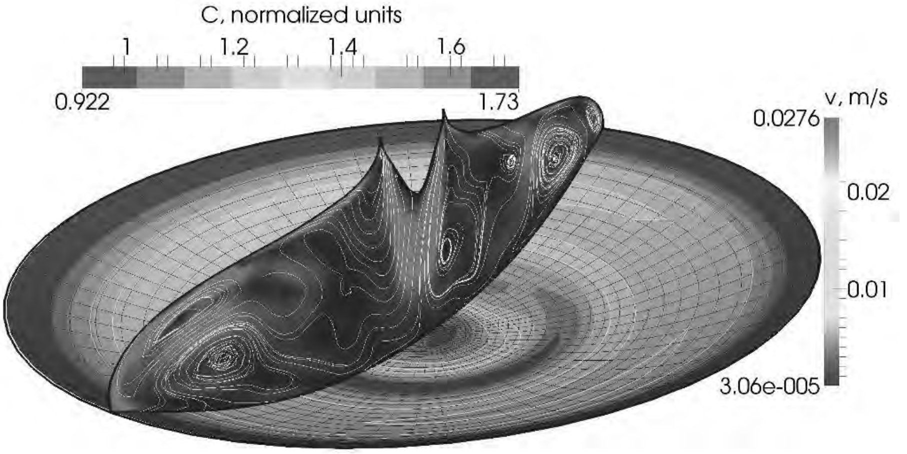

Figure 1. Vertical slice of the melt and crystallization interface. Melt velocity and its streamlines are shown in the vertical slice. Dopant concentration and mesh edges are depicted on the crystallization interface.

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GRAIN STRUCTURE OF MULTI-CRYSTALLINE SILICON : X-RAY SYNCHROTRON IMAGING CHARACTERISATION

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Improvement of multi-crystalline silicon (mc-Si) efficiency for photovoltaic applications is a key issue in the economic world and has thus attracted the scientific interest. In particular, the crystallisation phase is responsible for the grain arrangement and for major defects. Our contribution in this frame consists in the characterisation of the solidification mechanisms using a unique and original experimental set-up associating a high temperature furnace where directional solidification of silicon samples is carried out combined with two X-ray imaging techniques: radiography and topography. X-ray radiography based on absorption contrast enables to characterize the dynamics of the solid/liquid interface, its morphology (facets..) and kinetics (growth rate). The X-ray topography which relies on Laue diffraction principle helps in observing crystals shapes and to follow in real time the formation of the grains, strains and defects during growth [1–3].

We present results obtained by this technique and concerning facets at the solid-liquid interface and twinning. We demonstrate that twins are formed during growth in our samples. These latter are always related to presence of {111} facets. Moreover two twinning mechanisms are described: successive twinning which do not hamper the growth of the grains and, nucleation of grains in twin position which later modify the grain structure arrangement . The facets are also involved in another phenomenon which is the parasitic nucleation of grains at the sample edge. The occurrence of such nucleations is very detrimental when one wants to grow mono-crystalline silicon from a seed using directional solidification techniques [4].

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Modeling of Particle Engulfment during the Growth of Multicrystalline Silicon for Solar Cells

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With a reasonable balance between cost and efficiency, multicrystalline silicon (mc-Si) has been a mainstream material for solar cells, and these cells make up approximately 50% of the market of today's photovoltaics industry. There are significant opportunities for increasing quality and reducing cost of the mc-Si substrate material via a better understanding of crystal growth processes. One challenge is the formation of carbide and nitride precipitates in the melt that are engulfed by the solidification front to form inclusions in the mc-Si solid. These lower cell efficiency and can lead to wafer breakage and sawing defects. Minimizing these particles will promote lower cost and higher quality of solar-grade, multi-crystalline silicon and will advance progress in commercial solar cell production.

The primary goal of this research project is to understand the mechanisms that determine the dynamics of particle transport in silicon melts and the pushing or engulfment of these particles at a moving solid-liquid interface, specifically small silicon carbide (SiC) and silicon nitride particles (Si_3N_4) during the solidification of silicon. This work will coordinate with the ParSiWal (Partikeleinfang bei der Siliziumkristallisation im Weltall) project funded by the German DLR and involving the Fraunhofer IISB, University of Freiburg, and University of Bayreuth.

We present a finite-element, moving-boundary model to assess the dynamics of particle pushing and engulfment. This numerical approach allows for a rigorous representation of forces and dynamics previously inaccessible by approaches using analytical approximation or multi-scale formulations. Figure 1 shows the outcome of a transient simulation of particle engulfment by our approach. Here, all thermal properties are constant and the Gibbs-Thomson effect is turned off, so the solidification interface is flat; however, particle pre-melting is included. Under these conditions, the particle enters into the solid, but it never directly contacts the solidification interface because of the premelted layer. With this choice of parameters, the premelted layer is barely discernible in the images; however, our model is accurately resolving it.

We also present initial results to investigate various factors' influence on particle-solidification front dynamics. Of particular interest is to ascertain critical velocities for engulfment for a variety of different particle sizes and thermal gradients. We will also study the effects of shear and solidification flows, in the melt near the interface, on engulfment mechanisms and the effect of a grain boundary at the interface that locally modifies its shape and energy. Planned experiments by ParSiWal in the laboratory as well as during the TEXUS 50 mission are aimed to probe the effects of particle engulfment during silicon solidification and will be used to assess theoretical predictions.

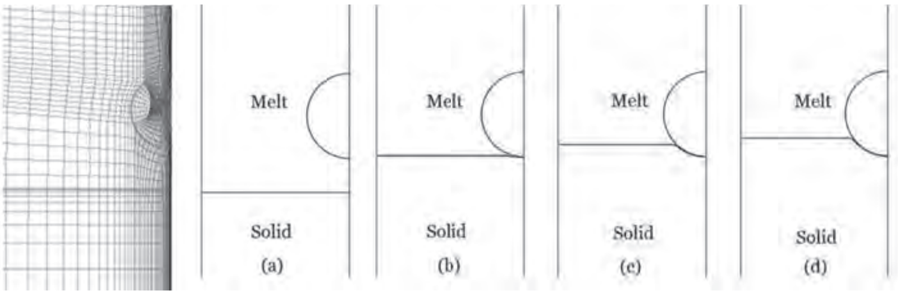

Figure 1: Computation of particle engulfment in the presence of a premelted liquid layer. Left: Snapshot of finite element mesh used in this calculation, with particle and solidification front indicated in red. Right: System geometry with advancing time. A thin layer of premelted melt of ~ 25 nm thickness always separates the particle from the crystal and is well resolved by our model. Such an approach circumvents the need for arbitrary cut-off values for determining minimum gap thickness prior to engulfment of the particle.

Supported in part by U.S. National Aeronautics and Space Administration, NNX10AR70G, the content of which does not necessarily reflect the position or policy of the United States Government.

Feed size dependence of suitable mirror position for silicon crystal growth by infrared convergent heating floating zone method

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In the crystal growth by the infrared convergent heating floating zone (IR-FZ) method, the heating lamp is usually set on one of the focus positions of each ellipsoidal mirror. The molten zone is formed at the other focus position. The number of the set of the heating lamps and the mirrors is dependent on convergent furnaces. Single-mirror type, double-mirrors type and four-mirrors type convergent furnaces are widely used. The layout of the heating lamp and the molten zone is usually in the same horizontal plane in these furnaces and the layout of the heated focus position, where the molten zone is formed, and the rotation axes of both the feed rod and the grown crystal are on the same vertical line. Recently, the systematic control of the interface shape between the molten zone and the grown crystal was achieved in the crystal growth of rutile (TiO_2) by the IR-FZ method using a tilting mirror type furnace [1]. The growth of a larger crystal in diameter by the IR-FZ method was examined [2]. With the increase of the diameter of the grown crystal, the volume of the molten zone is getting larger and the displacement between the molten zone surface where the convergent light is absorbed and the focus position of each ellipsoidal mirror which is on the rotation axes of the feed and the grown crystal is getting larger.

The heated focused position, however, does not have to be on the rotation axes of the feed and the grown crystal for the crystal growth by the IR-FZ method. In this IR-FZ growth of a silicon crystal, therefore, the positions of the mirrors were horizontally shifted from the position close to the molten zone to the more distant positions as compared with the conventional mirror position. The mirror position dependence of the required lamp power to form the molten zone was investigated to find a suitable mirror position. The feed size dependence of the suitable mirror position is also examined by the IR-FZ growth using silicon feed rods with various diameter in the argon gas flow.

The required lamp power was dependent on the mirror position. The mirror position, where the required lamp power was minimized, was observed. The more lamp power was required at the more distant mirror position than the mirror position of the minimum required lamp power. At the closer mirror position, the shapes of grown crystals of silicon were spiral in addition to the more required lamp power. The mirror position of the minimum required lamp power was also found to be dependent on the feed diameter. The more distant mirror position was suitable for the larger feed in diameter. These results indicate that the more effective convergent heating and the suppression of the spiral growth can be realized by the effect of the mirror position.

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The crystal growth process of titanium doped sapphire fibers by the micro-pulling down technique

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Abstract

In this work we have studied the solidification of crystalline fibers of titanium doped sapphire drawn by the micro-pulling down growing technique. The growth of titanium doped sapphire is performed using a relatively recent growing technique [1] that is the (μ-PD). This method presents several advantages over other growing methods [2] and allows a stable growth of shaped crystal fibers with very good optical quality. In this study we established a numerical, two-dimensional finite volume model in cylindrical coordinates with an axisymmetric configuration. The flow, the thermal transfer and the mass transfer are modeled by the differential equations of conservation of the mass, of quantity of the movement, energy and the species. This problem, which takes into account the convection-diffusion coupling, is discretized using the Finite Volumes Method (FVM). We focus on the physical properties of the melt zone and on the radial and axial distribution of titanium in the sapphire crystal fiber. Our model is in good agreement with experimental results.

Keywords: Micro-pulling down (μ-PD) growing technique, crystalline fibers titanium doped sapphire, the thermal transfer, the mass transfer, shaped crystals.

Fig.1: Dopants distribution for different pulling rate. (a) radial,(b)axial.

According to our numerical results, when the pulling rate increases, the dopants concentration of titanium increases in the center of the fiber (Fig. 1.a). Therefore a high pulling rate avoids the segregation of titanium towards the periphery of the fiber. This result is in a good agreement with the experimental results of A. Laidoune [1]. Our results of the dopants concentration along the axis of the fiber are shown in the Fig. 1. b For ($z<0.6$) the dopants concentration is low because the section of the molten zone is larger. As the liquid particles go downwards ($z>0.6$) the concentration increases and it stabilizes when the diameter becomes constant. This result agrees again with the experimental results shown [1]. The melt/crystal interface shape is essentially determined by the heat transfer in the growing system and has a convex shape towards the crystal. This important result agrees with the experiment [1]. The μ-PD method can gather the necessary conditions for optimization of the dopants concentration distribution for increasing the coupling between the laser wave and the ions of the doping agent in order to give the highest possible luminous power at the output of the laser.

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Bubbles defects observation during shaped sapphire crystal grown by the micro-pulling down techniques

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Abstract

Sapphire shaped single crystals contain specific defects called bubbles of average diameter higher than 100 µm or micro-bubbles of diameter smaller than 10µm. These defects strongly affect the crystal properties and decrease the optical performances. The comprehension of the mechanism of bubbles creation, their movement in the meniscus and in the vicinity of the crystallization interface and their incorporation inside the crystal are crucial to overcome their apparition and propagation [1]. Bubbles of 100 µm diameter average are observed in the molten zone. Before their propagation inside the crystal they have a periodic oscillation, and consequently deform crystallization interface [2]. We have studied the effect of the pulling rate on the bubbles size and their distribution in sapphire rods grown by the micro-pulling down (µ-PD) technique. Using a central circular capillary die, the bubbles diameters decreases as a function of pulling rate. The optical properties such transmission and light propagation are strongly affected by the pulling rate and the thermal isolation.

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E. A. Ghezal,, A. Nehari, K . Lebbou, and T. Duffar
CRYSTAL GROWTH & DESIGN Volume: 12 Issue: 11 (2012) 5715-5719

2-Effect of Pulling Rate on Bubbles Distribution in Sapphire Crystals Grown by the Micropulling Down (mu-PD) Technique
E. A. Ghezal, H. Li, A. Nehari, G. Alombert-Goget, A. Brenier, K. Lebbou, M. F. Joubert, and M. T. Soltani
CRYSTAL GROWTH & DESIGN Volume: 12 Issue: 8 (2012) 4098-4103

Nonstoichiometry and defect formation in scheelite-like double tungstates grown by the Czochralsky technique

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Double tungstates with scheelite structure are used as active laser media for the creation of efficient and compact diode-pumped solid-state lasers that operate in the near-infrared region. These compounds with the general chemical formula $(Na^{1+}_{0.5}TR^{3+}_{0.5})WO_4$ (TR^{3+} - a rare earth element) belong to the scheelite family (space group $I4_1/a$, Z=4). In crystal structure the Na^{1+} and TR^{3+} ions have dodecahedral environment by the O^{2-} ions with two sets of interatomic distances (c.n. = 4 + 4; c.n. – coordination number). The W^{6+} ions are located in the middle of slightly distorted WO_4 tetrahedra (c.n. = 4) with two sets of valent angles. Double tungstates with scheelite structure are characterized by the wide homogeneity region, the disordered crystal structure as well as by the absence of congruent melting when grown from the melt. They demonstrate a significant deviation from stoichiometry and the associated formation of structural defects. All the above mentioned affects the stability of double tungstates composition and physical properties as well as it results in the color center appearance in the crystals and, hence, it negatively affects the laser characteristics. The present study is devoted to the determination of sodium gadolinium tungstate crystal composition by X-ray diffraction analysis.

Three series of single crystals of the following initial melt compositions have been grown by the Czochralski technique: $(Na^{1+}_{x}Gd^{3+}_{1-x})WO_4$ (x=0.5, x<0.5, x>0.5) (I Series), $(Na^{1+}_{0.5+x}Gd^{3+}_{0.5})WO_4$ and $(Na^{1+}_{0.5}Gd^{3+}_{0.5+x})WO_4$ (x=0.05) (II Series), $(Na^{1+}_{0.5}Gd^{3+}_{0.5})(W_{1\pm y})O_4$ (III Series). The X-ray diffraction analysis of crystals microparts of ~0.2×0.2×0.2 mm in size was carried out on a STOE STADI VARI PILATUS-100K single crystal diffractometer (MoK_{α}).

The crystal structure refinement indicates the difference between refined crystal compositions and melt ones. The crystal compositions of the following general forms were determined for all the series: $(Na_xGd_{1-x})(W_y\square_{1-y})O_4$ ($x<0.5$, $y>0$) (Series I); $(Na_xGd_{1-x-z}\square_z)(W_y\square_{1-y})O_4$ ($x<0.5$, $y\geq0$, $z>0$) (Series II); $(Na_xGd_{1-x-z}\square_z)(W_y\square_{1-y})O_4$ ($x<0.5$, $y\geq0$, $z\geq0$) (Series III).

In some crystal structures the oxygen vacancies were revealed and the presence of tungsten ions with different formal charges (W^{6+} and W^{5+}) is not excluded. Determined correlation between the structural parameters (unit cell parameters, interatomic distances in the coordination polyhedra and valent angles) and compositions of (Na^{1+},Gd^{3+}) and W sites in the structures confirms the crystal refined compositions. The obtained results allow us to offer the crystallochemical approach for the refinement of melt composition with the uniform distribution of components over the crystal.

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Growth and thermoluminescence studies on rare earth orthogallate ($NdGaO_3$) single crystal by Floating zone technique

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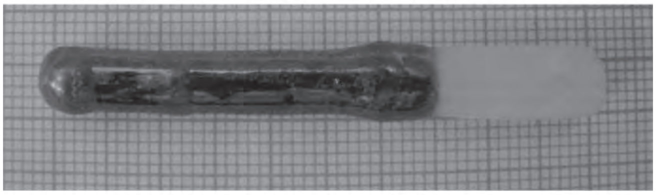
Abstract:

Rare-earth oxide compounds with perovskite structure have a long record of outstanding performance in solid-state physics. Many perovskite materials have been thoroughly studied and are now used in industry. Neodymium gallate, $NdGaO_3$ is one such compound. The growth of $Nd_{1-x}Sm_xGaO_3$ crystals (x =0.25, 0.50, 0.75, 0.9) has been reported by Aleksiyko et al [1]. Structure investigations of $Nd_{1-x}Sm_xGaO_3$ (x =0.25, 0.50) at RT were also reported in [2]. Polycrystalline feed and seed rods were synthesized by the conventional solid-state reaction technique. The crystalline phases of the sintered powder were identified by X-ray diffraction pattern analysis. Single crystal growth was performed in the optical floating-zone furnace (FZ-T-4000-H-HR-I-VPO-PC, Crystal Systems Corp.) having four halogen lamps as infrared radiation source. Fig.1 shows the photographs of as grown single crystals. The powder XRD pattern was recorded in the 2θ range 20 – 70 degree. All the X-ray diffraction peaks were indexed using STOE WinXPOW software. No impurity lines are observed, and the reflections can be well indexed to a perovskite type structure of $NdGaO_3$ with the Pbnm space group and the peak positions are in good agreement with the powder diffraction file (PDF Card NO. 83-0538). X-ray diffraction pattern of as grown crystal indicates that the grown crystal has (002) orientation with the nominal composition. The thermoluminescence readout on $NdGaO_3$ crystal shows an intense glow peak around 250 °C for the heating rate of 5 °C /s. The order of kinetics (b), activation energy (E) and other trapping parameters were calculated using peak shape method.

$NdGaO_3$



$Nd_{0.75}Sm_{0.25}GaO_3$

Fig.1 Photographs of as grown single crystal

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Growth of very large, stress-free YAG crystals with a new method

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Yttrium-aluminium garnet (YAG, $Y_3Al_5O_{12}$) is known for more than 40 years and is widely used as a host material mainly for solid-state lasers and scintillators. Czochralski method with automatic diameter control is commonly used for YAG production. The standard furnaces result in crystals with typical diameters below 100 mm. Larger crystals can be prepared by Kyropoulos, Heat Exchange Method, Temperature Gradient Technique or Horizontal Solidification Method, but their quality is typically insufficient, so these crystals did not find broader applications.

The newly developed method aims on production of very large and stress-free crystals. Crystals as large as 125 mm in diameter and 8 kg heavy without core will be presented. 150 mm crystals will be produced in the newly designed furnace this year. And since the system seems to be very robust, even larger crystals can possibly be achieved. The key features of the method are: i) tungsten crucible to cope with temperature gradient along the large area, ii) use of hydrogen protective atmosphere as gas with very high temperature conductivity, and iii) inside process configuration substantially different to the original Czochralski method. Homogeneous temperature distribution results in a very stable and flat growth front.

Technology of growth large garnet crystals can be used with advantage for several applications. Undoped YAG can, for example, replace sapphire as a material for high-power laser systems. Unlike sapphire, YAG is not birefringent. This brings a substantial advantage in any application where subtle differences in index of refraction can be a problem. Size matters also with doped materials. YAG:Ce is a perfect material for large imaging screens with submicron resolution using UV, X-ray, electrons or heavier radiation. Newly grown crystals will allow using much bigger “screens” to achieve larger field-of-view than it was ever possible. Yb:YAG is used for laser high-power application. This material is the key material considered to reach thermonuclear fusion within the HiPER reactor. Homogeneity of the grown material is good enough now to manufacture laser Yb/Cr:YAG slabs of the size and parameters necessary for this application. Laser slabs as large as 120x120mm are now being manufactured. Large Yb:YAG thus now offers attractive option to a large YAG ceramics, which might face problems with a high-power beam depolarization due to different orientation of small YAG grains.

Investigation of Second Harmonic Generation in SBN Crystals

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Second harmonic generation (SHG) is widely used to obtain radiation in the visible spectral region. The search for new efficient SHG nonlinear materials is very important. $Sr_xBa_{1-x}Nb_2O_6$ (SBN-x) is a perspective crystal for SHG applications due to its strong nonlinear optical properties [1]. Due to small birefringence of SBN the phase matching conditions for collinear SHG can hardly be satisfied. Coercive field in SBN is very weak, therefore, it is very attractive for manufacturing of periodically poled objects. SBN crystals with a periodically poled domain structure can be attractive for developing compact SHG converters. The aim of this work was to investigate SHG conversion efficiency in nominally pure and doped SBN crystals.

SBN belongs to relaxor ferroelectrics with ferroelectric polar phase at room temperature. The smooth phase transition to paraelectric nonpolar phase is observed with the increase of crystal temperature. The temperature of this phase transition depends on the composition of the crystal (*x*) and impurity dopants. In the earlier papers [2,3] the phase transition in SBN was investigated by measuring the temperature dependencies of dielectric constants.

The investigation of SHG in triturated materials can provide information on the value of the second order nonlinear susceptibility (χ). In this report we investigated SHG and its temperature dependence in triturated SBN crystals. The samples of nominally pure SBN-61, SBN-75 and SBN-61 doped with 0.5 wt.% Nd_2O_3, 0.5 wt.% Ni_2O_3, and 0.01 wt.% Cr_2O_3 were triturated into the powder with average single crystal size 2-4 μm. This dimention corresponds to the maximal coherence length of SHG process at 1064 nm wavelength in SBN crystal. The experimental setup utilized TEM_{oo} YAG:Nd laser passively Q-switched with $LiF:F_2^-$ color center crystal. The energy of laser pulses was 1.2 mJ, the duration of pulses was 13 ns with 5 Hz pulse repetition rate. This provided us the peak intensity density of 6,1 MW/cm^2 at the sample site. The backscattering radiation was collected by an optical collimator and fiber and delivered to the entrance slit of the spectrometer (USB-4000-UV-VIS-ES, Ocean Optics). The investigated sample was placed on a glass substrate located on a cupper block whose temperature was stabilized in the range from 5 to 90^{o}C.

The temperature dependences of SHG intensity in nominally pure and doped SBN are presented in Fig.1. The increase of the sample temperature results in the phase transition from polar to non-polar phase and vanishing of SHG conversion. It is important to note that increase and cooling dependencies exhibit no hysteresis behavior. The dependences of phase transition temperatures for all investigated SBN crystals were analyzed. These characteristics are in a good agreement with the results of measurements by traditional methods. The values of χ coefficient were calculated in comparison with the one in $LiIO_3$. With the increase of Sr content in SBN solid solution χ coefficient decreases from 16.1x 10^{-12} to 1.2x 10^{-12} m/V for SBN:61 and SBN:75, correspondingly. Among doped crystals SBN:61:Co is characterized by the maximum value of χ coefficient (16.3x10^{-12} m/V). The dependence of SHG intensity on pumping efficiency was also shown for triturated SBN samples.

Our investigations indicate that SBN crystal can provide us with SHG elements with a temperature controlled second order nonlinear susceptibility.

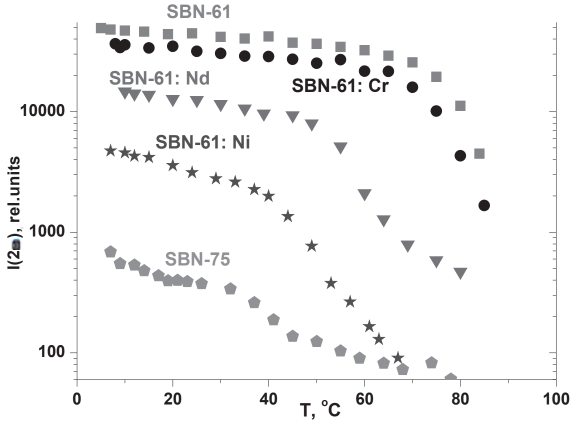

Fig. 1. The temperature dependences of SHG intensity in pure and doped SBN crystals exhibit smooth phase transitions for all investigated samples.

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Growth of Nd:GGG crystals with the diameter up to 190 mm by Czochralski method

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Considerable efforts have been devoted to search for good solid-state gain media, in which Nd:$Gd_3Ga_5O_{12}$ (Nd:GGG) crystal has been proved to be an excellent candidate for high power laser applications owing to its good mechanic properties, excellent thermal conductivity and high efficiency laser performance [1-4]. In comparison with Nd:glass, Nd:GGG boasts a better mechanical strength and higher thermal conductivity, which, as a result, can achieve the goal to rapidly cool the gain media between runs and reduce the turnaround time between laser firings [5]. Regarding to Nd:$Y_3Al_5O_{12}$ (Nd:YAG), one of the most excellent gain media for solid-state lasers, Nd:GGG crystal has the merits of lower melting temperature, easier to get larger size (no core growth), higher segregation coefficient, and wider phase homogeneity with high pulling rate (up to 5 mm/h) [6-8].

In the past few years, our research group also has been desired for proper growth parameters of large-sized Nd:GGG crystals. The crystal with the diameter of 120 mm was reported in 2007 [9]. In this paper, we report the growth of even larger, crack-free Nd:GGG crystals by using the Czochralski method. Large-sized Nd:GGG crystals with the diameters of 130, 156, 178 and 190 mm were successfully grown by Czchralski method, as shown in fig. 1 below. X-ray powder diffraction was used to characterize the phase purity of polycrystalline materials. All of the diffraction peaks are in good with the calculated one from the crystal structure of GGG, indicating the pure Nd:GGG polycrystalline materials. In addition, the optical homogeneity of as-grown 153 mm diameter Nd:GGG crystal was tested. The homogeneity value of 4.10×10^{-5}, with a RMS of 5.41×10^{-6}, was obtained, indicating that the as-grown crystal is of high quality. We also analyzed the relationship between the phase map of homogeneity result and crystal. Considering the crystal shape and ridge symmetry, the Nd:GGG crystal with the diameter of 190 mm should have a better quality than that of 156 mm one.

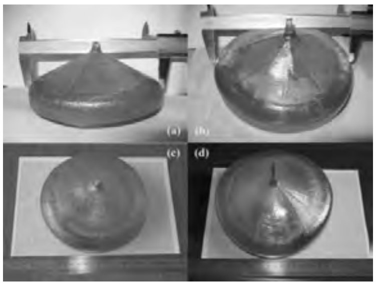

Fig. 1 As grown Nd:GGG crystals with dimensions: (a) 130 mm; (b) 156 mm; (c) 178 mm; (d) 190 mm

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Growth of $Ca_3Ta(Ga_{1-x}Al_x)_3Si_2O_{14}$ piezoelectric single crystals by Czochralski method and their piezoelectric properties

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Langasite-type single crystals have been investigated as a piezoelectric material due to the high piezoelectric constant and electromechanical coupling factor at high temperature and the langasite-type crystals are expected to be applied for various sensor devices at high temperature such as the combustion pressure sensor and temperature sensor [1][2]. Furthermore, they indicate the high frequency stability for temperature change as an oscillator. Recently, Rare-Earth (RE)-free langasite-type crystals such as $Ca_3TaGa_3Si_2O_{14}$ (CTGS) and $Ca_3NbGa_3Si_2O_{14}$ (CNGS) have been developed and there are many reports about the RE-free langasite-type crystals. They are attracting worldwide attentions as a piezoelectric material because their electrical resistivity at high temperature is higher than the previous langasite-type crystals containing RE such as $La_3Ta_{0.5}Ga_{5.5}O_{14}$ and $La_3Ga_5SiO_{14}$ [3]. In addition, the manufacturing cost can be decreased by decreasing the amounts of RE (La) and Ga ions in the crystals.

In our recent study, $Ca_3Ta(Ga_{1-x}Al_x)_3Si_2O_{14}$ crystals with x = 0, 0.2, 0.4, 0.6, 0.8 and 1 were grown by the micro-pulling-down (μ-PD) method and all crystals indicated a single phase of langasite-type structure without secondary phase. Therefore, in this study, we grew $Ca_3Ta(Ga_xAl_{1-x})_3Si_2O_{14}$ bulk single crystals by Czochralski (Cz) method to investigate their piezoelectric properties.

The mixed powders were prepared using $CaCO_3$, Ta_2O_5, β-Ga_2O_3, α-Al_2O_3 and SiO_2 powders as a starting material. $Ca_3Ta(Ga_{1-x}Al_x)_3Si_2O_{14}$ crystals were grown from the mixed powder by the Cz method. The chemical compositions of grown crystals were analyzed by the Electron Probe Micro-Analyszer (EPMA). The y-cut specimen was obtained from the bulk crystal, the piezoelectric properties were measured by the precision impedance analyzer using impedance-frequency curve.

$Ca_3Ta(Ga_{0.5}Al_{0.5})_3Si_2O_{14}$ crystal grown by the Cz method is shown in Fig.1. There was no crack in the crystal and it indicated high transparency with yellow color. The crystal growth, actual chemical compositions, crystallinity and piezoelectric properties of $Ca_3Ta(Ga_{1-x}Al_x)_3Si_2O_{14}$ crystals will be reported.

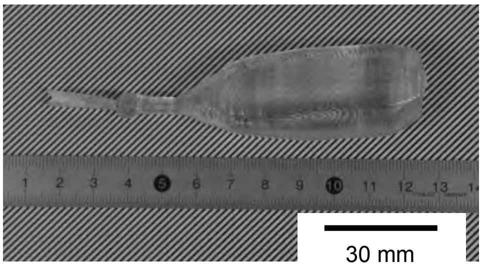

Fig.1 $Ca_3Ta(Ga_{0.5}Al_{0.5})_3Si_2O_{14}$ single crystal grown by the Cz method

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Growth and optical studies of bulk 4-Aminobenzophenone single crystal by modified vertical dynamic gradient freeze technique

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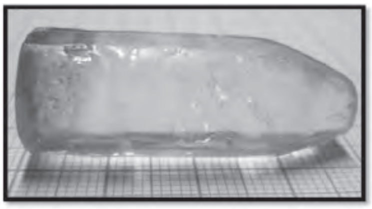
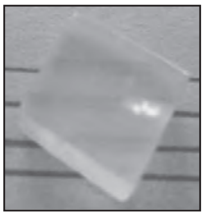
Abstract

Applications of organic materials have attained the superior level in recent technologies. The development of modern optical devices for the signal processing applications has increased the demand of electronically and optically functional organic single crystals. In general, melt growth techniques are suitable for the growth of bulk and unidirectional single crystals. But, growing bulk organic single crystals from melt technique is still a challenging task due to their thermal and chemical instability nature. To overcome this, making some modification in the existing or traditional crystal growth methods are the recent trends in crystal growth technology. Therefore in the present work, we have designed and constructed a modified melt technique, i.e., modified vertical dynamic gradient freeze (VDGF) system operating in the temperature range from 50 ˚C to 500 ˚C to grow bulk organic single crystals. Furnace was constructed with eight zones to achieve controlled thermal environment and multiple temperature gradients which are essential for the growth of organic single crystals. The transparent furnace enables direct observation to record and monitor the solid-liquid interface and growth of crystals through charge coupled device (CCD) based video camera. The system is fully computerized and hence it is possible to retrieve the complete growth and furnace history.

The efficiency of the designed VDGF system was illustrated by the growth of some well known organic NLO single crystals. 4-Aminobenzophenone is one among them which have higher SHG efficiencies than KDP (~150 times). Growth of 4 - ABP single crystals from solution and melt growth techniques was already reported. To improve the size and quality, we have employed the vertical dynamic gradient freeze technique (VDGF). The precise control of temperature and vibration less growth of the VDGF system provided the bulk 4-ABP single crystal with the size of 18 mm in dia and 40 mm in length. The structural and optical qualities of the grown crystal are analyzed. For nonlinear optical applications, along with the bulk growth, complete knowledge on linear and nonlinear optical properties of the single crystals is the essential requirement. Hence, in the present investigation, linear and nonlinear optical properties of the 4-ABP single crystal grown from the VDGF technique are studied using some simple methods.





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Czochralski growth of ferroelectric $LaBGeO_5$ single crystals for UV-generation

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Quasi-phase-matching (QPM) devices based on periodically poled structure are suitable for generating the second-
d third-harmonics, and ferroelectric crystals such as $LiNbO_3$ and $LiTaO_3$ are now used practically. However, they
not suitable for the UV region because of their limited optical transparency. Recently, we have realized the 350nm
neration by the QPM device made of an old but novel ferroelectric crystal of $LaBGeO_5$ (LBGO) [1]. LBGO has the
gonal symmetry belonging to the space group C_3^2. A few reports on the single crystal growth of LBGO have been
orted [2-4]. In order to make a QPM device, a crack-free single-domain crystal with diameter greater than 15mm
uired. Here, we present the Czochralski (Cz)-pulling of LBGO single crystal with good optical quality and
table size for device fabrication.

5N purity raw materials of La_2O_3, H_3BO_3 and GeO_2 were mixed in the stoichiometric ratio, and the mixture was
tered at ~1100 °C in air. The growth was carried out by the rf-heating Cz technique using a Pt crucible. A serious
blem of significant evaporation of components during the growth has
en reported [2-4]. We were able to resolve this issue by growing the
stal in dry atmosphere. The pulling and rotation rates were 0.4-1.0
n/h and 5-20 rpm, respectively. A typical example of the c-axis-grown
GO single crystal is shown in Fig.1. The crystal was a colorless
nsparency and exhibited a clear three-fold growth habit, which is a
aracteristic feature of LBGO. The optical transmittance of c-plate was
asured and the absorption edge was found to be around 195nm, as
wn in Fig.2. The short absorption edge makes LBGO useful for the
neration of UV region, shorter than 400nm [1].

By polishing with the colloidal silica suspended in water, the maze
main-like ferroelectric domain structure was revealed on the c-plate, as
wn in Fig.3(a). After performing a poling process and repolishing, we
nfirmed that it is a single domain structure, as shown in Fig.3(b). The
gle poling process conducted by applying about 40V/mm at 650°C.

Peculiarities of the crystal growth of LBGO will be presented in details.

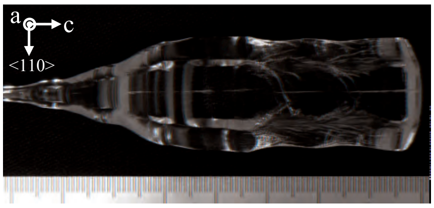

Fig.1: As-grown LBGO single

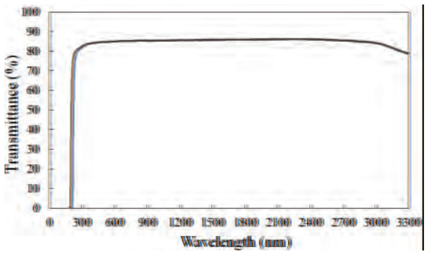

Fig.2: Optical transmittance

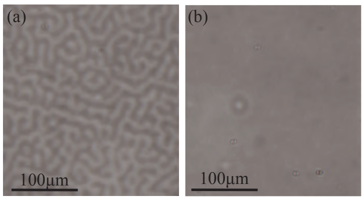

Fig.3: Domain structure on the c-plate
(a) as-grown, (b) after poling

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Single crystal growth of $KTa_xNb_{1-x}O_3$ by the Bridgman method

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June
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$KTa_xNb_{1-x}O_3$ (KTN) is an attractive material for optical devices, such as a laser beam scanner [1] and a variable focal-length lens [2], because of its large electro-optic effect above the phase transition temperature between cubic and tetragonal structures. In these devices, KTN single crystals grown by the Top-Seeded Solution Growth (TSSG) are used, and growth-induced striations exist inevitably in the crystals as pointed out [3]. Therefore, the incident beam should enter perpendicularly to the striations in order to avoid beam distortion caused by refractive index inhomogeneities due to the striation [3]. The striation in the KTN is a compositional fluctuation, a ratio of Ta/(Ta+Nb), which results in refractive index fluctuations [4]. The main origin of the striation in single crystals is related to temperature instabilities associated with complex convection flows in the solution during the TSSG growth. The vertical Bridgman and the vertical gradient freeze (VGF) growth methods are the promising solutions to eliminate convection flows in the solution.

The raw materials K_2CO_3, Ta_2O_5, and Nb_2O_3 (99.99% purity) were used. To avoid inclusions and/or precipitates, which would result in poly-crystallization, we examined the preparation of the starting charge materials prior to the growth experiments; K content and crystalline quality of sintered KTN compound. The <001>-oriented seed crystal was positioned in the bottom of crucible made of Pt. Both Bridgman and VGF growth experiments were conducted by lowering a crucible and by cooling the furnace, respectively.

Figure 1 shows an example of the Bridgman-grown boule. Four holed facets, which indicated single crystallinity, were sometimes observed on the crystal surface, and the X-ray diffraction pattern also showed that the grown crystals were in single crystalline. When the stoichiometric composition was used as the charge materials and soaking treatment was not conducted, $K_6Ta_{10.8}O_{30}$ intermediate compound was found to have contaminated at the beginning of the growth stage. The $K_6Ta_{10.8}O_{30}$ intermediate compound could be suppressed by using K-rich charge material as it was in the Bridgman growth of $KTaO_3$ [5].

The striation was confirmed under a polarized microscope, as shown in Fig. 2. Very weak striation could be only observed in the Bridgman-grown crystals (Fig.2b) in contrast to the existence of clear striation in the TSSG-grown crystals (Fig.2a). The refractive index fluctuation Δn in the Bridgman-grown crystals was ~$1x10^{-5}$, where the detectable minimum value of refractive index was $1x10^{-5}$ for our polarized microscope. Because the refractive index fluctuation Δn around $1x10^{-4}$ due to periodical striations causes Bragg diffraction of the laser light, refractive index fluctuation Δn around $1x10^{-5}$ is acceptable for most ptractical applications. The compositional fluctuation of Ta/(Ta+Nb) ratio Δx was also estimated to be 0.0001 from our early work for the relationship between Δn and Δx.

We established nearly striation-free KTN crystals grown by the Bridgman growth method.

Figure 1 an example of the Bridgman-grown boule.

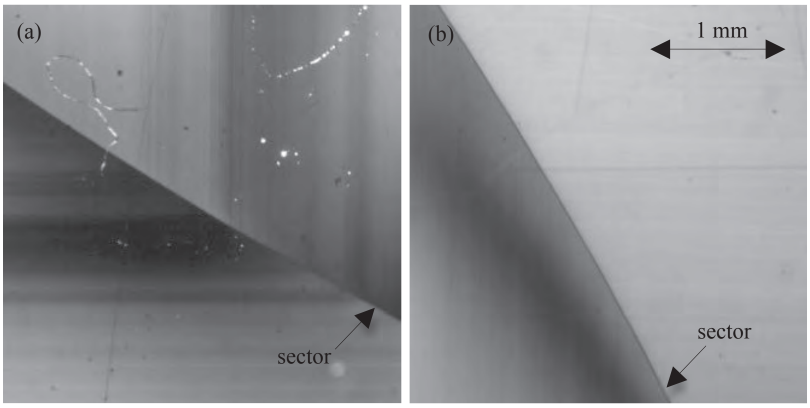

Figure 2 Striation characterizations under polarized microscope: (a) in the TSSG grown crystal, (b) in the Bridgman grown crystal.

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Investigation of phase equilibria and growth of BBO (β-BaB_2O_4) crystals in BaB_2O_4–LiF system

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The BaB_2O_4–$(LiF)_2$ system is of great interest for the crystal growth of the low-temperature form barium metaborate, β-BaB_2O_4 (BBO), which is widely used for frequency conversion in the visible through UV spectral region. The main method for growing β-BaB_2O_4 single crystals is crystallization from high-temperature solution using the technique of top-seeded solution growth **[1]**.

In this work phase equilibria in the BaB_2O_4–$(LiF)_2$ system have been studied. LiF is considered the promising solvent for β–BaB_2O_4 crystal growth due to the essential viscosity reduction. Also, lithium ions should not enter isomorphically into the structure of barium borate because of crystallochemical characteristics.

The phase formation in the BaB_2O_4–$(LiF)_2$ system has been studied by the methods of solid–state synthesis, modified visual polythermal analysis (VPA), spontaneous crystallization on a platinum loop and differential thermal analysis (DTA).

The experimentally determined optimal conditions for the solid–state synthesis were 690°C and 3 days. The criterion of reaction completion was the constant ratio of peak intensities. XRD characterization of the BaB_2O_4–$(LiF)_2$ samples prepared by solid–state reactions showed the presence of BaB_2O_4, $Li_2Ba_4B_{10}O_{20}$, BaF_2 at BaB_2O_4 contents above 83 mol % and $Li_2Ba_4B_{10}O_{20}$, $LiBaF_3$, LiF at BaB_2O_4 contents below 77 mol % and $Li_2Ba_4B_{10}O_{20}$, BaF_2, $LiBaF_3$ in the composition range from 77 to 83 mol % BaB_2O_4.

The chemical reactions in the solid state along the BaB_2O_4–$(LiF)_2$ section can be represented as follows:

at 83 mol % BaB_2O_4, $5\ BaB_2O_4 + (LiF)_2 = Li_2Ba_4B_{10}O_{20} + BaF_2$

at 77 mol % BaB_2O_4, $5\ BaB_2O_4 + 1.5\ (LiF)_2 = Li_2Ba_4B_{10}O_{20} + LiBaF_3$.

VPA and spontaneous crystallization on a platinum loop were applied to study the concentration range from 20 to 90 mol % LiF. It has been found that BaB_2O_4–LiF system is not quasi–binary. The liquidus of the BaB_2O_4–$(LiF)_2$ section consists of the primary crystallization fields of the α–BaB_2O_4, β–BaB_2O_4, $Li_2Ba_4B_{10}O_{20}$ and LiF phases. The powder XRD patterns of rounded boules, grown from melt composition from 82–75 mol % BaB_2O_4, exhibited a set of peaks corresponding to the β–BaB_2O_4 phase.

DTA was used to study the composition range 20 to 80 mol % LiF at 10 mol % intervals. The DTA curves of the samples from the primary crystallization field of BaB_2O_4 show small peaks at 887 °C, corresponding to the boundary between the β–BaB_2O_4 and BaB_2O_4 + $Li_2Ba_4B_{10}O_{20}$ crystallization fields. The splitting of the melting endotherm at 60, 70, 80, 90 mol % $(LiF)_2$ allowed us to locate the narrow crystallization field of $Li_2Ba_4B_{10}O_{20}$ + LiF.

BaB_2O_4 crystals were grown in a precise furnace with a vertical arrangement of heating elements and thermal field with L3 symmetry **[2]**. A high-temperature solution of the 0.65 BaB2O4–0.35 LiF composition with a mass of 1 kg was melted in a platinum crucible 90 mm in diameter and 95 mm in height. A crystal was grown on a single crystal seed with a cross section of 5 × 5 mm^2, oriented along the optical axis. After determining the equilibrium temperature with the seed brought into contact with the melt in the center of its surface, the growth process was conducted at a constant unidirectional rotation rate of 1 rpm and a constant pulling rate of 0.4 mm per day. The cooling rate was 0.3 to 1°C per day. Total temperature decrease was only 21.5 °C due to the very narrow crystallization area, but the yield coefficient was as high as 7.44 g/(kg·°C). The largest crystal was 60 mm in diameter and 25 mm in height, its weight was 160 g.

The high-temperature solution was used repeatedly. After first growth run, we added synthesized BaB_2O_4 in the crusible corresponding to the weight of the grown crystal. The crystal was 53 mm in diameter and 20 mm in height, its weight was 72 g in the second cycle. The yield coefficient is equals to 3.1 g/(kg·°C). Crystallization started at temperature about 920 °C, temperature interval of crystallization was 23.5 °C. Thus, the β-BaB_2O_4 crystals can be grown with a high output in the BaB_2O_4–LiF system only in one growth cycle due to the reactions occurring in the melt.

Table 1 contains the characteristics of the crystals grown in the BaB_2O_4–LiF system in two growth cycles. As follows from the data in Table 1, the transition from cycle I to cycle II is accompanied by a decrease of the yield and, accordingly, the sizes and weight of grown crystals.

Table 1. Experimental data on the growth of β-BaB_2O_4 crystals

System	Cooling range, °C	Pulling range, mm	Crystal weight, g	Crystal diameter and height, mm	Output, g/kg·°C
I BaB_2O_4–LiF	21.5	12	160	60 × 25	7.44
II BaB_2O_4–LiF	23.5	13	72	53 × 20	3.1

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Optimization of the growth of titanium doped sapphire fibers by the micro-pulling down technique

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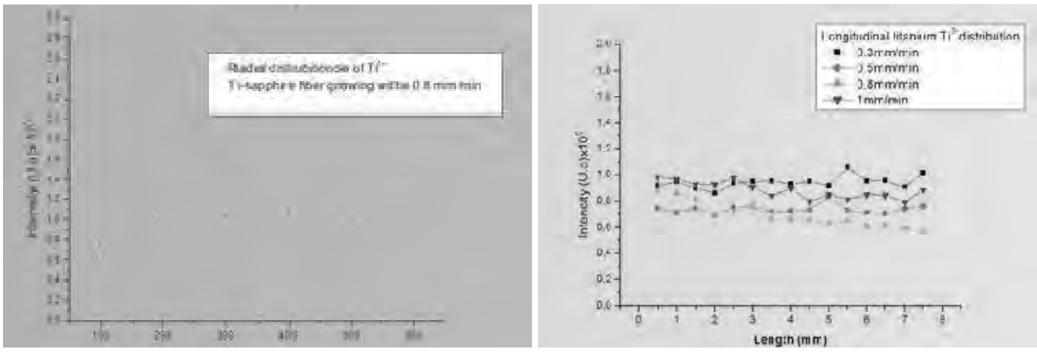
Abstract

In this study we present the optimization of the growth of undoped and titanium doped sapphire fibers crystals grown by micro pulling down (µ-PD) technique. The growth of titanium doped sapphire is performed using a relatively recent growing technique that is the (µ-PD). This method presents several advantages over other growing method and allows a stable growth of shaped crystal fibers with very good optical quality. The obtained fibers have good transparency and stable diameter, they are homogeneous are free from defects The minimization of segregation of titanium is realized through the optimization of the growth conditions (drawing rate, the heating power and the titanium concentration).. This work confirms the importance of crystalline fibers as good candidates in the design of new photonic devices for laser application. This experimental results are confirmed with the numerical study performed by H. Azoui in reference [1] that is a two dimensional finite volume model in cylindrical coordinates with an axisymmetric configuration. According to our results, when the pulling rate increases, the dopant's concentration of titanium increases in the center of the fiber (Fig. 1.a). Therefore a high pulling rate avoids the segregation of titanium towards the periphery of the fiber.



(a) (b)

Fig.1: Experimental dopant's distribution for different pulling rate.a) radial, b)axial.

Keywords: Micro-pulling down (µ-PD) growing technique, crystalline fibers titanium doped sapphire, the thermal transfer, the mass transfer, shaped crystals.

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The Synthesis, Crystal Growth, and Properties of Organic DAST

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4-N, N-diethylamino-4´-N´-methyl-stilbazolium tosylate (DAST) raw materials were synthesized by the reaction of 4-picoline, methyl toluenesulphonate, 4-N, N -dimethylamino benzaldehyd and purified by re-crystallization. The DAST crystals were grown by slop nucleation method (SNM), and the grown DAST crystals were characterized by single crystal X-ray diffraction and NMR (Nuclear Magnetic Resonance). Moreover, widely tunable THz waves ranging from 1.16 to 16.71THz were generated from 1mm-thick DAST crystals using the OPO, gaining the THz output energy of 27.4nJ(peak power of 2.74W) at 3.8THz.

Fig.1 The synthesized DAST raw materials

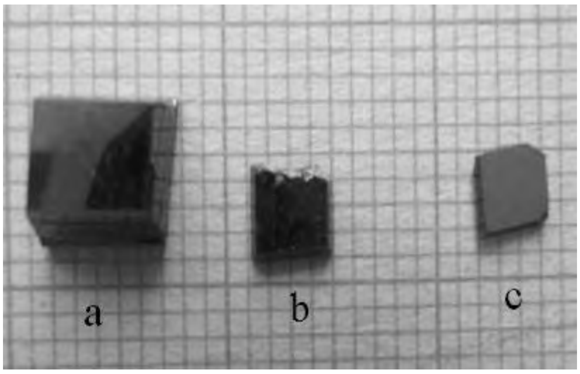

Fig.2 The grown DAST crystals（a：5×5×2mm^3；b： 4×4×1mm^3；c：3×3×1mm^3）

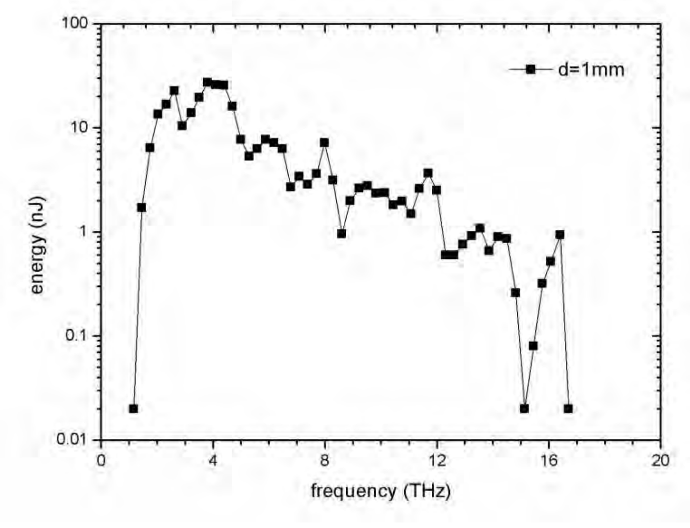

Fig.3 THz output energy as a function of THz frequency with 1-mm-thick DAST crystals.

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Comparison of the influences of in-situ doping using B_2H_6 and PH_3 on polycrystalline Ge layers

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We investigated the deposition of Polycrystalline Ge (poly-Ge) for application to channel layers 3-dimensional NAND flash memories in order to replace polycrystalline Si. In-situ doped poly-Ge layers were deposited by ultra-high vacuum chemical vapor deposition process. The influences of in-situ doping on the poly-Ge layers were studied by varying the flow rate of dopant source gases. The dopant source gases were B_2H_6 and PH_3 for the deposition process. Poly-Ge layers were deposited on a thermally oxidized Si(001) wafer. At 600 °C, the flow rate of GeH_4 was fixed at 200 standard cubic centimeters per minute (sccm), and the dopant source gas flow rates were varied from 0 to 200 sccm. Scanning electron microscopy (SEM) images showed that the growth rate of poly-Ge deposited in the presence of B_2H_6 increased with the increasing B_2H_6 flow rate, while the growth rate of in-situ P doped poly-Ge using PH_3 decreased as the PH_3 flow rate increased. At B_2H_6 flow rates of up to 50 sccm, island-shaped poly-Ge layers were formed. Poly-Ge layers were deposited as continuous layers after a B_2H_6 flow rate of 100 sccm. On the other hand, all poly-Ge layers deposited in the presence of PH_3 had island shapes. The area density of poly-Ge islands decreased with the PH_3 flow rate, which decreased to less than 10 μm^{-2} for PH_3 flow rates up to 50 sccm. The average diameters of in-situ P doped poly-Ge layers increased up to 150 nm for PH_3 flow rates of up to 50 sccm and then decreased above the PH_3 flow rate of 75 sccm. We found faceted islands in a pyramid shape in the in-situ P doped poly-Ge.

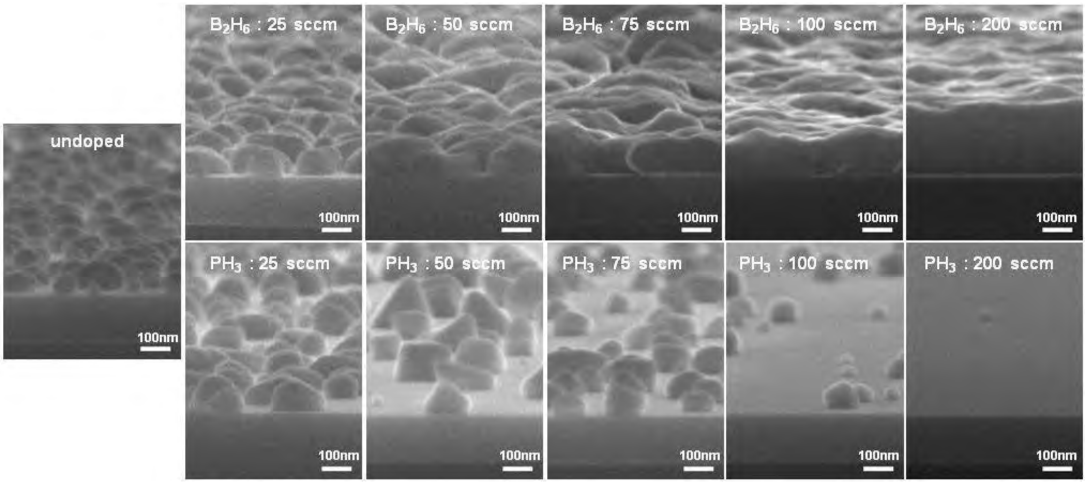

Fig 1. SEM Images of poly-Ge deposited from GeH_4 without additional doping and deposited in the presence of B_2H_6 and PH_3.

Effect of phosphorus on epitaxial growth of Ge layers on Si(111) substrates

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Research has been conducted on Ge for its applications in advanced nanoelectronics because of its higher mobility when compared with that of Si. In addition, it has been considered as a promising light source for optoelectronic devices because of its pseudo-direct bandgap property at 0.8 eV. For Ge applications in electronic and photonic devices, the growth of Ge with a considerable doping concentration on a Si substrate is required to acquire a substantial free carrier concentration and effective electrical pumping. Although extensive research has been undertaken on the growth of *p*-type epitaxial Ge films, the issue of a low phosphorus (P) doping concentration in Ge still remains unresolved because the equilibrium solid solubility of P in Ge is 2×10^{20} cm^{-3} and P atoms out-diffuse during growth. Therefore, there is a need to achieve a high P doping concentration. Ion implantation has been commonly used to introduce dopants, but a post-annealing process is needed to alleviate lattice damage and activate the dopants. In this study, we fabricated *in-situ* P-doped epitaxial Ge layers on Si(111) substrates at 600 °C by ultra-high vacuum chemical vapor deposition. The precursor of Ge and doping gas were germane (GeH_4) and phosphine (PH_3), respectively. To examine the effect of the flow rate of PH_3 on the growth of epitaxial Ge films, we varied the PH_3 flow rate from 0 to 200 standard cubic centimeters per minute (sccm) at a fixed GeH_4 flow rate of 200 sccm under the same growth time. Fig. 1 shows tilted-view scanning electron microscopy (SEM) images of the epitaxial Ge layers grown at different PH_3 flow rates. The P concentration as a function of PH_3 flow rate is shown in Fig. 2 and was obtained from secondary ion mass spectroscopy (SIMS) measurements.

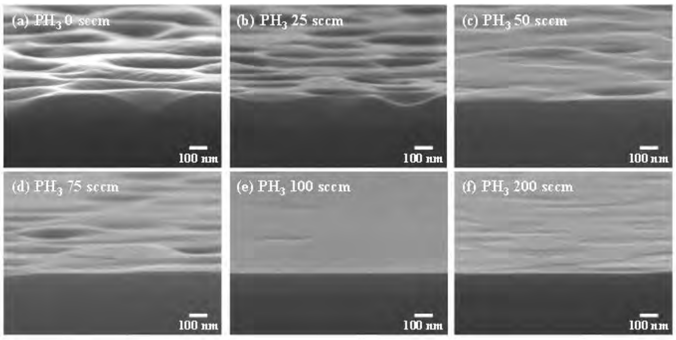

Fig. 1. SEM images of Ge films on Si grown at PH_3 flow rates of (a) 0 sccm, (b) 25 sccm, (c) 50 sccm, (d) 75 sccm, (e) 100 sccm, and (f) 200 sccm.

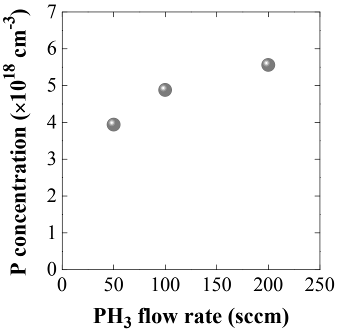

Fig. 2. P concentrations from SIMS measurements.

High temperature solution growth and characterization of V_2AlC single crystals

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V_2AlC (space group $P6_3/mmc$) belongs to the so-called $M_{n+1}AX_n$ (n=1-3) phases, where M is an early transition metal, A is an element of groups 13-16, and X is C or N. These MAX phases have attracted increasing attention due to a unique combination of interesting properties usually associated either with metals or ceramics. These properties make this family technologically interesting materials. Although polycrystalline MAX phases and their composites are well documented, there is only a limited number of references about MAX phase single crystals (see, *e.g.*, [1,3]). Yet, and due to the nanolamellar structure of these materials, fabrication of such crystals is required for evidencing and characterizing the expected physical anisotropies. In the present work, single crystalline flakes of the V_2AlC phase have been successfully synthesized using high temperature solution growth, with areas in the range of several mm^2 and thickness of 40µm (Fig1a). V_2AlC crystals ares identified using Raman spectroscopy (Fig1b) and X-ray measurements. As a member of the 211 MAX phase family, V_2AlC involves four active modes including A1*g* (361.2 cm^{-1}) +E1*g* (257.9 cm^{-1})+2E2*g* (157.3 and 239.5 cm^{-1}). X-ray pole figures (Fig2a) and ϕ-scans demonstrate the single crystalline character of the flakes. The morphology of the as-grown surface, which exhibits unit step heights and terraces with a constant width, indicates a conventional step flow growth mode (Fig.2b). We will also present additional data obtained by Nomarski optical microscopy and Scanning Electron Microscopy (SEM) (Fig2c).

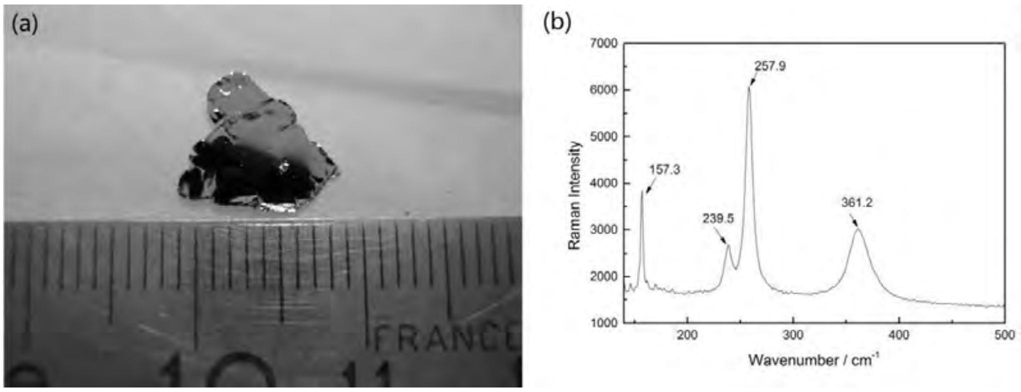

Figure 1 Photograph(a) and Raman spectrum (b)of the as-grown V_2AlC flake

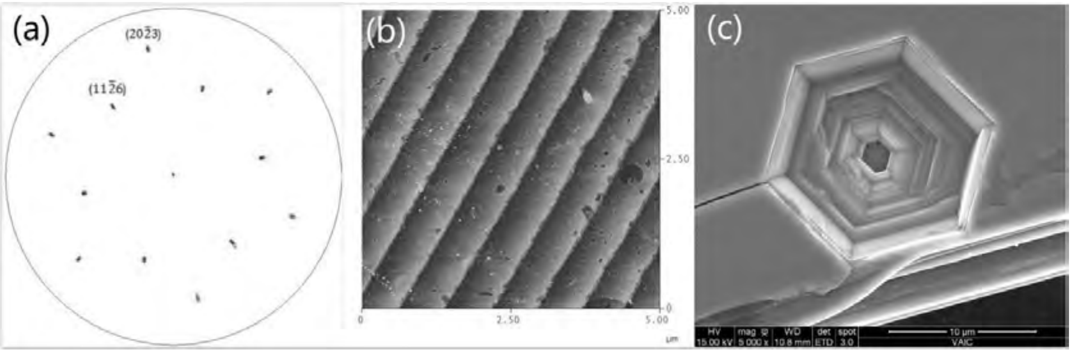

Figure 2 (a) (11$\bar{2}$6) (20$\bar{2}$3) X-ray pole figure of a V_2AlC flake (b) AFM image of the growth steps and (c) SEM image of the terrace structure

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CHARACTERIZATION OF LIQUID OXIDE BY SESSILE DROP METHOD ON REFRACTORY SUBSTRATES

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The study of eutectic ceramics has been highly promoted these last years. Indeed, these materials offer exceptional physical properties at very high temperatures[1,2]. However, these outstanding features depend drastically on the microstructure formed which is the result of the fabrication process conditions. It has been demonstrated that eutectic ceramics grown from the melt show much better mechanical properties than sintered materials. A large research activity has then led to the application of crystal growth technology to the numerous techniques as: Bridgman, micro-pulling down, floating zone..etc. The growth conditions may be thermal as temperature gradient, cooling rate and so on, but they can also be from chemical origin. The chemical impact is reflected by the interaction between the crucible and the studied material which modify the growth conditions and in some cases the grain structure.

In this frame, a high temperature experiment has been designed which consists of sessile drop technique. This apparatus allows imaging the oxide drop behaviour on various refractory substrates: molybdenum, tungsten and iridium.

A study of the capillary and wetting parameters are first extracted from the images: contact angles, surface energies and density of the studied materials. These parameters will enable optimising the fabrication processes, such as micro-pulling down or directional solidification.

Furthermore analyses of the reaction layers at the liquid/metal interfaces allow a better understanding of the chemical interactions. Particularly, partial pressures of oxygen should be well controlled to avoid oxidation of the substrates and consequently reactive wetting between the liquid oxide and the metal [3]. Moreover, it has been shown that partial pressure variations also affect the contact angles measurements [4]. In this aim, an additional device is used and allows depletion or addition of oxygen in the incoming gas during the experiment.

In this presentation, we show some preliminary results about the measurements performed using the described apparatus.

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Tuesday, June 17

Session 3		**Scintillators, piezo- and magnetoelectrics** Chair(s): Alexander Gektin (Institute for Single Crystals, Kharkov, Ukraine), Edith Bourret-Courchesne (Lawrence Berkeley National Laboratory, USA)
08:30	S3 / oral 1	Merry Koschan (University of Tennessee, Knoxville, USA) **A retrospective on the development of lutetium oxyorthosilicate (LSO)**
09:20	S3/ oral 2	Edith Bourret-Courchesne (Lawrence Berkeley National Laboratory, USA) **Crystal Growth of Alkali Earth Halides**
10:10		Coffee
10:30	S3 / oral 3	Akira Yoshikawa (Tohoku University, Japan) **Material Design and Crystal Growth of High Performance Scintillators**
11:20	S3 / oral 4	Jun Luo (TRS Technologies, USA) **Recent development on piezoelectric crystals for transducer and sensor applications - Understanding and overcoming the technical barriers to commercialization**
12:10		Break
12:30		Lunch
Session 4		**Substrates for wide band-gap and oxide semiconductors** Chair(s): Matthias Bickermann (IKZ Berlin, Germany)
14:00	S4 / oral 1	Tania Paskova (North Carolina State University, USA) **Status of HVPE grown GaN and AlGaN templates and bulk substrates: electrical and thermal conductivity**
14:50	S4 / oral 2	Dirk Ehrentraut (Soraa, USA) **SCoRA – New Technology for Scalable, High Rate Growth of Bulk Gallium Nitride**
15:40		Coffee
16:10	S4 / oral 3	Zbigniev Galazka (IKZ Berlin, Germany) **Bulk Single Crystals of Transparent Semiconducting Oxides: Growth and Properties**
17:00		Break
18:00		Gala Dinner
23:00		End

A retrospective on the development of LSO

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The late 1990s to early 2000s offered a rare opportunity to bring a new material from the R&D stage all the way through building a large-scale production facility. Cerium doped Lu_2SiO_5 (LSO), a scintillator useful for radiation detection, was initially developed by Chuck Melcher in the 1980s and a factory dedicated to the growth of LSO was constructed by CTI in 2000. However, the development of a material like this does not happen in a vacuum – many other things must first be in place.

This talk will follow the 'timeline' of the development of LSO, beginning with a brief review of the earlier work on rare-earth silicate materials [1-3] and advances in crystal growth technology [4-6] that were necessary prerequisites.

LSO was initially developed at Schlumberger, as part of an effort to develop new and better materials for use in "down-hole" oil exploration [7]. While it has many properties that were desirable, including good light yield, fast decay time, and high density, the thermal response is unfortunately not well suited for this application. It may have been left 'on the shelf', were it not for developments in a quite different field, medical imaging.

The detector material used in Positron Emission Tomography (PET) determines to a significant degree the sensitivity, the image resolution, and the count rates available. BGO had been a mainstay of the PET community since its initial development in the 1970s. While it's high density offers good stopping power at 511 keV, its light yield is unfortunately low and the 300 ns decay time was slower than desired. In a serendipitous event, people from CTI attended a talk on LSO in 1991 and realized that it would be a superior scintillator for PET. In 1995 they acquired an exclusive license for LSO from Schlumberger. In 1996, Chuck Melcher joined CTI and began a project to develop the growth processes and facilities necessary to supply enough LSO for use in their commercial tomographs; the author joined the project the following year.

The next few years were busy ones, with a transition from laboratory scale to a 10 station pilot plant operation in 1998-1999. Even at this scale it was possible to grow a large number of crystals, allowing for statistical analysis of factors such as boule homogeneity, light yield, and decay time [8]. Success at this stage was followed rapidly by construction of a large factory beginning in 2000.

Once the LSO project reached the production stage the development team returned to the research lab, founding the Scintillation Materials Research Center at the University of Tennessee. Experiments during this time revealed the impact of Ca^{2+} codoping on the scintillation performance and growth stability of LSO [9], which will be discussed.

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Crystal Growth of Alkali Earth Halides

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Large efforts in recent years to discover new scintillators have so far confirmed the superior performance of halide scintillators. The alkali halides NaI(Tl^+) and CsI(Tl^+) discovered more than 65 years ago are still dominating the market for applications that requires very large crystals and economical scintillators despites some limitations in their performance. The newer halide $LaBr_3:Ce^{3+}$ with superior performance is not as widely used mainly due to its high cost. This compound is very hygroscopic and crystals are produced with low yield due to defect and crack formation. Compounds containing alkali-earth halides and more complex halides (ternaries and quaternaries) have the potential to provide new choices for scintillators with energy resolution now less than 3%. The specifics of crystal growth of these new compounds and relevant properties will be discussed as they relate to fabrication of detectors for various applications.

This work has been supported in part by the U.S. Department of Energy/NNSA/NA22 and in part by the US Department of Homeland Security, Domestic Nuclear Detection Office, under competitively awarded contract HSHQDC-09-X-00075 and carried out at Lawrence Berkeley National Laboratory under Contract NO. AC02-05CH11231. This support does not constitute an express or implied endorsement on the part of the Government.

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Material design and crystal growth of high performance scintillators

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Important approach for the development and growth of high performance scintillators will be discussed.

1. Band Gap Engineering (BGE)

Multicomponent garnet is the typical example. Recently, it is found that Ce: $\{Gd,RE\}_3(M,Al)_5O_{12}$ (RE=Y, Lu, M=Sc, Ga) single crystals shows high light yield and high energy resolution [1]. Thuogh the lattice constant, volume and emission wavelength changes linearly, LY has maxima at the specific ratio (Fig.1). The is explained as the result of suitable BGE. Tranport efficiency will be changed depending on the position between the botom of conduction band of the host lattice and the level of 5d of Ce^{3+}[2].

In order to investigate BGE, consideration of phase diagram is also very important. For example, in the psude-binary system Gd_2O_3 - Al_2O_3, $GdAlO_3$ (perovskite) is congruent, however, $Gd_3Al_5O_{12}$ (garnet) is incongruent. In order to get garnet phase as initial phase, either the dodecahedral site must be smaller or the octahedral one bigger.

Recently, $(Gd,RE)_2Si_2O_7$ is also considered from similar point of view. $Gd_2Si_2O_7$ itself is incongruent. When larger cation such as La or Ce is partially substitute Gd, then it turned to be congruent. Scintillation performance is depend on the La concentration.

2. Crystal grwoth technology and crystal chemistry

Crystal growth technology is also the key to obtain high performance scintillators in your hand. Eu:SrI_2 is the typical example. Eu:SrI_2 is rediscovered by the progress of the precise atmosphare control during the crystal growth process. At the same time, machining, polishing and encapsulation are also very important. Similar items are importance for the elaboration of Ce:$LaBr_3$, Ce:CLYC [3,4]. Bulk crystal growth of Eu:SrI_2 will be introduced.

Control of segregation coefficient is also important. Interesting attempt to jump up the segregation coefficient of Eu in LiCAF will be discussed with crysta chemistry point of view.

Crystal chemistry study to find congurent composition also helps to obtain bulk single crystal. consideration of phase diagram in the psude-binary system Gd_2O_3 - Al_2O_3 as well as in the psude-binary system $Gd_2Si_2O_7$ - $La_2Si_2O_7$ will be introduced using the GAGG and La-GPS as the example [6].

Recently, eutectic scintillator with light guiding effect is proposed [7]. Ce:GAP phase plays a role of light guiding as well as high performance scintillator. They are the candidate for high resolution imaging.

Fig.1 GAGG single crystal grown by the CZ method.

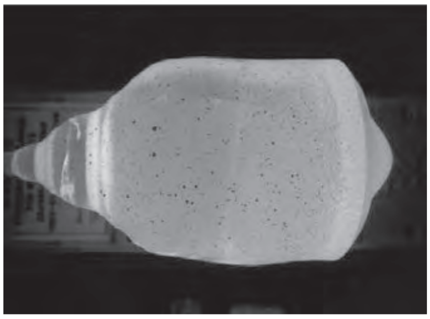

Fig.2 La-GPS single crystal grown by the CZ method.

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Recent development on piezoelectric crystals for transducer and sensor applications

- Understanding and overcoming the technical barriers to commercialization

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This talk reviews the recent developments on piezoelectric single crystals for transducer and sensor applications, from cryogenic (-200ºC) to extremely high temperatures (1000ºC). It covers the ferroelectric and non-ferroelectric piezoelectric crystals, which either have already been accepted by industries as the new generation piezoelectric materials or have shown great potentials for the near future, with emphasis on the crystal growth techniques, characterizations and how to bridge the gap between crystal growth and the industrial applications.

For ferroelectric piezoelectric materials, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramics with composition lie near the morphotropic phase boundary (MPB) have been the mainstay for the transducer and actuator fields since 1950's[1]. However, PZT crystals with similar composition have been grown neither in sufficient size nor with excellent piezoelectric performance. Some ferroelectric crystals, such as $LiNbO_3$ (LN) and the analogue $LiTaO_3$ (LT), offer inferior piezoelectric properties, with d_{33} about 10 times lower than PZT ceramics [2]. Development of the relaxor-based ferroelectric crystals of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) represents a revolutionary advance for piezoelectric applications. These binary relaxor-PT crystals provide several key advantages over conventional PZT ceramics, including high elastic compliances (4-5 times of PZT), large piezoelectric coefficients (3-5 times of PZT), and extremely high electromechanical coupling coefficients (k_{33}: 90-94%). By B-site substitution, ternary crystals, such as $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PIN-PMN-PT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ (PMN-PZT), and Mn doped ternary crystals, such as Mn:PIN-PMN-PT, have largely expanded the operational temperature and electric field [3]. The relaxor-PT crystals keep excellent piezoelectric performance for cryogenic applications; however, a ferroelectric-to-ferroelectric phase transition hinders any applications above 130°C. LN crystals possess a T_C of 1150 °C, but the low resistivity and oxygen loss at elevated temperature restrict application to below 600°C[4].

Non-ferroelectric piezoelectric crystals can be more attractive for high temperature sensing applications if they are lack of phase transition in the desirable temperature range, even though they usually present much lower sensitivity. Generally, non-ferroelectric piezoelectric crystals possess low piezoelectric coefficients, in the range of 1-20pC/N; however, the ultralow mechanical and dielectric losses, and high electrical resistivities, make them ideal candidates for high temperature sensing applications. Quartz analogues ($GaPO_4$, $AlPO_4$ etc.), langasite family crystals (LGS, LGT, LGN, STGS, CTGS, etc.) and rare-earth oxyborates ($ReCa_4O(BO_3)_3$), have been extensively studied for the high temperature sensing in recent years [4-6]. Considering the level of piezoelectric properties, electrical resistivity and temperature stability, some "ordered" langasite-structure crystals and some rare-earth oxyborates are potential candidates for the next generation high temperature sensing applications far outperforming the current materials [4].

TRS overcame several technical barriers during commercialization of relaxor-PT crystals, which may resonate with the common experiences among the crystal developers. The new material commercialization is always driven by the impact and scope of the potential applications, so it is crucial to identify such potentials and establish the industrial collaboration on the device or system levels even in the early stage of development. Cost reduction is a never-ending goal for commercialization, which can be achieved not only by scaling up the size of the crystals, but also by continuous improvement of the operational efficiency. Modern industries impose higher and higher standards on the finishes of crystal elements, so post-growth crystal processing presents more challenges as well as more opportunities than ever. Reproducibility and repeatability are great challenges in winning long-term customers, but they are achievable by applying SPC, lean manufacture and six sigma tools in the process control.

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Status of HVPE grown GaN and AlGaN templates and bulk substrates: electrical and thermal conductivity

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The current nitride technology employs two generally different groups of approaches. The first group is focused on development of bulk GaN and AlN substrates and the intensive research efforts during the last years have led to a demonstration of high-quality material with huge application potential, including for devices with nonpolar and semipolar alignment of the active regions. HVPE technique has led the effort during the last decade and is the only one offering GaN wafers in 2-inch or larger form factor for polar devices and all surface orientations of interest. The cost of this method, however, remains still high and several challenges have to be resolved to allow the cost to go down. The second group of research efforts is focused on template development of GaN, AlGaN and AlN on sapphire, SiC and Si substrates. Most of these efforts, using lateral overgrowth approaches, have showed devices with good performance and have been commercially implemented. Each of the approaches employs different buffer layers or nucleation schemas, as well different growth recipes, and results in as-grown substrates and templates with different thickness limitations. The doping alternatives, using either silicon or oxygen for achieving n-type conductivity and iron for achieving resistivity in wide ranges, respectively, were found to successfully alter the electrical properties of the materials, while the optical quality was largely maintained until reaching the saturation level. The defect ensembles and the charge transfer mechanisms were systematically evaluated in order to understand the Fe compensation mechanism and to achieve semi-insulating material with controllable characteristics. In addition, besides the reduced dislocation density achieved, the HVPE technique was proven capable of producing material of high purity, regarding residual impurities and point defects. This in turn leads to improved thermal conductivity, allowing better thermal management and device performance.

Recent advances in the research and development of a variety of optoelectronic and electronic devices produced on HVPE template and bulk nitride materials has resulted in a significant improvement of device performance for a number of applications. This motivates the increased demand for HVPE nitrides, which should boost the material availability and will drive down the production cost. In this talk, we will present a comparative summary of the most promising approaches for HVPE growth of GaN and AlGaN materials. The focus will be on the different doping approaches and their effect on the thermal transport in low-defect-density materials. High thermal conductivity values in wide temperature region will be presented and scattering mechanisms including at elevated temperatures, highly relevant for high power electronic and optoelectronic devices, will be discussed.

SCoRA – New Technology for Scalable, High Rate Growth of Bulk Gallium Nitride

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The vast majority of semiconductor device technologies are based on native substrates, and gallium nitride (GaN) is no exception with true bulk GaN generally regarded as the ideal substrate for GaN-based devices, including LEDs, lasers, and electronics. The latest development in LED devices shows a trend toward GaN as the substrate material of choice despite the currently high cost [1]. Soraa, Inc. recently introduced an LED-based MR16 reflector lamp whose LED light engine is fabricated on native GaN substrates [2, 3]. These lamps are the first LED-based MR16 to produce equivalent light quality as incumbent halogen-based lamps, including a high color-rendering index, CRI = 95, with a fraction of the power consumption and a greatly improved lifetime. The GaN-on-GaN LEDs operate at considerably higher current density than other commercially available LEDs and leverage reduced droop.

However, although HVPE GaN substrates have been available commercially for about a decade, bulk-GaN-based devices have largely remained in the realm of research, with the exception of laser diodes. Obstacles to commercial bulk-GaN-based devices include high cost, limited diameter, and complex microstructure [4].

Soraa has developed a novel ammonothermal approach for the growth of high quality, true bulk GaN crystals at a greatly reduced cost. Soraa's patented approach, known as SCoRA (Scalable Compact Rapid Ammonothermal) utilizes internal heating to circumvent the material-property limitations of conventional ammonothermal reactors. The SCoRA reactor has capability for temperatures and pressures as high as >700 °C and 600 MPa, respectively, enabling higher growth rates than conventional ammonothermal techniques, but is less expensive and more scalable than conventional autoclaves fabricated from nickel-based superalloys.

SCoRA GaN growth has been performed on seed crystals with *c*-, *m*-, and semipolar orientation with diameters up to two inch to thicknesses of 0.5-3 mm and high growth rates of 40 μm h^{-1}[5]. These values are easily sufficient for a very cost-effective manufacturing process. The crystals have been characterized by x-ray diffraction rocking-curve (XRC) analysis, optical and scanning electron microscopy, cathodoluminescence (CL), electron channeling contrast imaging (ECCI), electron beam-induced current (EBIC), optical spectroscopy, and capacitance-voltage measurements. The XRC scans are single-peaked, indicating that the GaN grown via the SCoRA process possess very high structural quality and are composed predominantly of a single grain. The FWHM values of the grown crystals are similar to or narrower than those of the seed crystals, about 25-50 arcsec, both for symmetric and asymmetric reflection. Dislocation densities below 1×10^5 cm^{-2} in vertically-grown and $<1\times10^4$ cm^{-2} in laterally grown SCoRA GaN have been obtained. High optical transmission was achieved with an optical absorption coefficient below 1 cm^{-1} at a wavelength of 450 nm. Crystals are typically n-type and transparent but yellowish, due to unintentional impurities. Epitaxial quantum well structures have been successfully grown on SCoRA wafers.

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Bulk Single Crystals of Transparent Semiconducting Oxides: Growth and Properties

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β-Ga_2O_3, In_2O_3, and SnO_2 are attractive transparent semiconducting oxides (TSOs) with wide bandgaps of 4.8, 2.8, and 3.5 eV, respectively. They are however, chemically unstable at elevated temperatures and tend to decompose, therefore growing such single crystals from the melt is a very challenging task. Bulk β-Ga_2O_3 (MP=1820°C) single crystals were grown by the Czochralski method (Fig. 1) using a self-adjusting dynamic growth atmosphere. The crystal appearance and electrical / optical properties are strongly dependent on applied growth conditions. In_2O_3 (MP=1950°C) is much more unstable than Ga_2O_3 and ZnO, and for the purpose of growing bulk In_2O_3 single crystals from the melt (Fig. 2) we have developed a novel crystal growth method under the name Levitation-Assisted Self-Seeding Crystal Growth Method (LASSCGM). SnO_2 is the most chemically unstable compound at high temperatures (MP>2100°C) among other TSOs so that single crystals of SnO_2 cannot be grown from the melt. Therefore, bulk SnO_2 single crystals were obtained by the physical vapor transport (Fig. 3). All these bulk TSO single crystals showed n-type conductivity with free electron concentrations in the range of 5×10^{16}–5×10^{18} cm^{-3} and electron mobilities between 120–220 $cm^2/(V\ s)$. A systematic annealing study of the bulk TSOs at different atmospheres, temperatures, and times revealed that all the crystals are thermo-chemically stable up to 1200°C in non-reducing and up to 600–700°C in highly reducing conditions. Moreover, in terms of electrical properties, bulk TSO single crystals are sensitive to annealing conditions: the free electron concentration of bulk crystals could be modified by 1-2 orders of magnitude, while bulk SnO_2 crystals could be even switched interchangeably between semiconductor and electrical insulator just by suitable annealing. An extensive characterization of the crystals showed that their physical and structural quality is fully compatible with their use as substrates for epitaxial deposition. Availability of truly bulk TSO single crystals combined with their unique electrical and optical properties opens the door to new applications, such as high power electronics, transparent electronics and light detectors.

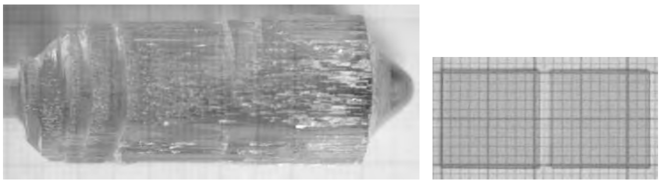

Fig. 1. Czochralski-grown bulk β-Ga_2O_3 single crystal (left) and wafers (right).

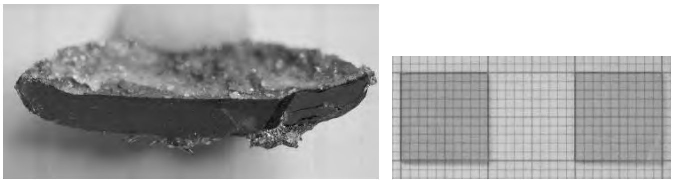

Fig. 2. LASSCGM-grown bulk In_2O_3 single crystal (left) and annealed wafers (right).

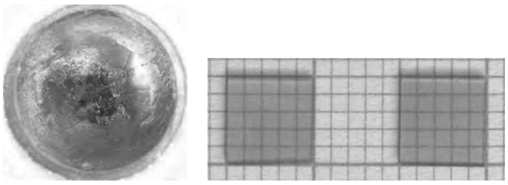

Fig. 3. PVT-grown bulk SnO_2 single crystal (left) and wafers (right).

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Wednesday, June 18

Session 6		**Crystal shaping and layer transfer technologies** Chair: Albrecht Seidl (Schott, Germany)
08:30	S6 / oral 1	Irina Shikunova (Russian Academy of Sciences, Chernogolovka, Russia) **Sapphire Shaped Crystals for Medicine**
Session 4		**Substrates for wide band-gap and oxide semiconductors** Chair: Matthias Bickermann (IKZ Berlin, Germany)
09:20	S4/ oral 5	Noboru Ohtani (Kwansei Gakuin University, Japan) **SiC epitaxial wafers for power device applications: present status and prospect**
10:10		Coffee
Session 5		**Growth control, quality assurance, and management of resources** Chair: Michael Neubert (IKZ Berlin, Germany)
10:30	S5 / oral 1	Patrick Berwian (Fraunhofer IISB, Germany) **Quality Assurance in the Epitaxy of SiC and its Relevance for Device Reliability**
11:20	S5 / oral 2	Jan-Freerks Rieken (ppm Pure Metals, Germany) **Origin and Supply Security of Minor Metals**
12:10		Break
12:30		Lunch
14:00	S5 / oral 3	Benno Orschel (MEMC Electronic Materials, USA) **Requirements for Model Predictive Control in Industrial Crystal Production by Czochralski Process**
Session 7		**Frontiers in crystal growth technology** Chair: Chung-Wen Lan (National Taiwan University, Taiwan)
14:50	S7 / oral 1	Andrea Ferrari (Cambridge University, Great Britain) **Graphene Future Emerging Technology**
15:40		Coffee
16:10	S7 / oral 2	Lain Jong Li (Academia Sinica, Taiwan) **Growth of Transition Metal Dichalcogenide Monolayers with Chemical Vapor Deposition**
17:00	S7 / oral 3	Mikael Syväjärvi (Linköping University, Sweden) **The cubic sublimation method: prospects for bulk 3C-SiC growth and photovoltaic applications**
17:50		Break
18:00		Dinner
19:15		Industry 2
20:00		Poster 2
21:45		End

SAPPHIRE SHAPED CRYSTALS FOR MEDICINE

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Sapphire has a high refractive index and a broad transmission band spanning the UV, visible, and IR bands. Sapphire also has high hardness, very good thermal conductivity, tensile strength, and thermal shock resistance. The favorable combination of excellent optical and mechanical properties of sapphire, together with high chemical inertness and biocompatibility, high resistance to human blood and body fluids, makes it an attractive structural material for medicine. We have developed a new kind of medical instruments and devices for laser photodynamic therapy and thermal therapy, laser surgery, fluorescent diagnostics, and cryosurgery based on sapphire crystals of various shape with capillary channels in their volume.

Sapphire smart scalpels with simultaneous incision and fluorescent diagnostics of a resected tissue immediately during surgical operation have been developed. The principle of the new system is based on the use of isolated capillary channels in the volume of the sapphire scalpel for introducing of quartz waveguides, Fig. 1. One of the waveguides is used for delivering the laser radiation directly to the narrow region of the cutting edge and local excitation of photoluminescence. Another one is used for catching and transfer of photoluminescence to spectrometer. The scalpel employs rapid real-time feedback analysis for on-line diagnostics of tissues during surgery to remove a tumor. A laser optically coupled directly inside the edge allows obtain effective concentration of the laser energy in the area of the cutting edge of the scalpel for coagulation blood adjacent incision.

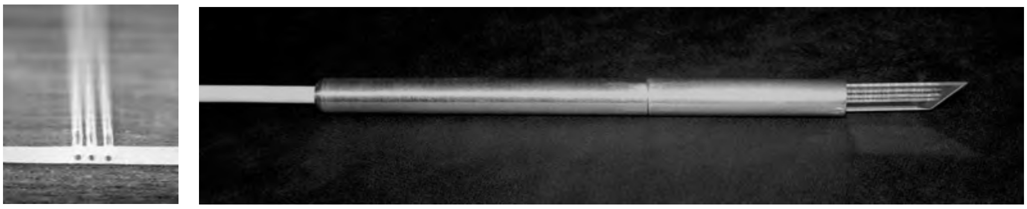

Fig. 1. Sapphire ribbon with three capillary channels of 0.5 mm in diameter (at the left). Sapphire scalpel for diagnostic and coagulation on incised tissue during a surgical operation (at the right).

Sapphire needle capillaries were developed as new laser waveguide introducers for delivery radiation into a tumour during interstitial laser photodynamic therapy, thermotherapy, and ablation oh tumors. These needles allow one to increase the irradiation volume substantially, to obtain an optimal temperature distribution, to simplify the design, and to eliminate a system for cooling the device. The high hardness of sapphire provides a stable point on the irradiator end for independent introduction of the irradiator into the tissue without using directors that lead to the increase in irradiator cross-section. The use of sapphire irradiators make it possible to improve the control over the dynamics of spatial photothermal distribution during the whole irradiation procedure, since the effective redistribution of released heat by the sapphire decreases the possibility of formation of overheating nuclei, leading to the appearance of thrombi, nontransparent to laser radiation.

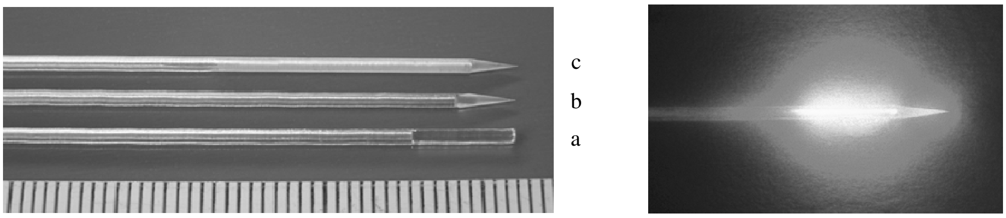

Fig. 2. At the left: sapphire needle capillaries (external diameter of 1.2 mm, internal diameter of 0.5 mm): (a) as grown closed capillary; (b) capillary with a point formed by mechanical operation of the butt; (c) capillary with a point and diffuser formed by mechanical operation. At the right: sapphire needle combined with quartz fiber (the geometry of light field).

Also the system for removal of brain tumors based on a sapphire multi-channel probe with demarcation of borders of a tumor by fluorescent diagnostics with simultaneous coagulation and aspiration was developed, Fig. 3. It carries out simultaneous laser coagulation for a hemostasis, tumor aspiration via the through channel of a sapphire probe, and also makes local optical measurements of properties of brain tissue for more exact and full removal of malignant tissue.

Fig. 3. Surgical operation on brain tumor removal using the sapphire probe for neurosurgery

SiC epitaxial wafers for power device applications: present status and prospect

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The development of silicon carbide (SiC) crystal growth technology over the last decade has brought about tremendous progress in SiC power devices. 100 mm diameter SiC epitaxial wafers with a low dislocation density have already been brought to market, and 4H-SiC wafers in diameter up to 150 mm have been successfully demonstrated in recent years. However, the commercialization of SiC power devices is still largely hindered by technological issues related to SiC epitaxial wafers, and thus it is abundantly clear that further successful development of SiC semiconductor technology relies on achieving an understanding of the Si bulk and epitaxial growth processes and, based on it, improving the technologies of manufacturing large high-quality SiC epitaxial wafers.

The first part of this presentation is aimed at describing the state of the art in the technology and quality improvement of SiC epitaxial wafers for power device applications. SiC bulk crystal growth, thin film epitaxy and device fabrication are reviewed, highlighting the recent achievements in the SiC material and device technology, which include diameter enlargement of bulk SiC crystals, morphological control of epitaxial films, and development of SiC power devices enabling high performance SiC-based power systems.

The second part will be dedicated to discussion of a range of issues yet to be addressed in further spreading the technology. Particularly, a better understanding of the defect formation mechanism is indispensable for implementing SiC crystals with increased diameter and higher crystallographic perfection. The presentaion focuses on dislocation-related phenomena and reviews recent important results regarding the formation mechanism of dislocations in SiC crystals, such as threading screw dislocations (TSDs) and basal plane dislocations (BPDs), from the viewpoint of crystal growth.

Quality Assurance in the Epitaxy of SiC and its Relevance for Device Reliability

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Quality assurance is defined as the systematic activities implemented so that quality requirements for a product will be fulfilled. With this in mind, quality assurance in crystal growth of commercial quality crystals and wafer should always focus on the requirements of the final product, i.e. the device the material is used for. In a next step a correlation of the required performance with crystals properties and production conditions is needed. For this correlation the relevant questions are "what are the quality requirements of the crystal, wafer?", "how can critical material defects be identified?" and "how can they be adequately measured and controlled in a production environment?"

An example for defect related device reliability issues is the degradation of bipolar high voltage silicon carbide diodes. There are currently two strategies for quality control of the devices: the first one is based on electrical characterization of the devices after fabrication and the determination of "pass" and "fail" diodes according to certain electrical selection criteria. This strategy is very successful but has certain limitations. The second strategy involves the abovementioned correlative approach. On the materials side, the crystal defects of the silicon carbide wafer have to be determined. In case of extended defects this is typically done by defect selective etching. As this method is not as unambiguous as it seems, it is necessary to optimize the defect identification and to use complementary methods to assure correct defect identification. This is the foundation for finding out which of the defects are critical. The determination of the detrimental defects is done by basic material scientific investigations as well as a direct correlation of defect content and device reliability.

Once the critical defects are identified, the crystal growth processes can be adapted to reduce their content in the crystalline material. In case of SiC for bipolar devices, the critical defects like stacking faults, basal plane dislocations, and epi defects can be reduced very far, but not to zero. For certain applications with very stringent reliability demands, like e.g. offshore wind power converters, the optimization of the crystal growth processes is therefore not enough. In this case, adequate quality control tools should be used during production of such devices to assure that only devices without critical defects are fabricated. The characterization techniques for such a defect mapping should be fast enough for a production environment, of course non-destructive, preferably non-contact, and selective enough to distinguish critical and non-critical defects. For silicon carbide epitaxial wafers, high resolution photoluminescence imaging is the currently most promising technique. In Fig. 1 the quality of a state-of-art SiC epi wafers is assessed by photoluminescence imaging.

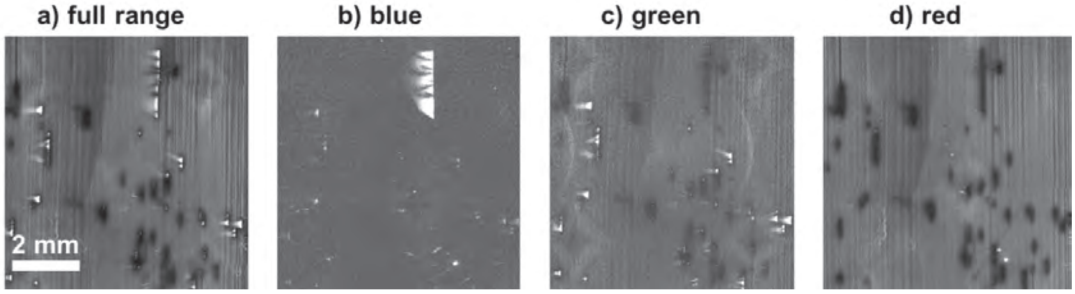

Fig. 1: Photoluminescence imaging of a SiC epi wafer surface with stacking faults, basal plane dislocations, step bunching and other defects. The PL signal at different spectral ranges is defect specific. This allows distinguishing the different critical defects and renders high resolution photoluminescence imaging a promising quality control tool for SiC device production.

Origin and supply security of minor metals with focus on Arsenic, Gallium, Germanium and Indium

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Despite of their high value, minor metals are becoming increasingly important for industrial applications. This is also observed in crystal growing. Beside of the production of compound semiconductor crystals, minor metals are used as dopant. In light of the current debate concerning the scarcity of rare earth metals finds the discussion about supply security of minor metals its way into the public spotlight.

Generally spoken, minor metals are not rare. But they can only be found in low concentrations. For this reason Arsenic, Gallium, Germanium, Indium are obtained almost exclusively as a by-product. Therefore, the production of these materials plays an economically subordinate role for the producers.

In the processing of ores not recovered metals remain in the primary product or the slag. Currently, this leads to a significant loss of minor metals. To increase the world production of minor metals it is not necessary to open new mines. Instead, Smelters that process suitable ores, must be convinced to extract the minor metals. This is a difficult task, because the integration of a method to extract minor metals necessarily means to intervene in the existing processes. A further impediment is that the revenue generated from the primary product (e.g. Aluminum, Lead or Zink) are significantly larger than those that can be achieved with the minor metals. Given the interlinked nature of these factors, potential primary producers take an increase of the production only into consideration if prices are sufficiently high.

The supply and the demand of production are normally in balance. However, the market volume is low and therefore it is extremely volatile and prone to exaggerations. Small changes in availability can lead to large distortions – especially if politics comes into play. This must be taken into consideration when it is planned to use minor metals for new purposes. Therefore, it is necessary to consider the recycling as early as possible in a development process. This helps to reduce raw material costs and the risk of a market distortion.

Requirements for Model Predictive Control in Industrial Crystal Production by Czochralski Process

Benno Orschel, Christian Spitaler, Markus Siegert, Bob Fuerhoff, Uwe Hermes (all SunEdison Inc)

Successful introduction of model predictive control (MPC) into industrial crystal production by Czochralski (Cz) process doesn't seem to happen as fast as one would expect, given the potential benefits MPC promises. Currently, the cascaded PID control (or slight variations thereof) is being used throughout the industry. Certain requirements must be met for MPC to give better performance than traditional PID control and only a significant performance improvement will justify such control system change in an industrial environment.

This presentation illustrates three concerns of a typical Cz puller. Mechanical design and actuator accuracy determine speed error; optical design and image processing determine diameter error. Furthermore, we present typical concerns of weight measurement. All three, speed, diameter and weight, are main properties in a model of the meniscus and growth interface. Unless simple and economical corrections can be found, these errors greatly limit the usefulness of MPC.

Predominately used throughout the industry, diameter control by PID suffers from significant model errors, which have significant implications for productivity. The most basic benefit from MPC would be tighter diameter and growth rate control. However, any model of the meniscus can only be as good as the accuracy of the crystal pull rate as output and the diameter measurement as input. Control systems used today, vary widely with respect to seed lift accuracy alone, not to mention crystal pull rate. The majority of crystal pullers still use analog servo motors for seed and crucible lift, resulting in significant pull speed deviations due to servo drift. Digitally controlled motors, used in advanced CZ pullers, eliminate these inaccuracies. However, crystal pull rate errors remain, due to crucible diameter deviations, and cable speed modulation, due to mechanical pull head design.

Crystal diameter measurement is another area, which needs improvement. The majority of crystal pullers do not have advanced camera systems that allow accurate tracking of the meniscus. However, even advanced 3D image processing solutions known in the industry today are coming close to their limits in terms of update rate and signal to noise ratio, due to the trend to larger diameters, restricted field of view, due to heat shields, as well as the drive to pull at faster rates for whenever possible.

If it was just for better diameter and pull rate control, solving the before mentioned issues would be almost enough. It has been shown, a simple PID that acts in length instead of time domain can already accomplish this. MPC control must deliver more than this to become successful in the industry. For instance, a properly designed model would allow controlling v/G simultaneously with diameter and pull rate, which would have tremendous benefits for a number of CZ products. To this end, the inclusion of weight tracking would be very beneficial. However, todays weight measurement systems suffer from significant noise, induced by mechanical pull head design.

Graphene Future Emerging Technology

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Disruptive technologies are usually characterised by universal, versatile applications, which change many aspects of our life simultaneously, penetrating every corner of our existence. In order to become disruptive, a new technology needs to offer not incremental, but dramatic, orders of magnitude improvements. Moreover, the more universal the technology, the better chances it has for broad base success. Does graphene have a chance to become the next disruptive technology? Can graphene be the material of the 21th century? Are the properties of graphene so unique to overshadow the unavoidable inconveniences of switching to a new technology, a process usually accompanied by large R&D and capital investments? In spite of the inherent novelty associated with graphene and the lack of maturity of graphene technology, a roadmap can be envisaged, including short-term milestones, and some medium- to long-term targets, intrinsically less detailed, but potentially even more disruptive. This should guide the transition towards a technological platform underpinned by graphene, with opportunities in many fields and benefits to society.

Growth of Transition Metal Dichalcogenide Monolayers with Chemical Vapor Deposition

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The direct-gap property of the semiconducting transition metal dichalcogenide monolayers are attractive for optoelectronics and energy harvesting. Here I would like to discuss the synthetic approach to obtain large-area MoS_2 (WSe_2) monolayer directly on arbitrary substrates using vapor phase reaction between metal oxides and S or Se powders. These layer materials can be transferred to desired substrates, making them suitable building blocks for constructing multilayer stacking structures. The significance of charge movement in the emerging field of 2d heterostructures, and the charge distribution strongly affects the properties of the 2d heterostructures. The band alignment between these 2d monolayers shall be discussed in details. The interaction between these layer materials are characterized by Raman, PL spectra and Second Harmonic Generation properties. Some possible applications based on these 2d heterostructures including photodetection and DNA detection shall be introduced.

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The cubic sublimation method: prospects for bulk 3C-SiC growth and photovoltaic applications

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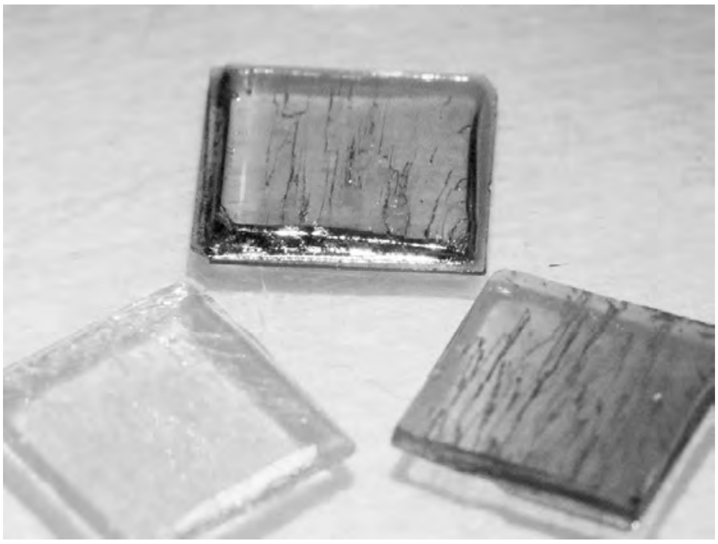
We describe a growth concept of cubic silicon carbide that can pave the way for approaches of growth technologies and applications based on this polytype. In comparison to hexagonal silicon carbide wafers that are commercially available, the cubic silicon carbide is known to provide challenges in polytype stabilization. High temperature physical vapor transport (PVT) growth methods have shown that the 3C-SiC polytype does not appear at temperatures slightly above 2000°C. Chemical vapor deposition approaches have low growth rates, and thick layers are challenging to produce, in particular of 3C-SiC on silicon due to the large lattice and thermal mismatch.

We have a modified sublimation growth concept at substantially lower growth temperatures and lower ambient pressure than in conventional PVT. Still, the method maintains the high growth rate that can be obtained in PVT, and growth rates up to 1 mm/hr have been obtained. It is shown that the quality can be similar to that of commercial SiC when using hexagonal SiC as substrate and polytype transformation. After transformation, the polytype of the 3C-SiC is maintained to at least 1.5 mm thickness. The competition between two 3C-SiC nucleation mechanisms is discussed. A domain enlargement is achieved by using off-axis substrates. Free standing 3C-SiC substrates have been produced.

Using the cubic sublimation method, we foresee several approaches that can be explored. The first one is bulk growth of 3C-SiC. The second one is 3C-SiC as highly efficient photovoltaic material since thick layers doped with boron fits nicely into the intermediate bandgap solar cell concept.



Free standing 3C-SiC substrates grown by the cubic sublimation method.

Growth and characterization of cerium doped LuAG fibers grown by µ-Pulling down for medical imaging devices and scintillators.

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Single crystalline scintillating fibers are considered the best candidate for high-energy physics detectors and medical imaging devices because they provide high granularity, highly efficient gamma ray detection and sub-millimeter position information due to their geometrical dimensions [1]. One of the best techniques for growing these single crystalline fibers is the micro pulling down technique. It has indeed the main advantage of allowing to grow directly shaped fibers and thus to avoid intensive cutting and polishing which is required by bulk crystal growth techniques.

Lutetium aluminum garnet (LuAG) is a good candidate material for these scintillating fibers because of its high density (6.73 g/cm^3) thus allowing having thinner screens with higher spatial resolution for medical imaging devices. Moreover, it has several interesting physical properties such as good radiation hardness, fast decay time and high light output. On the other hand, cerium is a very efficient luminescent activator and its incorporation in LuAG can produce an efficient high response scintillator. However, cerium forms cracks and defects in the LuAG matrix when substituting the Lutetium atoms due to its larger ionic radius. As a result, cerium does not homogenously spread in the host matrix thus leading to longitudinal and radial segregation which accumulates mainly on the peripheral part of the fiber. It leads to drastic reduction of the attenuation length.

We had already demonstrated attenuation lengths about 6 to 7 cm long for 1 mm diameter Ce:LuAG fibers grown with relevantly high Ce content [2]. Starting from this point, our aim was to improve the quality of the grown cerium doped LuAG fibers by optimizing growth parameters and checking the influence of Ce doping concentration on defects, surface quality, transparency and to consequently enhance the light output.

In this work, several concentrations of cerium were investigated on two different fiber diameters, and crystal quality was optimized by playing with the growth speed rates and crucible geometry. The obtained fibers had a much smoother surface, reduced cracks and defects and better transparency. Our interest was then to measure the intensity and light propagation throughout these fibers. So, light attenuation measurements were performed by exciting the fiber with 470 nm light from a CAEN ultrafast pulsed LED driver and detecting the results.

Attenuation lengths were enhanced and reached up to 15 cm for the 1mm diameter fibers and about 18 cm for the 2mm diameter fibers. Further improvements of 2 mm diameter fibers resulted in reaching even higher attenuation lengths of more than 30 cm. The enhancement in crystal quality and thus the light attenuation measurements will be discussed and detailed.

EU has supported this work in the framework of the Picosec project (PITN-GA-2011-289355-PicoSEC-MCNet).

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Floating zone growth and characterization of $SrFeO_{3-\delta}$ and $CaFeO_{3-\delta}$ single crystals

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$SrFeO_{3-\delta}$ and $CaFeO_{3-\delta}$ are interesting materials because they contain iron in the unusually high oxidation state +4, which has the same electronic configuration as the Mn^{3+} ion in $LaMnO_3$ a material that shows the giant magneto-resistance effect when doped with calcium and strontium. $SrFeO_{3-\delta}$ is a good ionic conductor at elevated temperatures, via oxygen vacancies. On crystal growth of $SrFeO_{3-\delta}$ the single crystals reach severely cracked at room temperature due to a phase transition with the changes in oxygen content on cooling from high temperature to room temperature [1, 2]. The dominant oxygen diffusion mechanism through such a crystal is via microcracks rather than oxygen vacancies, while the same cracks complicate the interpretation of transport measurements [3]. For the low temperature transport properties and intrinsic oxygen diffusion the cracking should be minimized. Some oxides of the brownmillerite structure with an oxygen deficient perovskite exhibit high oxide ion mobility [4]. Compounds like $SrFeO_{2.5}$ and $SrCoO_{2.5}$ can easily be oxidized by electrochemical oxidation to obtain the respective $Sr(Fe,Co)O_3$ perovskite. In this context it is rather surprising that $CaFeO_{2.5}$ equally showing the brownmillerite type structure, cannot intercalate oxygen atoms using electrochemical oxidation and that $CaFeO_3$ can be obtained under drastic conditions only, e.g. at elevated temperature and high oxygen partial pressure [5]. In this sense the comparison of $CaFeO_{2.5}$ with $Sr(Fe,Co)O_{2.5}$ should provide valuable information for a general understanding of the high oxide ion mobility at room temperature in the family of non-stoichiometric perovskites.

We reported here the floating zone growth and characterization of $SrFeO_{3-\delta}$ and $CaFeO_{3-\delta}$ single crystals. Polycrystalline $MFeO_{3-\delta}$ (M=Sr, Ca) were prepared by standard solid-state reaction. Stoichiometric amount of MCO_3 and Fe_2O_3 were mixed with ethanol, grounded and calcined at 1050 °C for 20 h in O_2 flow. The calcined powder was grounded and pressed into cylindrical shape rod by means of a hydrostatic pressure of 310 MPa. Crystal growth was performed using an infrared heating furnace (Crystal Systems Inc.) at the growth rate of 2-5 mm/h in O_2 or Ar flow. The feed and seed rods were rotated in opposite directions at 10 rpm and 30 rpm respectively during crystal growth. Thermogravimetric analyzer (TGA) was used to determine the oxygen content in the grown crystals from the weight loss on heating to 1000 °C in O_2 or Ar flow. The grown crystals were characterized by Powder XRD, Laue XRD and Optical microphotography. $SrFeO_{3-\delta}$ crystals grown in O_2 atmosphere were a metallic luster and contained many large cracks. This cracking into the $SrFeO_{3-\delta}$ crystals due to the phase transition from brownmillerite (δ =0.5) to the orthorhombic (δ=0.25) phase by the oxidation of Fe^{3+} ions to Fe^{4+} ions during cooling after growth in O_2 atmosphere. To prevent the oxidation of Fe^{3+} ions in $SrFeO_{3-\delta}$ we tried to grow $SrFeO_{3-\delta}$ single crystals in Ar atmosphere. The crystals grown in Ar atmosphere contained few cracks and twinned structure. The structure of the $SrFeO_{3-\delta}$ crystals grown in Ar and O_2 atmosphere were brownmillarite type (δ =0.5) and orthorhombic type (δ =0.25), respectively. The compositions of the $SrFeO_{3-\delta}$ crystals grown in O_2 and Ar flow were determined to be $SrFeO_{2.79}$ and $SrFeO_{2.51}$, respectively. On the other hand it is revealed from optical microphotographs that $CaFeO_{3-\delta}$ single crystals grown in O_2 and Ar atmospheres were crack free and there was no secondary phase or inclusion. Figure 1 shows the $CaFeO_{3-\delta}$ single crystal grown in Ar atmosphere. From the XRD patterns it was obvious that in both atmospheres the grown crystal structures were brownmillerite (δ=0.5). Another important result was that the $CaFeO_{3-\delta}$ single crystal grown in Ar atmosphere was not twinned like $SrFeO_{3-\delta}$. From TG analysis we found that at room temperature the oxygen content in $CaFeO_{3-\delta}$ single crystals grown in O_2 and Ar atmospheres were the same and their composition was determined to be $CaFeO_{2.5}$. It was also found from TG analysis that in O_2 atmosphere the higher oxygen content in $CaFeO_{3-\delta}$ was not stable above about 50 °C but in the case of $SrFeO_{3-\delta}$ the higher oxygen content was stable upto 400 °C.

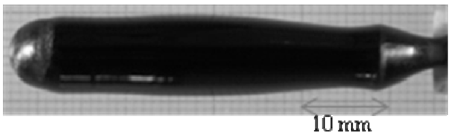

Figure 1: $CaFeO_{3-\delta}$ single crystal grown in Ar atmosphere

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Growth of N-benzyl-2-methyl-4-nitroaniline (BNA) single crystal fibers by micro pulling down method.

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Technology using terahertz (THz) region has recently being developed [1], and THz generation and detection technique attracts a interest for many application fields, such biomedical imaging, security, medicine, art conservation, and nondestructive testing [2]. A monochromatic THz-wave source using a nonlinear optical (NLO) process was employed in developing many of these applications, but the advancement of broadband sources and sources that possess some degree of frequency agility is desirable. In the developments on THz-wave technology, recently difference-frequency generation (DFG) was reported about its great advantage of ultra-broadband capability using the organic solid N-benzyl-2-methyl-4-nitroaniline (BNA) [3]. BNA, which was invented by Hashimoto, is a promising material for wideband, efficient, and high-power THz-wave generation because of its large second-order optical nonlinearity. The BNA-DFG monochromatic THz-wave was tunable over the range 0.1–15 THz. In order to improve efficiency of generating THz-wave and to realize position sensitive pallarel THz-wave generation and detection system, BNA thin fiber single crystal was required to directly couple with optical fiber line in DFG system.

In this report, BNA thin fiber single crystals were grown by micro pulling down method. Crucible materials and shape were designed according to wetness between BNA and the crucible materials. Finally BNA fiber single crystal with about 1mm diameter was successfully grown (fig.1). In my presentation, design of growth furnace and insulators, crystal structure and x-ray locking measurement result will be reported.

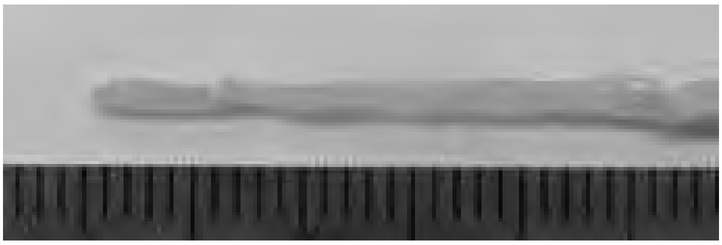

Figure 1, BNA fiber single crystal grown by micro pulling down method

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Crystal growth, scintillation and luminescence properties of Li_4SiO_4 single crystals for neutron detection

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A need for an efficient neutron scintillator has recently increased with the development of new neutron spallation sources, which are intended as a new probe for material sciences [1]. Other possible applications of a neutron scintillator include nuclear fusion monitoring, security scanning using neutron radiation, and medical therapy.

Recently, we have shown that 0.1% Ti-doped $LiAlO_2$ crystal can be a good candidate for novel neutron scintillation material due to Li-content and low density of about 2.75 g/cm^3 [2]. The light yield of the sample grown by micro-pulling-down method was determined to be around 6000 photons/neutron, which is as high as that of the commercial Li-glass scintillator. The leading luminescence process was ascribed to the Ti^{4+} charge transfer luminescence with its broad emission peak at 380nm and a reasonable decay time of 2.5µs. Positive influence of Mg codoping on the scintillation performance and the Fe^{3+} parasitic luminescence was discussed as well [3].

Another possible candidate can be the Ti-doped Li_4SiO_4 crystal with even lower density (2.35 g/cm^3) and higher Li content. Similarly as for the $LiAlO_2$:Ti the micro-pulling-down method [4] was optimized for crystal growth of Li_4SiO_4 taking into account the incongruent Li evaporation which requires adding an excess of Li_2O in the melt. The Li excess in the melt significantly influences the wettability of the crucible die and the crucible walls; therefore the melt composition needs to be optimized for the crucible die shape and the shape of the crucible bottom. The comparison of the X-ray-excited radioluminescence spectra of the Ti 0.2% -doped Li_4SiO_4 single crystal with $Bi_4Ge_3O_{12}$ (BGO) standard scintillator has shown that the overall scintillation efficiency exceeds 50% of that of BGO. It may be also influenced by slightly lowered quality of the sample surface. If we take account this fact and also possibility of further increasing the Ti concentration, Li_4SiO_4:Ti might be a promising neutron scintillator. The details and peculiarities of the crystal growth and preliminary luminescence studies of this material system will be presented and discussed.

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Growth of bulk CsI(Tl) crystal and its light output uniformity

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CsI(Tl) single crystal is an excellent scintillation crystal and has been applied in various radiation detection instruments. However, with the enlarging of the crystal size, its light output becomes more and more position dependent. The non-uniformity of light output is not acceptable for the application in such field as radiation imaging. But so far, most research work focus on the non-uniformity along the longitudinal direction, not on the transversal direction [1]. This paper presents a big CsI(Tl) crystal ingot with size ϕ280x300mm grown with vertical Bridgman method. The crystal is transparent, colorless and without any visible inclusions. As the volume of the entire crystal is too large to measure directly, some cubic samples with size of 20x20x20mm were dug out from different position of the ingot. Their light outputs and energy resolution excited by γ-ray from ^{137}Cs were measured with multi-channel pulse height spectra and the concentration of thallium was measured with ICP-Mass. It was found that the concentration of Tl increases from center to the margin of the large crystal and the light output shows the same trend as that of Tl concentration (Fig.1). This phenomenon demonstrates the interface between solid and melt is not a flat, but a convex during crystal growth. Therefore, to homogenize the light output of big size CsI(Tl) crystal, it's necessary to realize the homogeneous distribution of Tl concentration along radius. And the latter is proved to be related to the interface shape between the solid and melt. After several experiments, the thermal fields of the furnace were adjusted to reach a flat solid-melt interface.

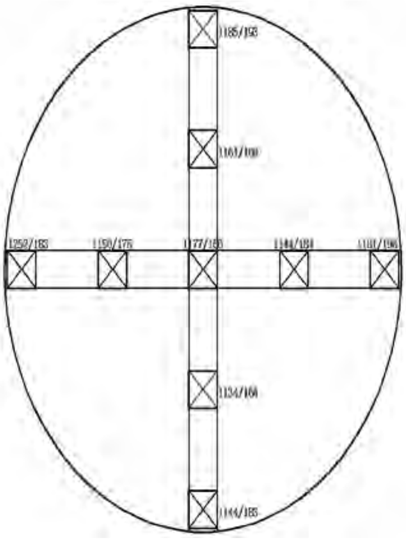

Fig.1 The channel number and Tl concentration (ppm) measured at different position of a cross section in CsI(Tl) crystal ingot with size of ϕ280x300mm

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Czochralski Growth of 2inch $(Gd_{1-x-y}La_xCe_y)_2Si_2O_7$ (Ce:La-GPS) single crystal and its scintillation properties.

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A number of halide and oxide scintillator materials have been developed in past decades. Currently, these materials are widely used in various fields including astronomy, medical imaging, and homeland security. Although halide scintillators, such as Tl:NaI, Tl:CsI, and Ce:$LaBr_3$, have high light outputs of more than 30,000 photons/MeV, they are extremely hygroscopic that makes their device application comparatively complicated. On the other hand, most of oxide scintillators are well resistant to moisture and humidity.

Ce-doped gadolinium pyrosilicate (or disilicate), Ce:$Gd_2Si_2O_7$ (Ce:GPS) crystals have also high light output of 30,000 photons/MeV and FWHM energy resolution of 6.0% at 662 keV at room temperature. However, Ce:GPS crystals need to be grown with heavy Ce-doping (approximately 10 at.% regarding Gd^+ host cations to be substituted) in order to modify the phase diagram and to stabilize the crystal growth process [1]. Such excessive Ce-concentration leads to reduced light output because of self-absorption or concentration quenching.

Recently, we found substitution of La into Gd site gives positive effect of the phase stability of this pyrosilicate [2].

In this study, the Czochralski growth of $(La,Gd)_2Si_2O_7$ type crystals was examined. The growth was performed from Ir crucible of Ø100x100 mm in dimensions that was surrounded with zirconia and alumina ceramics for thermal insulation. The crucible was heated inductively. The pulling-up rate applied was 0.5 mm/h and the environmental atmosphere in the growth chamber was mixed gas with Argon and Oxygen. The seed crystal was rotated at 10 rpm, and the crystal diameter was controlled to be about 51 mm that corresponded to solidification rate of approximately 8g/h (mass of solidified material per unit of time).

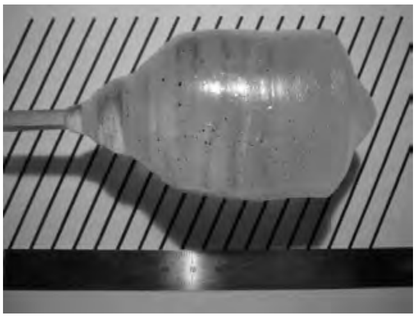

Fig1. 2inch Ce:La-GPS single crystal

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As grown crystal is shown in fig.1. After the crystal growth, photoluminescence, PL decay, radioluminescence, pulse height spectra and scintillation decay were measured and will be also reported in this relation.

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Growth and characterization of $AgGa_{0.5}In_{0.5}Se_2$ single crystal by vertical Bridgman method for IR applications

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Numerous potential applications of laser sources required output powers of several watts and pulse-repetition frequencies exceeding 10 kHz [1]. Optical parametric oscillators provided a shift in the output of a solid-state laser to longer wavelength, while SHG doubled the frequency of CO_2 lasers (9–11 μm), and sum frequency generation combined photons to produce longer wavelength photons in a large spectral range, generating an output of 3–5 μm and 8-14 μm atmospheric transmission windows [2]. $AgGaSe_2$ and related quaternary materials possessing the tetragonal chalcopyrite crystal structure are primary candidates for this application because of their high nonlinear coefficients (~39 pm/V) and excellent transmission in the mid-IR (1–18 μm) range [3]. Although $AgGaSe_2$ is available commercially, its strong birefringence properties severely diminish its conversion efficiency. Mixing this material with $AgInSe_2$ offers a practical means of significantly increasing $AgGaSe_2$ conversion efficiency with a noncritical phase matching. High purity $AgGa_{0.5}In_{0.5}Se_2$ polycrystalline material was synthesized by the melt and temperature oscillation method and it is shown in Fig.1 (a). Crack free $AgGa_{0.5}In_{0.5}Se_2$ single crystals of 12 mm diameter and 80 mm length have been grown using double wall quartz ampoule with accelerated crucible rotation technique by the vertical Bridgman method. Fig.1 (b) and (c) shows the as grown single crystal and cut & polished ingots respectively. The unit cell parameters were confirmed by single crystal X-ray diffraction analysis. The structural perfection of the grown crystals has been analyzed by high-resolution X-ray diffraction rocking curve measurements. The stoichiometric composition of $AgGa_{0.5}In_{0.5}Se_2$ was measured using energy dispersive spectrometry. The insignificant change in atomic percentages of Ag, Ga, In and Se along the ingot further reveals that the composition throughout its length is fairly homogeneous. The thermal behavior of the crystal has been studied using differential scanning calorimetry technique. As grown single crystal shows very high IR transmission of ~72 % in the spectral range 6000–510 cm^{-1}. Electrical property is measured using Hall effect measurements and it confirms the n-type semiconducting nature.

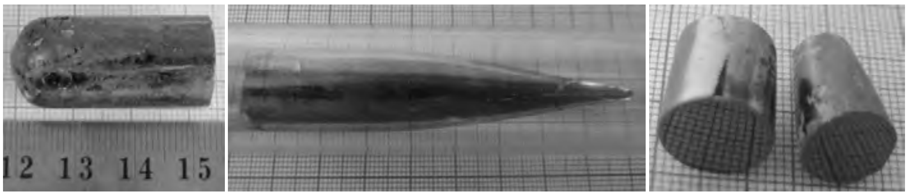

Fig.1 (a) Synthesized $AgGa_{0.5}In_{0.5}Se_2$ polycrystalline ingot, (b) As grown single crystal and (c) Cut & polished ingots

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Bridgman growth and scintillation properties of rare-earth doped $Bi_4Si_3O_{12}$ crystals

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Bismuth silicate ($Bi_4Si_3O_{12}$, hereafter abbreviated as BSO) is a new fast scintillator which has potential applications in high energy physics, nuclear physics, computed tomography and dosimetry [1-3]. Compared with widely used $Bi_4Ge_3O_{12}$ (BGO) crystal, BSO has some better scintillation properties such as a faster decay time, a greater radiation hardness and a lower raw material cost, so it is considered to be the substitute for an alternative to BGO crystals [4,5]. However, two main problems hindered its practical applications: (1) large size and high quality crystal is difficult to grow due to its compositional segregation; (2) relatively lower light yield.

In the present work, we developed a modified vertical Bridgman method and have grown large size BSO crystal successfully. By optimizing growth conditions, pure BSO crystals up to 30mm×30mm×200mm have been obtained, as shown in Fig.1. As grown crystal has good optical transmittance and the scintillation characteristics was measured. The energy resolution of the BSO single crystal was 18.9% (FWHM) with PMT for 662 keV gamma rays at room temperature when it was exposed to ^{137}Cs γ-ray and the relative light yield of the crystal was 7.2 with CsI(Tl) for absorbed gamma rays energy. Yb^{3+}, Gd^{3+}, Eu^{3+}, Ce^{3+}, Dy^{3+} doped BSO crystals have been grown in the same growth conditions. Their scintillation properties have been investigated and Table 1 shows the relative light yield of pure and RE-doped BSO crystal compared with BGO. Dy doping increased the light yield of BSO crystal considerably. It was suggested that Dy^{3+} ions replace some Bi^{3+} ions in BSO crystal and become new luminescent center. As a result, Dy doped BSO can be a potential excellent scintillator.

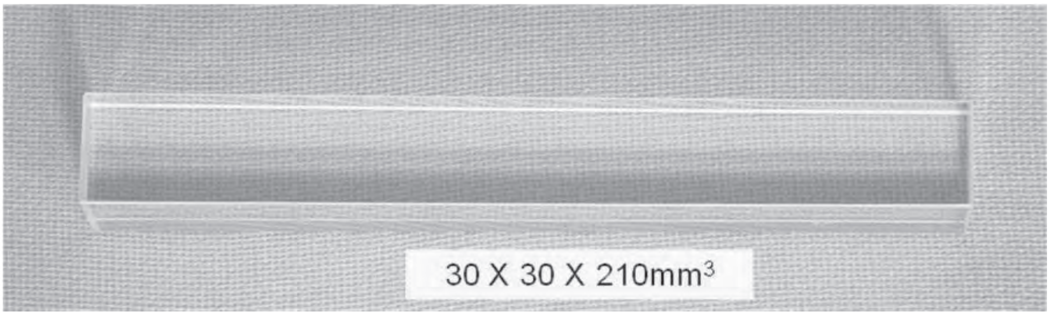

Fig. 1 BSO crystal with a dimension of 30mm×30mm×200mm

Table 1 Relative light yield of pure and RE-doped BSO crystal compared with BGO

	Crystal sample size(mm^3)	Light yield (relative)
BGO	10×10×40	100
BSO	10×10×40	21
Dy:BSO	10×10×40	35.2
Gd:BSO	10×10×40	25.1
Yb:BSO	10×10×40	27.2
Eu:BSO	10×10×40	21.3
Ce:BSO	10×10×40	20.2

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Crystal growth and luminescence properties of Cr:$Gd_3Ga_{5-x}Al_xO_{12}$ crystals for IR scintillator

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Inorganic scintillator crystals have been widely used for radiation detections such as high energy physics, security applications, oil logging and medical imaging. Recently, we have studied a real-time dose monitor system during the radiation therapy with a small scintillator into the tumor in the patient body [1]. When the scintillator is irradiated with incident X-rays, the intensity of the scintillation light give us information related to the dose in real time. Since human body had a low absorption in the region from approximately 700-1100 nm [2], near infra-red (IR) emission scintillator would be applied to the real time dose monitor system. Thus, we have investigated near IR emission scintillator materials. In the previous work, we evaluated the luminescent properties of Cr:$Gd_3Ga_5O_{12}$ crystals as IR scintillators, and the scintillation light yield of Cr 0.03%:$Gd_3Ga_5O_{12}$ crystal under 5.5 MeV alpha-ray was determined to be 30% of that of $Bi_4Ge_3O_{12}$ [3]. In this work, we studied the effect of the substitution of Ga for Al, which would shift the crystal-field. Then, we prepared the Cr:$Gd_3Ga_{5-x}Al_xO_{12}$ crystals with various Ga/Al ratio and evaluated their dopant distribution and luminescent properties for IR scintillators.

The crystal growths of Cr:$Gd_3Ga_{5-x}Al_xO_{12}$ crystals were performed by the micro-pulling down method using an Ir crucible with a radio-frequency heating system [4]. This method is useful for the survey of various compositions, because growth rate is relatively faster than other growth method. High purity Gd_2O_3, Ga_2O_3, Al_2O_3, Cr_2O_3, powders were used as starting materials. The pulling rate of crystal growth was 0.05 mm/min.

The powder X-Ray Diffraction (XRD) analysis were operated for these crystals using a X-Ray diffractometer (RIAGAKU RINT-Ultima). The analyses of the dopant distributions of growth direction and transverse cross-section to the growth direction were performed by the electron microprobe analysis (EPMA) (JEOL JXA-8621MX). Photoluminescence spectra of the crystals were recorded with an absolute photoluminescence quantum yields measurements system (Hamamatsu, C9920-02G). X-ray excited radioluminescence spectra in the near IR region was measured by using a photo-sensor module (Hamamatsu, H9305-03) and an X-ray tube (Amptek, Mini-X). The detailed results are presented on the presentation.

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Growth and Scintillation Properties of 1 inch Eu:SrI_2 Bulk Crystals Grown by the Bridgeman Method Using High-Frequency Induction Heating

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Eu doped SrI_2 [Eu:SrI_2] crystals have been investigated due to the greatly high light yield and energy resolutions. However, the Eu:SrI_2 crystal has strong hygroscopicity and it is difficult to make the bulk single crystal without any special technique and equipment. Therefore, we have developed the modified micro-pulling-down (μ-PD) method and the Eu:SrI_2 fiber crystals with a diameter of 2 mm were grown by the modified μ-PD method [1]. In addition, we have improved the growth technique to grow the Eu:SrI_2 bulk crystal and the bulk crystals 1 inch in diameter were grown by the Bridgeman (BS) method using the modified μ-PD furnace and the special-designed carbon crucible [2]. However, the grown bulk crystal included some cracks in the crystal and only small specimens with 10 x 10 mm^2 cross-section were obtained. Therefore, in this study, we achieved the growth of the 1 inch Eu:SrI_2 bulk crystals without cracks by the improvement of growth conditions.

EuI_2 and SrI_2 powders (4N purity) were mixed in the glove box as nominal compositions, $(Sr_{1-x}Eu_x)I_2$ $x = 0.03$ and 0.05. The mixed powder was entered into the carbon crucible with an inside diameter of 1 inch and the crucible, insulator and quartz cover were set in the removable chamber. After the vacuuming in the chamber, the crucible was heated by the high-frequency induction coil up to the melting point of SrI_2 and the crystal growth was performed by pulling-down the crucible. After the crystal growth was finished, the crucible was cooled to room temperature for 12 hours. Crystal structures and chemical compositions of grown crystals were evaluated by the X-ray diffraction measurement and Inductively-Coupled Plasma mass spectroscopy. In addition, the specimens with 1 mm thickness for measurements of scintillation properties were cut from the bulk crystals and they were polished in the glove box.

Eu5%:SrI_2 bulk crystal was grown by the BS method using μ-PD furnace and grown crystal is shown in Fig.1. There was no visible crack in the crystal and the bulk crystal indicated high transparency. The light yield and energy resolution were estimated from the pulse-height spectrum of the specimen obtained from the bulk crystal under γ-ray irradiation from ^{137}Cs radiation source. The estimated light yield and energy resolution were approximately 87,000 ph/MeV and 3.2%, respectively. Details of crystal growth and other scintillation properties will be reported.

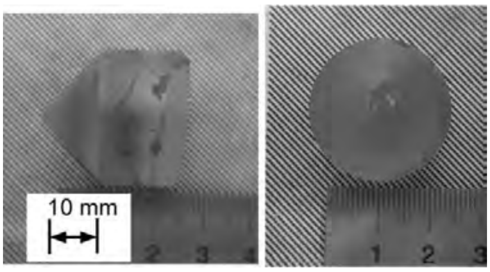

Fig.1 1 inch Eu5%:SrI_2 single crystal grown by the BS method using high-frequency induction heating.

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Large Size Single Crystal Growth, and Multifunctional Properties of Materials $LiMP_2O_7$ (M = Fe, Cr).

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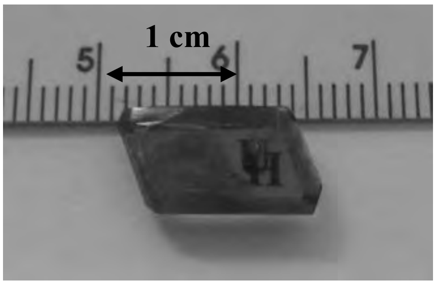
Multifuctional materials, especially multiferroics, have attracted much attention attributable to their coexistence and mutual interaction of magnetic and electric orders.[1,2] However, ferroelectricity and magnetic ordering are often mutually exclusive, which leads to the rarity of materials exhibiting both properties.[3] On the other hand, large single crystals of advanced functional materials are necessary for detailed physical property measurements. This is particularly true with low symmetric systems, such as polar oxides. $LiFeP_2O_7$ and $LiCrP_2O_7$, both crystallize in polar structures with the monoclinic space group $P2_1$ (No. 4). Meanwhile, Fe^{3+} and Cr^{3+} are magnetic ions. The coexistence of the magnetic order with the electrical polarization makes $LiFeP_2O_7$ and $LiCrP_2O_7$ interesting candidates for studying the magnetoelectric coupling in electrically polarized materials. Using a flux growth method, we have grown centimeter size crystals of new polar materials - $LiFeP_2O_7$ (Figure 1), and $LiCrP_2O_7$. SHG, piezoelectricity, and polarization were measured. In addition, the magnetic, thermodynamic, and pyroelectric properties of oriented single crystals are investigated. Crystal growth details and functional property measurements will be described.

Figure 1. $LiFeP_2O_7$ single crystal



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Unsteady thermodynamical analysis of the polytype stability in PVT growth of SiC using 2D nucleation theory

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1. Introduction

SiC has great potential as a power device material that can present a solution to the energy-saving problem. The physical vapor transport (PVT) method is the most successful and commonly used method to grow bulk SiC crystals. However, different polytypes are easily formed in a SiC crystal during crystal growth and mixing of polytypes decreases the quality of SiC. In this study, we performed a thermodynamic analysis of the growth condition dependence of polytypism, which occurs in the nucleus formation process of SiC PVT growth using 2D nucleation theory.

2. Theory

Changing the form inside a crucible in consideration of growth of a crystal, we culculated the temperature and partial pressure of the chemical species in a crucible from the global heat transfer [1]. To calculate the vapor pressure above the substrate, the evaporation flux at the powder source and the deposition flux at the seed are calculated by the Hertz–Knudsen equation. Based on the result of this heat transfer analysis, the free energy of nucleus formation is given by

$$\Delta G_2^* = \frac{\sigma_l^2 b^4}{\Delta\mu - \sqrt{3}/2b^2\left(\sigma_l + \sigma_i - \sigma_S\right)} \quad , \qquad (1)$$

where, b is the lattice constant, and σ_S, σ_i, and σ_l are the surface energies of substrate surface, of the layer/substrate interface and layer surface, respectively. $\Delta\mu$ is the bulk chemical potential change associated with the molecular change from the vapor state to the condensed state [2,3].

3. Calculation result and discussion

Figure 1 shows the difference of nucleation energy between 3C and 6H polytypes. The substrate was set to 6H (Si-face). The growth temperature and pressure were set to 2300 K and 1 Torr, respectively. The nucleation energy of 6H is small in a whole crystal. This means 6H is the most stable polytype in a whole ingot. The difference of between the 3C and 6H polytypes near the center of a crucible is small and gradually increases towards the edge and growth front. This means that the area near the center of a crucible at the early stage of growth is the most unstable in the growth of 6H-SiC.

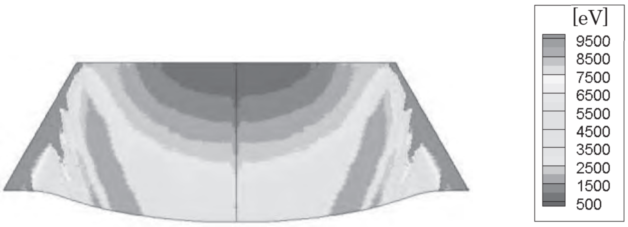

Fig. 1. Difference of nucleation energy between 3C and 6H

(Substrate : 6H-SiC C-face, Growth temperature : 2300K, Growth pressure : 1Torr)

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Free-standing HVPE-GaN crystals obtained from ammonothermal GaN substrates as seeds for the HVPE growth

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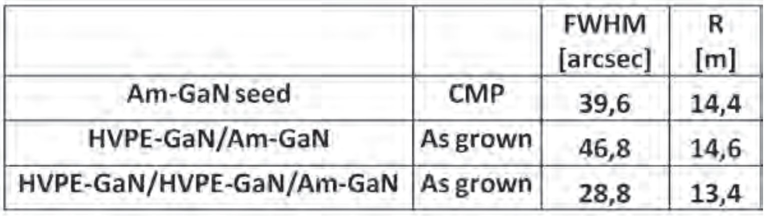
It has been shown that the ammonothermally grown GaN crystals can be successfully used as seeds for the Hydride Vapour Phase Epitaxy (HVPE) growth. Thicker than 2 mm and not cracked HVPE-GaN layers have been obtained [1]. The free-standing (F-S) HVPE-GaN crystals have been sliced from the seeds. The structural properties of the F-S HVPE-GaN have not differed from the well-known and excellent structural properties of the ammonothermal GaN seeds. Slicing procedure produces two types of crystals: F-S HVPE-GaN and its seed, Ammono-GaN (Am-GaN) when the slicing is carried out along the interface. However, if the slicing is carried out above the interface between Am-GaN and new grown HVPE-GaN, one can obtain the Am-GaN seed covered by the thin (100-200 μm) HVPE-GaN layer (HVPE-GaN/Ammono-GaN crystal). All these crystals, described above, can be used as seeds for further HVPE growth. In this work it will be shown how to prepare and use them to such growth. The starting conditions for the HVPE crystallization on the seeds presented above will be determined, demonstrated and discussed. Smooth HVPE-GaN layers of excellent crystalline quality of 2 mm thick, without cracks, and with dislocation density of the order of $5x10^4$ cm^{-2} will be shown. The result of the next slicing (second slicing) of a new HVPE grown material will be demonstrated. Structural, optical and electrical properties of this new sliced F-S HVPE-GaN will be examined and presented. It will be shown that the most perspective seeds for re-growth procedure seem to be the HVPE-GaN/Ammono-GaN crystals. Structural properties of the typical Am-GaN seed and the HVPE-GaN grown on it as well as the HVPE-GaN grown on the HVPE-GaN/Ammono-GaN crystal are presented in Tab. 1. Fig. 1 represents the XRD FWHM spectrum for the HVPE-GaN grown on the HVPE-GaN/Am-GaN couple.

Tab. 1. Structural properties of the ammonothermal GaN seed, and F-S HVPE GaN.



		FWHM [arcsec]	R [m]
Am-GaN seed	CMP	39,6	14,4
HVPE-GaN/Am-GaN	As grown	46,8	14,6
HVPE-GaN/HVPE-GaN/Am-GaN	As grown	28,8	13,4

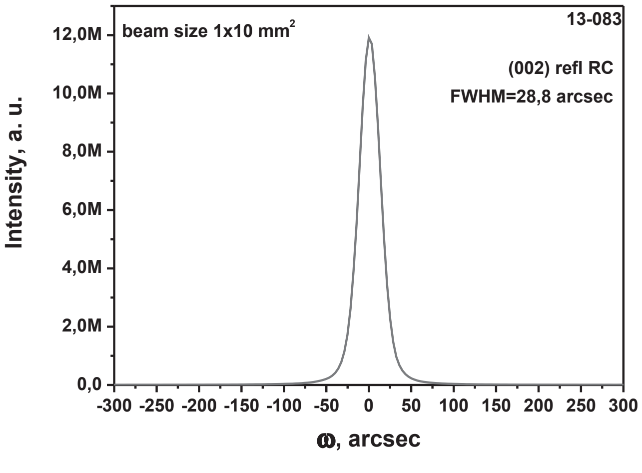


Fig. 1. X-ray diffraction spectra of the HVPE GaN grown on the HVPE-GaN/Ammono-GaN seed.

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HVPE-GaN growth on non-polar and semi-polar seeds

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In this paper an influence of growth directions and growth conditions on a growth rate, morphology, structural quality and contaminations with oxygen and silicon of new grown non-polar and semi-polar HVPE-GaN crystals was investigated in detail. The non-polar and semi-polar seeds were obtained from a thick bulk GaN crystal (grown in [0001] direction by the HVPE method), by slicing it in the appropriate crystallographic directions. Four crystals with four different crystallographic non-polar and semi-polar surfaces: (10-10), (11-20), (20-21) and (20-2-1), and two polar crystals with two different crystallographic surfaces: (0001) and (000-1) plane were used as seeds for the HVPE processes. Two crystal growth experiments were carried out. They were performed in the same growth conditions (in sense of geometric configuration of the HVPE reactor, growth temperature, reagents flows) but with different carrier gas used: H_2 and N_2, respectively. Both were performed in well-known conditions (for the authors) for stable growth in the [0001] direction.

Generally, the observed growth in non-polar and semi-polar directions was macroscopically unstable. Only the crystallization in the [20-21] direction showed some characteristics of stable growth like a macrosteps flow. In other morphological cases the growth mode was difficult to be detected and described. The higher growth rate was observed when the nitrogen was used as a carrier gas. On the other hand, in this carrier gas the differences in the growth rates in all examined directions were the smallest. During the crystallization with the hydrogen as a carrier gas the difference between the growth rates in the [10-10] and [11-20] directions were relatively high; almost three times.

The X-ray measurements showed that the quality of all crystals grown in non-polar and semi-polar directions was improved. The DSE showed that the defect density was not strongly reduced in all examined directions and for both carrier gases used. Probably, the significant defect reduction could be observed for thicker layers. It was not expected that the treading dislocation density could be reduced to the value lower than 10^6cm^{-2}. However, the DSE results obtained in the material grown in the [20-2-1] direction were opposite. The threading dislocation density was reduced to the level of 6×10^5 cm^{-2} for both carrier gases used. The TEM analysis showed that there were no stacking faults in the non-polar (10-10) layers grown with nitrogen and hydrogen as a carrier gas. It is opposite to the results obtained by Bryant et al. [1].

The PL measurements suggested that the examined samples had various levels of doping. The layers crystallized in [0001], [11-20] and [20-2-1] directions with hydrogen as a carrier gas showed strong excitons emission lines, suggesting a low level of impurity contents. On the other hand, the crystals grown in [10-10] and [20-21] directions had probably a high level of doping, presenting weak excitons emission lines in their PL spectra. When nitrogen was used as a carrier gas the layers crystallized in [0001], [10-10] and [20-2-1] directions showed strong excitons emission lines. The crystals grown in [11-20] and [20-21] presented weaker emission lines, thus higher level of doping. These PL measurements and suggestions about various doping were absolutely confirmed by the SIMS analysis. It showed that all layers were mainly doped by the oxygen and silicon. The lowest concentration of impurities was introduced during the growth in the [0001] direction. It was detected for both carrier gases applied. In the non-polar and semi-polar directions the donor impurities concentration was always higher and depended on the growth direction and the carrier gas used. It should be noted that the impurities concentration, especially the oxygen concentration, also depended on the growth rate. For the higher growth rate the lower impurities concentration was detected. The highest donor impurities concentration (5×10^{19} cm^{-3}) was detected for the crystallization in the [20-21] direction with the hydrogen as a carrier gas. It is a very interesting result because intentional doping to the high n-type in the HVPE technology is still a big challenge and maybe by using the appropriate growth direction this doping will not be needed.

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The effect of rotation on the macro-steps formation during 4H-SiC solution growth

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Solution growth is known as the mostpromising technique for growth of high quality SiC single crystals with low defect density, since growth occurs close to the thermodynamic equilibrium [1-2]. However, there are still some important issues to tackle for a further development of the process. Among those, the stability of the growth front over long growth time is really a keypoint as it can give rise to polytype and solvent inclusions. Such morphological instability which forms since the early period of growth has been attributed to non-uniform distribution of supersaturation [3]. In this paper, we will bring new insights about morphological instabilities, pointing out the effect of rotation of the crystal on the formation of instabilities.

A standard top seeded solution growth (TSSG) process has been implemented using pure Si as solvent and a temperature ranging from 1600 to 1900°C (see the details in [4]). We employed Si-face 4H-SiC crystal 4° off-axis towards [11-20] as seeds. We applied a clockwise rotation to the crystal. As grown surface morphology has been observed using Nomarski optical microscopy (NDIC). Polytype of grown crystals are investigated by Raman scattering microscopy. For a matter of clarity, we will differentiate the different steps as follow: i) “steps” correspond to unit bilayer height (2.5 Å) or a few bilayers, ii) “micro-steps” correspond to bigger steps (few tens of nm) coming from bunching of steps, and iii) “macro-steps” which correspond to µm scale height steps. This latter comes from the bunching of micro-steps.

Fig. 1 shows as grown morphologies observed by NDIC microscopy on the same crystal but different locations. If we compare the direction of the fluid flow (close to the crystal surface) and the direction of the step flow on the surface, we can define four different areas. The formation of micro-steps as shown in fig. 1(a) and (d), the development of macro-steps is provoked by the interaction between the direction of the rotation of the crystal (i.e. the direction of the fluid) and the original micro-step morphology. On the other hand, Fig. 1(b) area morphology results from a fluid flow having the parallel direction with step flow. Fig. 1(c) area is characterized by a fluid flowing to the antiparallel direction with step flow. Fig. 2 shows the schematic of the different possibilities. Fig. 2(a) shows the step morphology on the melt droplet area. In this area, the micro-steps formed on the surface with the common facetting of the step edges, typical of an off-axis substrate misoriented to the [11-20] direction in contact with a liquid phase. While the macro-steps was observed only on the right and left side of crystal (same areas compare to Fig. 1(b) and 1(c) with Fig. 2(b) and 2(c)), i.e. along the [0-110] and [-1010] directions, respectively. The terrace width of the fig. 2(b) area was 5.9 µm and that of the Fig. 2(c) area was 5.1 µm. Thus the step velocity of the Fig. 2(b) area is slower than the Fig. 2(c) area with 15%. All these results can be explained by considering the local variations of supersaturation. In addition to the direction of the fluid, we will show that the fluid flow rate (here linked to the crystal rotation rate) has also a strong effect on the density of macrosteps. We will show that those macro-steps edges are the origin of solvent inclusions and can give rise to a single- to polycrystalline growth transition.

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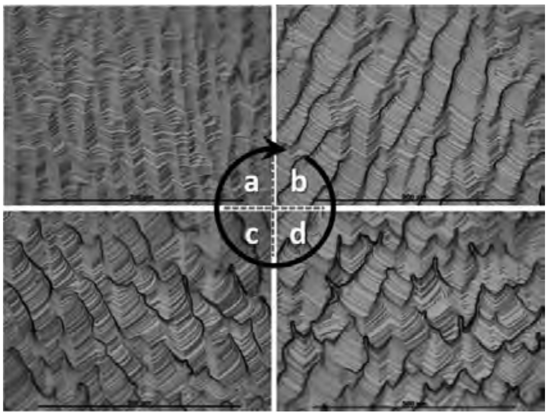

Figure 1. NDIC microscopy images of the as grown surface of the same sample. We can define four different areas; from a to d, and the seed had rotated in a clockwise direction. The black elongated lines in the Fig 1b and 1c are the so called “macro-steps”.

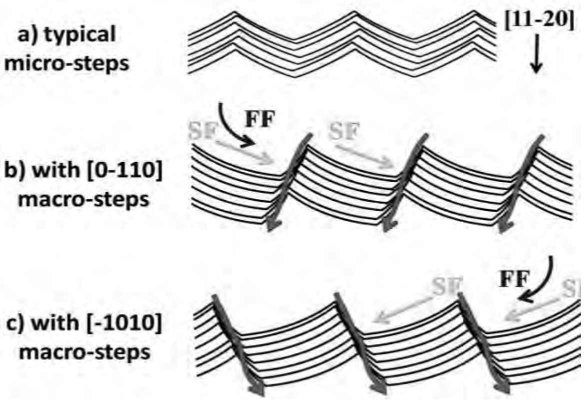

Figure 2. The schematic of the macro-steps development (depicted by the red lines) and the direction of step flows (SF; green arrow) and fluid flows (FF; blue arrow), respectively.

Examination of growth rate during Hydride Vapor Phase Epitaxy of GaN on ammonothermal GaN seeds

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The Hydride Vapor Phase Epitaxy (HVPE) is the most common approach for manufacturing GaN substrates. Generally, this involves crystallization from the vapor phase at ambient pressure, with GaN deposited on a foreign substrate through the reaction of ammonia with gallium chloride at temperatures of about 1300 K. Etching or self-lift-off techniques are used to separate the nitride film from the foreign substrate (typically sapphire or GaAs) and yield a large-diameter, freestanding GaN substrates. Deposition on a foreign substrate enables the growth of large-diameter GaN crystals, but these often suffer from lattice bowing. This meaning from significant differences between the lattice constants and thermal expansion coefficients of the foreign substrate and the nitride film. When GaN is grown by the HVPE on sapphire, the bowing radii of crystallographic planes is usually below 10 m. This relatively low value means that there is a little benefit in using HVPE-grown GaN as a seed for subsequent crystallization runs.

It is possible to form GaN crystals from the solution in supercritical ammonia. The ammonothermal GaN crystals (Am-GaN) have many great attributes: they are extremely flat, with bowing radii of the crystallographic planes reaching up to 100 m and dislocations density is of the order of $5x10^4$ cm^{-2}.

Recently, it has been shown that the ammonothermally grown GaN crystals have been able to be successfully used as seeds for the HVPE growth and that it is possible to combine the HVPE and ammonothermal methods and crystallize perfect HVPE-GaN(see Fig. 1a). Thicker than 2.5 mm and not cracked HVPE-GaN layers were obtained. The free-standing HVPE-GaN crystal was sliced from the seed showing high structural and optical quality. The structural properties of the F-S HVPE-GaN did not differ from the structural properties of the Am-GaN seeds.

In this paper the examination of growth rate during Hydride Vapor Phase Epitaxy of GaN on ammonothermal GaN seeds is presented. Various growth rates in the c-direction were determined. The growth rate was changed in two ways. First, the HCl flow was changed at a constant III/V ratio. Second, the HCl flow was changed (increased or decreased) at all other experimental parameters constant during the process (see Fig. 1b). An influence of the fastest and the slowest rate on a structural quality, materials' purity, their optical quality as well as on a morphology of the growing crystal's surface will be analyzed in this paper. The optimal growth rate (for stable crystallization) and the way to its achieving will be shown and discussed.

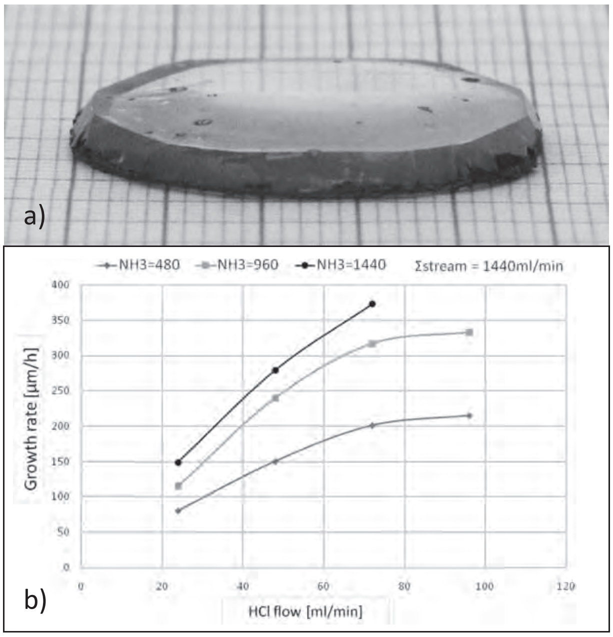

Fig. 1 a) 1900 µm thick HVPE-GaN layer grown on Ammono-GaN seed; b) Growth rate versus HCl flow at constant NH_3 flow.

Combined computational fluid dynamics and quantum chemistry calculations for the gas phase nucleation of GaN

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Metal-organic chemical vapor deposition (MOCVD) is a key technique for producing GaN thin film. As a general precursor, NH_3 and $Ga(CH_3)_3$ cause complex gas-phase and surface reactions at high temperature, especially the pre-reaction which forms the Lewis acid-base adducts and polymer. The polymer condense on the cold wall of the reaction chamber and cause the formation of nanoparticles, which then worsen the film quality and cause the precursor loss. Since the complex chemical reaction has a great influence on the growth of GaN, the understanding of the reaction paths of the growth of nanoparticles is essential to increase the utilization rate of $Ga(CH_3)_3$.

Parasitic chemical reactions lead to the formation of gas-phase nanoparticles. However, the nanoparticles growth reactions are still not completely understood. Creighton[1] reported that the parasitic chemical reactions occur in the boundary layer near the growing surface and eventually lead to the formation of nanoparticles. Thon and Kuech[2] reported that the TMG:NH3 adduct transforms into $[Ga(CH_3)_2NH_2]_3$. In this study, we proposed that the nanoparticles are mixtures consist of ring adducts ($[Ga(CH_3)_2NH_2]_3$ or $[GaN]_6$) and C and GaO. The mechanism of the formation of nanoparticles in $Ga(CH_3)_3/NH_3/H_2$ systems were then investigated using computational fluid dynamic and density functional theory simulations.

Fig.1 shows the serial reaction paths and molecular structures. Adduct reactions start with the reaction between TMG and NH_3 at room temperature. As temperature increases, the CH_4 escapes from the TMG:NH_3 and $DMGNH_2$ is consequently generated. Two $DMGNH_2$ molecules then oligomerize into a dimer $[DMGNH_2]_2$, and simultaneously three $DMGNH_2$ molecules oligomerize into a trimer $[DMGNH_2]_3$. Fig.2 shows that the thickness of adduct concentration boundary layer is in good agreement with that of the thermal boundary layer, indicating dissociation reactions begin to occurs as adduct enters the hot thin layer.

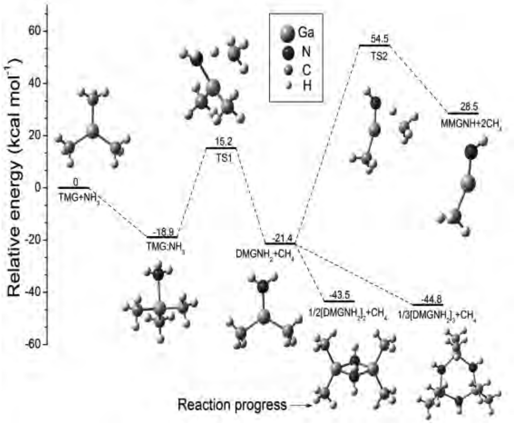

Fig.1 Potential energy surfaces of TMG+NH3 adduct reaction path.

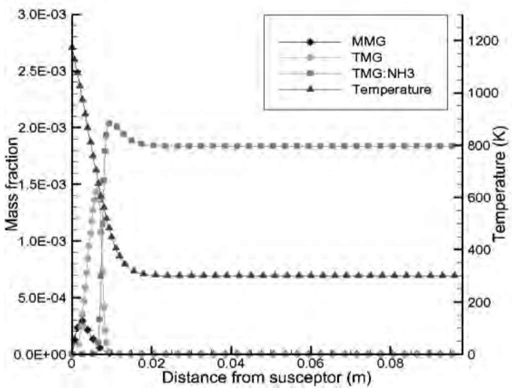

Fig.2 Temperature and mass fractions of Ga-containing particles along the symmetry axis.

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A perspective on the history and future of Bridgman crystal growth

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Percy Williams Bridgman received the 1946 Nobel Prize in Physics *"for the invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics."* He also invented an apparatus that has arguably proven to be even more important and pervasive, when in 1926 he developed a method to grow single crystals of non-cubic metals needed for his high-pressure studies. This technique, depicted in Figure 1, is now commonly referred to as the Bridgman method.

The initial realization of the Bridgman method was quite crude, with a cylindrical tube being lowered into the air of the room or into a cooling bath of oil. Bridgman noted, "It is important that air drafts be kept from the emerging mold, as otherwise new centers of solidification may be started." In a "radical change of technique," Stockbarger (1935) pulled his samples of lithium fluoride from an upper furnace maintained at a temperature above the melting point into a lower furnace, whose temperature was set to achieve a suitable axial gradient. Thus, Stockbarger was perhaps the first to advance the idea that careful control of temperatures and gradients would be needed to carry out the growth of high-quality single crystals. Wang and Witt (1984) further refined the notion of Stockbarger's zones via the heat-pipe furnace that provided well-defined thermal boundary conditions. Today, modern electrodynamic gradient freeze (EDG) systems provide nearly limitless possibilities for thermal control via dynamic computer control of individual heating zones. However, to the knowledge of the authors, only very simple profiles have been used with these furnaces.

The idea of better controlling conditions to improve crystal growth will be examined in this presentation, which endeavors to highlight many of the prior advances in understanding and technique that have led to the Bridgman-Stockbarger and gradient freeze processes of today. In particular, we will emphasize the role of heat transfer and furnace design in setting the macroscopic shape of the solidification interface. It will be argued that modern ideas of model-based design and control can be used to influence this important characteristic of growth. Several examples from recent modeling of electrodynamic gradient freeze growth of cadmium zinc telluride will be presented. Notably, a strategy is presented to dynamically adapt the furnace profile so that uniform, convex interface shapes are maintained through an entire growth run. Realizing a convex solidification interface is postulated to result in better crystallinity and higher yields than obtained via conventional approaches.

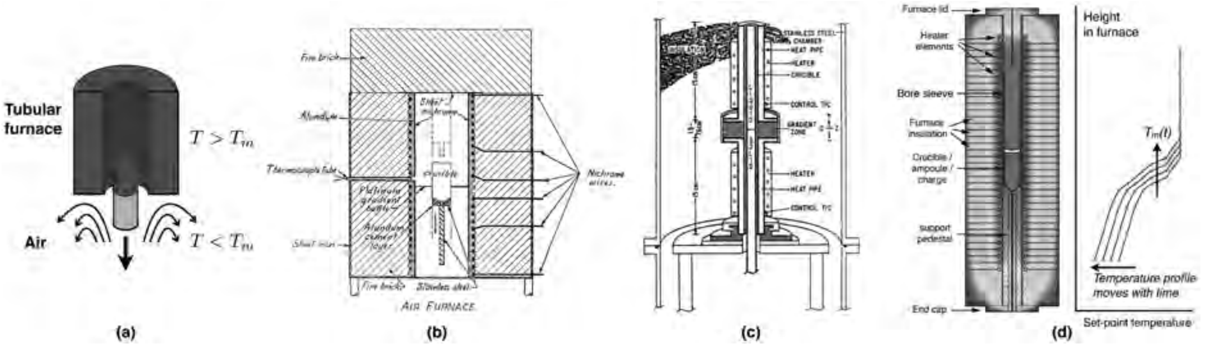

Figure 1: The evolution of the Bridgman crystal growth process. (a) Bridgman's device for growing large, single crystals featured an ampoule pulled from a heated furnace directly into ambient surroundings. (b) Stockbarger's multiple zone furnace was a "radical change in technique" that provided for higher gradients and more control. (c) The heat-pipe, Bridgman-Stockbarger furnace of Wang and Witt was designed to provide extremely well-specified thermal boundary conditions. (d) Depiction of a modern, electrodynamic gradient freeze furnace for crystal growth that can apply flexible thermal profiles for growth.

Supported in part by DOE/NNSA, DE-FG52-08NA28768, the content of which does not necessarily reflect the position or policy of the United States Government, and no official endorsement should be inferred.

OPTIMIZED ALGORITMS OF ATOMATED BULK CRYSTAL GROWTH

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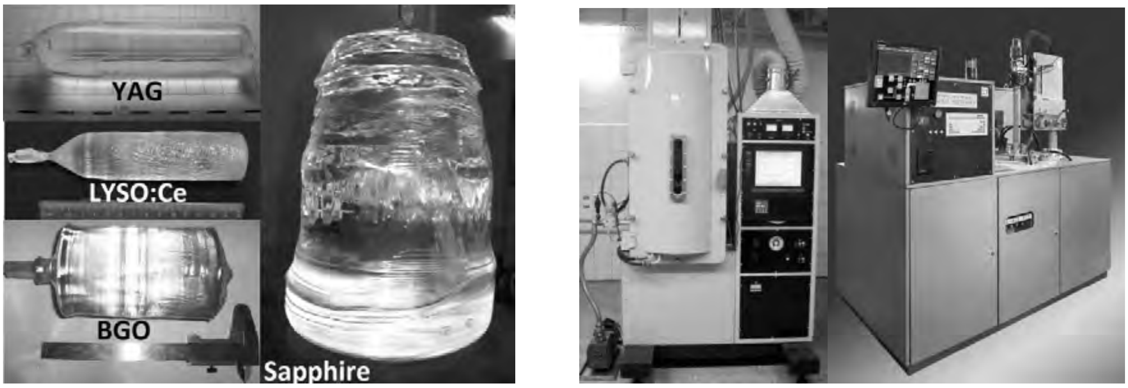
Single crystal materials have a wide range of applications in medicine, science, electronics, military equipment, and many other areas. An appropriate method should be chosen for every material to produce single crystals with the required dimensions, and with the acceptable cost. Shape of growing crystal is also an important issue. Growth of crystals good cylindrical shape can provide an increase of production yield at mechanical treatment. Therefore, a lot of attention should be paid to these issues at development of the crystal growth technology.

This work is devoted to the improvement of control principles for automated bulk crystal growth. This is the result of cooperation of equipment constructors and crystal growth team.

The authors have been jointly developed control algorithms of bulk crystal growth from the melt by the Czochralski method. PID regulator by weight sensor is implemented for crystal diameter control. The accuracy of crystal diameter stabilization within ± 0,5 mm was achieved. It has been found that the optimum PID regulator coefficients depend not only on the static characteristics of the crystallizer (thermophysical properties of insulating materials, heater, crystal, and melt), but on the growth conditions and parameters as well (growth speed, thermal gradients, crystal to crucible diameter ratio).

Growth of crystal upper cone when diameter increases from the neck diameter to a required value is the most difficult stage in the Cz process. Quite often, variations of crystallization interface shape occur on this stage leading to erroneous diameter regulation in systems with weight sensor control. The crystals obtained with this erroneous diameter control have a distorted shape and, quite often possess a lot of inclusions. The improved control algorithm of the upper cone growth was developed to avoid crystal shape deformations. The essence of the improved algorithm is the tracking of crystallization interface shape changes and its stabilization by the switching off the weight sensor and using heater power change by the preset algorithm.

The optimized growth control algorithms were implemented by the authors at growth of large RE silicates, bismuth germanate, sapphire (Fig. 1a) in induction and resistive heating setups (Fig. 1b).



a b

Fig. 1. a – as grown crystals, b – growth setups: left - induction heating “Oxide”, right – resistive heating “Omega”.

FORCED CONVECTION EFFECT ON HEAT EXCHANGER CRYSTAL GROWTH

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Forced convection has been found to play a main role in Czochralski crystal growth. However, this convection mode has not been studied before in HEM technique. Heat transfer is a phenomenon that exists in several physical processes. Therefore, its study is necessary and interesting. In our case we carry out a numerical study of heat transfer by natural and forced convection into a cylinder where all walls are hot. The heat exchanger is placed in the bottom. First, the crucible and the heat exchanger are held stationary. Second, the crucible is subjected to different speeds of rotation and the exchanger is kept fixed.

Numerical computation has been performed to investigate temperature, velocity distributions and pressure field in HEM process. The finite-volume method is employed to solve the governing equations with proper boundary conditions.

Keywords: HEM, fluid flow, natural convection, forced convection, heat transfer, finite-volume method.

Growth and luminescence properties of pure and RE-doped $RbPb_2Cl_5$ crystals prepared by vertical Bridgman method

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Recently, there has been growing interest in congruently melting ternary alkali lead halides (ternary halides), which are considered as a suitable host for solid state lasers operating in broad spectral range from mid-IR to vacuum ultraviolet [1]. Our attention was focused on crystals of ternary halides, with a stoichiometric relation of corresponding alkali halide and lead halide equal to 1:2, especially on $RbPb_2Cl_5$ (RPC).

However, crystal growth of above mentioned compounds is difficult due to their high affinity to react with atmospheric moisture under formation of hydroxy-halides which convert to oxy-halides when heated. These impurities must be unconditionally removed from starting halides before the crystal growth [2]. In our laboratory a very efficient purification method of ternary halides was developed. This method is based on introduction of gaseous mixture of halogenation agents into molten halide followed by zone refining [3].

Rubidium lead chloride ($RbPb_2Cl_5$) melts at 423 °C without any solid-solid phase transition in temperature range from room temperature to its melting point. This compound belongs to the structural homogeneous family of lead-based perovskite-like (MPb_2X_5) materials crystallizing in monoclinic structure [3].

RPC starting material was prepared by direct synthesis in molten state of refined rubidium chloride and lead chloride in stoichiometric relation 1:2. RE admixtures of nominal concentration 0,1 mol% (Dy) and 0,5 mol% (Nd and Pr), which were added into RPC host as $DyCl_3$, $NdCl_3$, and $PrCl_3$, were prepared from commercially available RE carbonates by reaction with hydrochloric acid.

Spectroscopic investigations on the prepared samples were performed in Prague laboratory, where the absorption, radioluminescence, photoluminescence, and photoluminescence excitation spectra and decay kinetics were measured in UV-visible range. The time-resolved excitation spectra in VUV range were measured at DESY synchrotron. In doped samples, the host band edge is shifted to the long wavelength side with respect to the undoped sample due to an excess positive charge in the lattice after Pb^{2+} cation substitution by trivalent activator [4]. The emission spectra of all studied samples are represented by broad host related emission band as well as corresponding activator-related emission bands. All the emission bands could be excited in the host intrinsic absorption region. The decay of the dominant emissions is described by single exponential functions in microsecond time range.

This contribution deals with preparation of high purity RPC starting materials, their doping with Dy^{3+}, Nd^{3+}, and Pr^{3+} ions, and crystal growth by vertical Bridgman method. Fundamental optical and luminescence properties of prepared samples in the visible, UV, and VUV spectral regions are characterized. This work continues in successful preparation and optical characterization of halide single crystals grown by the atmosphere controlled micro-pulling-down (μ-PD) method such as RE:RPC [4] and $Pr:PbCl_2$ [5].

June
18

P5.4

This work was supported by the research project MSMT KONTAKT II no. LH14266 and by Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for JSPS Fellows relating to JSPS Postdoctoral Fellowship for Foreign Researchers (P14040).

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NUMERICAL INVESTIGATION OF HYDRODYNAMIC STABILITY IN CZ PROCESS

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Abstract

The technology of production of semiconductors is essentially based on silicon Cz crystal growth process. Among the solidification defects encountered in this process we mention striations. To remedy to this problem and in order to find an alternative to the magnetic field application to control the behavior of turbulent flows, we propose a set of numerical investigations to study the combination effect of the geometry of the crucible, free surface and the crystal-melt interface on hydrodynamic stability in Cz crystal growth.

Keywords: Silicon Cz crystal growth, geometry, crystal and crucible, hydrodynamic stability.

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FREE SURFACE STUDY IN SILICON CZOCHRALSKI MELT

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A numerical study on the free surface of silicon melt in CZ growth is conducted. The free surface shape has not been studied before to our best knowledge. A set of numerical computations are conducted using the finite volume method. The time-dependent VOF formulation is used to track the shape of the free surface and the flow field inside the silicon crucible. The VOF formulation relies on the fact that two fluids (liquid silicon and argon gas) are not interpenetrating. The volume fraction is introduced as a new variable of the phase in the computational cell. In each control volume the volume fractions of all phases sum to unity. The fields for all variables and properties are shared by the phases and represent volume-averaged values, as long as the volume fraction of each of the phases is known at each location.

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A Comprehensive Model of the Growth of Cadmium Zinc Telluride (CZT) by the Traveling Heater Method (THM)

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The traveling heater method (THM) has enjoyed particular success for the growth of cadmium telluride (CdTe) and cadmium zinc telluride (CZT). In THM, unlike in conventional melt growth, crystalline material grows from a liquid phase that is enriched by a suitable solvent. Notably, crystalline CZT is grown from a liquid phase that contains excess tellurium. This solvent phase is produced in a liquid zone that is simultaneously dissolving a charge of CdTe or CZT as it is moved via a traveling heater. Desirable attributes of THM include lower growth temperatures and material that contains less excess tellurium than material grown from the melt. However, growth rates in THM are typically orders of magnitude smaller than those obtained in melt growth processes.

THM is inherently more complicated than melt growth methods, since compositional effects, including both phase equilibria and phase change kinetics, are of paramount importance. Hence, our fundamental understanding of THM is limited in comparison. Therefore, the primary objective of this research is to study and understand THM growth characteristics. Toward this goal, this work involves an international collaboration between research groups at the University of Minnesota (UMN) and the Albert-Ludwigs-Universitaet (ALU) in Freiburg, Germany. Research teams at ALU are focussing on experimental aspects of the traveling heater method, while UMN researchers are developing sophisticated mathematical and numerical models to analyze the process.

In this presentation, we formulate a comprehensive mathematical model for the THM process, employing a rigorous phase diagram within the framework of our prior crystal growth models that account for heat and species transfer, fluid mechanics, and moving, phase-change interfaces. We employ the CrysMAS code (Fraunhofer IISB) to predict heating profiles that arise from different furnace designs and provide these as boundary conditions to our finite element codes for growth. We summarize the finite element methods employed for solution of this model and present initial results on THM growth characteristics, such as interface shape, thermal gradients, interfacial stability, and crystal composition (both tellurium excess and zinc distribution). We will examine parametric process sensitivity to factors such as growth rate, heater profile, and size of the melt zone. In particular, we examine several phenomena that limit achievable growth rates in this system, such as constitutional supercooling, growth kinetics, and dissolution rates of the feed into the zone. Preliminary comparison with experimental systems will also be presented.

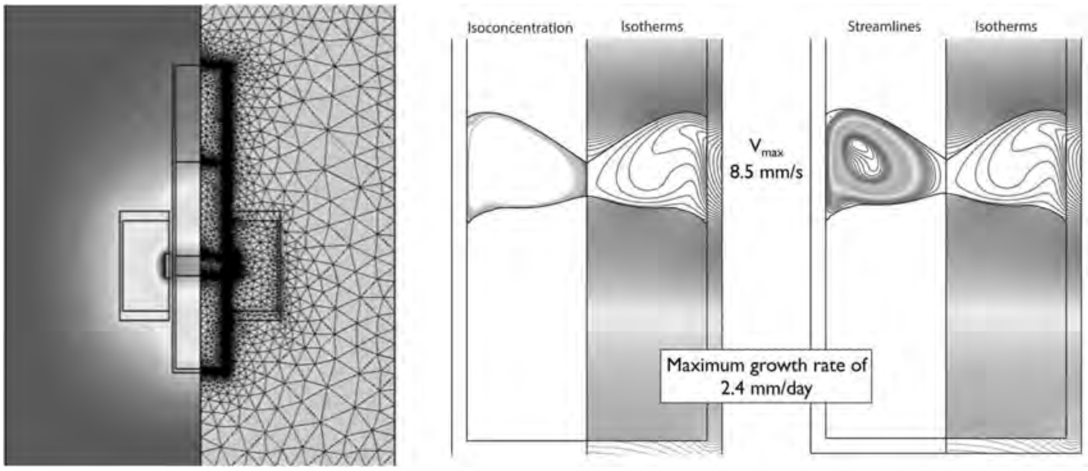

Figure 1: Heat transfer computations (left) are employed to provide thermal boundary conditions to a rigorous, finite-element model for the traveling heater method (THM) growth of CZT.

Supported in part by U.S. National Science Foundation, NSF DMR-1007885, the content of which does not necessarily reflect the position or policy of the United States Government, and no official endorsement should be inferred.

Verification of numerical model of AVC technique for crystal growth from melt

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Axial vibrational control (AVC) technique for a crystal growth from melt consists in low-frequency oscillation of a baffle submerged into melt. The baffle is made from an inert material-regarding to the melt. The AVC technique was successfully applied to Bridgman [1] and Czochralski [2] configurations. However, there has not been created a universal numerical model to predict a behavior of high temperature melts until now.

We made a test bench for physical simulation of heat and mass transfer in liquid with a control viscosity and AVC application to the liquid. The bench allows to measure liquid flows with high space-to-speed resolution (0.01 mm/0.05 m×s^{-1}). 3D temperature mapping is measured by an optical thermoluminescent probe with 0.3 mm space resolution and 0.05°C accuracy in 20-90 °C range.

An influence of a baffle shape on heat and mass transfer was studied by physical and numerical analyses. We found out the baffle shape which allowed to organize intensive laminar vibrational flows both in the central part of the crucible to dissolved a very convex interface and near the crucible walls to dissolve the “tails” resulted from a low crystal thermal conductivity and a high crystallization heat in case of large diameter crystal growth.

For developing a verified numerical model we made a special UserDefineFunction for a dynamic mesh behavior. We also adjusted a quadrilateral cell mesh (Fig. 1 left) which reduced in dimension more than 30 times approaching the baffle edge. The developed mesh allowed detecting very small and fast primary flows generated on the baffle sharp edge. A comparison of calculated (red) and experimental (white) flows in a water-glycerol solution activated by AVC (*f*=15 Hz and A=0.6 mm) demonstrated a good correlation between the model and experiment both in the flows mapping and their velocity (Fig. 1 right).

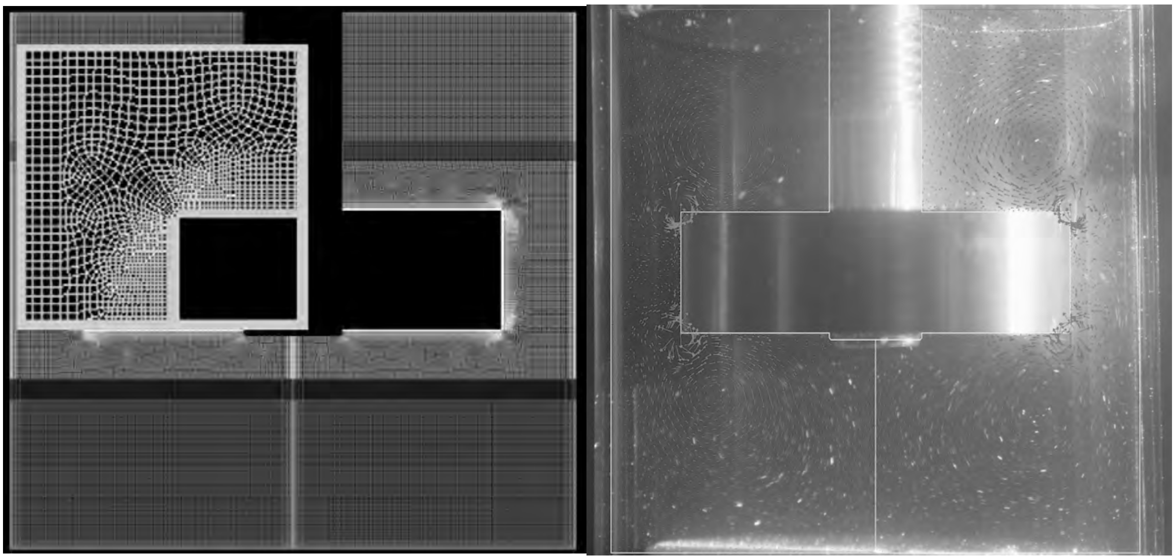

Fig.1. Quadrilateral cell mesh for AVC technique numerical simulation in Bridgman configuration (left) and a comparison of calculated (red) and real (white) flows in a water-glycerol solution (right) under AVC action with *f*=15 Hz and *A*=0.6 mm.

The study was supported by the Russian Foundation of Basic Research. Grant No. 13-02-12199

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Growth of sapphire capillaries for X-ray studies under supercritical conditions

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Sapphire, the single crystal of aluminium oxide, is a desired material for many demanding applications thanks to its unique physical and chemical properties, e.g., high mechanical durability, excellent optical properties, chemical stability against most substances and high melting point [1].

The production of sapphire crystals in Crytur is achieved via the “Edge-defined Film-fed Growth” technique (abbreviated as EFG). This way profiled crystals are manufactured, mostly in the form of tubes [2]. The principle of this crystal-from-melt pulling process is that the melt rises through a die, thanks to capillary effects, from the heated crucible into a small basin of defined shape from which the single-crystal filament is slowly drawn. We used newly designed shaping elements to produce capillaries with inner diameter from 1.5 mm down to 0.6 mm and outer diameter 1.0 - 2.0 mm. The crystals were pulled at a rate of 60–300 mm/h. The crystallographic orientation of sapphire capillaries is along the c-axis. The capillaries can be sealed on one end with single-crystal sapphire cap grown directly onto the profiled tube. This is achieved by the same crystal growth method (EFG) employing a different shape of the orifice (a full disc cross-section instead of an annulus used for tubes).

Sapphire capillaries are able to withstand internal pressures several hundred times higher than is the atmospheric pressure. Therefore they are being employed in many kinds of experiments where their penetrability for various regions of electromagnetic spectrum as well as electrical, thermal and chemical resistance is useful. Sapphire capillaries are successfully used for X-ray diffraction studies in non-ambient environments [3], e.g., under supercritical conditions of water ($p > 22$ MPa, $T > 647$ K) or other fluids in the process of crystallization of new nanoparticles in material research.

The burst pressure of thin single-crystal sapphire tubes was measured using a hydrostatic testing apparatus. These measurements were conducted under room temperature as well at elevated temperature of 1000 °C. Strength of sapphire tubes was determined, which can be used for computing the pressure durability. Single-crystal sapphire capillaries can be pressurized up to ca. 100 MPa. Therefore sapphire vessels can be applied in various high-temperature, high-pressure and other hi-tech applications.

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June
18

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Thursday, June 19

Session 4		**Substrates for wide band-gap and oxide semiconductors** Chair: Matthias Bickermann (IKZ Berlin, Germany)
08:30	S4 / oral 4	Zlatko Sitar (North Carolina State University, USA) **Growth of AlN crystals and AlGaN epitaxy on AlN wafers**
Session 6		**Crystal shaping and layer transfer technologies** Chair: Albrecht Seidl (Schott, Germany)
09:20	S6/ oral 2	Shinichi Shikata (Diamond Research Labs, AIST, Japan) **Diamond Wafer Prospect for the Power Device Application**
10:10 - 10:30		Coffee
10:30	S6 / oral 3	Noah Smick (GT Advanced Technologies, USA) **Using Proton-Induced Exfoliation to Manufacture Low-Cost, Device-Quality Single Crystal Substrates**
11:20	S6 / oral 4	Sarah Kajari-Schröder (Institute for Solar Energy Research IFSH, Germany) **Kerfless Wafering for Photovoltaics**
Session 1		**Advances in bulk crystal growth of semiconductor & photovoltaic materials** Chair: Michael Neubert (IKZ Berlin, Germany)
12:10	S1 / oral 5	Xingming Huang (JA Solar, China) **Development of High-quality Multi-crystalline Silicon Ingots**
13:00		Closing
13:10		Lunch

Growth of AlN crystals and AlGaN epitaxy on AlN wafers

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Any crystal growth from the vapor phase relies on one of the two strategies to achieve large-area wafers: growth of thick layers on non-native seeds and subsequent seed removal, or gradual crystal-size expansion through an iterative re-growth process. While the former technique produces large diameter wafers faster, the latter approach yields crystals of much higher quality. This presentation contrasts the two approaches and focuses on challenges inherent to high-temperature growth of AlN.

AlN boule expansion was pursued in an inductively-heated reactor, capable of temperatures in excess of 2400°C. Sintered AlN powder was used as a source material and growth was performed in a nitrogen atmosphere. Detailed finite element analysis was used to design radial and axial gradients to follow the desired boule expansion; realistic expectations and limitations of this technique will be discussed.

Stable facets observed in AlN crystals grown close to the thermal equilibrium are c, m and r. Single crystalline AlN boules were grown on c+, c-, a and m oriented high-quality AlN seeds. The growth on the N-polar seeds was controlled by one growth center leading to a mirror-like growth facet, while the growth on the Al-polar seeds resulted in numerous competing growth centers. A surface energy model in conjunction with the BCF theory, developed as a framework for AlN crystal growth on different facets, supported experimental observations. AlN boule growth on non-polar seeds was controlled by step-flow growth emanating from one growth center and was always terminated with m-facets, regardless of seed orientation. AFM measurements were performed on the as-grown c- and m-surfaces and showed step-flow growth mechanism. Gradual crystal expansion was achieved through a scalable, iterative re-growth process in which the volumetric defect formation is suppressed and high crystal quality is maintained over many generations of boules.

The availability of low defect density ($<10^3$ cm^{-2}) native AlN substrates offers an opportunity for growth of AlGaN alloys and device layers that exhibit million-fold lower defect densities than the incumbent technologies and enable one to assess and control optical end electrical properties in absence of extended defects. UV LED structures and laser diodes were fabricated on these materials that exhibit low turn-on voltages and record low lasing threshold.

This presentation will review state-of-the-art of AlN-based technology and give examples of potential applications in future devices and contrast these with other wide bandgap technologies.

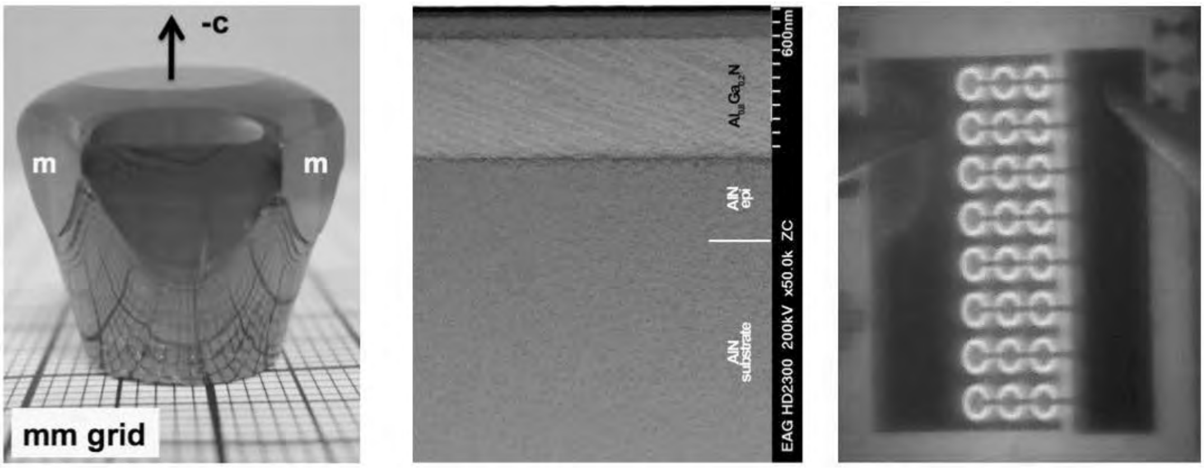

Figure 1: From left: as grown AlN boule, STEM image of homo end heteroepitaxial layers, fabricated deep UV LED array.

Diamond Wafer Prospect for the Power Device Application

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Diamond is known as a hopeful candidate material for the low loss high power switching devices due to its extreme properties such as high breakdown, high thermal conductivity, high mobility and so on [1]. We have started the R&D program aiming for this application at Jan. 2005 on the basis of new concept “Cooling module free” power device operating at elevated temperature from 200 to 250°C (self-heated temperature of the active power device) [2], where the activated carriers contribute to reduce conduction loss.

As the equilibrium state can only be realized by HPHT for diamond, large diameter wafer realization rely entirely on CVD method. The first technology carried out toward large size diamond was 3D growth technique, which resembles to RAF method for SiC. Starting from several mm sq. HPHT substrate, up to approximately 10mm size was obtained. Second, we have developed a wafer copying technology. Here, we have employed ion implantation to form “damaged layer” in sub-surface, which was followed by diamond growth and lift-off process from “mother crystal” by removing “damaged layer” to form a daughter wafer without using slicing[3]. Here, the mother crystal can be re-used to form the sister wafers. The feature of this method is the affinity of obtained “sisters” that have same crystallographic off-angle and direction, as if they have installed same DNA. The sisters are joined by CVD growth, and applying the “lift off method” again to this jointed substrate, we can obtain large size monolithic substrate [4], which we call “Mozaic wafer”. Fig.1 shows the photograph of the wafers of the initial plate of 9x10mm^2, 20x20mm^2 plate which consist of 4 single crystal plates, 20x40mm^2 consist of 8 plates. On the right, 40x60mm^2 by 24 plates before the lift off is shown [5]. These technologies are now leading the road to realize large single crystal diamond wafer in the near future.

Additionally, we are applying this technology to realize low defect density wafer using high quality HPHT seed (defect density: lower than 100cm^{-2}) and successful epi growth with UV assisted polishing technique which lead to high quality copying techniques is recently confirmed [6,7]. For the device, we already confirmed the advantages of diamond using SBD as a test device and found low loss switching operation at 250C [8,9] The latter two topics are abbreviated in this abstract because of the space limitations, but will be presented intensively in the talk with future prospect and challenges to be solved.

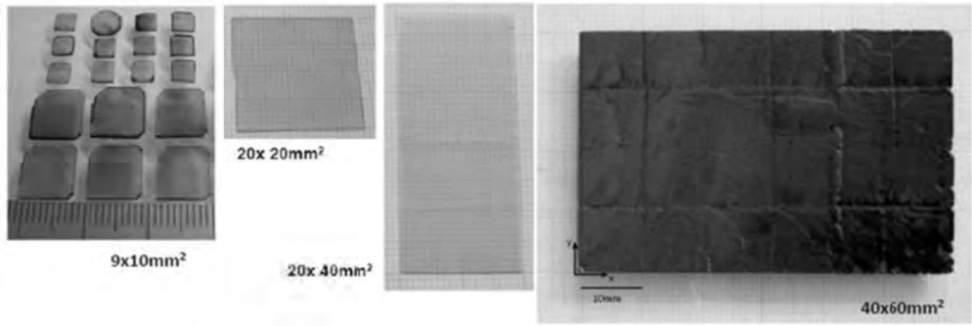

Fig.1 Photographs of mosaic single crystal diamond wafers. Left to right; Initial 9x10mm^2, 20x20mm^2 by 4 plates, 20x40mm^2 by 8 plates, and the last 40x60mm^2 by 24 plates before the lift-off.

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Using Proton-Induced Exfoliation to Manufacture Low-Cost, Device-Quality Single-Crystal Substrates

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High substrate cost continues to be one of the primary factors preventing wide-scale adoption of compound semiconductor substrates in areas such as power electronics and LED manufacturing. Silicon-based devices are widely used in applications where SiC, GaN or AlN would make much more suitable substrates, if the costs of these alternative substrates were lower. GT Advanced Technologies continues to make progress towards the commercialization of its proton-induced exfoliation ("PIE") technology, starting with fully-integrated photovoltaic cells and extending to other compound semiconductor materials, allowing substrate and device manufacturers to reduce substrate cost dramatically. PIE introduces a controlled proton doses to bulk crystalline materials, followed by a cleaving step that leaves the manufacturer with a thin, low-cost but epitaxy/device-ready substrate. We will present results showing our progress towards commercialization of this technology in a number of industrially relevant materials, including thin-lamina handling and other important post-processing strategies.

Kerfless wafering for photovoltaics

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Cost-competetive photovoltaics (PV) requires high-quality absorbers for the lowest possible prize. Traditional wire-sawing of wafers has a significant fraction of silicon that is lost as kerf. Kerfless wafering techniques aim to drastically reduce the silicon consumption per absorber by eliminating the kerf loss. The techniques currently in development are varied: kerfless wafers can be produced directly from the silicon melt [1], or a single thick wafer can be split in many thinner wafers e.g. by thermo-mechanical exfoliation of thin silicon layers with a stessor layer [2]. A third way is to grow monocrystalline silicon wafers directly from the gas phase. One such technique is the porous silicon (PSI) layer transfer technique [3,4]. Here, a thick monocrystalline wafer is electrochemically porosified with a low porosity layer at the surface and a buried high porosity layer. A hydrogen bake closes the surface, enabling a high-quality epitaxy of silicon on a monocrystalline silicon template. The high-porosity layer forms into a mechanically weak layer, enabling the subsequent lift-off of the epitaxial layer from the growth substrate. In this way the PSI process produces monocrystalline silicon foils with thicknesses in the range of 20-60 µm, which is sufficient for high-efficiency solar cells. We will review the recent progress in the development of the PSI process, discuss the challenges in adopting this technique for high-volume production in PV and outline a variant for producing kerfless PSI wafers with standard thicknesses, thus reducing the challenge of handling the thin silicon layers.

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Development of High-quality Multi-crystalline Silicon Ingots for Solar Cells

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Many new directional solidification (DS) technologies have been developed to meet the product quality requirements of the newly developed photovoltaic market. These technologies include the dendrite growth for multi-crystalline silicon (mc-Si) ingot, the seed-assisted growth for quasi-mono Silicon (QSC-Si) ingot, and the seed-assisted growth for high-performance mc-Si ingot.

For the mc-Si ingot of the dendrite growth, many twin grain boundaries generated by enhancing the cooling rate with low dislocation density at the initial stage. But with the crystal growth, the dislocation density increased evidently due to the competition between different grains. For the QSC-Si ingot, wafers with a large <100>-orientated area can be obtained and the cell efficiency had a great advantage in comparison with the conventional mc-Si by using alkaline texturing method. But high dislocation density and insufficient single area yield were the main problems which impacted the solar cell efficiency and made the production cost high. For the high-performance mc-Si ingot via the seed-assisted growth, the distribution of grain size was effectively controlled by the application of mc-Si seeds. Uniform grains with lower dislocation density and higher minority carrier lifetime were obtained in high-performance mc-Si ingot than in the conventional mc-Si ingot. About 0.5% absolute values in average solar cell conversion efficiency were higher with the same cell production process.

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Printed by:
Polyprint GmbH
Newtonstr. 18
12489 Berlin, Germany

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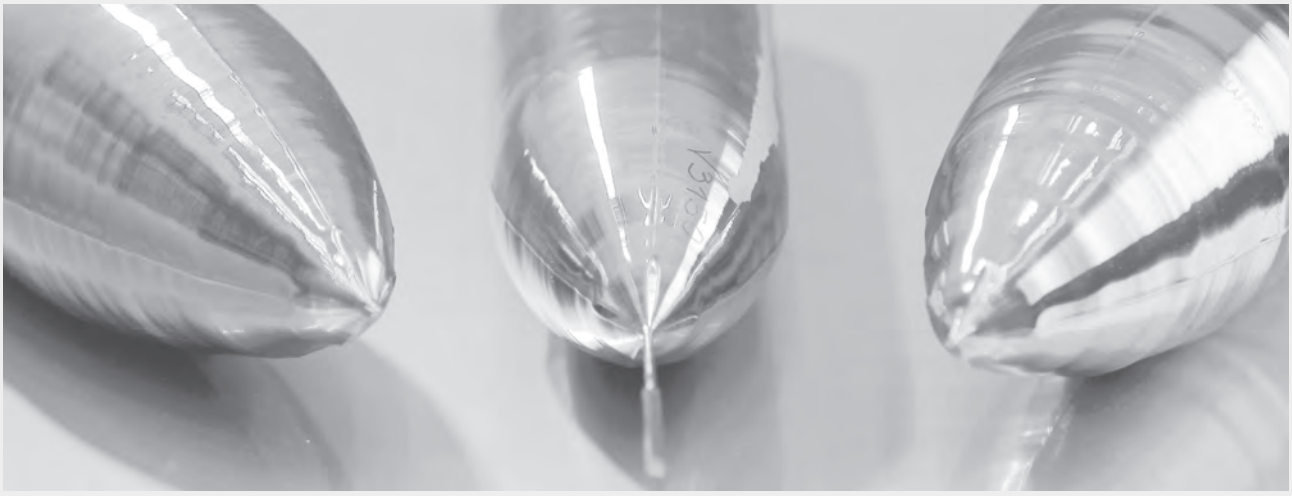
The Leibniz Institute for Crystal Growth (IKZ) is dealing with the research on scientific and technical aspects of the growth of crystalline materials. These materials play a fundamental role in e.g. photovoltaics, micro-, opto-, and power electronics, sensor applications, optics, and laser techniques. Our activities cover fundamental research up to industrial growth processes. IKZ provides crystals and technologies as a service for research and industry.



Materials prepared at the IKZ include:

- Wide band-gap nitride and oxide semiconductors (AlN, GaN, Ga_2O_3, In_2O_3, SnO etc.)
- Oxide and fluoride crystals for laser, optical components, sensors, and substrates for multi-ferroic applications
- Silicon crystals for high power electronics and photovoltaics,
- Crystalline epitaxial oxide layers for oxide semiconductors and ferroelectric applications,
- Si/Ge layers and nanostructures for photovoltaics and thermoelectrics.

The research and service of the IKZ comprise:

- Developing methods for growth, wafering, and characterization of bulk crystals as well as layers and nanostructures,
- Developing of cross-material crystal growth, wafering, and charcterization technologies,
- Provision of crystals with unique specifications,
- Modeling and experimental research of crystal growth processes,
- Characterization of materials properties and their interpretation,
- Development of construction components, equipment, and materials for crystal growth, wafering, and characterization.

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IWCGT-6
TIMETABLE

	June 15	June 16	June 17	June 18	June 19
08:30		S 1 / 1 Kimbel	S 3 / 1 Koschan	S 6 / 1 Shikunova	S 4 / 4 Sitar
09:20		S 1 / 2 von Ammon	S 3 / 2 Bourret-Courchesne	S 4 / 5 Ohtani	S 6 / 2 Shikata
10:10		Coffee	Coffee	Coffee	Coffee
10:30		S 1 / 3 Kakimoto	S 3 / 3 Yoshikawa	S 5 / 1 Berwian	S 6 / 3 Smick
11:20		S 1 / 4 Jouini	S 3 / 4 Luo	S 5 / 2 Rieken	S 6 / 4 Kajari-Schröder
12:10		Break	Break	Break	S 1 / 5 Huang
12:30		Lunch	Lunch	Lunch	13:00 Closing
14:00		S 2 / 1 Tao	S 4 / 1 Paskova	S 5 / 3 Orschel	13:10 Lunch
14:50		S 2 / 2 Kraenkel	S 4 / 2 Ehrentraut	S 7 / 1 Ferrari	
15:40		Coffee	Coffee	Coffee	
16:10	Registration	S 2 / 3 Isaenko	S 4 / 3 Galazka	S 7 / 2 Li	
17:00		S 2 / 4 Kolis	Break	S 7 / 3 Syväjärvi	
17:50		Break		Break	
18:00	Dinner	Dinner	Gala Dinner	Dinner	
19:15	Panel	Industrial Session Industry 1		Industry 2	
20:00		Poster 1		Poster 2	
21:45	End	End		End	
23:00			End		