7th INTERNATIONAL WORKSHOP ON CRYSTAL GROWTH TECHNOLOGY

GERMANY, JULY 02 - 06, 2017

IWCGT-7

POTSDAM NEAR BERLIN

TOPICAL SESSIONS	SINGLE CRYSTALS OF SILICON AND III-Vs MULTI-CRYSTALLINE SILICON FOR PV OXIDE CRYSTAL GROWTH WIDE BANDGAP SEMICONDUCTOR GROWTH EMERGING FIELDS IN CRYSTAL GROWTH
PANEL DISCUSSION	TRAINING AND EDUCATING CRYSTAL GROWTH TECHNOLOGY
ORGANISED BY	LEIBNIZ INSTITUTE FOR CRYSTAL GROWTH (IKZ)

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7th International Workshop on Crystal Growth Technology

Potsdam near Berlin, Germany, July 02 - 06, 2017

Welcome message

Dear participants of the IWCGT-7,

We are very happy to welcome you at the 7th International Workshop on Crystal Growth Technology (IWCGT-7), which takes place at the Seminaris SeeHotel Potsdam, Germany, on July 2–6, 2017. 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). The German Association for Crystal Growth (DGKK) sponsors a poster prize.

Crystal growth has enabled a substantial part of modern technology, from piezoelectric, optical, and laser applications to today's booming photovoltaic market and overwhelming use of electronic devices in information technology, communication, system control and power conversion. Producing 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. Crystal growth technologists address this demand, and this workshop is where they meet.

Since its initiation in 1998 by Hans Scheel, the workshop is perceived as a meeting of experts in crystal growth technology, where invited renowned speakers give in-depth presentations about a particular challenge in application-oriented crystal growth, and with lots of space for discussions and networking opportunities.

This approach has proven very successful and is continued at IWCGT-7. The retreat-type of scenery around the hotel, long coffee breaks and the barbecue dinner, but also the two evening poster sessions are means to stimulate a lively networking atmosphere between the participants. All attendees, and in particular young researchers, have been asked to prepare abstracts and posters to present their own work.

The IWCGT-7 is intended to bridge R&D and the actual production and go beyond academic treatment as presented e.g. in the other existing series of crystal growth conferences. We intend to discuss the latest developments in crystal preparation, industrial production, machining, and equipment, and talk about the challenges of bringing novel materials to a commercial stage.

We sincerely 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 invited speakers, the members of the steering committee, the IKZ local organization team, the session chairs, our exhibitors and sponsors, and all attendees for their most valuable contributions.

Meet the experts in crystal growth technology at IWCGT-7!

Matthias Bickermann, Hanna Dabkowska, Kazuo Nakajima
IWCGT-7 chairpersons

Chairs

- Matthias Bickermann, IKZ Berlin, Germany
- Kazuo Nakajima, Tohoku Univ., Japan
- Hanna Dabkowska, McMaster Univ., Canada

Steering Committee

- Edith D. Bourret-Courchesne, LLNL, USA
- Peter Capper, SELEX Galileo Infrared, UK
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- Ben Depuydt, Umicore, Belgium
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- Roberto Fornari, University of Parma, Italy
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- Frank M. Kiessling, IKZ Berlin, Germany
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- Maria Porrini, SunEdison Semiconductor, Italy
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- Nathan Stoddard, SolarWorld, USA
- Deren Yang, State Key Lab., Zhejiang Univ., China
- Evgenii V. Zharikov, D. Mendeleev University, Moscow, Russia

Local Organization

The IWCGT-7 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)
- Andrea Lepper (organization)
- Uwe Rehse (registration, organization)
- Maike Schröder (organization, sponsoring)
- Dietmar Siche (program, exhibitation)

Workshop Program

Sunday, July 02

16:00		**Registration**
18:00		Dinner
Panel		**Training and educating crystal growth technology** Chair: Matthias Bickermann (IKZ Berlin, Germany)
19:30		Panel Discussion

Monday, July 03

Session 1		**Single crystals of silicon and III-Vs** Chairs: Maria Porrini (SunEdison Semi, Italy), Koichi Kakimoto (Kyushu Univ., Japan)
09:00	a)	Michael Rosch (FCM, Germany) **III-V bulk growth (GaAs, InP)**
09:50	b)	Joel Kearns (NASA, USA) **Czochralski silicon and wafer processing in the PV and semiconductor device industry**
10:40		Coffee
11:00	c)	Ludwig Stockmeier (Fraunhofer IISB, Germany) **Approaches for highly n-doped silicon**
11:50	d)	Shin-ichi Nishizawa (Kyushu Univ, Japan) **Improvement of Si Materials and Processes for Si power devices**
12:45		Lunch
Session 2		**Wide Bandgap Semiconductor Growth** Chairs: Dietmar Siche (IKZ Berlin, Germany), Henryk Teisseyre (Institute of Physics PAS, Poland)
14:30	a)	Akito Kuramata (Tamura Corp. and Novel Crystal Technology, Japan) **Ga_2O_3 bulk crystal growth technology**
15:20	b)	Michal Bockowski (IHPP and UniPress, Poland) **Status, perspectives, and trends on bulk growth of gallium nitride**
16:10		Coffee
16:30	c)	Robert Bondokov (Crystal IS, USA) **The Development of High-Quality, UV-transparent Two-inch AlN Single-Crystal Growth**
17:20	d)	Thomas Straubinger (SiCrystal AG, Germany) **SiC bulk crystal growth**
18:30		Dinner
Poster		**Presentation**
19:30		Session I

P1 Single crystals of silicon and III-Vs

01 Kaspars Dadzis, Robert Menzel, Helge Riemann, Nikolay V. Abrosimov
Leibniz Institute for Crystal Growth, Berlin, Germany
Thermal simulation of silicon crystal growth using a granulate crucible

02 Wataru Fukushima, Satoshi Nakano, Hirofumi Harada, Yoshiji Miyamura, Koichi Kakimoto
Research Institute for Applied Mechanics, Kyushu Univ., Fukuoka, Japan
Numerical analysis of dislocation density in Si single crystal using oxygen diffusion

03 Xin Liu, Xue-Feng Han, Satoshi Nakano, Koichi Kakimoto
Research Institute for Applied Mechanics, Kyushu Univ., Fukuoka, Japan
Control of crucible movement on melting process and carbon contamination in Czochralski silicon crystal growth

04 Xue-Feng Han, Satoshi Nakano, Xin Liu and Koichi Kakimoto
Research Institute for Applied Mechanics, Kyushu Univ., Fukuoka, Japan
3D Numerical analysis on the shape of free surface in floating zone (FZ) method for silicon single crystal growth

P2 Wide Bandgap Semiconductor Growth

01 Agnieszka Pieniążek, Henryk Teisseyre, Dawid Jarosz, Bartłomiej S. Witkowski, Anna Reszka, Krzysztof Kopalko, Adrian Kozanecki, Marek Godlewski, Bogdan J. Kowalski
Institute of Physics, Polish Academy of Sciences, Warsaw, Poland
Fabrication and Optical Properties of Axial ZnO/ZnMgO Multiple Quantum Wells on Vertical ZnO Microrods

02 Dawid Jarosz, Henryk Teisseyre, Marcin Stachowicz, Jaroslaw Domagala, Adrian Kozanecki
Institute of Physics, Polish Academy of Sciences, Warsaw, Poland
Incorporation of magnesium into ZnMgO layers grown by PA-MBE

03 Michal Fijalkowski, M. Iwinska, T. Sochacki, B. Lucznik, M. Amilusik, M. Bockowski
Institute of High Pressure Physics PAS, Warsaw, Poland
Comparison of structural, optical, and electrical properties of highly conductive HVPE-GaN doped with Si or Ge and grown on native seeds

04 Mikolaj Amilusik, Tomasz Sochacki, Malgorzata Iwinska, Boleslaw Lucznik, Michal Fijalkowski, Michal Bockowski
Institute of High Pressure Physics PAS, Warsaw, Poland
Highly resistive HVPE-GaN grown on native seeds with solid iron or methane as a source of dopants

05 Tom Schneider, G. Lukin, F. Zimmermann, C. Röder, M. Barchuk, E. Niederschlag, C. Schimpf, O. Pätzold, M. Stelter
Institute f. Nonferrous Metallurgy & Purest Materials, TU Bergakademie Freiberg, Germany
Investigation of GaN layers grown by high temperature vapor phase epitaxy

06 Yudai Maji, Satoshi Nakano, Koichi Kakimoto
Research Institute for Applied Mechanics, Kyushu Univ., Fukuoka, Japan
Analysis of Mass Flux of AlN Crystal Growth at a Seed Face in PVT Method

07 Yeong-Jae Yu, Dae-Seop Byeon, Su-Hun Choi, Myung-Hyun Lee, Won-Jae Lee, Seong-Min Jeong
Korea Institute of Ceramic Engineering and Technology
Residual stress analysis on the 4H-SiC crystal grown by top seeded solution growth technique

P3 Halides

01 Akkanur Thangavelu Ravichandran, M. Senthil Pandian
Research Department of Physics, National College, Tiruchirappalli, India
A Comparative Study of Solution Grown and Sankaranarayanan-Ramasamy (SR) Method Grown Diglycine Zinc Chloride (DGZC) Single Crystal

02 Alexandra Yu. Tarasova, A. A. Goloshumova, L. I. Isaenko, A. P. Yelisseyev
South Ural State University, Chelyabinsk, Russia
New $SrPb_3Br_8$ crystals

03 Volodimir Taranyuk, A. Gektin, A. Kolesnikov, V. Shlyakhturov
Institute for Scintillation Materials NAS of Ukraine, Kharkiv, Ukraine
Bulk halide single crystal growth by skull technique

P4 Oxide crystal growth I

01 Dmitrii Kokh, V. Shevchenko, A. Kokh, V. Vlezko, A. Vakulenko
Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia
Paratellurite bulk crystals growth

02 Jian Zhang, Yanru Yin, Zhitai Jia, Xutang Tao
State Key Laboratory of Crystal Materials, Shandong University, Ji'nan, China
Mechanism of surface cracking in a $Ca_{12}Al_{14}O_{33}$ crystal during the cooling process

03 Lei Lin, Haijun Dong, Xiuai Lu
Photop Optics, Inc., Fuzhou, Fujian, China
Melt drop method in the growth of defect-free TeO_2 single crystals

04 Paul Sass, Robert Schöndube
ScIDre GmbH – Scientific Instruments Dresden, Dresden, Germany
Optical floating zone crystal growth under high pressure atmospheres: advantages and applications

05 Anatoly M. Balbashov, M. E. Voronchikhina, M. S. Frantsishin
Moscow Power Engineering Institute, Moscow, Russia
Pequiliarities of single crystal growth of oxide multiferroics by floting zone melting

P5 General Topics

01 Nathan Morgan, Kerry Wang, Jeffrey J. Derby
Dep. of Chemical Engineering and Materials Science, Univ. of Minnesota, Minneapolis, MN, USA
Mitigation of Second-Phase Particles via Post-Growth Treatment: Temperature Gradient Zone Melting and Annealing

02 V. V. Atuchin, L. I. Isaenko, V. G. Kesler, A. Yu. Tarasova, Alexandr B. Tarasov
Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics SB RAS, Novosibirsk, Russia
Single crystal growth and surface chemical stability

03 A. E. Kokh, Vasily A. Vlezko
Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia
An experience of creating the growth station control systems based on the low-cost general-purpose controllers and specialized peripherals

Tuesday, July 04

Session 3 Oxide crystal growth I

Chairs: Hanna Dabkowska (McMaster Univ., Montreal, Canada), Aleksander Gektin (ISC NAS, Ukraine)

09:00	a)	John Frank (Saint-Gobain Crystals, USA) **Oxide crystal growth in industry**
09:50	b)	Zuo-Guang Ye (Simon Fraser University, Canada) **Development of high-Tc and high-performance piezo-/ferroelectric single crystals based on PZT and other systems**
10:40		Coffee
11:00	c)	Christo Guguschev (IKZ, Berlin, Germany) **Perovskites and other substrates for multiferroics**
11:50	d)	Georgy Dosovitskiy (IREA, National research center "Kurchatov Institute", Russia) **High purity raw materials for scintillators and other single crystals - development, production and control**
12:45		Lunch
		Free Time

Session 4 Emerging Fields in Crystal Growth I: Materials

Chair: Thierry Duffar (INP Grenoble, France)

16:30	a)	Kuei-Hsien Chen (National Taiwan University) **Vacancy and Phase Control of the GeSeTe for Thermoelectric Applications**
17:20	b)	Vera Manomenova (Shubnikov Inst. of Crystallography, Moscow, Russia) **Ni and Co sulfate crystals for solar-blind UV-filters**
18:30		**Workshop barbecue**

Wednesday, July 05

Session 5 Multi-crystalline silicon for PV

Chairs: Christian Reimann (Fraunhofer IISB, Germany), Kader Zaidat (SIMAP Grenoble, France)

09:00	a)	Anne Karin Søiland (Elkem Solar, Norway) **From upgraded metallurgical-grade silicon feedstock to high quality wafer**
09:50	b)	Gunter Erfurt (MeyerBurger, Germany) **Industrial perspective of silicon PV**
10:40		Coffee
11:00	c)	Zhixin Li (Linton Machine, China) **Trend of Crystal Growth Technology in Solar Industry**
11:50	d)	Julien Laurent (Vesuvius, France) **Crucibles for HP mc-Si**
12:45		Lunch

Session 6 Emerging Fields in Crystal Growth II: Technologies

Chairs: Stephan Riepe (Fraunhofer ISE, Germany), Matthias Bickermann (IKZ Berlin, Germany)

14:30	c)	Matthias Schreck (Univ. Augsburg, Germany) **Single crystal diamond wafers by heteroepitaxy**
15:20	d)	Siddha Pimputkar (LeHigh Univ., USA) **Technology of ammonothermal growth for gallium nitride**
16:10		Coffee
16:30	e)	Christiane Frank-Rotsch (IKZ, Berlin, Germany) **Status of KRISTMAG® technology and its impact on crystal quality**
17:20	f)	Nathan Stoddard (SolarWorld, USA) **Silicon Crystal Doping: Pesky Problems and Exotic Options for Batch and Continuous-feed Growth**
18:30		Dinner

Poster Presentation

19:30	Session II (next page)

Thursday, July 06

Session 7 Oxide crystal growth II

Chairs: Merry Koschan (Univ. of Tennessee, USA), Steffen Ganschow (IKZ, Germany)

09:00	e)	Encarnacion Garcia Villora (NIMS, Tsukuba, Japan) **Part 1: Single-crystal phosphors for high-brightness lighting** **Part 2: Ultimate UV-IR Faraday rotators, CeF_3 and $(Tb_{1-x}Lu_x)_3Sc_2Al_3O_{12}$**
09:50	f)	Jiyang Wang (Shandong Univ., China) **Laser and scintillator crystals**
10:40		Coffee
10:10		**DGKK poster award ceremony**
11:20	g)	Igor Pritula (ISC NAS, Ukraine) **Growth of Ti:Sa crystals for producing of large-size laser elements**
12:10		Workshop Closing
12:20		Lunch

P6 Multi-crystalline silicon for PV

01 Ahmed Nouri, G. Chichignoud, Y. Delannoy, K. Zaidat
Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, Grenoble, France
Achieving a square horizontal cross section of monocrystalline silicon ingots using Kyropoulos technique

02 Ingrid Schall, Erwin Peiner, Andreas Waag, Gerhard Palm, Stefan Ebbinghaus
sameday media GmbH, Schneverdingen, Germany
Crystalline silicon on glass by low-temperature reduction using Al

03 Jose Luis Plaza, E. Diéguez
Laboratorio de Crecimiento de Cristales, Departamento de Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, Spain
Design of a Compact Multifunctional Heat Exchange-Directional Solidification System For Industrial Multi-Crystalline Silicon Casting

04 Kader Zaidat, M. Cablea
Univ. Grenoble Alpes, SIMAP, Grenoble, France
Metallic impurities segregation controlled by electromagnetic field: Application to Silicon for PV

05 Tomoro Ide, S. Nakano, H. Harada, Y. Miyamura, K. Kakimoto
Department of Aeronautics and Astronautics Engineering, Kyushu Univ., Fukuoka, Japan
Effect of Oxygen on Dislocation Multiplication during Growth of Crystalline Silicon for Solar Cell

06 Thi Hoai Thu Nguyen, Jyh Chen Chen, Chieh Hu, Chun Hung Chen, Yen Hao Huang, Michael Yang
Department of Mechanical Engineering, National Central University, Jhongli, Taiwan
Numerical study of temperature, velocity, stress and dislocation-density distributions during the growth process of 800 kg and 1600 kg silicon feedstocks

P7 Oxide crystal growth II

01 Martin Klejch, S. Sýkorová, D. Petrýdes, M. Korjik, V. Dormenev, R. Novotny,
Hans-Georg Zaunik, J. Houžvička
CRYTUR spol. s r.o., Turnov, Czech Republic
Growth of radiation hard PWO crystals in open furnaces towards reproducibility

02 Abdeldjelil Nehari, I. Lasloudji, C. Stelian, J. Boy, M. Allani, H. Cabane, M. Dumortier,
P. Jeandel, K. Lebbou
Institut Lumière Matière, UMR5306 Université Lyon1-CNRS, Lyon Villeurbanne, France
Large LGT ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) Langatate crystal growth by Czochralski technique for BAW and SAW applications

03 A. E. Dosovitskiy, Ilya Yu. Komendo, A. L. Mikhlin
National Research Center “Kurchatov institute”, IREA, Moscow, Russia
Development and producing of high-purity potassium dihydrogen phosphate for the large scale single crystals

04 Carmen Stelian, Thierry Duffar
SIMAP-EPM, Saint Martin d’Hères, France
Modeling interface shape in Czochralski growth of sapphire crystals

05 Guohao Ren, Chao Wang, Huanying Li, Jian Shi, Yuntao Wu
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China
Growth of and Scintillation Properties of $(Gd,Y)_3(Ga,Al)_5O_{12}$:Ce Crystals

06 Jan Polák, Martin Klejch, K. Bartoš, J. Houžvička
CRYTUR spol. s r.o., Turnov, Czech Republic
EFG method for novel garnet and perovskite materials development

07 Zhitai Jia, Jian Zhang, Qiangqiang Hu, Xutang Tao
State Key Laboratory of Crystal Materials, Shandong University, Ji'nan, China
Improvement of CALGO crystal: a promising host material for ultrafast laser application

08 C. L. Melcher, M. Koschan, M. Zhuravleva, F. Meng, Y. Wu, S. Donnald, M. Tyagi, J. Hayward, N. Cherepy, S. Payne
Scintillation Materials Research Center, University of Tennessee, Knoxville, TN, USA
Scintillation Properties of Single Crystal Garnet Scintillators

09 Haohai Yu
State Key Laboratory of Crystal Materials, Shandong University, Ji'nan, China
Growth and Characterization of Zinc tungstate ($ZnWO_4$) Raman crystal

P8 Other Materials

01 Magdalena Szubka, P. Zajdel, E. Talik, A. Guzik
A. Chełkowski Institute of Physics, University of Silesia, Katowice, Poland
Synthesis and characterization of $CaCoSinO_{2(n+1)}$ ceramic pigments by X-ray diffraction, SQUID magnetometry, scanning electron microscopy and X-ray photoelectron spectroscopy

02 S. Aron Rabi, A.T. Ravichandran, C. Ravi Dhas
Research Department of Physics, Bishop Heber College, Trichy, India
Growth and optical, structural, mechanical, thermal and dielectric studies of Zinc Thiourea Sulphate single crystal

03 Sergey Grazhdannikov, A. Kurus, L. Isaenko, P. Krinitsyn, V. Drebuschak
Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia
The newest $LiGaTe_2$ crystal thermal data and mathematical modeling of the crystal growth process

04 Tian Tian, Yumeng Li, Min Jin, Jiayue Xu
Institute of Crystal Growth, School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, China
A novel horizontal Bridgman growth of SnSe crystal and its thermal properties

05 Vladimir Artemyev, Andrey Smirnov, Vasif Mamedov, Alex Galyukov, Vladimir Kalaev
STR Group, Inc. and Soft-Impact, Ltd., St. Petersburg, Russia
Analysis of dislocation density in CZT Bridgman crystal growth using computer modeling

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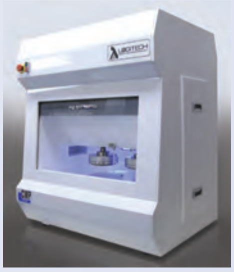

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IWCGT-7 2017 - Sunday, July 02

16:00	**Registration**
18:00	Dinner
Panel	**Training and educating crystal growth technology** Chair: Matthias Bickermann (IKZ Berlin, Germany)
19:30	Panel Discussion

IWCGT-7 2017 - Monday, July 03

Session 1		**Single crystals of silicon and III-Vs** Chairs: Maria Porrini (SunEdison Semi, Italy), Koichi Kakimoto (Kyushu Univ., Japan)
09:00	a)	Michael Rosch (FCM, Germany) **III-V bulk growth (GaAs, InP)**
09:50	b)	Joel Kearns (NASA, USA) **Czochralski silicon and wafer processing in the PV and semiconductor device industry**
10:40		Coffee
11:00	c)	Ludwig Stockmeier (Fraunhofer IISB, Germany) **Approaches for highly n-doped silicon**
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16:30	c)	Robert Bondokov (Crystal IS, USA) **The Development of High-Quality, UV-transparent Two-inch AlN Single-Crystal Growth**
17:20	d)	Thomas Straubinger (SiCrystal AG, Germany) **SiC bulk crystal growth**
18:30		Dinner
Poster		**Presentation**
19:30		Session I

III-V bulk growth (GaAs)

M. Rosch[1], S. Eichler[1],
[1] *Freiberger Compound Materials GmbH, Am Junger Löwe Schacht 5, 09599 Freiberg, Germany*

GaAs mono-crystalline substrates are used for application on RF electronics, for generation and sensing of IR/red/orange light, and photovoltaic mono/multi junction cells. The crystals can be grown from the melt – critical topics are the high arsenic partial pressure and the composition. Historically (until year 2000), Liquid Encapsulated Czochralski (LEC) technique was used – today, the Vertical Gradient Freeze (VGF) and Vertical Boat (VB) method dominate.

The paper will discuss limitations and scalability for crystal growth technologies material properties as well as their impact on material properties (electrics, real structure). Several aspects of mass production of crystals under industrial conditions will be touched.

Czochralski silicon and wafer processing in the PV and semiconductor device industry

Joel K. Kearns
National Aeronautics and Space Administration, USA
joel.k.kearns@nasa.gov

Semiconductor silicon has been the foundation of the world microelectronics industry since the 1950s. Although considered a “mature” industry, the growth of silicon crystals is still under technological development to enable greater device functionality. Silicon is grown from the melt, using Czochralski (pulling) technique, as threading dislocation-free single phase single crystals. These provide a unique technological material for use and a model material for study. Decades of purification of the starting poly-silicon provide extremely low concentrations of unwanted impurities, besides those introduced during the Czochralski process itself (primarily oxygen and carbon). Introduction of dislocation-free growth allowed the increase of crystal diameter from c.a. 50 mm to the 300 mm standard of today, while efforts to continually reduce crystal growth costs have resulted in long length crystals to maximize yield from the batch crystal growth process. However, maximizing crystal length is not always compatible with minimizing property variation along that length. Crystal diameter has been repeated increased by defined standard diameters, to provide more devices on each round wafer cut from the crystal, reducing cost per device. Since the crystals are dislocation free, thermodynamic point defects and impurities combine during post-solidification cooling to produce unusual bulk microdefects, some of which can give desired properties while others must be avoided as device killers (e.g., “crystal originated particles”/D-defects). Since the crystal is single phase single crystal, there is no classical “microstructure”, but the final distribution of properties can be related to bulk microdefect and chemical structure and to the Czochralski process. Both oxygen concentration and solute striations can be influenced by the application of a magnetic field to affect the melt heat and mass transfer during crystal growth. The performance of devices fabricated into slices of these Czochralski crystals are set by the chemical, electrical and structural “defect” distributions of the crystal and post-slicing processing. Post growth processes such metal-gettering defect nucleation and growth, or annealing to reduce voids, can be used to modify various regions of slices from the crystal. Each commercial wafer supplier worldwide has developed proprietary and trade-secret approaches for the Czochralski growth process and associated equipment (“puller”) to grow crystals which provide wafers with the desired properties.

Semiconductor silicon crystal growth has different performance optimization paths, depending on whether the crystal is intended to produce substrates for later epitaxial layer growth, or must be used as a “defect-free” polished wafer for direct device fabrication, or a substrate for silicon-on-insulator, or will be used for specialized applications such as “ink jet printer” heads, MEMS, or mechanical parts. For semiconductors, initial studies to grow crystals of 450 mm diameter have already been pursued to meet the future international semiconductor roadmap targets, and 675 mm diameter crystals have been discussed as a far future goal. For low voltage power devices, the crystal needs to be heavily doped during growth, as much as 0.1% atomic percent electronic impurity (near the dopant solubility limit), so constitutional supercooling and secondary phase nucleation must be avoided.

Czochralski silicon for the PV industry is focused on lowering costs while increasing photovoltaic conversion efficiency. Unlike semiconductor wafers, “solar cells” are large area, full wafer devices, with a very small number of p-n junctions and metal-semiconductor contacts. “Mono” silicon pulled by Czochralski method competes with directionally solidified multi-crystalline silicon as a higher performance alternative for smaller area residential installations and to lower total system cost for utility and commercial systems. The lightly doped Silicon crystals must be grown at extremely low cost to meet stringent cost targets for cost per watt peak per solar cell and solar module installation. The traditional boron-doped 1- to 3 ohm-cm crystal for screen print cells has been modified to enable advanced p-type PERC cells and will likely be succeeded by lightly phosphorous doped crystals for advanced n-type cells. The batch Czochralski process has been extended to a multiple batch recharge process, but the crystal-to-crystal build-up of minority carrier lifetime killing impurities such as carbon and metals must be carefully controlled. Crystals are grown to produce “pseudo-square” cross section wafers of either 125mm or 156mm side to side dimension, the standard for solar cells. The “wings” sliced off the full length of the sides of the bulk crystals must be recycled to reduce ingot cost.

The history and current status of the Czochralski growth of dislocation-free silicon will be reviewed, with a focus on the crystal growth processes and equipment needed to grow large diameter crystals exhibiting desired bulk properties or bulk microdefects. The recognized trade-offs between bulk property value and distribution, and crystal conversion cost will be outlined, for different crystal types such as those needed for semiconductor, photovoltaic or mechanical application. Process modifications such as continuous Czochralski (CCz) are under development to both further reduce cost and provide more uniformity to specific properties, and will be described.

Approaches for highly n-doped silicon

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Heavily As- or P-doped silicon is grown by the Czochralski method. The material is needed as substrates for power electronic devices. In recent years there has been an increasing demand for lowering the electrical resistivity and increasing the diameter of the crystals. Nowadays, the typical achievable lower resistivity limit is about 0.003 Ωcm for As-doping and 0.001 Ωcm for P-doping.

However, there are several challenges when growing heavily n-type doped silicon by the Czochralski method. Therefore, the growth process of heavily n-type doped will be looked on more closely in comparison to not heavily doped silicon. For the growth of silicon by the Czochralski method it is known that the incorporation of intrinsic point defects at the solid/liquid interface and their agglomeration behavior during the growth process is governed by a ratio of pulling velocity V to axial temperature gradient G. Surprisingly, the high doping concentrations affect the agglomeration behavior of the intrinsic point defects. The agglomeration behavior of intrinsic point defects in heavily doped Cz silicon will thus be viewed at.

When comparing the growth process of heavily and not heavily doped silicon the enrichment and the evaporation of the dopant is always of great concern and needs to be highlighted. The segregation of the dopants can also lead to the phenomena constitutional supercooling, which limits the maximum achievable dopant concentration (see fig. 1).

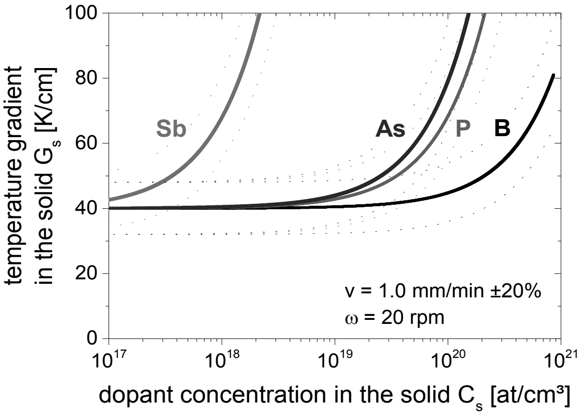

Fig. 1: Necessary temperature gradient Gs in the solid to prevent constitutional supercooling from occurring.

The crystal yield is affected by the formation of dislocations primarily during the growth of the top cone of such heavily n-type doped silicon crystals. The dislocations multiply during the growth process, causing the loss of the so-called growth ridges. As a result of the dislocation formation the crystal becomes poly crystalline. Thereafter it is of great importance to prevent the formation of dislocations. With the help of XRT measurements it was possible to analyze the dislocation dynamics and confine the place of origin of the dislocation formation. Hence it was possible to ascertain the cause for the dislocation formation in heavily n-type doped Czochralski silicon.

Improvement of Si Materials and Processes for Si Power Devices

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For the future power electronics system, one of the key issues is to make more high power densities of PE systems. At the moment, several types of silicon devices are widely used from the low voltage to high voltage PE systems. Fig.1 shows the history of the bulk power semiconductors materials development. Since the start of solid state electronics in 1950's, silicon has been developed as the key materials. In this paper, the current status and future prospect of silicon wafer technology is discussed.

On the device points of view, the on-resistance should be decreased to fabricate high efficiency and low loss PE system. In case of unipolar devise, several developments have been done by electric field management of reverse biased active layer, such as super junction structures, floating junction structures. In the case of bipolar devices, ex IGBT, the most of the development have been done to optimize storage carrier profile through active layer. Trench MOS structure is used to control electron injection by injection enhancement. Filed stop and transparent p-emitter structures are used to control hole injection by controlling p-emitter local doping amount. And thin wafer is also used to reduce the on resistance. Si power device are still on the way of developing 1). Further improvements of Si power devices are expected. On the power wafer points of view, the increasing of wafer volume might be a big issue. In case of LSI technology, a rapid increasing of Trs numbers has been supported by the devise downsizing (high bit densities) and the wafer mass production technologies. The device downsizing leads to the Trs yield from the unit wafers area, and the wafer mass production technologies support the demands of huge number of Trs by increasing the wafer diameter. For the power devices, the both device downsizing and wafer mass production should be tried based on the analogy with LSI technology. However, in the case of power devices, the device downsizing will meet limitation such as the thermal limit by heat losses. Wafer mass production for high power devices also has several difficulties. FZ technique is mainly used for high power devices because of its low oxygen concentration compared to MCZ technique. But in FZ technique, it might be difficult to make enlargement in diameter, currently 6 and 8 inches. To support the big demand of power wafers, MCZ technique is strongly expected. But MCZ technique has a disadvantages of crystal quality. In order to support the urgent and strong demands of large volume increasing of high power wafers, high quality and low impurities MCZ technique should be developed.

Recently, Nagai, et al. demonstrated the low carbon silicon wafer by MCZ technique2). They analyzed and managed the mass transportation in the MCZ furnace and achieved the very low carbon concentration in grown silicon, which is lower than FZ materials. Their objectives are to produce more long life-time wafers by MCZ. The one of the life-time killer defects is the oxygen clusters. And carbon acts as the heterogeneous nucleation sites for oxygen precipitates. By reducing the carbon concentration, the elimination of oxygen precipitates, and consequently, long carrier life-times are expected. The another effect of carbon impurities are also discussed by Schulze, et al.3). They mentioned that carbon impurities compose the CiOi-H complexes and its behaves like a donor. They showed the impact of this complexes in the filed stop layers in IGBT, and concluded that CiOi-H complexes lead the low break down voltages. For the next generation of IGBT with longer carrier life time and precise carrier distribution control, the reduction of carbon impurity is one of the key issues.

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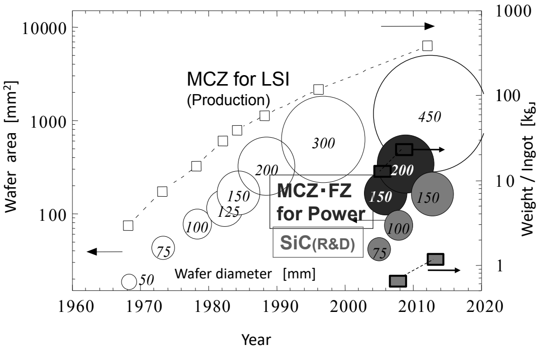

Fig.1 The history of bulk power semiconductors

Bulk Crystal Growth of Ga_2O_3

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Gallium oxide (Ga_2O_3) is a semiconductor material that has both a large band gap energy and good electrical conductivity. It has been attracting attention because it has high potential for power device applications[1-3)]. β-Ga_2O_3 can be grown from a melt source; therefore, its growth rate is high. This means it has a lower production cost compared with other wide band gap semi-conductor materials such as silicon carbide, gallium nitride, aluminum nitride, and diamond, whose growth rates are relatively low because they can be grown from only diluted vapor sources. In this presentation, we report on bulk crystal growth of β-Ga_2O_3 substrates using an edge-defined film-fed growth (EFG) process[4)].

Figure 1 shows the picture of β-Ga_2O_3 bulk crystal. Despite the tendancy that twin boundaries are easily generated in β-Ga_2O_3 bulk crystal, semiconductor substrates containing no twin boundaries with sizes up to 4 inches in diameter have been demonstrated as shown in Fig. 2. We examined what impurity elements were included in the Ga_2O_3 source powder and the EFG-grown crystals by taking GDMS and SIMS measurements and found that the major residual impurity elements contained in unintentionally doped crystals were Si and Ir. Intentionl doping was tried using SnO_2 or SiO_2 as a dopant source, and successful control of n-type carrier concentration was acheived in the range between $2x10^{17}$ cm^{-3} and $2x10^{19}$ cm^{-3}. The crystal defects were examined by observing substrates surface after wet etching using heated H_3PO_4. It was shown that there are two kind of prominant defects in β-Ga_2O_3 bulk crystal and that they are dislocations and long and narrow voids elongated in the [010] direction. The density of dislocations was between 10^3 cm^{-2} and 10^4 cm^{-2}on ($\bar{2}01$) and (010) sufaces, and that of void was 10^2 cm^{-2} on (010) surface.

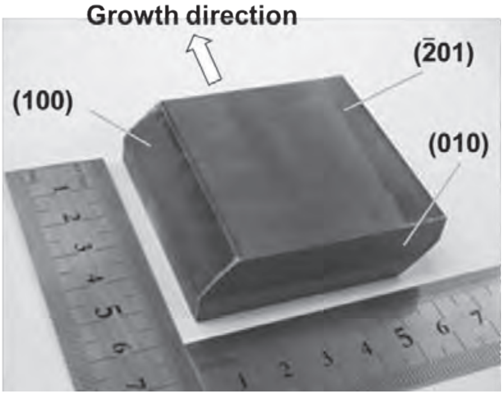

Fig. 1 β-Ga_2O_3 bulk crystal.

Fig. 2 4-inch β-Ga_2O_3 substrate.

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Status, perspectives, and trends on bulk growth of gallium nitride

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For more than two decades crystallization of bulk gallium nitride (GaN) has remained a big challenge for the nitride community. GaN-based devices, like light emitting diodes (LEDs) or high electron mobility transistors (HEMTs), are mainly built on foreign substrates (sapphire, silicon, or silicon carbide). Nevertheless, the nitride community is still looking for GaN substrates in order to advance the existing generation and develop the new one of the products. For many years work on developing bulk GaN has mainly been motivated by the laser diodes market. Today, the main driving force for crystallizing bulk GaN seems to be the electronic industry and a demand for vertical high power transistors and diodes. For this application GaN wafers of high structural quality and with a high free carrier concentration are necessary. Some electronic applications also require GaN substrates with low free carrier concentration and impurities level ($\sim 10^{15}$ cm^{-3}) as well as semi-insulating ones. However, crystallization of GaN is quite a challenging process. The gallium nitride compound melts at extremely high temperature (>2500°C) and the nitrogen pressure necessary for congruent melting of GaN is expected to be higher than 6 GPa [1]. Thus, today, it is impossible to crystallize GaN from the melt. This compound should be grown by other techniques requiring lower pressure and temperature. Crystallization from gas phase, solution, or any combination thereof must be included.

Firstly, single crystals of GaN (seriously, thin crystalline films grown on sapphire) were obtained by H.P. Maruska and J.J..Tietjen in 1968 [2]. GaN was grown from the vapor phase using relatively new technology at this time, halide vapor phase epitaxy (HVPE). It crystallized as a product of reaction between gallium chloride and ammonia at temperature of 1000°C and at atmospheric or even lower pressure. Unfortunately, this time an ammonia gas, which was used, had a water content as high as 1000 ppm [3]. Due to contamination of dopants it was impossible to crystallize high purity and structural quality material. Single crystals of gallium nitride appeared again in 90s of 20th century as small hexagonal platelets (up to 1 cm^2) of extremely high structural quality and high oxygen content ($5\text{x}10^{19}$ cm^{-3}). They were crystallized from solution of atomic nitrogen in liquid gallium under high nitrogen pressure (~1 GPa) at temperature of 1400-1500°C by a method called high nitrogen pressure solution (HNPS) [4]. As a result of the explosion of interest in nitride semiconductors in 90s, there appeared other methods for GaN growth. Crystallization of high quality nitride crystals by sodium flux (growth in the mixture of gallium and sodium under nitrogen pressure of approximately 5 MPa and at temperature of 900°C) has been developed in Japan [5]. Also, the HVPE method has returned to favor with much higher purity of ammonia and other reactants gases than it happened before. Using foreign seeds 2-inch free standing GaN crystals and then substrates of high purity and quite high structural quality have been demonstrated [6]. At the beginning of the 21st century ammonothermal growth method (crystallization in supercritical ammonia under pressure up to 0.6 GPa and temperatures from 300°C to 750°C) has begun to develop, presenting the highest structural quality, highly conductive as well as highly resistive 2-inch crystals and wafers [4]. However, it should be remarked that all these methods allow to crystallize only a few millimeters thick GaN, and in general, allow to produce one new crystal from one seed used. Therefore, they represent a wafer to wafer technology. Up to now, no one has demonstrated real bulk GaN crystal and convenient technology for growing it.

Today, only three technologies are applied for GaN crystal growth: sodium flux, ammonothermal and HVPE. The first two of them represent growth from solution, the third one, as mentioned, growth from the vapor phase. In this paper a current status of these three methods will be presented and described in detail. They will be compared in terms of numbers and quality of seeds used in one crystallization run, morphology of growing crystals, their structural quality and growth rate. The electrical and optical properties of new-grown material will be presented, too. The main advantages and disadvantages of each method as well as their main limiting factors will be analyzed. Recently, a combination of ammonothermal or sodium flux growth with HVPE technology has been demonstrated (ammonothermally or sodium flux grown crystals have been used as seeds in the HVPE method). Its perspectives will be discussed. Based on the results of the HVPE growth on ammonothermal seeds a doping technology to obtain highly conductive and highly resistive crystals will be demonstrated. Seed point technique and tailing technology (lateral connection of small crystals to obtain a bigger one) in sodium flux and HVPE methods, respectively, will be shown and discussed. Some new trends in GaN crystal growth will be also presented. The HVPE process on nitrogen polar (000-1) plane of GaN will be shown and compared to traditional crystal growth run using the Ga polar (0001) surface. A variety of crystallization from gas phase, halogen-free vapor phase epitaxy (HF-VPE) will be demonstrated. A possibility to grow bulk GaN crystals by described methods will be analyzed. Comparison with commonly used wafer to wafer technology will be performed. The main advantages and disadvantages of these two approaches will be discussed.

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The Development of High-Quality, UV-transparent Two-inch AlN Single-Crystal Growth

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The rapid growth of III-Nitride electronics in the past several years ensured that the aluminum nitride (AlN) became a key member of the Nitride semiconductor family. AlN unique properties, such as direct wide bandgap of ~ 6.1 eV, high thermal conductivity, mechanical rigidity and chemical stability made it the material of choice for wide spectrum of deep ultra-violet (UV) devices. The AlN substrates are used to fabricate high performance, long lifetime UVC LEDs for air purification, water disinfection, and environmental sensing. Significant progress was made over the past two decades in improvement of AlN quality and increasing the size of the wafers. The availability of high-quality, large area AlN substrates promises to further widen the AlN commercialization. AlN substrates can be used to grow Al-rich epitaxial layers for LEDs that operate in the entire UV region. Furthermore, the AlN substrates with standard sizes are viable necessity for the future generations of high-power and RF-device electronics. The accessibility of AlN single-crystal material will continue to drive further development of novel electronic and opto-electronic applications due to its distinctive semiconductor, thermo-physical, and mechanical properties.

We report on the current status of the industrial growth of bulk aluminum nitride single crystals. The AlN single-crystals are grown using a proprietary sublimation-recondensation approach, similar to the Physical Vapor Transport (PVT) method. A Tungsten crucible with AlN seed and source material is placed in a hot zone ensuring well-controlled thermal gradients. The AlN source material sublimes and decomposes into Al atoms and N_2 molecules. These species are then transported to the AlN seed where they incorporate into the growing crystal. The seeds are oriented with their Al-face exposed to the vapor phase. The crucible with growing crystal is subjected to sufficient axial thermal gradient to ensure the crystal enlargement. The thermal gradient uniformity during the growth can be achieved by either moving the heater (usually an RF coil) with respect to the crucible or vice versa. In order to expand the crystal in lateral direction without quality deterioration, a proper balance between radial and axial gradients is needed. Increasing the crystal dimensions demands careful thermal gradients tailoring in order to lower the thermally induced stresses.

Currently, AlN single crystals with diameter > 2 inch are grown using the method described above. It should be noted that this method shows very high potential in terms of growing large bulk AlN crystals; yet, some challenges have to be resolved en route to 100 mm diameter crystals. Large bulk crystals could be beneficial for production of non-polar and semi-polar substrates which are used to reduce the internal electric fields due to polarization.

The AlN crystals are sliced into wafers and subsequently polished. Special attention is paid to the wafer bow, thickness variation, surface roughness, and sub-surface damage. At the present, the 2” AlN wafers have bow ≥ 20 m, RMS ≤ 5 Å, and are free off sub-surface damage confirmed by Transmission Electron Microscopy (TEM). The crystalline quality is measured by X-ray diffractometry (XRD) rocking curves, etch pit density, and photo-elastic birefringence pattern (cross-polar imaging). We have demonstrated AlN wafers with narrow rocking curves and with full width at half maximum (FWHM) < 30 arcsec; the fabrication process is being transferred to production. The AlN wafers with highest transparency in the UV region are exhibiting absorption coefficient < 30 cm^{-1} at 265 nm. The very low UV absorption is linked to the material purity measured by Secondary Ion Mass Spectrometry (SIMS) and Glow Discharge Mass Spectrometry (GDMS). For our applications, the promises of AlN material to produce high-power, high-lifetime UVC devices are fulfilled only when both high-quality and high UV transparency substrates are used.

High quality pseudomorphic epitaxial layers are grown using Metal-Organic Chemical Vapor Deposition (MOCVD) process to form the device structure. Commercially available SMD product (Klaran™) achieve germicidal power outputs that exceed 30 mW at 400 mA at a nominal wavelength of 265 nm. The devices feature a wide radiation pattern with a viewing angle of 105° and L50 lifetimes in excess of 6000 hours at 400 mA and 45 °C.

SiC Bulk Crystal Growth

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During the last years alternative sources of energy became more and more popular. Provisional highlight of this development is the announcement of major car manufactures like VW to focus on the switch to electric drives in the upcoming years. Silicon carbide based devices like schottky-barrier-diodes but also more complex devices like the MOSFET are finally considered to be used by the automotive industry in mass production and the sector of silicon carbide substrate and device fabrication is therefore facing a strong increase of production volume in short time.

Fig. 1: schottky-barrier-diode (Rohm semiconductor)

Since the start of international SiC-conferences in the 1990th several methods were discussed for the growth of silicon carbide crystals. Advantages and disadvantages of the three most popular methods high-pressure-solution, high-temperature-CVD and physical-vapor-transport will be discussed.

The development of special characterization methods and the adjustment of existing methods to the special needs of silicon-carbide are mandatory for the improvement of growth processes and the resulting quality of SiC-substrates. Defects and characterization methods will be discussed as well as the present quality of 150mm substrates produced by SiCrystal. In paticular the separation of threading screw- and edge-dislocations will be shown.

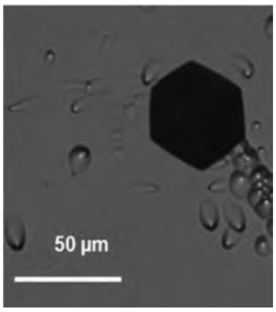

Fig 2: Etch Patterns on SiC-4H-Wafers after etching in liquid KOH
Hexagonal shape: screw dislocation (micro-pipe); Round shape: Threading Edge/Screw Dislocation; Oval shape: Basal Plane Dislocation

Precondition for the growth of silicon carbide crystals with diameters up to 150mm is the availability of seeds with sufficient quality and diameter. Unlike other semiconductor crystals grown from the melt the SiC-crystals do not grow on small seeds and strongly increasing diameter in the first growth phase but on a seed with the same or even larger diameter as the targeted crystal. During more than 20 years seed diameters at SiCrystal were increased step by step from Acheson platelets to 6 inch with special seed-processes which had to be adjusted.

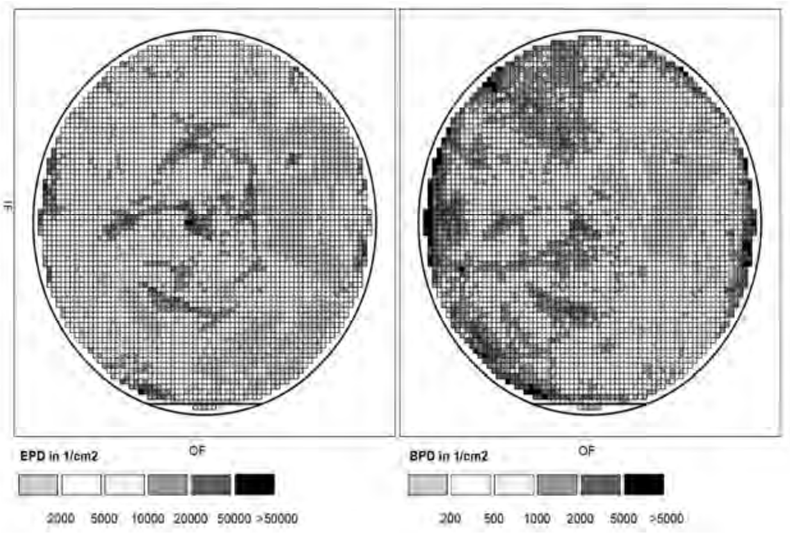

Fig 3: Dislocation density (EPD: 5k/cm2; BPD: 1k/cm2) in 6 inch SiC Wafer

Thermal simulation of silicon crystal growth using a granulate crucible

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In the last decade, growth of bulk silicon crystals from the melt has experienced a series of new developments, especially, for photovoltaic applications. The classical Czochralski (CZ) and float zone (FZ) techniques were modified for the growth of quadratically-shaped crystals [1, 2]. The costs caused by the feed rod in FZ growth were addressed in a combined CZ-FZ process, where the feed rod is obtained from a rapid CZ process [3], as well as in the granulate FZ process [4]. Bridgman growth of large silicon ingots was modified for top seeding [5] or bottom seeding using monocrystalline or multicrystalline seeds [6]. Nevertheless, a major problem in most of these techniques remains melt contamination from the quartz crucible. A novel method has been proposed recently, where the melt is contained by a silicon granulate bed, thus avoiding any contact with a foreign material [7]. The so-called *granulate crucible* method (Si-GC) consists of the following main steps (see Fig. 1):

1. Melting (generation of the initial melt pool). Silicon granulate is placed in a quartz container and melted from above using a high-frequency inductor. Since undoped granulate is susceptible to heat induction only above 650 °C, a susceptor is usually placed in the central inductor hole during the initial melting stage. This step is finished when melt has reached a stable shape, with a remaining solid granulate layer of several cm thickness between the melt and the quartz container. Both the unmolten granulate and the quartz container are reusable.
2. Seeding. The center of melt surface is touched by a seed as in the CZ growth. Note that in the Si-GC process the maximum melt overheating is limited to preserve the granulate bed, and the melt center typically experiences both small induction heating and high radiation losses. Therefore, special inductor and susceptor design is required to support the seeding.
3. Growth (and continuous melt replenishment). A cylindrical crystal is pulled out of the melt through the central inductor hole while solid granulate is continuously replenished through a small hole at the inductor rim. In contrast to CZ growth, the additional influence of heat induction at the triple point must be considered for crystal diameter stabilization. The control of the melt-granulate phase interface requires special attention, too.

Numerical simulation of this process requires complex multi-physical models including heat transfer by conduction, convection, and radiation as well as phase change, electromagnetic induction, and a free melt surface. Tight coupling of all phenomena is caused by temperature-dependent material properties and by the influence of electromagnetic pressure on the free melt surface. We present a 2D thermal model of the Si-GC process based on the Comsol software. The process stages are analyzed in a steady-state approximation, numerical results are compared to experimental observations. This allows us both to discuss the justification of various approximations in the numerical model and to support further optimization of the furnace geometry and and process parameters.

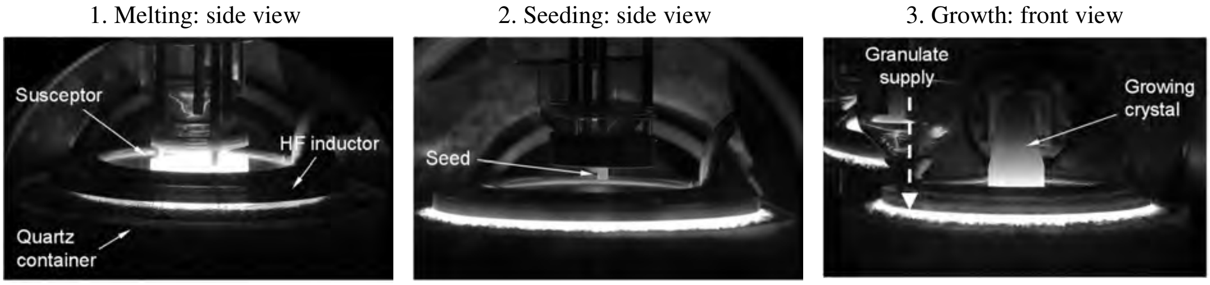
1. Melting: side view
2. Seeding: side view
3. Growth: front view

Figure 1: Photographs from various stages of a 2 inch process (quartz container Ø200 mm, inductor central hole Ø60 mm).

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Numerical analysis of dislocation density in Si single crystal using oxygen diffusion

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It has been reported that oxygen atoms in the Si single crystal adhere to dislocation and immobilize it [1]. Therefore, dislocation multiplication in the Si single crystal is suppressed during high-temperature processing because oxygen atoms about 10^{18} atoms/cm^3 are in the Si single crystal grown by Czochralski growth method. We developed Haasen-Alexander-Sumino model to analyze the effect of oxygen atoms in the Si single crystal on dislocation density during annealing process. We took into account unlocking stress which could release the fixing of oxygen atoms on dislocation core. The model of dislocation multiplication by J. Cochard, et al., was used [2]. We also solved the diffusion equation for oxygen atoms around the dislocation core to obtain oxygen concentration at dislocation core.

Fig. 1 shows relationship between oxygen concentration in the Si single crystal and maximum dislocation density. The results show that maximum dislocation density decreased as a function of oxygen concentration in the Si single crystal. Fig. 2 shows relationship between temperature profile and maximum dislocation density in the crystal. We found that dislocation density rapidly increased in the temperature range of 1200-1300K.

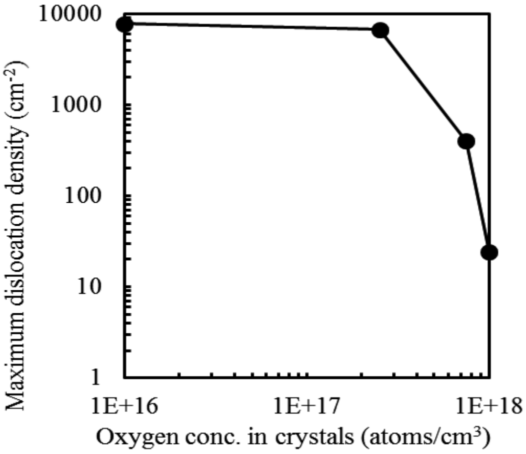

Fig. 1 Relationship between oxygen concentration and dislocation density.

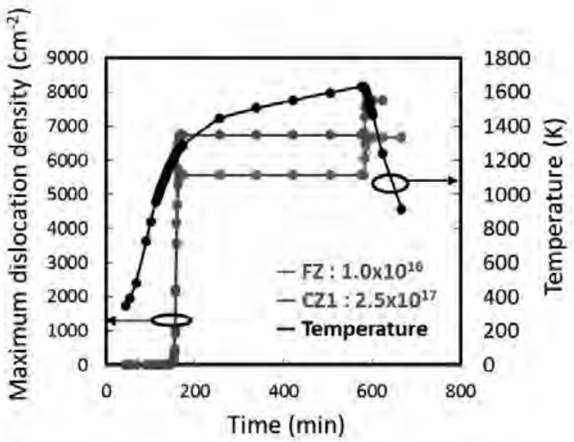

Fig. 2 Temperature profile and maximum dislocation density in the crystal.

Acknowledement

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Control of crucible movement on melting process and carbon contamination in Czochralski silicon crystal growth

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The bulk lifetime of Czochralski silicon (CZ-Si) crystal is shortened by the oxygen (O) precipitates, which are enhanced by the carbon (C) contamination [1]. Reduction of C contamination in the grown crystal is required for the production of Si wafer with long carrier lifetimes. Contamination of C in Si crystal mainly originates from carbon monoxide (CO) generation on the graphite component, which is triggered from the preheating stage and reaches the maximum during the melting stage. Therefore, it is essential to control the CO generation and C incorporation from the preheating to the tailing stage. The packed Si chunks experience the collapsing and volume shrinking during the melting process. Axial movement of the crucible is generally applied to adjust the level of Si feedstock. Melting process, as well as the species transport, must be modeled by transient global simulation according to the crucible movement and the Si volume change.

Due to the porosity of packing Si chunks, the heat transport modeling should take into account the effective thermal conductivity (ETC) of Si feedstock. The ETC model proposed by IAEA [2] was applied in the transient global simulation of the melting process. Axial movements of the crucible and the melting of Si feedstock in CZ-Si crystal growth lead to the dynamic thermal and flow field, as well as the affected species transport. To study the effect of crucible movement control on the melting process and C contamination, the fixed and lifting crucible cases were investigated by the transient global simulation with dynamic mesh. Intermediate thermal and flow fields for the lifting crucible case were shown in Fig. 1 with 20% melt fraction. The gap width between the gas-guide and the top surface of Si feedstock was kept constant during the crucible lifting process. Heat and impurity transport and accumulation of C in Si feedstock were compared for the static and dynamic crucible cases. Comparison of C accumulation for the fixed and lifting crucible cases indicate that the lifting crucible case resulted in higher C contamination than the fixed crucible case, as shown in Fig. 2. Furthermore, different gap width cases with the lifting crucible were also investigated to clarify the control strategies of crucible movement on the melting process and C contamination in CZ-Si crystal growth.

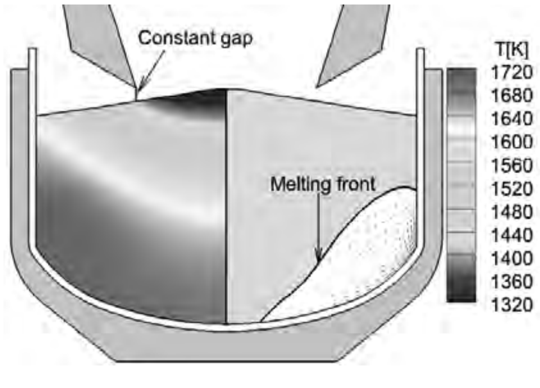

Fig. 1 Thermal and flow field for 20% melted Si feedstock

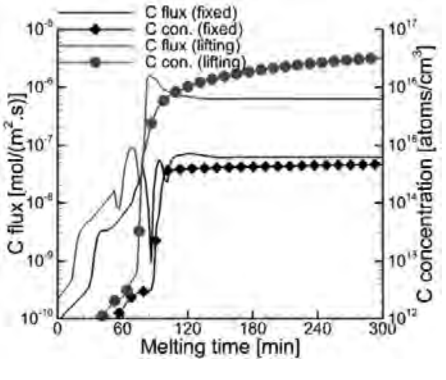

Fig. 2 C accumulation for the fixed and lifting crucible

Acknowledgements

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3D Numerical analysis on the shape of free surface in floating zone (FZ) method for silicon single crystal growth

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July
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P1.4

Floating zone (FZ) silicon is most widely used in the power electronics due to its high purity. In the FZ growth processes, the stability of free surface is important to produce single crystal silicon with high quality. Therefore, previous studies have theoretically calculated the shape of free surface in 2D axisymmetric model [1-3]. However, in the industrial FZ processes, in order to improve the homogeneity of radial resistivity, the crystal and the feed are not coaxial. Hence 3D calculation becomes an important research to precisely analyze the shape of free surface. By using volume of fluid (VOF) model, 3D asymmetrical free surface has been obtained (Fig. 1). In order to validate the accuracy of this model, 3D calculation results of free surface are compared with previous studies and provide a good fit with 2D calculation results and experimental results (Fig. 2).

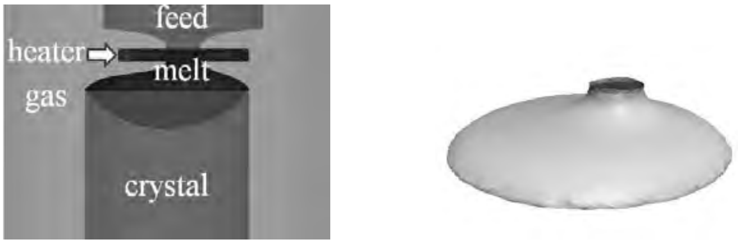

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Fig. 1 (a) Front view of calculation results of free surface; (b) 3D view of free surface in asymmetrical process.

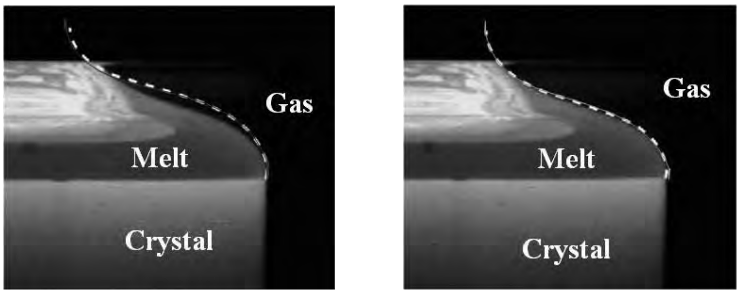

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Fig. 2 Comparison between 3D calculation results (red line in (a) and green line in (b)) with 2D calculation results (dotted line) and experimental results [3]: (a) without electromagnetic pressure (b) with electromagnetic pressure.

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Fabrication and optical properties of axial ZnO/ZnMgO multiple quantum wells on vertical ZnO microrods

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P2.1

We report on the fabrication and cathodoluminescent (CL) properties of axial ZnO/ZnMgO multiple quantum well (MQW) heterostructures with various quantum well and barrier layer thicknesses on the top of the ZnO microrods. Growth method consists of two steps.

The first step of the growth is the fabrication of the ZnO microrods by the microwave-assisted hydrothermal method. Growth of the ZnO microrods proceeds in the aqueous solution on c-plane, non-intentionally doped GaN substrate. The reaction mixture containing deionized water, zinc acetate dihydrate and sodium hydroxide (used as pH regulator) is placed in a microwave hydrothermal reactor. A microwave-assisted version of a hydrothermal reactor is exploited as uniformity of heating of the solution is very important in our method and provides the extremely high growth rate of the ZnO microrods. Prepared microrods are overgrown by plasma-assisted molecular beam epitaxy technique and this is the second step of our method. Before the growth, the ZnO microrods on GaN substrate are annealed in a loading chamber, and then in a buffer chamber to remove the surface contaminants. During the growth, the high purity Zn (6N) and Mg (6N) are evaporated using the conventional effusion cells. The radio-frequency power of oxygen plasma is fixed at 390 W with a O2 gas flow rate of 2.8 sccm.

Scanning electron microscopy (SEM) image (Fig. 1(a)) reveals the general morphology of the axial ZnO/ZnMgO MQW heterostructures. The top-view SEM image shows the well-defined hexagonal shape and vertical alignment of the axial MQW heterostructures. The CL map of individual MQW heterostructure (Fig. 1(b)) composed of two images taken for the two spectral features (QW and barrier emission) show the spatial distribution of the emission bands with respect to position in the microrod. It is clearly visible that the ZnMgO layers are located only on the top end of the microrod. Emission at 3.36 eV is localized between the ZnMgO layers and most likely is related to recombination in QW.

The presence of the axial heterostructure grown on the top of ZnO microrods is confirmed by low-temperature CL. Luminescence lines are observed at the spectral positions expected for the QW and barrier emissions from the top part of the microrods.

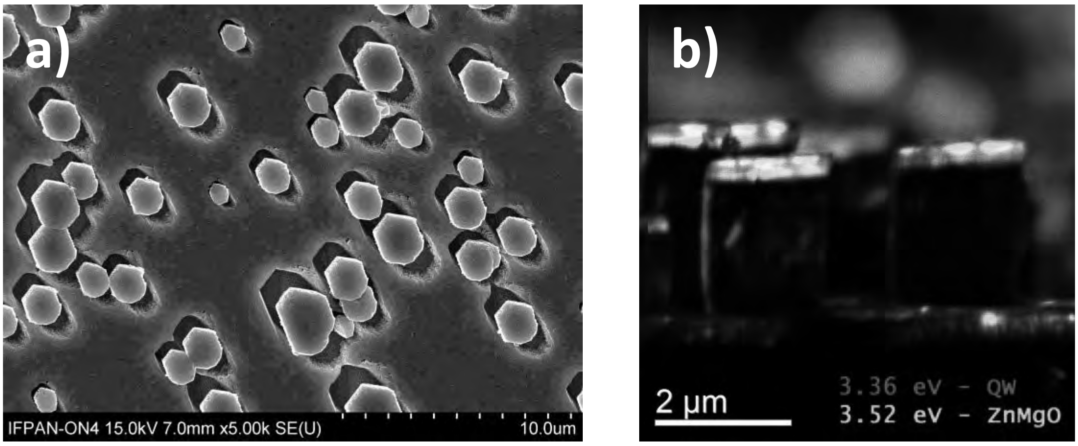

Fig. 1 (a) Top-view SEM image of the axial MQW heterostructures. b) False colour CL image of the axial MQW heterostructure.

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Incorporation of magnesium into ZnMgO layers grown by PA-MBE.

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A large 60meV exciton binding energy of wide 3.37 eV (at 300K), direct band gap ZnO exhibits stable excitonic emission at room temperature and promotes it as a potential candidate for optical active element in optoelectronic devices. ZnO is a serious rival to GaN because of similar crystal symmetry and large band gap, much larger exciton binding energy and low production costs in comparison to GaN.

PA-MBE (Plasma-Assisted Molecular Beam Epitaxy) is a unique growth technique as it holds the most precise control of growth parameters such as growth rate, substrate temperature, Mg/Zn/O flux ratio. The band gap engineering in MBE is realized by increasing magnesium concentration in ZnMgO alloys and it gives high uniformity of Mg content in the layers and well resolved interfaces between ZnO/ZnMgO/Substrate layers.

As the ratio of fluxes of metals to oxygen is the most important growth parameter, the substrate temperature is second and has crucial influence on Mg incorporation. Elevation of the substrate temperature enforces higher Zn flux to get stoichiometric conditions. [1] The same is in the case of ZnMgO alloys but here one must take under account all three elements.

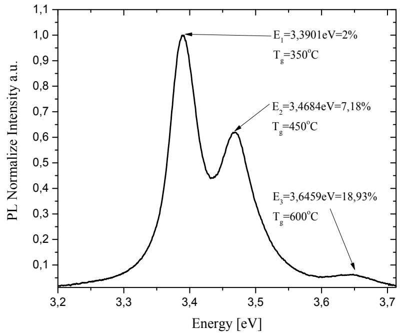

Fig.1 Photoluminescence spectra at 10K for ZnMgO thin films grown with the some Mg and Zn fluxes in different substrate temperature.

In this work the influence of the substrate temperature on the composition of magnesium in ZnMgO epilayers is investigated. The growth rate evolution versus substrate temperature was studied by means of *in situ* laser reflectometry. ZnO and ZnMgO epilayers on a-plane Al_2O_3 substrates were grown by PA-MBE. PL measurements were conducted to determine the Mg concentration in the alloys. At given fluxes of metals and oxygen the composition of magnesium changes with growing substrate temperature. The Mg content in ZnMgO alloys as a function of substrate temperature can be explained with the difference of vapor pressure between Mg and Zn elements at high growth temperatures. At higher growth temperature Zn can be easily desorbed yielding Mg enriched films. Effectively, there is a higher Mg concentration in the alloy films when grown at higher temperatures.[2] The effect of higher composition of magnesium in ZnMgO epilayers on crystallographic structure has been studied by PL and X-ray diffraction. This work was partly supported by the Polish National Science Centre (NCN) Grant No. 2014/13/B/St7/01773.

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Comparison of structural, optical, and electrical properties of highly conductive HVPE-GaN doped with Si or Ge and grown on native seeds

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Currently available commercial grade GaN substrates are prepared from crystals grown by HVPE. This method involves crystallization from gas phase and has two advantages – fast growth and high purity of HVPE-GaN. Without intentional doping the material is n-type with free carrier concentration of the order of 10^{16} cm^{-3}. However, controllable doping of HVPE-GaN to prepare substrates of specific parameters is still a challenge. In this work influence of two different donor dopants, Ge and Si, on structural, optical, and electrical properties of GaN is presented.

Photoluminescence (PL) spectrum of undoped HVPE-GaN contains a weak yellow luminescence (YL) peak. This can be attributed to presence of gallium vacancies (V_{Ga}) in the material. When the material is intentionally doped with Si the YL peak increases with Si content. According to SIMS, Raman, and Hall measurements, concentration of Si is always higher than the free carrier concentration in GaN:Si. This shows that part of Si donors is compensated by an acceptor state. The strong YL suggests that this deep acceptor is V_{Ga} or its complexes. The assumption is in good agreement with theoretical calculations of energy of V_{Ga} formation decreasing for highly n-type material [1]. However, when Ge is incorporated into HVPE-GaN, no YL is observed and there is no significant difference between concentration of Ge and the free carrier concentration. It may suggest that in this case V_{Ga} are not formed.

Advantages and disadvantages of doping with Si and Ge will be presented and two types of highly conductive n-type HVPE-GaN will be compared.

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Highly resistive HVPE-GaN grown on native seeds with solid iron or methane as a source of dopants

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HVPE is the most commonly used crystallization method for GaN crystals. One of HVPE's assets is the high purity of grown material. When no intentional doping is applied, HVPE-GaN is n-type with free carrier concentration of the order of 10^{16} cm^{-3}. Controllable doping of HVPE-GaN to prepare substrates of specific parameters remains challenging. This work presents influence of different acceptor dopants on structural, optical, and electrical properties of GaN.

In case of undoped HVPE-GaN a weak yellow luminescence (YL) peak is observed in the photoluminescence (PL) spectrum. The YL can be associated with gallium vacancies (V_{Ga}) in the material. When C is introduced to HVPE-GaN, using CH_4 as a precursor, a strong YL peak is observed in PL spectra. The material is highly resistive ($>10^8$ Ωcm) at 296 K. Hall measurements performed up to 1000 K showed p-type conductivity with hole concentration 4×10^{15} cm^{-3}. Activation energy of ~1 eV was calculated from Arrhenius plot. This is an experimental confirmation of DFT calculations performed for C substituted for N [1]. It is also an explanation for strong yellow luminescence (YL) present in PL spectra for GaN:C in this case not related to V_{Ga} but to C. When a solid iron source was used for doping, no YL is visible in PL of these samples and only a peak from internal transition of Fe^{3+} at ~1.3 eV is noticible. Calculated activation energy is ~1.8 eV and it suggests the presence of a different deep acceptor in the material. This prediction was confirmed by SIMS measurements. A significant concentration of Mn, originating from the source of Fe, was detected. The crystallized HVPE-GaN, co-doped with Mn and Fe, was highly resistive at 296 K and n-type at 1000 K with carrier concentration of 2×10^{13} cm^{-3}. Properties of highly resistive HVPE-GaN with different acceptors used will be discussed and compared.

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Investigation of GaN layers grown by high temperature vapor phase epitaxy

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GaN layers were grown on sapphire substrates by high temperature vapor phase epitaxy (HTVPE), which is a physical vapor transport based technology [1, 2]. This method uses thermally evaporated, elemental gallium and ammonia as precursors. Fig. 1a) shows a scheme of the inductively heated Ga evaporation cell with an optimized local temperature field and gas flow. In order to carry the Ga vapor, a mixture of Ar/H_2 gas (A) is introduced via nozzles incorporated in the crucible wall. The evaporation cell is surrounded by a fused silica tube channeling an inert gas flow (B), which prevents the diffusion of ammonia (C) towards the evaporation cell. The components of the evaporation cell are made of molybdenum, tungsten, fused silica and glassy carbon. The second key component of this setup is a separated heat zone for the sapphire substrate in a distance of 70 mm from the Ga source (not shown).

In this contribution, experimental results on the HTVPE growth of GaN layers on 15 x 15 mm² sapphire substrates are presented. Typically, GaN is deposited by the following process: At first, the substrate is thermally pre-treated at a temperature of 1350°C under an Ar/N_2 atmosphere with 10% hydrogen admixture. In a further step, a low temperature (LT) nucleation layer is deposited at a substrate temperature of 500°C and recrystallized at 1080°C under different hydrogen contents in the carrier gas. Subsequently, the nucleation layer was overgrown for 1 h at a crucible temperature of 1300°C and a substrate temperature of 1100°C. The resulting GaN layers reveal FWHMs of the 002 rocking curves of about 300". Finally, these layers are used as templates for overgrowth experiments under various conditions. Fig. 1b) shows the dependence of the FWHMs of the 002 and 105 rocking curves on the layer thickness. The crystal quality increases with the thickness of the layers. Raman investigations reveal compressively strained layers with free carrier concentrations lower than 10^{17} cm^{-3}, which is the detection limit of the method. The main impurities are silicon and iron with concentrations up to ~ 10^{17} cm^{-3} as determined by glow discharge mass spectrometry.

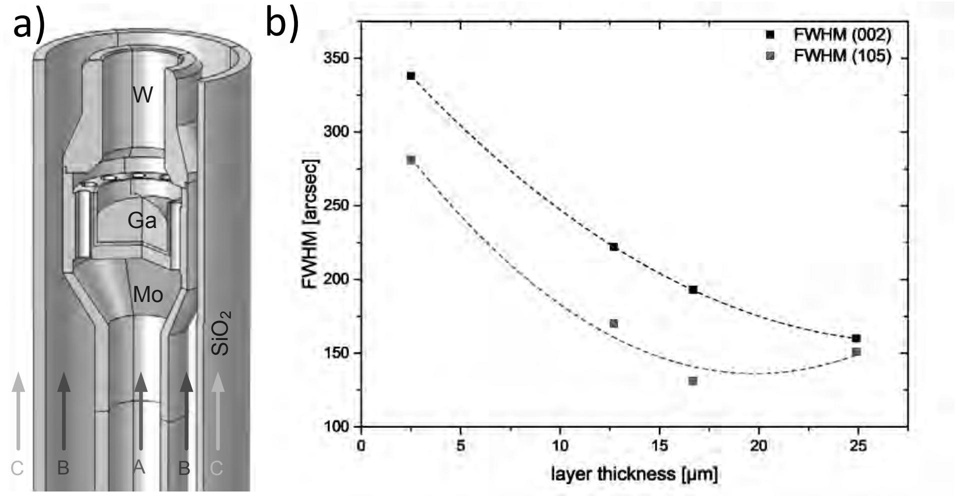

Figure 1: Scheme of the evaporation cell of the HTVPE setup. b) Dependence of the FWHMs of the 002 and 105 rocking curves on the layer thickness.

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Analysis of Mass Flux of AlN Crystal Growth at a Seed Face in PVT Method

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AlN crystals have the following properties, wide band gap, high electron mobility and high breakdown electric field [1]. It is expected for high power devices that are high temperature tolerance and low loss. It is reported that types of defects in AlN depends on whether growth condition is Al-rich or N-rich [2]. Main method of AlN bulk crystal growth is physical vapor transport (PVT). However, growth mechanism of AlN bulk crystal in PVT method has not been studied. If growth conditions are clear, it can reduce types of defects to be considered when it makes devices. The purpose of this study is to clarify growth mechanism by calculations of mass fluxes of Al and N to growth front in PVT.

We assumed that vapor phase only consists of aluminum and nitrogen gases and are compressible fluid in a furnace. Sublimation and deposition mass fluxes at a source face and a seed face are calculated by Hertz-Knudsen equation [3]. In this study, the so-called stoichiometry condition that aluminum and nitrogen are equally incorporated into crystals is not used, sticking coefficients of aluminum and nitrogen that were reported values [4-6]. Furthermore, we assumed that equilibrium total pressure is equal to total pressure in a furnace, and calculated equilibrium partial pressures of aluminum and nitrogen as a function of total pressure and temperature.

Figure 1 shows mass flux ratio of aluminum to nitrogen distributions along a seed face at different total pressures. Mass flux ratios of aluminum to nitrogen were about order of ten along a seed face. Figure 2 shows partial pressure distributions of aluminum (left) and nitrogen (right) in a furnace, respectively. Aluminum pressure decreased while nitrogen pressure increased from a source to a seed. These indicate that aluminum gas diffuses from a source to a seed and nitrogen gas diffuses from a seed to a source. Therefore, it is included that nitrogen flux incorporating into crystals is smaller than aluminum flux.

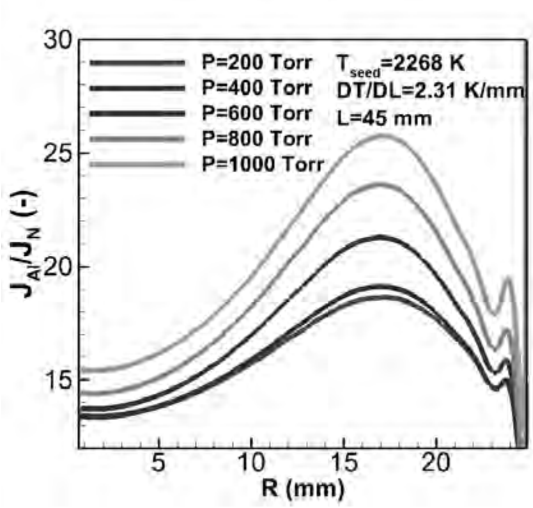

Figure 1. Mass flux ratio of Al to N distributions along a seed face at different pressures.

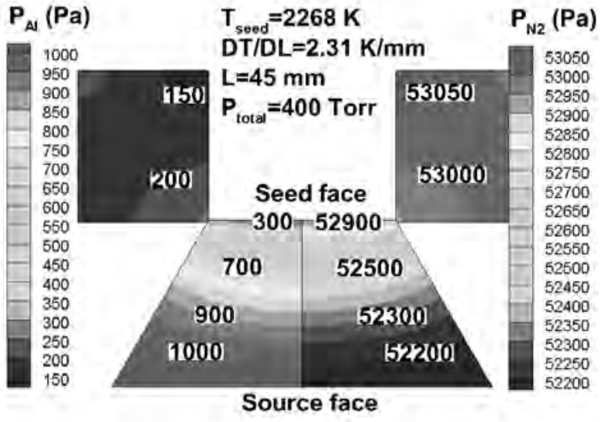

Figure 2. Partial pressure distributions of Al (left) and N_2 (right) in a furnace, respectively.

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Residual stress analysis on the 4H-SiC crystal grown by top seeded solution growth technique

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Top seeded solution growth technique (TSSG) is actively being studied as an alternative method growing silicon carbide (SiC) bulk crystal because it is advantageous to fabricate high quality crystals from point of defect level.[1-3] With TSSG, the SiC seed crystal is attached to a seed holder made with graphite and is dipped into a Si-rich solution containing C to grow SiC on it at quite high temperatures normally below than ~2000°C. The graphite and Si have different physical properties especially including the coefficient of thermal expansion (CTE) and elastic modulus. The mismatch in the physical properties could invoke large residual stress which is harmful to post processes after growing. Thus, in this study, we tried to analyze the residual stress on the grown SiC crystals after TSSG process. Because some liquid droplet remains on the SiC grown surface in many cases of TSSG experiments, we analyzed the residual stress loaded by liquid droplet as well. The average residual stress and strain of the 4H-SiC single crystal are quantitatively characterized by the X-ray Diffraction (XRD), not only before and after the TSSG process, but also inside and outside Si droplet regions. Those values are verified by the micro-Raman spectroscopy using deep UV source with short wavelength of 244 nm. And the dislocation distribution and crystalline quality are characterized using the synchrotron X-ray topography (XRT) and high-resolution X-ray diffraction (HRXRD), respectively.

As results, we found that the residual stress of the SiC single crystal increased by the TSSG process, which was assumed by the CTE difference between SiC seed crystal and graphite seed holder. Remarkable stress difference was also observed inside the liquid droplet. It was interesting to note that many micropipes (MPs) were found inside the liquid droplet compared to the outside. The high density of MPs inside liquid droplet was assumed to be due to stress relaxation by dislocation movement by slow cooling inside the liquid droplet with relatively large heat capacity.

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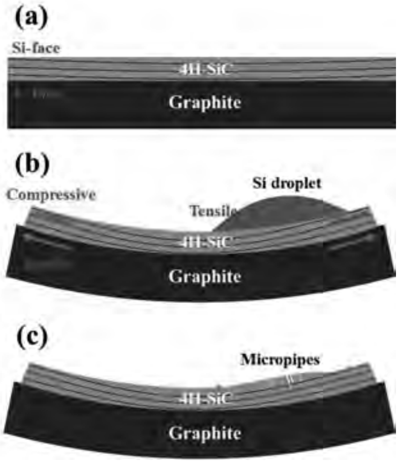

Figure 1. Cross-sectional schematic diagram of 4H-SiC growth mechanism by TSSG with thermal stress effect of Graphite and Si droplet. (a) Before an experiment; (b) During the cooling process after extracting from Si melt; (c) After etching in an HF solution. The black curves represent the stress field inside the 4H-SiC single crystal.

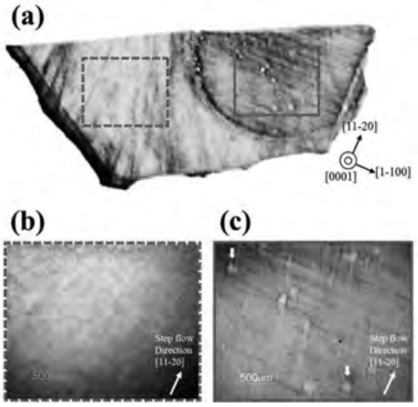

Figure 2. (a) XRT images with **g** = (11-28) of a piece of 4H-SiC grown crystal showing both Outside and Inside Si droplet regions; (b)~(c) Optical microscope (OM) images of the red dashed and solid rectangle sections in Figure 2-(a), respectively.

A Comparative study of solution grown and Sankaranarayanan-Ramasamy (SR) method grown diglycine zinc chloride (DGZC) single crystal.

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Abstract

Diglycine zinc chloride, a semi-organic nonlinear optical crystal was grown by conventional slow evaporation solution method and Sankaranarayanan-Ramasamy method. By employing this unidirectional method, diglycine zinc chloride single crystals of diameters 10 mm, 30 mm and length upto 60 mm were grown. The growth conditions and growth rate have been optimized. A maximum growth rate of 1.5 mm per day was observed. A comparative damage threshold analysis made on the diglycine zinc chloride crystals by conventional and unidirectional method shows that the crystal grown by Sankaranarayanan-Ramasamy method has higher damage threshold. The conventional and Sankaranarayanan-Ramasamy method grown diglycine zinc chloride crystals were also characterized by chemical etching, UV-Vis analysis, dielectric constant, dielectric loss, Vicker's microhardness analysis and the results were compared. The present study indicates that the crystal quality of Sankaranarayanan-Ramasamy method grown diglycine zinc chloride is good compared to conventional slow evaporation method grown crystal.

Keywords: Directional solidification, Impurities, Optical microscopy, X-ray diffraction, Growth from solutions, Nonlinear optic materials

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New $SrPb_3Br_8$ crystals.

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Halogenide crystals are of big interest as the functional materials for various applications because of their high transparency in a wide spectral region and a resistance for optical damage. The subject of present investigations is the new $SrPb_3Br_8$ crystal. It is transparent from about 360 nm to 20 microns, the estimated band gap value is 3.20 eV. $SrPb_3Br_8$ crystal has orthorhombic symmetry Pnma. The composition contains strontium, which ionic radius is comparable with rare-earth ions, that provides for their good distribution coefficient in doped crystals. $SrPb_3Br_8:Pr^{3+}$ crystals were grown by the Bridgman method. X-ray excited luminescence and transmission spectra were obtained, and they indicated the presence of Pr^{3+} ions in the crystal structure (Fig.1).

Obtained results allow to consider $SrPb_3Br_8$ doped with Pr^{3+} as a laser medium with low energy phonon spectrum for mid IR region, for up-conversion processes along with well-known halogenides of APb_2Cl_5:RE (A=K, Rb) [1]. Since $SrPb_3Br_8:Pr^{3+}$ has the high density (6.242 g/cm^3) and rare-earth distribution coefficient it also can be deemed as a potential scintillator for gamma radiation [2].

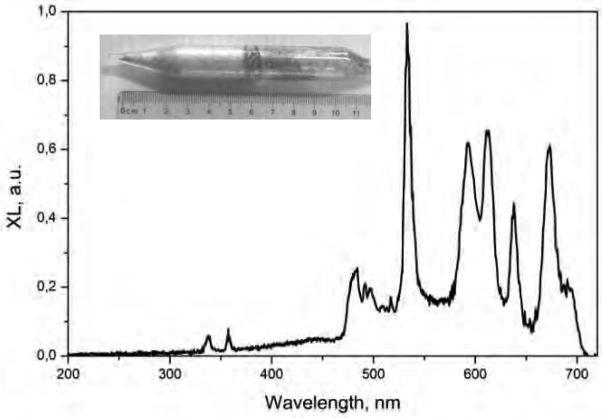

Рис.1 $SrPb_3Br_8:Pr^{3+}$ crystal and its X-ray excited luminescence and transmission spectra.

This work is supported by Russian Foundation for Basic Research (grant №16-32-00545) and by Act 211 Government of the Russian Federation, contract № 02.A03.21.0011 and by the Ministry of education and Science of the Russian Federation (№№10.9639.2017/BP).

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Bulk halide single crystal growth by skull technique.

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The claim for quality halide scintillators at reasonable price lead to the search of alternatives to conventional Bridgman or CZ that dominate at this area last decades. Finally at [1-3] the skull technique was successfully implemented to alkali halide bulk scintillator growth. This approach looks like poly silicate in semiconductor technology and base on ability to use poly crystalline bulk chunks for many types of radiation detector production. The lack of Pt crucibles and simple growth furnace construction (no any rotated parts like in CZ) make this approach very cost efficient.

But at the same time the better uniformity, scattering, mechanical properties and so on initiate request for single crystal growth. It was the main goal of this work.

The problem was resolved by the introduction to the bottom of the skull layer the seed crystals. Several approaches and modifications of the seed crystal sizes, place, distances from seeds were studied simultaneously with optimization of the temperature field along the crucible bottom. Experiments were carried out for NaI(Tl) and CsI(Tl) ingots of 250x180x45 mm and 450x450x100 mm size. Other words all experiments were performed in industrial scale furnaces.

The growth conditions that allows to nuclear on the seed substrate single crystalline layer and successfully continue the axial growth were revealed. The large area single crystals were obtained. Comparison of functional scintillation parameters (light yield, energy resolution, uniformity etc.) show the full correspondence with Bridgman or continuous growth technologies [4]. So, finally, the technology of the single crystal halides growth by skull technique is developed.

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P4.1

Paratellurite bulk crystals growth

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Paratellurite (TeO_2) crystals are widely used in acusto-optics and as a birefringent element. Inclusions and defects in elements made from this crystals are highly unwanted. TeO_2 crystallize with P_{422} space group and melts congruently at 734°C. Though it is good way to grow the crystal from its melt by Czochralski method. The growth of TeO_2 crystals by the Czochralski method with low-gradient thermal conditions (1–2 °/cm) allows producing faceted crystals with low thermo- elastic stresses and high optical homogeneity [1] (see fig. 1).

Since the other paratellurite growth stations are made with autonomous cooling system, that make them a little complicated. We decided to try paratellurite growth in furnace designed and constructed for LBO (LiB_3O_5) growing process.

The setup consisting of zones heating furnace and regulating devices. In the light-weight fireclay bricks body installed three levels of 4 segment heaters. The bottom and middle zones connections are realized through two separate load commutators. Each one allows to simultaneously switch on any of the heating elements in any sequence and for any time period. The top zone provides favorable axial gradient in the growth medium. Adjustment of the surface temperature distribution during seeding and control of the heat field symmetry during crystal growth are set mainly by the middle zone. The bottom zone is responsible for switching of the ‘‘hot spots’’ on the bottom part of the crucible wall stimulating buoyancy convection with azimuthal component. So the furnace provides dynamically changing (rotating) heat fields with various and controllable distributions of temperature along both the central axis and crucible walls.

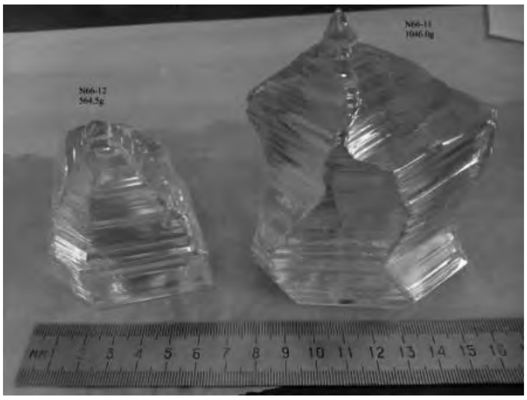

Fig. 1 Two examples of bulk crystals grown in furnace designed for LBO growth.

Experimentally shown that by changing times of solid state relay closure the temperature profile can be effectively changed, that also means that temperature gradient in melt can be adjusted to that needed for chosen crystal to grow. That furnace have bit thicker thermo isolation and no outer cooling. Few successful experiments we done last year. Faceted crystals with no visible inclusions and little “hair-like” scattering were obtained weighted up to 1.2 kg.

We grow bulk crystals along [110] direction platinum crucible loaded with 1.8 kg of TeO_2. Temperature regulation controlled by Eurotherm 6402 with 4 thermocouples on every level close to each heater.

By shortcircuiting one or more relays the corresonding heaters are swiched off for a period prescribed causing the local cooling and changing temperature gradient field. Peacture 2 shows the variety of temperature profiles measured in center of the crucible. The station is equipped with the distributed system of automatic control of the crystal-cross section By varying wanted section (calculated via diametre) yield coefficient can be changed.

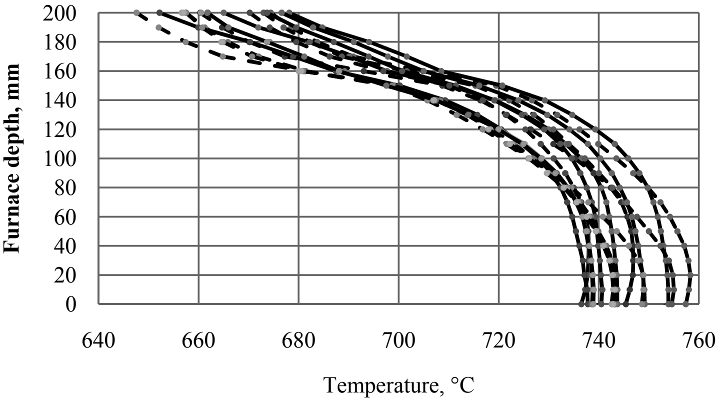

Fig. 2 Temperature profiles measured in the growth station. Solid lines are center and dotted lines are edge profiles.

Conclusions:
Designed and produced growth stations initially for LBO crystals are meet well the conditions of TeO_2 growing process. Grown TeO_2 faceted crystals have no visible inclusions and optical quality satisfied the standard of birefringent material in commercial polarizers.

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$Ca_{12}Al_{14}O_{33}$ is a calcium aluminate with the molecular structure $12CaO{\cdot}7Al_2O_3$ (C12A7). The unit cell of C12A7 consists of two molecules, and its chemical formula is represented as $[Ca_{24}Al_{28}O_{64}]^{4+} + 2O^{2-}$ with two freely bonded oxygen ions[1]. Zeolite-like crystal structure provides C12A7 a unique environment for the selective incorporation of anions such as OH^-, F^-, O_2^-, O_2^{2-} and electrons as substitutes for O^{2-}[2-4]. Because of these exceptional characteristics, C12A7 crystals are expected to be applied in many applications such as cold electron emission, active anion beam emission, optical writing of conductive wires, and as various catalytic agents for chemical reactions. To realize some of these applications, high quality single crystals are indispensable. A bulk C12A7 crystal with dimensions of Φ 30×67 mm was successfully grown by the Czochralski (Cz) method. During cooling of the crystal to room temperature, the surface exhibited severe cracking to a depth of about 1 mm. To determine the mechanism of the surface cracking we have measured powder and single crystal X-ray diffraction, Raman spectroscopy, thermal analysis and infrared absorption measurements of the OH-stretching band. We find that the lattice parameters of the cracked crystal surface and the core are different. An exothermic peak in the DSC and a weight increase in the TGA are observed. Furthermore, the OH^- ion content of the crystal increases with the number of the annealing cycle. It can be concluded that hydration of the C12A7 single crystal caused the surface cracking of the grown crystals.

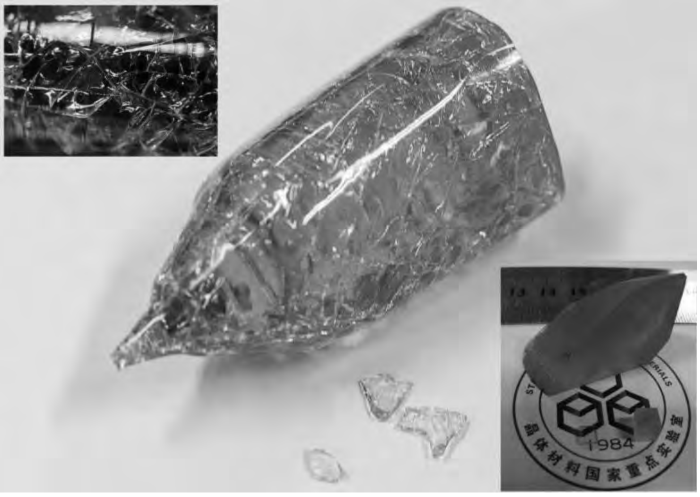

Fig1. The as-grown C12A7 crystal, and small pieces of the surface layer. The inserts show the inner part of the as-grown C12A7 crystal (bottom right) and detail view of the skin (top left).

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Melt drop method in the growth of defect-free TeO2 single crystals

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P4.3

Large-sized α-TeO_2 single crystal is well known and extensively used for it attractive acousto-optic properties. This crystal has also found in the last decade years strong interest in nuclear physics. Both applications require volume yield of crystals of large dimension and defect free remains as a challenging topic. Today, numerous works have been carried out mainly based on the Czochralski method for crystal of acousto-optic application and the Bridgman method for the crystal of neutrinoless double-beta decay experiments. Whatever the technique employed, the growth of crystals is performed from pure TeO_2 powder melted in a platinum crucible. It is reported a clear evidence of a chemical interaction between the liquid phase of TeO_2 and Pt container. As a consequence, this leads to the occurrence of several kinds of defects in grown ingots like striations, black inclusions (Pt + [Te_yO_{2y-x}]) and entrapment of gas bubbles (O_2). For industrial volume production, the Pt loss of Pt crucible in growth is incremental waste as well. The purpose of this work is to find a way to avoid the catalyzing of Pt and TeO_2. Based on thermodynamic analysis, the catalyzing can be neglected at the temperature of melt of less than 800 °C. With a properly heat insulator, the temperature of melt could be closed to the melting point of TeO_2 (733 °C) at pulling phase then cool down. So the process of material charges of Pt crucible to be observed for control of catalyzing. When the material in Pt crucible is charged by melting powder several times, the overheating of temperature and time is frequently followed by black inclusions in the ingot, "scum" on the melt surface and gray interior of Pt crucible. However, if the Pt crucible is charged by melt drop method, the temperature of melt to be charged is controlled easily at melting point of TeO_2. Few scums can be found in the charged Pt crucible. Benefit from melt drop method, clear ingot and shining interior of Pt crucible after pulling and annealing. Meanwhile, cycle time is saved by a furnace of charging to support multiple automated Czochralski pullers.

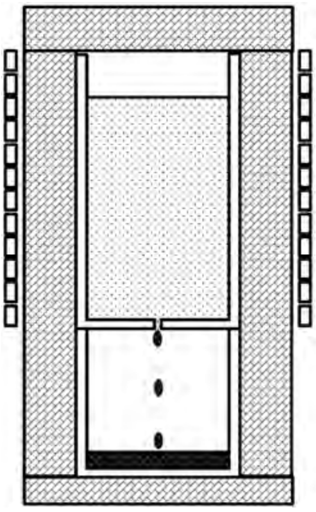

Fig. 1. Furnace of melt-drop for material charge.

Fig. 2. Czochralski-grown bulk α-TeO_2 single crystals.

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Optical floating zone crystal growth under high pressure atmospheres – advantages and applications

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Floating zone (FZ) technique with optical heating belongs to the most important crystal growth methods in science. The possibility to melt contactless very different materials and to control parameters like growth atmosphere and temperature in a wide range can lead to the creation of heretofore unknown compounds with striking properties. In recent times, FZ crystal growth with gas pressures up to 300 bar becomes feasible. We illuminate the potentials of high gas pressures and other non-standard growth parameters for the FZ process and show recently published examples from correlated oxides and intermetallic compounds.

High pressure atmospheres substantially restrain the evaporation from the molten zone and thus prevents melt stoichiometry changes and instrument pollution. During the FZ growth process of intermetallic compounds, high-purity protective gases like argon are used to avoid contaminations and reactions with the melt. On the other hand, a well-controlled partial pressure of oxygen directly affects the thermodynamical phase selection of oxides, since it interacts in subtle way with the thermodynamic stability of cationic valence states at melting temperature. Depending on the intended process, this influence might lead to the need for elevated pressures of pure oxygen, inert gases or precise gas mixtures during the growth process. The gas diffusion between the melting zone, the crystal and the atmosphere can be controlled by applying a wide range of ambient O2 pressures during the growth process. Furthermore, for some incongruently melting materials, congruent melting can be achieved with significantly increased O2 pressure. Thus, the O2 partial pressure and generally the total gas pressure affects not only the solidification mode and crystallisation process but also the composition, homogeneity and physical properties of the crystals themselves.

Pequiliarities of single crystal growth of oxide multiferroics by floting zone melting.

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Study of physical properties of oxide multiferroics appropriately using these materials in the form of fairly perfected single crystals. This allows to more accurately identify the subtle features of physical processes and examine the properties associated with the crystalline anisotropy of solid. This paper presents the results of technology development and implementation processes of crystal growth multiferroics by floating zone melting method on crystal growth equipment with light heating type of URN-2-ZM [1] allowing for cultivation processes in a wide range of gas environment over melt, including enhanced gas pressure up to 100 atm., and high-temperature annealing the crystal in growing process. To obtain rather quality crystals of various multiferroics growing conditions on dynamic parameters of the process and composition and pressure gas environment should vary widely. The optimal growth parameters are defined usually experimentally. The most famous and widely researched the types of oxide multiferroics and conditions to obtain enough quality crystals by floating zone melting with light heating are presented in Table.

Composition	Structure type	Melting type	Gas atmosphere	Crystallization speed	Crystal rotation velocity	Crystal size
$RMnO_3$ R-Gd÷Lu	Hex., Perovs.	Congr.	Ar flow, air	5 mm/h	40 r/min	Ø 8 x 60mm
$WMnO_4$:Co	Monoclin.	Congr.	Ar- flow	6 mm/h	40 r/min	Ø 8 x 60 mm
$Ba(Sr)Fe_{12}O_{19}$	Hexag. M	Incongr.	O_2 60 atm.	6 mm/h	40 r/min	Ø 8 x 60mm
$Ba(Sr)\ CoTi_x\,Fe_{12-x}\,O_{19}$	Hexag. M	Incongr.	O_2 60 atm.	4 mm/h	40 r/min	Ø 6 x 60mm
$Ba(Sr)Sc_x\,Fe_{12-x}O_{19}$	Hexag. M	Incongr.	O_2 60 atm.	4 mm/h	40 r/min	Ø 6 x 60 mm
$Ba_3Co_4Fe_{24}O_{41}$	Hexag. Z	Incongr.	O_2 60 atm.	4 mm/h	40 r/min	Ø 6 x 60 mm
$BaMe_2Fe_{16}O_{27}$	Hexag, W	Incongr.	O_2 60 atm.	4 mm/h	40 r/min	Ø 6 x 60 mm
$Ba_2Zn_2Fe_{12}O_{22}$	Trigon. Y	Incongr,	60 O_2 atm	2 mm/h	40 r/min	Ø 6 x 60 mm
$Ba(Sr)_3Nb(Ta)Fe_3Si_2O_{14}$	Trigonal	Incongr,	O_2, Ar flow	2 mm/h	40 r/min	Ø 6 x 60 mm
$CoTiO_3$	Romboedr,	Congr,	Ar flow	2 mm/h	40 r/min	Ø 6 x 60 mm
$CoTi_2O_5$	Orthoromb.	Incongr,	Air	2 mm/h	40 r/min	Ø 6 x 60 mm
Ca_2FeAlO_5	Perovskite	Incongr,	Ar flow	2 mm/h	40 r/min	Ø 6 x 60 mm

Pecuiliarities of crystal growth of each material and quality parameters in more details will be described.

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Mitigation of Second-Phase Particles via Post-Growth Treatment: Temperature Gradient Zone Melting and Annealing

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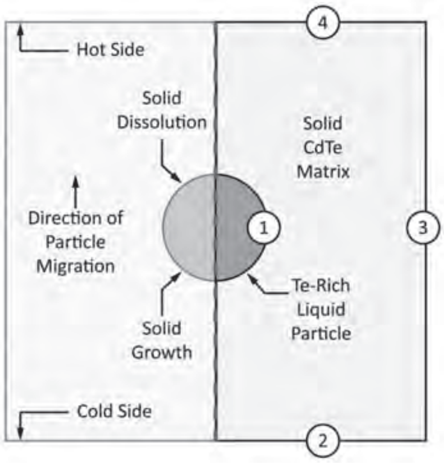
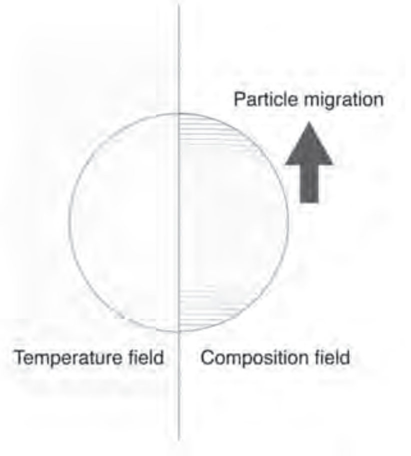
Second-phase particles are often unavoidable during the growth of binary semiconductor crystals from liquids, due to effects arising from non-congruent solidification and thermodynamics of the solid state. This presents a special challenge for the growth of large, high-quality crystals of cadmium telluride (CdTe) and cadmium zinc telluride (CZT) needed for gamma spectrometers, in which tellurium-rich particles are deleterious to the performance of such devices.

This poster first presents the most plausible mechanisms by which these second-phase particles arise during the growth of CdTe and CZT from the Bridgman process and the traveling heater method (THM). Since it may not be possible to prevent the formation of these particles during crystal growth, we discuss possible mitigation strategies that involve post-growth processing. Specifically, we analyze and assess post-growth strategies that involve treatment of the crystalline material under controlled temperatures and gas-phase environments over time.

We first discuss the temperature gradient zone melting (TGZM) technique, whereby particles can be induced to migrate by heating to slightly above the eutectic temperature and applying a temperature gradient across the sample. Under such conditions, the now-liquid particle dissolves on the hot side and re-solidifies on the cool side, with a net effect of the particle migrating toward the hotter region. We next consider how annealing under a cadmium-rich atmosphere can reduce the size of second-phase particles. Finally, we consider the combined strategy of TGZM and cadmium-overpressure annealing.

Our assessment relies upon mathematical and computational models for these post-growth treatments. We briefly present the formulation of mathematical models for particle migration via TGZM and particle shrinkage under the effect of solid-state diffusion of an enriched constituent. We provide analytical solutions that give good estimates for the overall outcomes of these strategies. We also describe the implementation of a moving-boundary, finite-element method that solves for particle position and shape, with no simplifying assumptions about mechanistic interactions. This model allows for a computation of the evolution of particle velocity, size, and shape over time and comparison to experimental observations.





Single crystal growth and surface chemical stability

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Optical bromide crystals offer unique combination of physico-chemical properties, in particular wide transparency range up to 30 mm, relative chemical stability in air and appropriate mechanical and thermal properties. Monoclinic KPb2Br5, space group P21/c, a=8.854(2), b=7.927(2), c=12.485(3), b=90.05(3)°, Z=4, accept effective doping by rare earth lasants and are promising for creation new laser host mediums for middle infrared spectral range. This study is devoted to single crystal growth of KPb2Br5 and evaluation of top-surface properties after contact to air atmosthere.

The synthesis of RbPb2Br5 compound was performed from high purity bromide salts. Crystals of KPb2Br5 were grown using the Bridgman method from a batch of stoichiometric composition in soldered ampules in halogen atmosphere. The melting temperature of the bromides is T = 655 K. The initial compounds PbBr2, and KBr were dried under pumping, followed by multiple purification through directed crystallization. The growth setup was a vertical single-zone furnace with a temperature gradient of no less than 5 K/mm. Single crystals of up to 15 mm in diameter and 40 mm in length were grown in evacuated quartz ampoules at an average rate of 2–4 mm/day.X-ray photoelectron spectroscopy (XPS) was used for the evaluation of chemical state of KPb2Br5 surface. To have a developed surface area, a peace of crystal was grinded up to powder state at room conditions. Observation of electron parameters of KPb2Br5 was produced by using surface analysis center SSC (Riber) with XPS method. The nonmonochromatic Al Kα radiation (1486.6eV) was used for the excitation of photoemission. Photoelectron energy drift due to charging effects was taken into account in reference to the position of C 1s (284.6eV) line generated by adventitious hydrocarbons. The photoemission lines and Auger-lines of the constituent elements were detected. Besides those, the C 1s line related to adventitious hydrocarbons and low intensity O 1s line appeared. Low intensity of O 1s line confirms high tolerance of KPb2Br5 to air agents.

An experience of creating the growth station control systems based on the low-cost general-purpose controllers and specialized peripherals

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P5.3

This paper presents the structure of the control system (CS) for crystal growth which supports various growth methods and control algorithms and can function in the growth stations with a wide range of peripheral equipment, including the equipment for control of symmetry and dynamics of the heat field in the growth furnace. This CS has been implemented for the methods of Czochralski and Kyropoulos. The various modifications of this CS have been used for the growth of LBO, BBO, TeO_2, etc. crystals.

From the outset the main requirements for the control system were its openness, flexibility and liveness (recovery after an emergency power failure). As well as use as a process controller of the low-cost PC-controller with ISaGRAF programming system. At the initial stage, a low-power, but quite reliable i-7188EG was chosen. Then for some tasks a bit more powerful uPAC-7186EG was required. As the development of CS progressed, the more high-end controllers WP-5147 (ISaGRAF) and WP-5238 (WinGRAF) were also tested. On the host-computer (operator station) we applied a SCADA programm Indusoft Web Studio (IWS). To simplify the synchronization between the ISaGRAF target in the process controller and the SCADA system, especially after a power failure, all the main control functions (algorithm implementation, calculations, parameter assignment functions, interaction with the peripherals and the host-computer) are transferred to the ISaGRAF project. SCADA is charged with the parameters indicating, the processes displaying, the interaction with operator, archiving, administration, etc. Nevertheless, even i-7188EG is quite able to cope with the tasks assigned to it. For example, it ensures the continuous process control for several months.

Some peripheral equipment, specially developed for the CS, helps also to solve the control tasks and reduce the load on the process controller. In our case, these are the controllers of the step motors for line moving and rotating of crystal MD1-VL and MD2-VL as well as the load commutator LC8-VL controlling the symmetry of the heat field by switching the segments of the growth furnace according to the specified program. The communication protocol and the set of commands of the step motor controllers are optimized from the point of view of loading the process controller and reliability of the control system. In particular, the process controller transmits to the MD1-VL a speed value and receives in the response a values of the current and absolute motions. Thus even if the connection is stopped, the movement of the rod continues. The figure shows a block diagram of one of CS modifications for LBO crystal growth station.

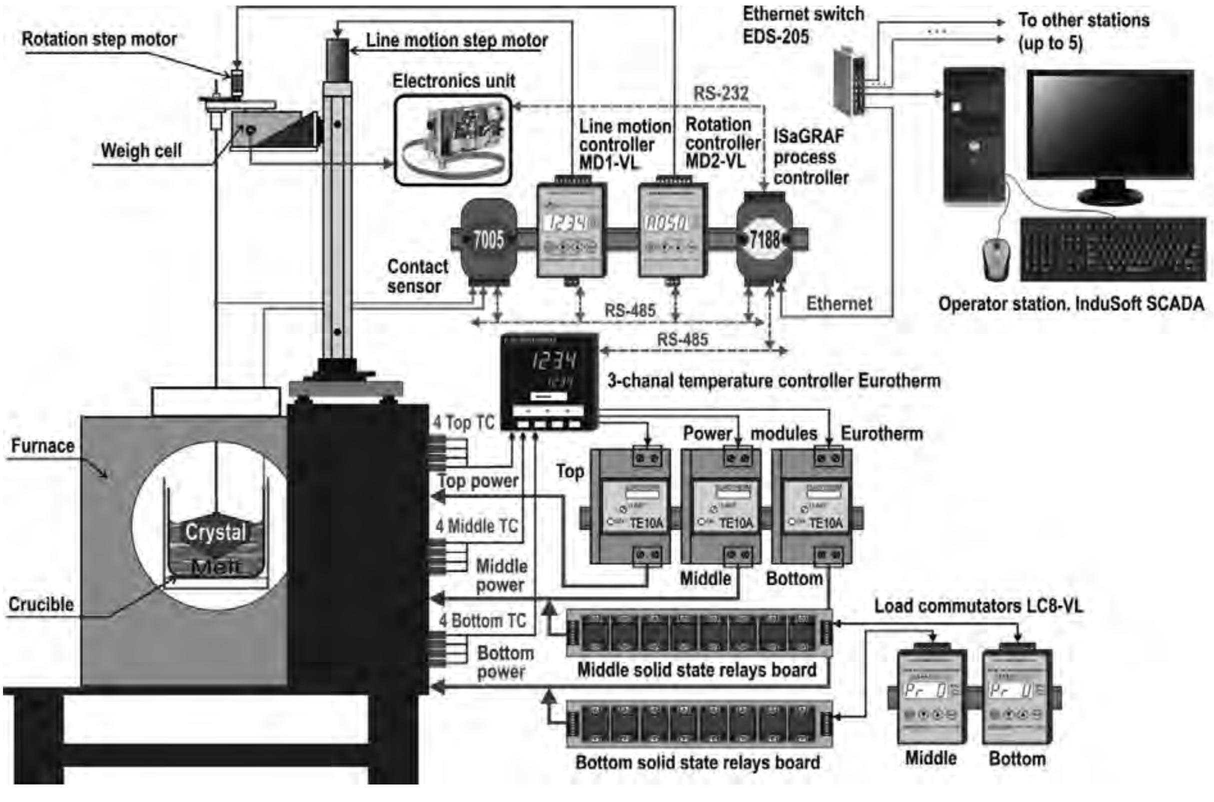

Figure. LBO growth station

IWCGT-7 2017 - Tuesday, July 04

Session 3		**Oxide crystal growth I** Chairs: Hanna Dabkowska (McMaster Univ., Montreal, Canada), Aleksander Gektin (ISC NAS, Ukraine)
09:00	a)	John Frank (Saint-Gobain Crystals, USA) **Oxide crystal growth in industry**
09:50	b)	Zuo-Guang Ye (Simon Fraser University, Canada) **Development of high-Tc and high-performance piezo-/ferroelectric single crystals based on PZT and other systems**
10:40		Coffee
11:00	c)	Christo Guguschev (IKZ, Berlin, Germany) **Perovskites and other substrates for multiferroics**
11:50	d)	Georgy Dosovitskiy (IREA, National research center "Kurchatov Institute", Russia) **High purity raw materials for scintillators and other single crystals - development, production and control**
12:45		Lunch
		Free Time
Session 4		**Emerging Fields in Crystal Growth I: Materials** Chair: Thierry Duffar (INP Grenoble, France)
16:30	a)	Kuei-Hsien Chen (National Taiwan University) **Vacancy and Phase Control of the GeSeTe for Thermoelectric Applications**
17:20	b)	Vera Manomenova (Shubnikov Inst. of Crystallography, Moscow, Russia) **Ni and Co sulfate crystals for solar-blind UV-filters**
18:30		**Workshop barbecue**

Advances, Results and Perspectives in Industrial Scale High Temperature Oxide Crystal Growth

John Frank Saint-Gobain Crystals USA, Drew Haven Saint-Gobain Crystals USA and Vladimir Ouspenski Saint-Gobain Recherche France

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As a leader in crystal growth, Saint-Gobain continues to work with and improve upon various technologies to produce cost effective high temperature oxide crystals at industrial scale (i.e. greater than 1 metric ton produced annually). This includes transitioning materials and technologies from the laboratory to a stable manufacturing environment. With the objective of illustrating the transition from academic research to manufacturing, key performance indicators will be contrasted between fundamental research and manufacturing, including the use of Technology Readiness Levels (TRL) to guide efforts. Two examples of recent advances will be shown. The first is a process to manufacture more than 10 sapphire crystals up to 1.5mm thick per crystal in one furnace using multi-tip EFG at > 2300 cm^2 surface area per crystal. The second is an improvement in LYSO scintillator performance that impacts crystal growth quality, requiring process modifications that are only apparent at scale. Perspectives for the direction of future improvements in oxide crystal growth, including process methods and material families, will be shared.

Fig. 1 15-Tip EFG Sapphire Crystal

Fig. 2 LYSO Scintillator with Ca induced spiral

Developments of High-T_C and High-Performance Piezo-/ferroelectric Single Crystals of Complex Perovskite Structure

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Single crystals of relaxor-based complex perovskite solid solutions, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ [PMN-PT] and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ [PZN-PT], exhibit extraordinary piezoelectric performance with extremely high piezoelectric coefficients, very large electromechanical coupling factors and exceptionally high strain levels, making them the materials of choice for the next generation of high-end electromechanical transducers for a wide range of applications, including (i) high-power underwater projectors and medical therapy, (ii) medical diagnostic imaging and nondestructive evaluation, (iii) sensors and receivers, such as hearing aid devices and pyroelectric applications. However, to further improve the binary materials' properties, new generations of piezocrystals have been developed, including ternary relaxor-PT solid solutions (Generation II), doped relaxor-PT solid solutions (Generation III), and other crystal systems with higher Curie temperature (T_C) and high performance. On the other hand, understanding the relationship between the complex domain structures and macroscopic properties is a key to this development.

In this talk we present an overview on the recent developments in high-performance piezo-/ferroelectric single crystals, and the fundamental understanding of their complex domain structures, phase transitions and structure - property relations. The design, crystal growth, phase symmetry, domain structure, and dielectric, piezoelectric and ferroelectric properties of several crystal systems will be discussed, including (i) ternary solid solution $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ [PIN-PMN-PT]-based Generation II piezocrystals with a complex morphotropic phase boundary region where the rhombohedral $R3m$ → monoclinic M_A (Cm) phase transition preserves the piezoelectric performance of the rhombohedral phase up to T_C, overcoming the depoling effect and extending the operating temperature range of the piezocrystals; (ii) $Bi(Zn_{0.5}Ti_{0..5})O_3$ [BZT]-based binary and ternary crystals that exhibit a high-T_C; (iii) $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbSnO_3$-$PbTiO_3$ [PMN-PSn-PT] ternary system which shows high piezoelectricity with a piezoelectric memory effect attributed to a self-polarization mechanism based on the defect-dipoles due to the presence of mixed valence states of $Sn^{2+/4+}$; and (iv) $Pb(Zr_{1-x}Ti_x)O_3$ [PZT] single crystals that form a class of high-T_C and high-performance piezo-/ferroelectric materials potentially useful for high-power electromechanical transducers that can operate in a wide temperature range and at high fields.

In addition, the development of the Standard for Piezoelectric Single Crystals will be presented. This document covers the physical and electromechanical requirements for relaxor-based piezoelectric single crystals of PMN-PT and PZN-PT solid solutions.

This work is supported by the U. S. Office of Naval Research (Grants No. N00014-12-1-1045 and N00014-16-1-6301) and the Natural Science and Engineering Research Council of Canada.

Perovskites and other substrates for multiferroics

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Zbigniew Galazka, Rainer Bertram, Steffen Ganschow, Matthias Bickermann

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Several mixed oxides with interesting ferroelectric, ferromagnetic, multiferroic, or simply electronic properties crystallize in the perovskite structure; quite often the structure is orthorhombically distorted. If such materials are grown epitaxially on almost, but not completely, lattice-matched substrates, the Gibbs free energy of the layers is influenced by a contribution of elastic distortion at the interface. Rare earth scandates $\mathrm{REScO_3}$ (RE = Pr ... Dy) proved to be especially well suited as substrates, because they are orthorhombic from their high melting points near or beyond 2000°C down to room temperature and exhibit almost square (101) lattice meshes with spacings around 4 Å, which is close to the lattice parameters of many advanced perovskite oxides. Haeni et al. (2004) [1] could shift the Curie temperature for the transition of ferroelectric (low T) to the paraelectric (high T) phase of $\mathrm{SrTiO_3}$ from almost absolute zero to room temperature by epitaxial growth of 1% strained layers on $\mathrm{DyScO_3}$ substrates. Depending on the epitaxial layer, the choice of appropriate substrates allows the adjustment of elastic strains stepwise, by the choice of proper RE ions. This talk will report how solid solutions of several perovskite mixed oxides, (e.g. $\mathrm{(LaLuO_3)_{1-x}(LaScO_3)_x}$ [2] , $\mathrm{Sm_{1-x}Gd_xScO_3}$ and $\mathrm{Nd_{1-x}Sm_xScO_3}$ [3]) can fill the gap between neighboring $\mathrm{REScO_3}$, and can even extend the range of accessible substrate lattice parameters (Fig. 1). Furthermore, improvements in crystalline quality will be presented for established, commercially available substrate crystals (like $\mathrm{SrTiO_3}$) and for not yet commercially available crystals which belong to the pyrochlore family.

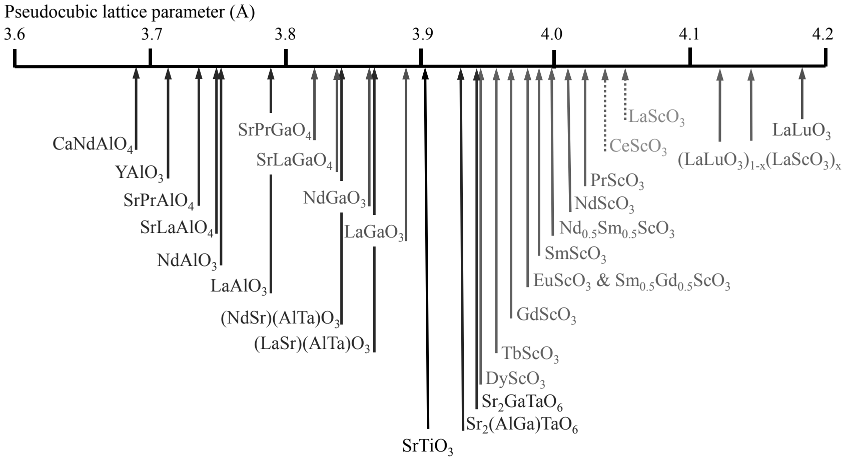

Fig. 1: Pseudocubic lattice parameters of perovskite substrates. This list is based on the one in Ref. [4]. Except for $\mathrm{LuAlO_3}$, $\mathrm{CeScO_3}$ and $\mathrm{LaScO_3}$, all crystals are grown at the Leibniz Institute for Crystal Growth (IKZ).

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High purity raw materials for scintillators and other single crystals - development, production and control

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Single crystal form of substance is used to produce advanced materials with strict performance requirements. In order to produce a crystal, meeting these requirements, one of the key issues is to choose a right raw material. High purity, i.e. low (or controlled) content of impurity atoms, is, usually, one of the first controlled parameters.

One group of single crystalline materials, which are rather demanding to raw materials purity, are scintillators. For example, to be used in experiments on fundamental particle physics, scintillator, usually, must have extremely high level of certain one or two impurity-dependent characteristics:
- high transparency and radiation hardness of $PbWO_4$ crystals for LHS CMS and ALICE detectors [1,2] and even higher radiation hardness for FAIR PANDA detector;
- isotopic purity and extra-low natural radioactivity background of $CaMoO_4$ crystals for Y2L AMoRE detector [3].

To reach the necessary scintillator performance certain impurities have to be strictly controlled in raw materials. E.g., 3d impurities, such as Cr, are detrimental to radiation hard $PbWO_4$ properties at 0.5 ppm level, and U and Th even at content of 0.1 ppm in $CaMoO_4$ create unacceptable background signal.

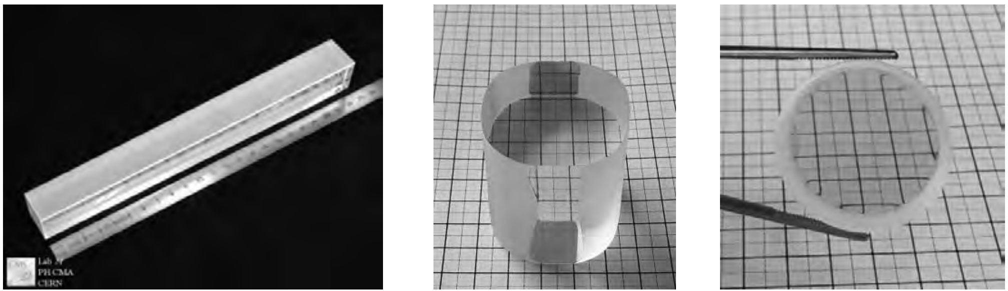

Fig. 1. Scintillator single crystals. From left to right: $PbWO_4$ for LHC detectors, courtesy of CERN [cds.cern.ch], $^{40}Ca^{100}MoO_4$ and $Gd_3Ga_3Al_2O_{12}$:Ce crystals, courtesy of Fomos-Materials OAO.

High purity raw material production technology development includes steps of finding suitable initial compound(s) and reagents, development of purification procedures, scaling these procedures to a level of technological processes. In order to maintain a stable product quality, in-process and final product control methods should be implemented. Besides mere final compound purity, technological solution should take into account factors of reliability, reproducibility, scalability, costs.

Work should start from setting goal purity of a needed compound – basing on it, suitable analytical techniques and purification procedures are chosen. But precise specification of impurities content in raw material could be unknown, especially for a new product (crystal). So, close link between producers of crystals, users of crystals and producers of raw materials speeds up work and helps to find optimal purity/performance/cost ratio.

There are some commonly established groups of impurities, classifying them by their chemistry (e.g. anionic/cationic, 3d, RE – La-Lu), harmful effect (e.g. "coloring"), abundance (e.g. "common" – Na, Ca, Mg). Some impurities could be eliminated using efficient small scale production processes (e.g., most of 3d); getting rid of the other at a reasonable cost is possible only in large-scale manufacturing (e.g. RE). There are some common approaches to types of purified compounds and types of impurities; however, purification of each certain compound is a special task.

Requirements for raw materials may differ for various crystal growth techniques and other forms of materials – ceramics, glasses. Besides purity, other important characteristics of raw materials are: Chemical composition in the sense of main components ratio, which should take into account possible difference between raw material and crystal composition. Microstructure, which is especially important for ceramics production. Starting material price and availability – in some cases it makes serious recycling efforts reasonable.

These subjects would be covered in a talk with examples from laboratory and production experience.

Current work on scintillator materials is supported by grant of Ministry of Education and Science of Russia 14.625.21.0033, project ID RFMEFI62515X0033.

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Vacancy and Phase Control of the GeSeTe for Thermoelectric Applications

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Germanium antimony telluride (GeSbTe) alloy is a popular material in optical and non-volatile memory devices. In the recent years, it has attracted renewed attention due to its potential for thermoelectric applications. In this work, we controlled the phase and vacancy in the alloy to achieve high thermoelectric performance. In order to ehance thermoelectric property in GeSbTe we attempted both bulk and thin film growth of this alloy. For the bulk samples, the compound was prepared by solid state reaction utilizing high-purity Ge, Sb, and Te to be melted under vacuum at 950 °C, then slowly cooled to 500 °C, followed by a rapid quenching in water or in the air. The sample is pulverized to powder, and followed by single crystal growth in a vertical Bridgman furnace. By careful control of the growth condition such as Ge content and rapid quenching condition we can turn the vacancies and defects in the crystal. For the thin film samples, we use magnetron sputtering to deposit GeSbTe on a Si substrate. Due to the interface effect between the GeSbTe film and Si substrate, we can sustain the high temperature cubic phase down to room temperature and study their thermoelectric properties.

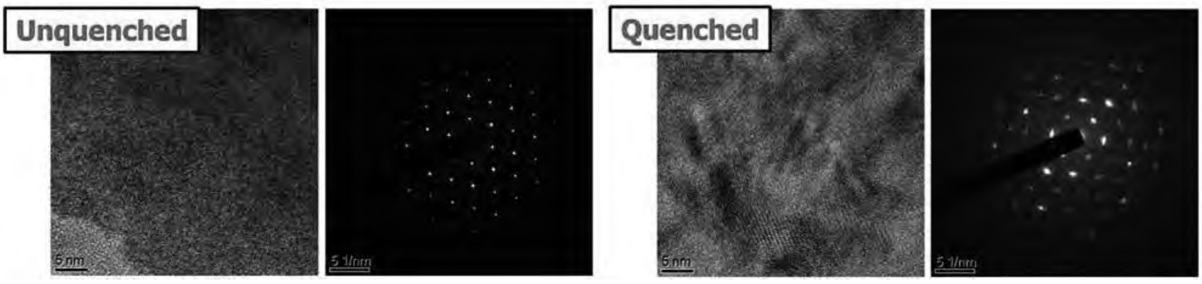

Figure 1. TEM images and SAD of the unquenched and quenched GeSbTe samples, showing the effect to quenching to induce disorder of the crystal.

High thermoelectric performance has been observed for cubic phase GeSbTe thin films compared that of the rhombohedral bulk samples. Systematic characterization of the thin film samples reveals that enhanced electric conductivity above 150 °C contribute mainly to the TE performance without compromising the Seebeck coefficient and thermal conductivity. Detailed investigation has been performed including TEM, XPS, UPS to unveil the mystery of the GeSbTe film. Further extension of the film properties to a bulk sample is underway.

Ni and Co sulfate crystals for solar-blind UV-filters

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The ozone layer of the Earth efficiently absorbs solar light in the wavelength range of 200–300 nm. UV radiation sources (such as electric discharges and flame) can be detected in this solar-blind spectral range because these sources have a significant radiation component in the wavelength range of 250–280 nm. Detectors operating in this spectral range are used for the remote inspection of power lines and for the ecological monitoring of terrestrial and aqueous environments. An essential element of these devices is an effective band filter transparent in the range of 200–300 nm and opaque beyond it. Such filter allows operate in solar light. Currently, the main materials for solar-blind filters are simple and complex nickel sulfates: α-$NiSO_4 \cdot 6H_2O$ (α-NSH), $K_2Ni(SO_4)_2 \cdot 6H_2O$ (KNSH) and $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ (ANSH) [1-5].

We have determined the conditions for growing of $Rb_2Ni(SO_4)_2 \cdot 6H_2O$ (RNSH) and $Cs_2Ni(SO_4)_2 \cdot 6H_2O$ (CNSH) crystals and for the first time we have grown these large single crystals of optical quality. We have also improved techniques for growing of α-NSH, KNSH and ANSH crystals.

The real structure of all growing crystals was studied by projection X-ray topography. We have defined the common features of the $Me_2Ni(SO_4)_2 \cdot 6H_2O$ (Me = K, Rb, Cs) crystals real structure.

For the first time we have studied the thermal stability of the single crystals RNSH, CNSH and the polycrystalline samples of ANSH, RNSH and CNSH. Thermo-gravimetric analysis of the grown crystals allowed to define the relative thermal stability of the α-NSH and $Me_2Ni(SO_4)_2 \cdot 6H_2O$ (Me = NH_4, K, Rb, Cs) crystals. It turned out that RNSH and CNSH crystals have the highest thermal stability. It was found out that with increasing radius of the alkali cation the onset dehydration temperature of Tutton nickel salts changes nonmonotonic.

The crystal structure of RNSH, CNSH was refined. And as a result, we have found the dependence of the onset dehydration temperature of Tutton nickel salts on their structural characteristics.

It has been found out that all investigated crystals have high transmittance in the solar-blind range of the UV and therefore they can be used as materials for UV optical filters.

We have chosen the α-NSH and CNSH crystals as an advanced material for UV filters and we have improved the technology of their growth. Namely, we have determined the optimal methods of growing crystals, we have studied the distribution of impurities in different crystal growth sectors, we have proposed methods of raw salts purification and we have determined the optimal pH of solutions and growth temperature conditions.

The application of these crystals as UV filters has made it possible to create highly sensitive monophotonic devices: UV C direction finders and UV C corona discharge sensors, monophotonic microrelief sensors, sensors for hyperspectral systems.

However, the nickel sulfate crystals have the transmission band in visible range of spectrum (near 500 nm). So the next step to improve the device efficiency is the complete suppression of unwanted bands in the visible spectrum range. So the report will discuss also the growth of mixed $K_2Ni_xCo_{(1-x)}(SO_4)_2 \cdot 6H_2O$ single crystals, because these crystals can improve the filtration efficiency 10 times comparing with the nickel sulfate crystals [6].

This work has been supported by Russian Science Foundation (project no. 15-12-00030).

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IWCGT-7 2017 - Wednesday, July 05

Session 5		**Multi-crystalline silicon for PV** Chairs: Christian Reimann (Fraunhofer IISB, Germany), Kader Zaidat (SIMAP Grenoble, France)
09:00	a)	Anne Karin Søiland (Elkem Solar, Norway) **From upgraded metallurgical-grade silicon feedstock to high quality wafer**
09:50	b)	Gunter Erfurt (MeyerBurger, Germany) **Industrial perspective of silicon PV**
10:40		Coffee
11:00	c)	Zhixin Li (Linton Machine, China) **Trend of Crystal Growth Technology in Solar Industry**
11:50	d)	Julien Laurent (Vesuvius, France) **Crucibles for HP mc-Si**
12:45		Lunch
Session 6		**Emerging Fields in Crystal Growth II: Technologies** Chairs: Stephan Riepe (Fraunhofer ISE, Germany), Matthias Bickermann (IKZ Berlin, Germany)
14:30	c)	Matthias Schreck (Univ. Augsburg, Germany) **Single crystal diamond wafers by heteroepitaxy**
15:20	d)	Siddha Pimputkar (LeHigh Univ., USA) **Technology of ammonothermal growth for gallium nitride**
16:10		Coffee
16:30	e)	Christiane Frank-Rotsch (IKZ, Berlin, Germany) **Status of KRISTMAG® technology and its impact on crystal quality**
17:20	f)	Nathan Stoddard (SolarWorld, USA) **Silicon Crystal Doping: Pesky Problems and Exotic Options for Batch and Continuous-feed Growth**
18:30		Dinner
Poster		**Presentation**
19:30		Session II

"From UMG silicon feedstock to high quality wafer"

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Elkem Solar
anne-karin.soiland@elkem.no

Upgraded metallurgical (UMG) silicon is a term that is used to describe metallurgical grade silicon, which has been subjected to one or several purification steps. The term has lately been adopted by the photovoltaic (PV) industry to distinguish silicon from a metallurgical refining route from the conventional gas decomposition routes (as e.g, the "Siemens" process). Elkem Solar has developed its proprietary process, which consists of three main purification steps; 1) Slag refining 2) Acid leaching and 3) Directional solidification [Odden *et al*., 2012]. An industrial plant has now been running with this process since 2009, producing Elkem Solar Silicon® (ESS®), with an initial capacity of 5000 MT to a targeted capacity for this year of 7900 MT. The plant also comprises a silicon arc furnace for production of a specific silicon for the refining processes. Through the merger with REC Solar, the whole value chain from quartz to solar modules is covered. This gives unique possibilities to further development of the feedstock and processes, for optimization and tailoring of the final product.

The most characteristic material difference between the UMG-Si and polysilicon lies in the dopants. Because of limitations in the refining processes, there will always be significant amounts of both dopant types, boron and phosphorus present, thus giving a compensated silicon. One asset of this concurrent presence of the two dopant types is that it is possible to obtain flat resistivity profiles for the ingots when gallium is used as a co-dopant (figure 1). The dopant concentrations will also influence other properties like carrier mobilities. Most metallic impurities exhibit low segregation coefficients, which makes it possible to achieve low levels, also with a metallurgical refining route, see Table 1 [Søiland *et al.*, 2012]. Light element impurities (CON) will usually be present in higher amounts than for conventional polysilicon. However, the balance of these elements is strongly influenced by the ingot crystallization step due to various equilibria in the furnace environment (crucible/coating/graphite chamber/) and process conditions (e.g. melt convection) [Reimann *et al.*, 2010, Møller *et al*. 2009, Søiland *et al*., 2005].

To obtain a high quality wafer, a proprietary high performance multi-crystallization process has been developed, resulting in a wafer with small and randomly oriented grains, which exhibit low density of dislocation clusters [Stokkan *et al*., 2014]. To reduce the extent of red-zone and further improve both yield and cell efficiencies, EMMA® additive is used. [Søiland *et al*., 2015]. Today, REC Solar's current technology has shown the potential to achieve 20.47% with ESS®-based p-type multi.

The metallurgical refining route offers a solar grade silicon production with low energy use and low carbon footprint compared to conventional gas decomposition routes [Odden et al., 2012]. It has become more crucial to endeavor a low carbon footprint in competition with other solar panel producers and other alternative energy sources. ESS® has been certified in France with a carbon footprint of 10.87 kg CO_2 eq/kg (by Ademe) and in Japan with 14 kg CO_2 eq/kg. It is expected that the future will further emphasize on this feature. Together with the continuous cost reduction demands, the challenge lies in meeting these requirements while keeping the necessary product quality.

Method	Na	K	Ca	Ti	Fe	Ni	Cu	Zn	Ga
NAA^1 / ppbw	0.3	<0.5	<40	<100	1.0	1.0	1.0	<0.02	0.2
GDMS^2 / ppbw	<50	<50	<100	<5	<50	<10	<10	<50	<10

Table 1: Analyses of metallic impurities in ESS® performed at external laboratories.
^{1} Average from 3 laboratories. ^{2} Average from monthly sampling over 6 months production of ESS®

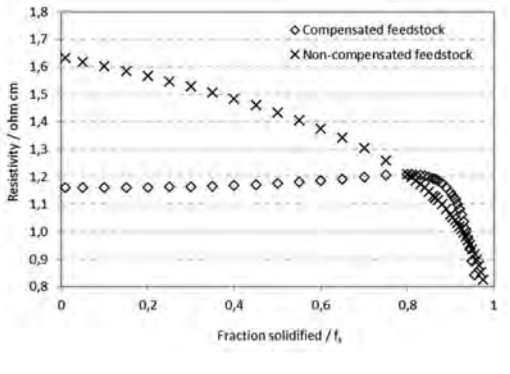

Figure 1: Resistivity profiles for a compensated feedstock with Gallium co-dopant vs. a non-compensated feedstock (only boron dopant)

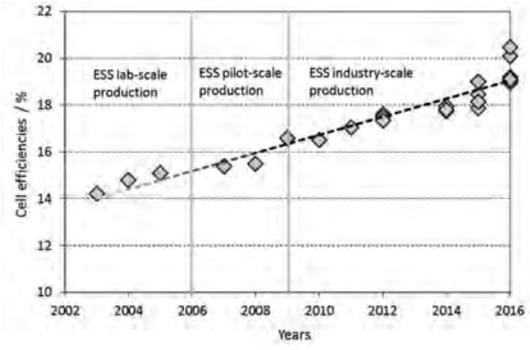

Figure 2: Cell efficiencies (averages) by year obtained with ESS® in different mixes at various producers

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Industrial perspective of silicon PV

Gunter Erfurt, Meyer Burger Technology AG

Industrial photovoltaic has fulfilled economic and energy pay back promises in the past years by continually improving the overall cost structure as well as by pushing efficiencies of solar cells and modules up. Improving the bulk quality of crystalline silicon and combining this with improved passivation and metallization techniques can be found among the biggest cost down influencers within the modern production process of cells and modules. Nevertheless, current bulk quality of industrially used silicon is holding back the full potential of highly surface passivated PERC, PERT and HJT solar cells using both dielectric layers such as AlOx or SiOxNy as well as a-Si passivations. Further cost down potential by improving bulk quality lies in the range of up to -10% which has a direct impact on the levelized cost of electricity (LCOE) that is - depending on the geographical region of installation - already as low as \$25/MWh. Furthermore, dopants for both, n and p crystalline silicon will play a dominant role within the next years in the continued cost down as well as efficiency increase efforts undertaken by the academic community in collaboration with the photovoltaic industry. The presenter will provide an overview on current technology trends as well as on challenging scientific problems to be tackled in order to make solar even more cost competitive in the energy market and to pave the way for full deployment of this sustainable and renewable source of energy.

Trend of Crystal Growth Technology in Solar Industry

Dr. Zhixin Li, Linton Machine

ABSTRACT

More than a quarter million tons of silicon crystals are used in solar industry to make crystalline silicon solar cells. In order to grow such a large number of crystals, specialized equipment is used and advanced process technologies are developed. In manufacturing of solar cells, two major types of silicon crystals are utilized: mono-crystals and multi-crystals.

Mono-crystals (Mono-C) are typically grown using Czchoralski (CZ) method. Mono-crystals have better structural quality and result in higher photo-voltaic conversion efficiency. However, it consumes more electric power to grow, and has a slower crystal growing process, thus lead to higher production cost. For the past a few years, many technical approaches are utilized to achieve fast growth and lower power consumption, greatly enhanced the competitiveness of mono-crystals.

Multi-crystals (Multi-C) are typically grown using Directional Solidification Systems (DSS) method. It has evolved through many generations, currently the most popular being G6 and G7, with G8 being developed. Each Multi-C furnace has larger production capacity compared with Mono-C, with ingot weight being 800 Kg or higher. It also consumes less power per Kg of ingot weight. An additional advantage is that poly-silicon of lesser quality can be used to produce Multi-C. The downside of Multi-C is that its photo-voltaic conversion efficiency is typically lower than that of Mono-C. For the past a few years, much effort has been made to enhance the PV conversion efficiency of Multi-C.

Wafering technology also affect the relative competitiveness of Mono-C and Multi-C. Recently competitiveness of Mono-C wafers has greatly enhanced due to earlier and faster application of diamond wire slicing technology in producing Mono-C wafers. The utilization of diamond wire in slicing Multi-C wafers has been slowed down because of compatibility issues with current surface etching technologies.

In this work, the above topics are discussed in detail in relation to the development of solar industry background.

Crucibles for HP mc-Si

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Abstract:

Electricity from solar cells is widely recognized as one of the most promising sustainable energy sources of the future. Today, 90% of commercial solar cells are made from crystalline Si (c-Si) and market projections for the next 15-20 years indicate that Si will continue to be the preferred material for solar cells. The cells are made from wafers cut from ingots grown from a Si melt; either by solidification inside a crucible (mc-Si) or pulled up from a melt in the crucible (sc-Si).

Since Si melts at a very high temperature (1412 ºC) and is highly reactive, only few materials are suitable for solidification of Si ingots. Crucibles made of silica (SiO_2) are most commonly used commercially. A coating layer of silicon nitride (Si_3N_4) is usually applied to the inner crucible surface to reduce the interaction between melt and crucible, thus reducing the amount of introduced oxygen.

High performance multi wafers is now supplanting multi-crystalline silicon wafers and its market share will be increasing over the next years up to 50% [ITR15]. This new casting technology by using small randomly oriented seeds was proposed for the so-called high-performance mc-Si (HPM) [YAN15] and demonstrated that by using an unmelted silicon grain layer as seed a small grained microstructure can be obtained which is able to generate high efficiency silicon solar cells. But this process induces larger bottom red zone and lost area due to remaining unmelted seed. To reduce the cost, this red zone has to be reduced. In this context a self-nucleating crucible has been developed to reduce the bottom red zone while keeping good electrical properties of the silicon wafers all along the silicon ingot without using a silicon seed layer.

The presentation will be divided into two different parts. First we will explain exactly the role of the crucible and the coating on the chemical and electrical quality of an mc-Si ingot. Secondly, we will present the results we obtained with the Vesuvius self-nucleating crucible. This study explores lifetime results on ingots and wafers obtained with this newly developed self-nucleating crucible. Standard and self-nucleating crucibles were used to grow laboratory-scale and industrial silicon ingots. Length of the bottom red zone, minority carrier lifetime, grain structure, and recombination active wafer area were compared.

The results show clearly that ingots originating from the self-nucleating crucible can reach a similar quality than HPM ingots grown from a silicon seeding process. It will be shown that using a self-nucleating crucible can lead to a significant saving in term of usable length and then subsequently can contribute to a significant wafer cost reduction.

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7th International Workshop on Crystal Growth Technology, Potsdam, July 2 – 6, 2017

Single crystal diamond wafers by heteroepitaxy

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Two alternative concepts are currently explored to synthesize single crystal diamond by chemical vapor deposition (CVD): homoepitaxy on diamond seed crystals or heteroepitaxy on foreign single crystal substrates. In order to obtain the highest structural and electronic quality in homoepitaxy, first of all seed crystals (e.g. from the HPHT technique) with minimum dislocation density can be chosen. In addition, careful surface pretreatment as well as optimized growth procedures have to guarantee that the nucleation of new dislocations during the CVD process is avoided. In contrast, heteroepitaxy generally starts with a high dislocation density which has to be reduced in the subsequent growth process. Its specific strength is in the scaling to large areas.

In this presentation the concept of heteroepitaxial diamond growth is reviewed. Important milestones, like the selection of Ir as growth surface, the use of the bias enhanced nucleation (BEN) procedure to generate oriented nuclei, the transformation of oriented diamond layers into real single crystals, the development of the multilayer substrate Ir/YSZ/Si and its scaling to 4” wafer size are described. Special attention is paid to threading dislocations, their role in stress formation and strategies to reduce their density. The state of the art in terms of material quality for (001)- and (111)-oriented layers is presented and the potential for further improvement is critically discussed. Finally, several fields of possible applications for single crystal diamond grown by heteroepitaxy and first steps towards commercialization (http://www.audiatec.de/) are described.

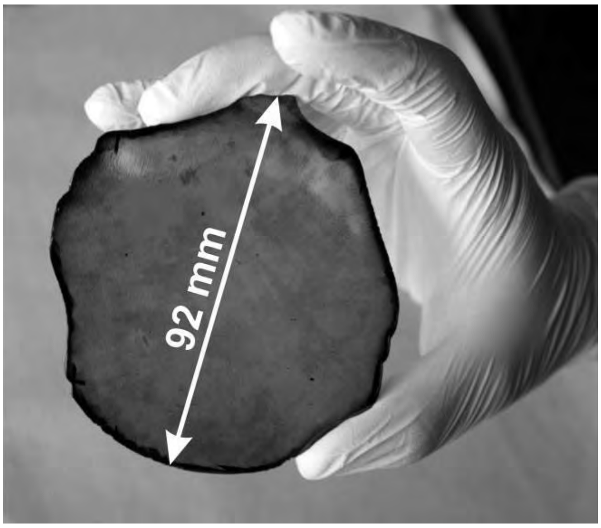

Figure 1: Freestanding unpolished diamond single crystal synthesized by heteroepitaxy on Ir/YSZ/Si(001). The thickness of the disc is 1.6±0.25 mm and its weight is 155 carat [1].

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Technology of Ammonothermal Growth of Gallium Nitride

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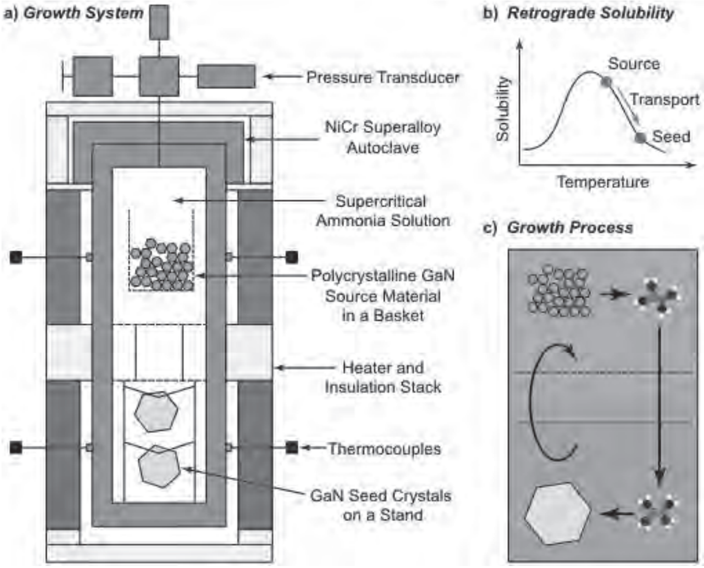
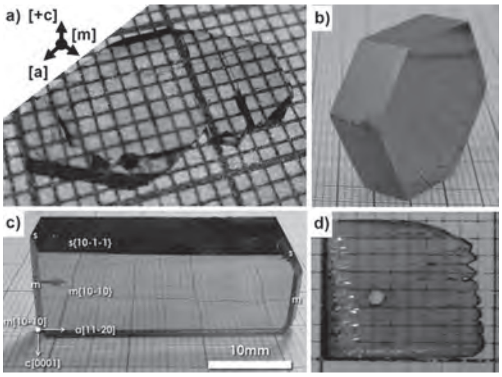
Gallium nitride (GaN) is a wide bandgap semiconductor which has received widespread attention as it has enabled the development of short wavelength (UV, blue) optical emitters and promises highly efficient, high power electronics. Common to these fields is the need for a high quality, single crystal bulk GaN substrate to minimize efficiency losses caused by dislocations, permit growth of GaN epitaxial layers in arbitrary crystallographic orientations and enable vertical device structures to further increase the operating breakdown voltages for GaN power electronics.

Bulk GaN growth is challenging due to the inability to readily melt the material ($T_{melt} >$ 2200 K, $P_{melt} > 6$ GPa).[1] The ammonothermal (AT) method[2] circumvents this challenge by dissolving GaN into a supercritical ammonia solution under elevated temperatures (~ 600 °C) and pressures (~ 2000—3000 atm). Mineralizers, such as alkali metals or halides, are added to the solution to increase GaN solubility leading to basic or acidic solutions, respectively. Basic solutions are less corrosive than acidic solutions permitting use of unlined Ni-Cr superalloy autoclaves, whereas acidic autoclaves typically require precious metal lined autoclaves. Recently, molybdenum-based autoclaves have for the first time demonstrated their suitability as an unlined autoclave for use in both acidic and basic growth environments.[3] Non-hermetically sealed capsules have been developed enabling higher purity growths of GaN in basic environments.

Important advances in the field which will be highlighted include improvement of growth rates leading to demonstrated peak growth rates of 60—340 µm/day for basic systems[4] and 250—960 µm/day for acidic systems[5], development of an equation of state to thermodynamically describe the decomposition of ammonia at typical operating conditions[6], and a reinvestigation of the observed retrograde behavior of GaN solubility in basic ammonothermal systems[7]. Properties of ammonothermally grown GaN crystals will be presented, including improvements in crystal purity, explanations for their observed sub-bandgap optical absorption[8] and coloration due to the presence of point defects[9], including most notably hydrogenated gallium vacancies.





Left Figure. Overview of a) AT autoclave, b) solubility for basic process and c) growth process. **Top Figure.** a) 1 mm thick slice from basic AT-GaN grown in Ag-capsule, b) unlined basic growth of AT-GaN boule, c) acidic AT-GaN boule, d) acidic AT-GaN grown in Mo-based autoclave. **Refs. in [9].**

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Status of KRIST*MAG*® technology and its impact on crystal quality

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The benefit of magnetic fields in crystal growth is well-known since many years. Mostly steady magnetic fields are applied in industrial scale to damp melt flow oscillations. Compared to steady magnetic fields the application of travelling magnetic fields (TMF) is also very promising since similar effect in the melt can be obtained already by a significantly lower induction. A detailed overview on magnetic field features and their pros and cons is given by Rudolph [1]. The idea to use the heater itself in a modified configuration to generate a suitable TMF very close to the melt was put in practice at the Leibniz Institute for Crystal Growth (IKZ). The KRIST*MAG*® technology was developed in close cooperation with industrial and academic partners, within three related project frames during the period from 2005-2014 and furthermore continuously improved too. The acronym KRIST*MAG*® stands for "**Krist**allzüchtung im **Mag**netfeld" (crystal growth in magnetic field). The developed so-called heater-magnet module (HMM) combines the simultaneous operation with direct current (dc) and alternating current (ac) that enables decoupled generation of heat and TMF. The acting Lorentz forces ensure the control of melt flow. They can be used to improve the crystal quality by: i- increasing or decreasing the melt mixing, ii- shaping the solid/liquid interface, and iii- damping possible temperature oscillations at the growing interface. The direction and magnitude of the TMF can be adjusted by the variation of ac/dc ratio, frequency and phase shift between the heater coils. The suitable parameter field is estimated with the help of numeric simulations and according to the desired growth conditions.

The KRIST*MAG*® concept proves to be favorable for various materials and has been already successfully applied in numerous growth techniques like Czochralski [2], liquid encapsulated Czochralski [3], vertical gradient freeze [4, 5], directional solidification [6] and liquid phase epitaxy [7]. It has been successfully applied to the growth from electrical conducting melts, among them semiconductors like Ge, Si, GaAs and $Hg_{1-x}Cd_xTe$.

HMM´s have been designed and realized in various geometries and scales for the crystallization in single as well as multi-crucible use and were transferred from laboratory to industrial scale [8].

The improved quality of crystals grown in TMFs has been shown by diverse investigations. Results of the positive impact of the KRIST*MAG*® technology on crystal quality, such as enhanced homogeneity of electrical parameters, reduced defect content, improved solid-liquid interface morphology and increased crystallization rates due to TMF melt flow controlling, will be illustrated.

Fig. 1a shows an image of a 4 inch GaAs VGF single crystal grown in a HMM furnace at IKZ. In Fig. 1b a multi crystalline G5 Si ingot is seen.

Up to now about ten crystal growth equipment based on KRIST*MAG*® technology have been realized, some of which are even used for industrial scale. Furthermore, the recent developments of the KRIST*MAG*® technology, which are currently tested at IKZ will be presented. The technology is protected by 16 patents. The term is registered as trademark. KRIST*MAG*® was awarded by the Innovation Price Berlin-Brandenburg in 2008 and the Bavarian State Prize in 2012.

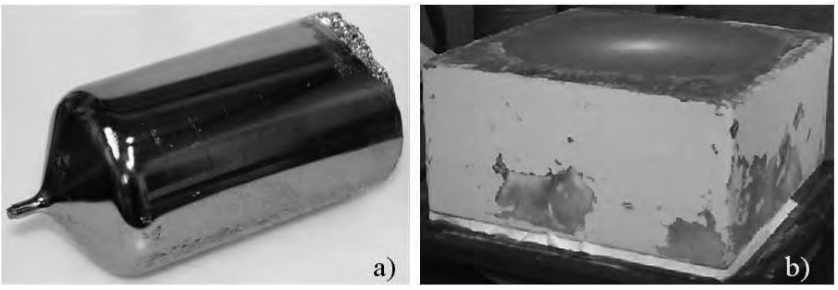

Fig. 1: Images of crystals grown by the KRIST*MAG*® technology: a) 4" VGF GaAs single crystal (9 kg), b) G5 mc-Si ingot (640 kg)

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Silicon Crystal Doping: Pesky Problems and Exotic Options for Batch and Continuous-feed Growth

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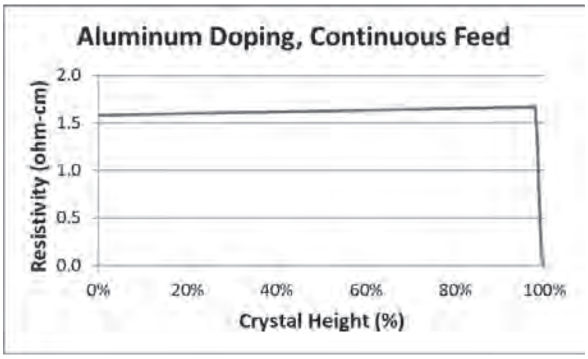
Silicon without dopants is a most un-useful material. With the necessity to control doping concentrations, perhaps no equation is more useful in semiconductor crystal growth than Scheil's equation for the segregation of impurities. While boron doping is well understood for cast-in-place and batch Czochralski growth, and the semiconductor industry has extensive experience with phosphorus and arsenic, there are many possibilities for doping control and process options that bear consideration. We present a study of doping techniques applied to different crystal growth schemes and the relationship to cost drivers such as yield and minority carrier lifetime.

In cast-in-place growth for multicrystalline and mono-like ingots, the main investigations have revolved around the use of upgraded metallurgical silicon and a compensated doping scheme where the phosphorus in the material overtakes the boron at the top of the ingot, but the first time yield impact is minimal. Current low poly prices have dried up most of the interest here, but rising prices will inevitably bring the topic back. The real difficulty comes in the recycling loop, where the top of the ingot is at worst unusable and at best perhaps 50% salvageable with a further directional solidification. Similarly, purely n-type studies have produced wafers with a wide range of resistivity, often from 3.0 – 4.0 at the bottom down to 0.2 – 0.3 ohm-cm at the top. While some cell architectures do better than others at handling the range, none can be optimal for the whole range, meaning that the n-type efficiency advantage is tempered.

The interesting possibility for crucible grown ingots is the option to integrate the crucible growth with a technique for continuous or semi-continuous supply of liquid silicon. Here, it is possible to operate at high atmospheric pressures and to incorporate strongly segregating dopants such as aluminum or even bismuth. A small quantity of the dopant is sufficient to dope the entire ingot and can provide a highly uniform doping distribution. In Fig. 1 the doping profile for an aluminum doped ingot is shown for continuous and semicontinuous feeding cases. Note that no dopant metering is used. The same can be done for other highly segregating p-type dopants if the minority carrier lifetime issues of aluminum are a problem. N-type doping is trickier since the relatively high segregation coefficients of phosphorus and arsenic demand a metering of dopant during the process, see Fig. 2.



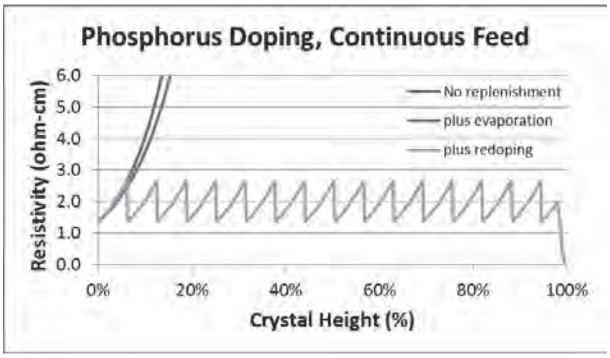


Fig. 1, P-type aluminum doping profile in a continuously fed ingot

Fig. 2, N-type phosphorus doping profile in a continuously fed ingot with small relative melt volume, with and without periodic dopant additions

A similar approach can be taken in Czochralski silicon, although here the low operating pressure has to be accounted for. It has been shown that continuous Czochralski technology can result in high doping uniformity. However, even in the simpler case of batch recharging, aluminum, indium, arsenic or phosphorus doping can be used to supply a batch process. The dopant uniformity of the ingots is traded off here against the length of the crystal and the accompanying yield loss associated with extra tops and tails.

Finally, it is possible to look at counterdoping schemes in some select cases in order to increase yield lengths. In CZ growth, the pulling of the tail and the leaving of potscrap works to lessen the yield impact of the highly concentrated last melt that results from compensation schemes, and the lifetime impact is less than is seen with UMG compensated material where metallic impurities necessarily accompany the dopants.

Achieving a square horizontal cross section of monocrystalline silicon ingots using Kyropoulos technique

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Abstract:

Production of silicon ingots for photovoltaic application can benefit from the combination of mono crystalline growth and shape control to obtain monocrystalline ingots with a square horizontal cross section.

The Kyropoulos crystal growth technique is investigated numerically and experimentally to grow monocrystalline ingots of silicon from a seed using a square crucible. The investigation shows that it is possible to grow unconfined single crystals of silicon from the seed inside the melt. The numerical results highlights that both radiation and convection will consequently influence the final crystal shape and size. Obtained experimental results show that ingots with a square horizontal cross section can be grown using facet growth kinetics. The square shape in this case is due to the faceted growth of the <111> crystalline orientation in a melt at low temperature gradient. In parallel, presented numerical results suggest that it is also possible to control the shape of the final ingot using a balance between heat conduction and advection in the melt. In the case of low Péclet number, the horizontal cross section of the ingot inherits the square shape of the crucible due to heat diffusion from the wall. The sides of the resulting ingot are facing the sides of the crucible. On the other hand, in the case of high Péclet number, the square shape of the horizontal cross section of the ingot is the result of strong flow loops coming from the four corners of the crucible where the sides of the ingots are facing the four corners of the crucible. The later square shape was rotated 45° compared to the crucible according to the vertical central axis.

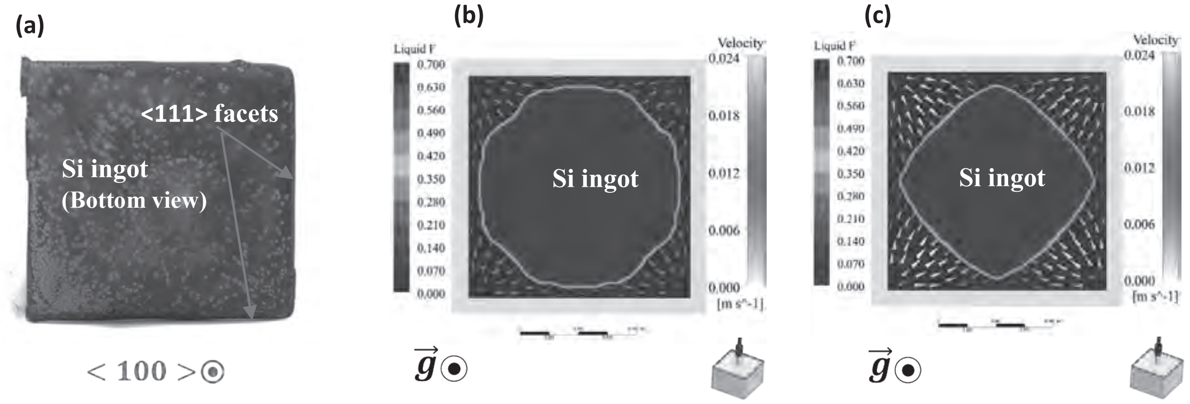

Figure 1. (a) experimental results of obtained Si ingot with square horizontal cross section using facetted growth, (b) Numerical results displaying the top view of the surface with shape control of the square horizontal cross section of the ingot using heat conduction in the melt (low Péclet number), (c) Numerical results displaying the top view of the surface showing shape control of the square horizontal cross section of the ingot using heat advection in the melt (higher Péclet number).

'Crystalline silicon on glass by low-temperature reduction using Al'

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Crystalline silicon thin films on glass substrate as wafer equivalent for the crystalline silicon-photovoltaics is a most attractive way to consiberably reduce the energy consumption for silicon production. Unfortunately due to its amorphous structure the processing of crystalline silicon on glass proved very complex, at least for a good electronic quality, offering so far little prospect of substantial cost reduction.
In this contribution, formation of multicrystalline silicon on standard floatglass, without the need of subsequent recrystallization steps is described for the first time.

The novel approach 'crystalline silicon synthesis (CSS)' has the potential for providing considerably less elaborate wafer equivalents, because it is based on low-cost soda-lime glass and aluminum, without requiring elemental silicon. The silicon-synthesis process is based on an aluminothermic reduction of SiO_2 in a chemically closed system, which takes place well below the aluminum melting temperature (< 660.4°C).

By means of the solid-state reaction during CSS ideomorphical crystalline silicon surfaces which by suitable process control can further coalesce towards a coherent crystalline silicon layer formed, building flakes of several hundred µm in lateral size and about 20 µm in thickness (Fig. 1). X-ray diffraction in Bragg-Brentano geometry of a contiguous c-Si layer (Fig. 1, right) confirm a high crystallinity by strong reflexes of the clearly separated Cu $K\alpha_{1,2}$-doublet, a clear texture along the the [111] direction and a narrow 111 reflex of 0.042°.
Raman measurements show the LO phonon line of crystalline silicon (3.64 cm^{-1}) with no evidence an amorphous phase or nanocrystalline grains (Fig. 2). By fitting the asymmetric part of the line shape according to (Fig. 2) a hole concentration from process-induced Al-doping in the order 10^{18} cm^{-3} was estimated at the surface. Furthermore, using electrochemical carrier concentration profiling prerequisite thin-film crystalline silicon photovoltaics evidence was obtained for decreasing doping concentration towards the glass substrate [2].

This work was sponsered by 'Deutsche Bundesstiftung Umwelt' DBU AZ-32945 – 24/2

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Einseitig kontaktierte amorph/kristalline Silizium Heterosolarzellen
Vom Wafer zur kristallinen Silizium-Dünnschichtsolarzelle auf Glas

Design of a Compact Multifunctional Heat Exchange-Directional Solidification System For Industrial Multi-Crystalline Silicon Casting

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The use of casting methods to produce multi-crystalline silicon (mc-Si) for solar cells is being currently used due to the relatively cheap production costs, compared with the production of higher quality but more expensive single-crystalline silicon (sc-Si) by using the more conventional Czochralski (Cz) growth method. In an attempt to bridge this quality gap, novel growth methods have emerged in recent years, using casting methods and sc-Si seeds to produce high quality mono-like silicon (ml-Si) ingots [1,2]. The wafers obtained from these ingots have been shown to result in high efficiency solar cells. However, several challenges have emerged, preventing a more widespread use of industrial mc-Si production.

In this work we report on the design and development of a multifunctional system (see fig. 1) at the industrial scale that can operate both as a Heat Exchange (HE), Directional Solidification (DS) furnace, or even as a combination of both techniques. This system will provide the benefits of both HE and DS techniques enabling an more accurate control of the mc-Si ingot quality both in terms of dislocation and impurity distribution due to a more complete control of the thermal field.

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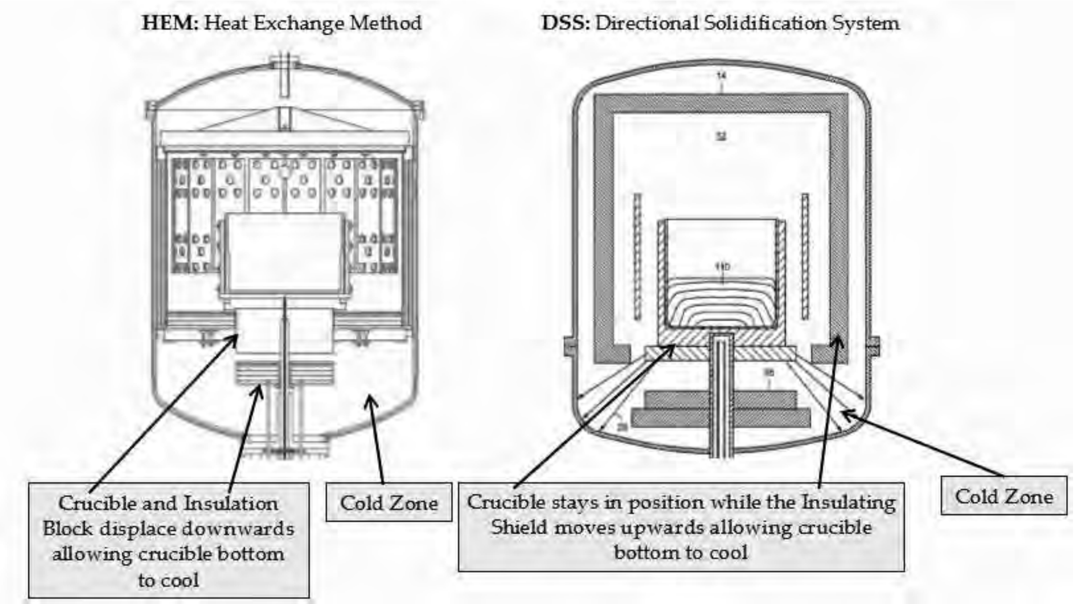

Fig. 1. Overview of the Multifunctional HEM-DSS Furnace Design for mc-Si Casting .

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Metallic impurities segregation controlled by electromagnetic field: Application to Silicon for PV

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Abstract

Chemical segregation of the dopants or of the solute is a major problem during the crystal growth from liquid phase. It has been proved that under purely diffusive transport conditions in the liquid phase, axially homogeneous crystals are obtained after an initial transient. On the contrary, when natural convection (buoyancy convection due to the thermal gradient) is present in the liquid the concentration of dopants or solute evolves continuously in the final crystal.

Silicon continues to be the most used material for the development of solar cells in the photovoltaic industry. Far from the performances of mono crystalline silicon obtained from expensive crystal growth methods like Cz method, the less expensive multi-crystalline silicon, obtained from a directional solidification process, is used as a base material for solar cells in order to keep a low production cost especially if the high performances of the cells are not a top propriety. Metallurgical materials could provide even a lower production cost if the impurities contamination could be controlled during the process. In order to reach the best possible electrical performances for the cells, a reduced number of crystal defects as grain boundaries and dislocations is desired. The impurities are generally trapped at the grain boundaries, but also they could precipitate and then decrease the quality of the solar cells. Another option is to induce a controlled fluid flow in the liquid. That could enhance the segregation and allows the imposing of a desired interface shape in a controlled way.

A vertical Bridgman type furnace (VB2) equipped with an electromagnetic stirrer was developed in order to study the solidification process of silicon under travelling magnetic field. The furnace was equipped with a Bitter type electromagnet that can provide a travelling magnetic field able to induce a convective flow in the liquid. As a result the axial segregation of metallic impurities is improved while controlling the interface deflection. A numerical model was developed in ANSYS Fluent commercial software to support and complete the experimental set-up. This paper will present experimental and numerical results of this approach.

Effect of Oxygen on Dislocation Multiplication during Growth of Crystalline Silicon for Solar Cell

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Multicrystalline silicon is the most widely used material for solar cells because of its mass productivities and cost-effectiveness. However, it has been known that high dislocation density is generated in a silicon ingot during the production process, which reduces minority career life time [1]. Therefore, it is necessary to reduce the dislocation density in order to improve the conversion efficiency of solar cells. It has been reported that oxygen in silicon crystals immobilizes dislocations by interaction between dislocations and oxygen atoms [2]. In other words, the oxygen atoms suppress multiplication of dislocations in silicon crystals.

We performed three-dimensional analysis of the dislocation density using a model considers oxygen atoms from the solidification process to the cooling process. We used the calculation model reported by Cochard and co-workers [3]. Temperature and oxygen concentrations used in the model were calculated with numerical simulation by vertical Bridgeman method [4], [5]. This paper reports the effect of oxygen on dislocation multiplication in silicon crystals.

We focused on two different portion, both of which are the bottom of the Si crystal and are high dislocation density and high oxygen concentration ($c_O = 8.71 \times 10^{17}\mathrm{cm}^3$). Figure 1 shows that mobile dislocation density distribution in the bottom of the Si crystal. Figure 2 shows that the history of difference of mobile dislocation density (N_m) between with and without taking into account the oxygen concentration at P and Q during growth and cooling processes. Difference of N_m at position P is larger than that at Q at first. However, final difference of N_m at P is smaller than that at Q. In summary, our calculation obtained that the effect of oxygen on dislocation density is large when dislocation density is small.

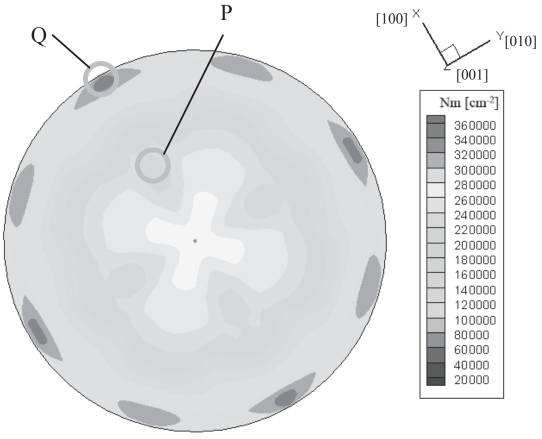

Figure 1. Mobile dislocation density distribution in the bottom of the Si crystal.

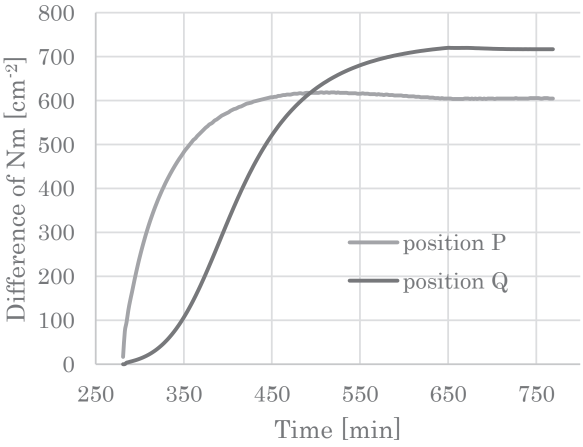

Figure 2. History of difference of mobile dislocation density at P and Q.

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Numerical study of temperature, velocity, stress and dislocation-density distributions during the growth process of 800 kg and 1600 kg silicon feedstocks

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Abstract:

Transient numerical simulations have been performed to investigate the evolution of the thermal and flow fields as well as stress and dislocations during the growth of multi-crystalline silicon ingots with two different silicon feedstock capacities, 800 kg and 1600 kg. The simulation results show that there are differences in the structure of the melt flow. In the 1600 kg case, the size and the strength of the upper cell generated by both the buoyancy and thermos-capillary force are much larger than the lower one generated by only the buoyancy force. On the contrary, those of upper cell for the 800 kg case are lower than the lower one. For the 1600 kg case, there is a reduction in the concavity of the crystal-melt interface near the crucible wall and an increase in the convexity of the interface with the melt at higher solidification fractions. Moreover, at the end of the solidification process, Von-Mises stress and dislocation densities in the ingot get lower about one order of magnitude in the case of 1600 kg in comparison with those in the case of 800 kg.

Growth of radiation hard PWO crystals in open furnaces – towards reproducibility

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Lead tungstate (chemical formula $PbWO_4$) is an intrinsic scintillator of fast decay time and high stopping power which is mostly utilized in high-energy physics experiments, e.g. in the Large Hadron Collider (LHC) in CERN, Geneva, Switzerland, where approx. 80,000 crystals are installed in the Electromagnetic Calorimeter (ECAL) of the CMS detector.

PWO is the desired scintillation material for the PANDA experiment (under construction) in the Facility for Antiproton and Ion Research (FAIR) in Darmstadt, Germany [1] and various ongoing detector projects. Crystals of improved properties (also known as PWO-II) were developed at Gießen jointly with the CMS/ECAL collaboration, the group at RINP (Minsk) and the former manufacturer BTCP (Bogoroditsk Technical Chemical Plant) in Russia (closed down and bankrupt in 2011) in standard Czochralski isolated pullers using RF heated Pt crucibles and nitrogen atmosphere. The project for production of lead tungstate was restarted in CRYTUR in summer 2014 aiming to compete for the lacking two thirds of the 11,000 PANDA crystals. The crystals are grown by the Czochralski method in resistively heated platinum crucibles placed in open-air furnaces, which are more cost effective than expensive closed systems. The chamber is purged with inert gas (argon or nitrogen) during the growth.

We achieved the growth of clear, straight and crack-free ingots (diameter 38 mm, weight over 2 kg) with good homogeneity. All-faces polished prisms of irregular shape ca. 25×22×200 mm are machined from the boule crystals. The measurements of key physical properties (a) light yield and (b) radiation hardness are performed at Justus-Liebig-University (JLU) in Gießen giving the final approval of acceptance. In-house measurement setups of light yield and transmission spectra (for on-site control) have been finished and are being calibrated to match with the JLU data. Currently (Mar 2017) almost forty prisms matching the PANDA specification [1] with light yield of 16-24 ph/MeV and radiation hardness 0.3-1.1 m-1 were produced, after starting semi-serial production in September 2016.

The performance of the lead tungstate scintillating material is greatly affected by point defects (mostly lead and oxygen vacancies) as PbO evaporates from the melt. Careful compensation of these defects is necessary in order to produce radiation hard material [2]. The origin and pre-treatment of raw materials seem to play significant role in radiation hardness as well. These effects are not fully understood, however various ratios in the mixture of smelted and pre-crystallized material with crystal cut-offs are providing consistent results.

It was demonstrated that radiation hard crystals (with very low density of crystal structure defects) can be reproducibly grown in open chambers, where fixed atmosphere is hard to achieve. The growth process is stable providing crystals of all key properties within the selected specification. The current progress is to map the technological limits in which the growth of PWO crystals with desired parameters is possible. The on-going goal is to decrease the cost of the product, e.g., by shortening the production cycle. All technologies (esp. crystal growth and machining) are under constant improvement in order to achieve that and increase yield.

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Large LGT ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) Langatate crystal growth by Czochralski technique for BAW and SAW applications

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Abstract

Recently, the development of electronic technology towards higher frequencies and larger band widths has led to interest in finding new piezoelectric materials, which could be used to make filters with larger pass band widths and oscillators with better frequency stability. So, LGT Langatate ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) gaining in popularity due to their superior piezoelectric material properties and performance [1]. This material have similar crystal properties as the quartz material, which is widely used in BAW, SAW applications such as resonators and piezoelectric vibratory gyroscopes. The langatate crystal has good stability at high temperatures and can be grown from the melt by Czochralski technique.

Large size LGT crystals have been successfully grown by several companies and laboratories [2,3]; however, it did not yet meet the wide commercial production requirements and especially the performance reproducibility. The main reason limiting this commercialization was the inhomogeneous properties of the crystals which caused by "disorder" structure. Whereas we realized that this inhomogeneous property could be improved by increase the quality of the crystal through controlling crystal growth technology.

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Development and producing of high-purity potassium dihydrogen phosphate for the large scale single crystals

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Potassium dihydrogen phosphate (known as KDP) with chemical formula KH_2PO_4 and its deuterated isomorph KD_2PO_4 (DKDP) are widely used as Q-switches, parametric oscillators and frequency convertors in laser technic [1]. High laser damage resistance (> 5 GW/cm^2) and optical transparency range (200 – 1500 nm) are the properties of KDP single crystals that made them almost irreplaceable material in very high peak power laser facilities [2]. The main line of the research on such type laser facilities is the realization of a pulsed scheme of controlled laser thermonuclear fusion, the most known of them are «National Ignition Facility» USA и «Megajoule» France. Besides above-mentioned benefit properties of KDP, possibility of large scaled (40-60 cm in aperture) single crystal growth from aqueous solutions is also very important. For realization such ambitious projects as National Ignition Facility more than several hundreds of optical elements made from large KDP single crystals with high degree of optical and crystalline perfection are required. This circumstance was the one of the main that triggered the development of fast growth methods of KDP large crystals [3]. It is certain, that optical properties either growth rate of crystals depend on purity of raw material. In case of rapid growth this dependence is more dramatic. Low crystal growth speed achieved by a low over-saturation allows structural units from taking the “right” lattice positions, thus supressing crystal defects formation and improving crystal quality; therefore, decrease of a growth rate causes superior crystalline structure. In growth process of large scaled KDP single crystals the most unfavorable is a presence of polyvalent metals like Al, Fe, Cr, Ti in growth solution [4-6].

Widespread industrial methods to produce high purity inorganic salts are crystallization, coprecipitation, purifying with chelating agents and ion exchange. Consideration of them with goal of obtaining high purity potassium dihydrogen phosphate gives us following disappointing conclusions: above-mentioned polyvalent metals have segregation coefficient > 1 [7], in other words they are co-crystallizing, therefore purifying of KDP by the crystallization method is impossible. Using coprecipitants and chelating agents is associated with exposure to foreign substances which could be a source of contamination. Ion exchange method would be rather effective, however even crystallization from purified solutions may cause concentrating of polyvalent metals in crystals. Moreover, designing of suitable regenerant for expensive ion exchange resin is a quite a bit of problem.

In this conference poster we are sharing our successful experience in development of technology producing high purity potassium dihydrogen phosphate applicable in processes of rapid growth of large scaled single crystals. Requirements to raw material for rapid growth of large scaled single crystals are also considered and likewise usability and comparison of efficiency of common industrial methods to produce high purity inorganic salts relating to KDP. To obtain high purity potassium dihydrogen phosphate we focused efforts on purification KDP solution using coprecipitant and then evaporated solution in the presence chelating agent.

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Modeling interface shape in Czochralski growth of sapphire crystals

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Numerical modeling is applied to investigate the influence of the forced convection in Czochralski growth of sapphire crystals (10 cm in diameter). The forced convection is generated by the crystal and crucible rotation. Global modeling is applied to compute the thermal field in the furnace and the convection in the melt. The shape of the growth interface is computed by using the deformable mesh technique. Internal radiative effects are taken into account inside the semi-transparent sapphire crystal. The modeling is performed at different stages of the crystallization process. Numerically computed shape of the crystal-melt interface is compared to experimental results taken from literature [1].

Numerical results show that the conical shape of the interface depends essentially on the internal radiative heat exchanges in the crystal, being less influenced by the buoyancy convection. The Marangoni effect enhances the flow near the triple solid-liquid-gas point, and generates a convex-concave shape of the interface (see Fig.1). As shown in Ref. [1], a convex-concave shape of the growth interface, along with the temperature gradient, determines the formation of facetted regions, which will be areas of localized stress.

Applying crystal rotation at rates greater than a critical value changes drastically the flow pattern in the melt. Computations performed at early stages of the growth, show a reversed convection at the sample center, underneath the crystal, when the rotation rate exceeds 20 rpm. In this case, the growth interface is less curved and exhibits a convex shape, so the facets formation could be avoided. If the crystal rotation rate is increased up to 30 rpm, the interface is distorted by the flow, and is therefore prone to facet formation.

Applying sole crucible rotation enhances the downward flow at the sample center, leading to increased interface curvature. Rotating both the crystal and crucible in opposite directions generates a complex flow pattern with three main vortices. The local change in flow direction near the growing crystal, has impact on the interface shape, which becomes distorted.

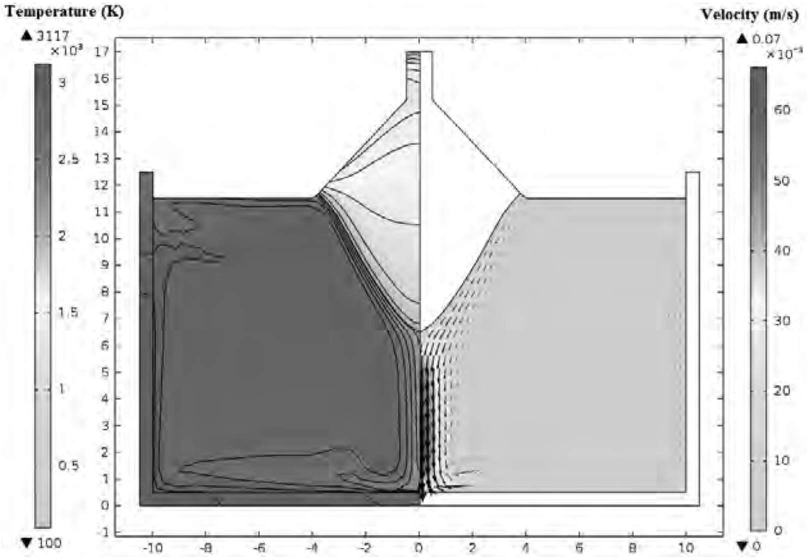

Fig. 1 Temperature distribution (left side) and velocity field (right side) computed without rotation in the early stage of the growth.

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Growth of and Scintillation Properties of $(Gd,Y)_3(Ga,Al)_5O_{12}$:Ce Crystals

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Ce doped $(Gd,Y)_3(Ga,Al)_5O_{12}$ multicomponent garnet was reported to be an excellent scintillation crystal because of its high yield and good energy resolution, however little attention was paid on the optimal Gd/Y and Ga/Al ratio within the crystal. This work focuses on the optimization of $(Gd,Y)_3(Ga,Al)_5O_{12}$:Ce^{3+} scintillators using a combination strategy of pre-screening and scale-up. Ce-doped $Gd_xY_{1-x}Ga_yAl_{5-y}O_{12}$ (x= 1, 2 and y=2, 2.2, 2.5, 2.7, 3) polycrystalline powders were prepared by high-temperature solid state reaction method. The structure of the synthesized garnet phase was analyzed using X-ray diffraction measurement. By comparing the radioluminescence intensity, the highest scintillation efficiency was achieved at a component of Ce^{3+}: $Gd_2Y_1Ga_{2.7}Al_{2.3}O_{12}$. A Ce1%: $(Gd_2Y_1)Ga_{2.7}Al_{2.3}O_{12}$ single crystal with dimensions of Ø35×40mm was grown by Czochralski method using [111] oriented seed. The growth atmosphere contained 30% CO_2 in the Ar to depress the vaporization of Ga_2O_3. The transmittance of the grown crystal is around 84% in the concerned wavelength from 500 to 800 nm. Its 5d-4f emission of Ce^{3+} is at 530nm (Fig.1). The light yield of a Ce1%: $Gd_2Y_1Ga_{2.7}Al_{2.3}O_{12}$ single crystal slab at a size of 5×5×1 mm^3 can reach about 65,800±3290 photons/MeV(Fig.2)， which is the highest value ever reported in the literature on garnet scintillators, along with two decay components of 94 and 615 ns under excitation of ^{137}Cs source.

Key words: GYGAG:Ce garnet; Scintillation crystals; Czochralski method.

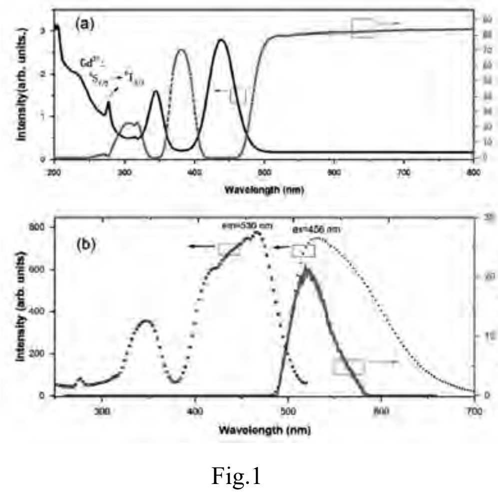

Fig.1

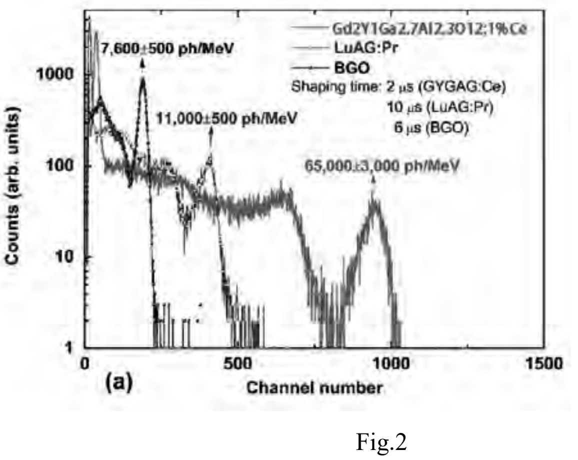

Fig.2

Fig.1 Optical transmission, absorption (a) and photoluminescence (b) of GYGAG:Ce crystals

Fig.2 Pulse height spectra of GYGAG:Ce crystal exicted with ^{137}Cs

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EFG method for novel garnet and perovskite materials development

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The EFG (Edge-defined Film-fed Growth) method introduced in 1971 by La Belle[1] enables production of sapphire single crystals in various shapes. The EFG method is similar in principle to the older Stepanov's (1953) method focused for the growing of the shaped single crystals of metals[2].

The EFG method is based on rising of the melt by capillary action[3] through a channel. The profiled crystal is grown from a thin layer of melt on the top of the shaping element which defines the cross-section of the crystal. Although the EFG method is primarily applied in sapphire production, it can also be used for a wide range of materials like are metals, silicon and oxides.

Our aim was to carry out material screening for laser and scintilating applications with low cost and in short time. For novel materials development the µPD (Micro Pulling Down) technique is today commonly used. The EFG method can well serve for the same purpose. The first material which we started was *Sapphire* (Al_2O_3) and D-elements as a dopant. The second tested materials were garnets *YAG* ($Y_3Al_5O_{12}$) and *LuAG* ($Lu_3Al_5O_{12}$) doped with various RE (Rare-earth dopant). The last and most complex matrix was perovskite *YAP* ($YAlO_3$) doped with RE.

All the prepared crystals either in the form of rod, plate, tube or fibre were in sufficient optical quality to enable spectroscopic measurement, however not enough for laser radiation measurement.

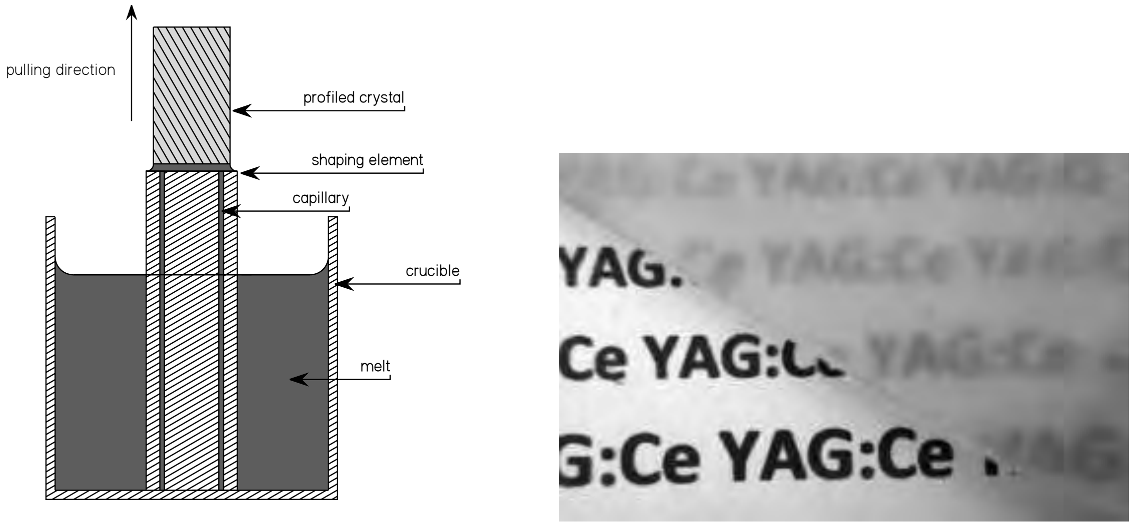

Figure 1. *EFG method scheme and (as grown) transparent YAG:Ce plate*

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Improvement of CALGO crystal: a promising host material for ultrafast laser application

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$CaGdAlO_4$ (CALGO) crystal is a promising laser host crystal since it has a disordered structure and should be a good candidate for the ultra-fast laser[1-3]. Structural disorder can lead to differing crystal-field potentials at spatially differing active ion sites. As a result, the absorption and emission spectra can be inhomogeneously broadened, which provides great convenience for laser diode pumping and mode locking in the generation of ultrafast laser. So far, remarkable achievements have been made by Yb^{3+} doped CALGO crystals in the output of ultrafast laser due to its broad spectra and good thermal conductivity.

However, it was interesting to find that the commercial Yb:CALGO crystals of different batches and producers were usually with different shades of brown color, and the color always became deeper after annealed in air at high temperature[4]. This color issue of the CALGO crystal should be the first puzzle to be faced, especially if it was used in the Vis-UV region in future.

In this work, the CALGO single crystals have been grown in different oxygen concentration atmospheres by the Czochralski method, as shown in Fig. 1. The origin of coloration was studied by the density functional theory, which showed that the brown coloration was due to the interstitial oxygen atoms. The colorless CALGO was grown under inert gas atmosphere and exhibits a wide transparency range of 227-7140 nm. The maximum phonon energy was determined to be as low as 618 cm^{-1}. The colorless CALGO host crystal with disordered structure, good thermal conductivity, low maximum phonon energy and wide transparency is promising for ultrafast ultraviolet and visible laser applications.

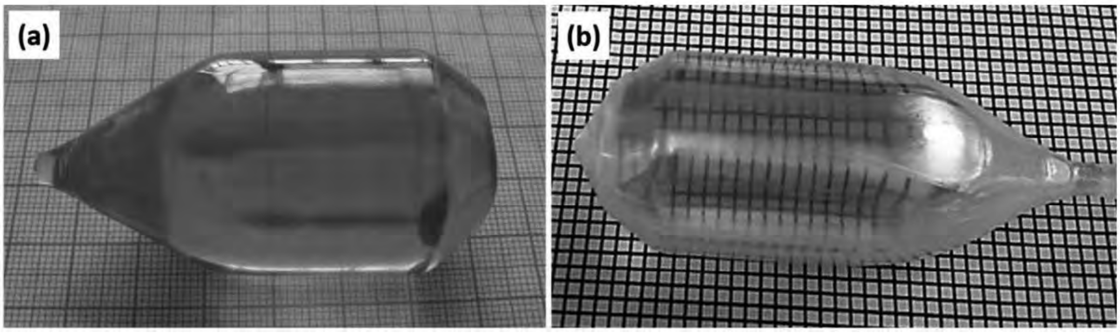

Fig1. CALGO single crystals grown in different oxygen concentration atmospheres by the Czochralski method

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Scintillation Properties of Single Crystal Garnet Scintillators

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Rare earth based garnet structures are attractive matrices for scintillators due to their relatively high density, cubic symmetry, lack of cleavage planes, congruent melting, lack of solid-solid phase transitions, large band gap, insensitivity to moisture, and existence of a trivalent site to accommodate Ce^{3+} doping. They have been successfully synthesized in both single crystal and polycrystalline forms with similar, although not identical, properties. In this report we review the scintillation properties of simple and mixed cation garnet scintillators in single crystal form. Particular attention is paid to light yield, energy resolution, and scintillation time profile as function of rare earth species and dopant concentration. In addition, we consider the use of codoping for tailoring various scintillation properties.

July
05

P7.8

Growth and Characterization of Zinc tungstate ($ZnWO_4$) Raman crystal

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Stimulated Raman scattering (SRS) is an important technique for broadening the laser spectra. As an inelastic scattering process, there is a mass of heat generated during the SRS process. Thus the Raman-active crystals with high thermal conductivity are favorable. In this work, a large size $ZnWO_4$ crystal with good quality was successfully grown by the Czochralski method and the dimensions are up to Φ 35 mm × 70 mm as shown in figure 1(a). The anisotropic thermal properties were measured including specific heat, thermal expansion, and thermal conductivity. The coefficients of thermal conductivity are calculated to be 3.06 $Wm^{-1}K^{-1}$ along X direction, 3.17 $Wm^{-1}K^{-1}$ along Y direction and 4.52 $Wm^{-1}K^{-1}$ along Z direction. An *a-cut* crystal was used to for realizing the SRS process with the laser wavelength shifted from 532 nm to 558.95 nm as shown in figure 1(b). These indicate that $ZnWO_4$ crystal is a good Raman material with excellent thermal and optical properties.

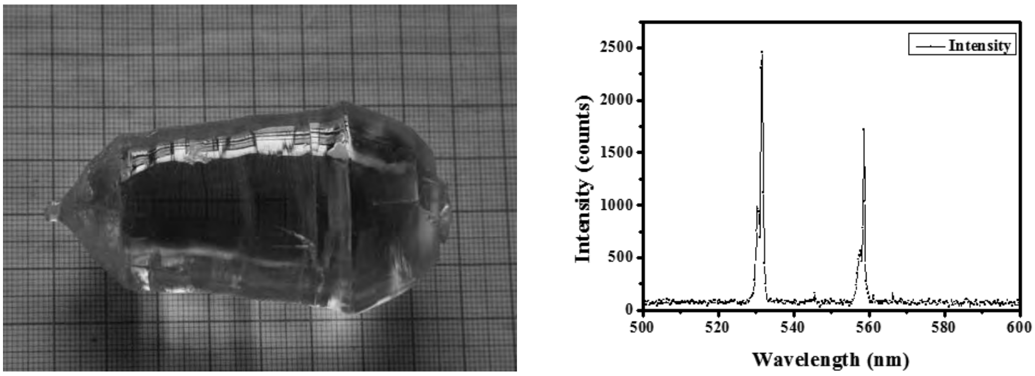

Figure 1. (a) The as-grown $ZnWO_4$ crystal by CZ method; (b) Relationship between output light and input light of the SRS performance experiment.

Synthesis and characterization of $CaCoSi_nO_{2(n+1)}$ ceramic pigments by X-ray diffraction, SQUID magnetometry, scanning electron microscopy and X-ray photoelectron spectroscopy

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Cobalt-based pigments are being commonly used in the ceramic industry as blue glazes and also for bulk coloration of unglazed porcelain stoneware [1]. Cobalt is usually connected with blue colorization, though the color palette includes also pink, green, violet, brown and black. The color of Co^{2+} compounds depends on the ligands coordination around its ion in the host lattice. If cobalt is in tetrahedral coordination, the color is deep blue [2] while, if it is surrounded by six or eight atoms of oxygen the hue shifts to pink or violet [3]. In case of glasses and many crystal structures Co^{2+} prefers the tetrahedral coordination, but in case of $CaCoSi_nO_{2(n+1)}$ ceramic it does occupy the octahedral or cubic site.

Cobalt based phases like $CaCoSi_nO_{2(n+1)}$ are interesting candidates as ceramic colorants particularly as in comparison to the commonly used Co-olivine Co_2SiO_4 and spinel $CoAl_2O_4$ they can host a lower cobalt content maintaining a bright pink color. It is important in order to minimize the use of cobalt because of its toxicity, and expensiveness [4].

The aim of this work was to prepare different compositions of $CaCoSi_nO_{2(n+1)}$ ($n = 1, 2, 3, 4$) ceramic using solid state reaction. The obtained samples were characterized by the following methods: X-ray diffraction, SQUID magnetometry, scanning electron microscopy (SEM/EDX) and X-ray photoelectron spectroscopy (XPS).

Polycrystalline samples with nominal stoichiometry $CaCoSi_nO_{2(n+1)}$ $n = 1, 2, 3, 4$ (called later on N1, N2, N3, N4) were synthesized using ceramic method in the following way. Stoichiometric amounts of $CaCO_3$ (Sigma), Co_3O_4 (Sigma) and amorphous silica (Sigma) in quantity appropriate for 2 g of the final products were mixed together in a planetary mill for 2 h at 350 rpm. The powders were removed from the cell using acetone, dried and pelletized in a 10 mm pressure die into several discs, each around 1 mm thick. Starting materials were gray with N3, N4 samples being visibly brighter. The discs were placed in Al_2O_3 based boats in a chamber furnace. All samples were heated at 1150 °C in 48 h and cool down to room temperature. After that, the N1, N3 and N4 specimens were bright pink and N2 slightly blue with visible signs of glazing of the pellet. This led to the conclusion that the N2 material might have been close to its melting point so a new synthesis N2 was carried out at a lower temperature of 1100 °C. The obtained sample was pink with slight blueish hue, without glassy surface. After the first heating, the pellets were again ground in a planetary mill. A second round of pelletizing and reheating was carried out and after that, sample N2 lost its blue hue.

Despite earlier reports [4, 5] claiming the existence of phases N3 and N4 only one the (N2) $CaCoSi_2O_6$ was found to exist as a well characterized phase. Compositions N3 and N4 were found to be dual phase consisting of N2 and the excess of SiO_2. Additionally the crystalline samples were pink not blue.

For stoichiometric composition N2 synthesized at 1100 °C we have found monophasic pink $CaCoSi_2O_6$ pyroxene with cobalt in octahedral coordination. X-ray diffraction and SQUID magnetometry confirmed a single phase with magnetic transition at about 12 K.

Samples made at 1000 °C or lower had a slight violet hue which was found to be connected with the presence of Co-äkermanite $Ca_2CoSi_2O_7$ with Co^{2+} in tetrahedral coordination. The presence of $Ca_2CoSi_2O_7$ was also clear from SQUID measurements as an additional transition at 4 K.

One sample N2 synthesized at > 1150 °C melted in the furnace creating a deep blue glaze, which was caused by tetrahedral Co^{2+} in a glassy phase.

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Growth and optical, structural, mechanical, thermal and dielectric studies of Zinc Thiourea Sulphate single crystal

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ABSTRACT

The growth of Zinc Thiourea Sulphate (ZTS) Single Crystals is analysed in this study. The crystals were grown by slow evaporation technique. The X-Ray diffractions study indicates that the prepared grown crystals confirm the crystal structure for ZTS crystal. The presence of Sulfur- to- Zinc bonds in the complex has been revealed by Fourier transform infrared analysis. The optical characterization shows that the grown crystal having ZTS crystal has low UV cutoff of 220nm and has a good transparency in the visible region. The thermal analysis shows that the Zinc Thiourea Sulphate can be expoliated up to 240°C of ZTS Single Crystal. The Vicker's microhardness number was found to increase ZTS crystal which studies the mechanical stability of the grown crystal. The dielectric properties of dielectric constant as function of frequencies 80KHz room temperature for electro optic modulators of ZTS Single crystal.

Keywords: ZTS, FTIR, UV-Visible, Micro hardness test, Powder XRD, Thermal analysis, electrical studies.

July
05

P8.2

The newest LiGaTe$_2$ crystal thermal data and mathematical modeling of the crystal growth process

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LiGaTe$_2$ (LGT) is a perspective laser radiation converter in the mid-IR range. The crystal has a wide transmission area (T = 0.52 – 21 µm), high nonlinear susceptibility (d_{36} = 43 pm/V) in combination with a high birefringence coefficient (Δn = 0.09) [1].

In a series of experiments the elementary Li, Ga and Te were used as starting materials. During the research we found the charge composition from which stoichiometric crystals had been grown. The melting point was determined by DTA as 945 K. LGT crystals were obtained up to 8 mm by the Bridgman-Stockbarger technique using the furnace with controlled heat exchanger.

The thermal field behavior was modeled for this system. The crystal growth process mathematical model based on the thermodynamic characteristics of the material using the STR Group Crystal Growth Simulation (CGSim) was constructed. On its basis the optimal thermal unit configuration was developed and thermal conditions were defined ensuring the convex solidification front maintenance throughout the growth process. The 4-zone Bridgman-Stockbarger crystal growth vessel with the low radial and constant axial gradients was engineered. Evaluation experiments with positive results were obtained.

According to the temperature heat capacity dependence of the LGT crystal there was no material decomposition up to 673 K recorded by TGA.

The heat capacity equation was obtained [2], the curve Cp (T) was constructed Eq. (1).

$$Cp(T) = 100.01 + 0.0219 \cdot T - 191210 \cdot T^{-2} \qquad (1).$$

It is noted that all the experimental points and curve, respectively, lie above the classical limit 3R per average gram-atom (for LGT – 100 J/mol·K) (Fig 1a.). The sample mass lack absence has been proved up to 673K by TGA (Fig. 1b).

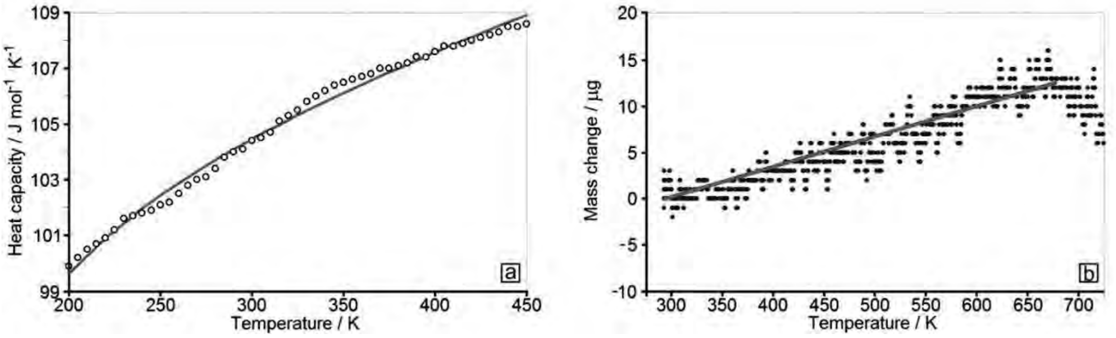

Fig. 1. The circles show the experimental values, and the line - smoothed dependence in the Maier-Kelley polynomial form (a) and TGA data (b).

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A novel horizontal Bridgman growth of SnSe crystal and its thermal properties

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The semiconductor of SnSe with different dimension has attracted extensive interest because of its interesting thermal, electrical and optical properties, as well as its widespread applications in thermoelectric device, infrared electronic devices, switching devices and so on. Among them, the theoretical calculation, crystal growth, property adjustment of SnSe crystal were reported in many works. However, the growth of large size SnSe crystal is seldom reported and the as-grown SnSe crystal is always easy to break as the structure undergoes a phase transition from Cmcm to Pnma phase during crystal growth. Moreover, the different thermal properties of SnSe crystal should be measured, because they were of great importance for large size crystal growth and fabricating devices. Here, a novel horizontal Bridgman method and B_2O_3 encapsulant was employed to grow the pure SnSe crystal and maintaining the stoichiometry ratio. The SnSe crystal was grown in a PBN crucible and the size up to 2 mm×15 mm×10 mm. The TGA and DTA curve of SnSe crystal were measured, which were helpful to choose suitable temperature in different growth process. Besides, the thermal expansion coefficients in different axial direction were also examined. According to the results, the thermal shock resistance and thermal expansion of SnSe crystal can be evaluated and benefit to fabricating SnSe-based devices.

Analysis of dislocation density in CZT Bridgman crystal growth using computer modeling

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$Cd_{1-x}Zn_xTe$ (CZT) crystals are used for manufacturing of room temperature radiation detectors, IR filters and used as a substrate for epitaxial growth of HgCdTe (MCT). Quality and performance of devices manufactured using CZT crystal and wafers depend on the concentration of crystal defects, such as dislocations, inclusions, grain boundaries, and on the homogeneity of Zinc concentration distribution over the crystal volume. The traditional approach for crystal growth technology optimization is experimental. Due to very low growth rates of CZT crystal, such approach is expensive and time-consuming. Accurate and detailed computer models help to significantly reduce the time and cost of process optimization [1]. In the present work, we demonstrate advanced computer model of CZT crystal growth, which includes multiple novel capabilities.

Presented computer model of CZT Bridgman crystal growth process is created in CGSim software. Crystal growth stage is calculated coupled with the melt flow with an account of the effect of Zn concentration on the melt convection. Calculated results also include distribution of Zn concentration in the grown crystal to analyze the effect of growth conditions on radial and axial uniformity of Zn concentration.

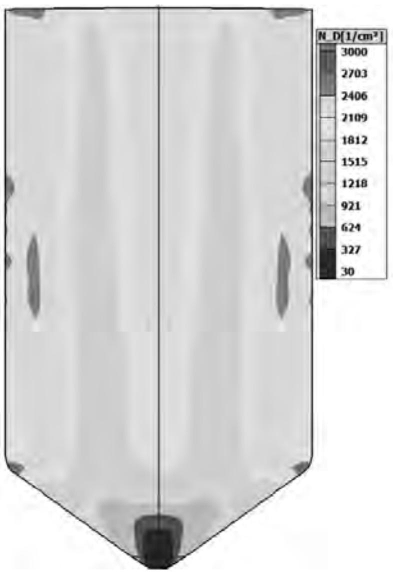

Figure 1. Example of calculated dislocation density distribution in CZT crystal.

Plastic crystal deformation due to thermal stresses during growth and cooling stages is analyzed within Alexander-Haasen model [2]. Effect of growth and cooling conditions on dislocation density is analyzed and discussed. Calculated dislocations density distributions for different process conditions are compared to commonly used criterions of crystal quality: melt/crystal interface shape and temperature gradients.

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IWCGT-7 2017 - Thursday, July 06

Session 7		**Oxide crystal growth II** Chairs: Merry Koschan (Univ. of Tennessee, USA), Steffen Ganschow (IKZ, Germany)
09:00	e)	Encarnacion Garcia Villora (NIMS, Tsukuba, Japan) **Part 1: Single-crystal phosphors for high-brightness lighting** **Part 2: Ultimate UV-IR Faraday rotators, CeF_3 and $(Tb_{1-x}Lu_x)_3Sc_2Al_3O_{12}$**
09:50	f)	Jiyang Wang (Shandong Univ., China) **Laser and scintillator crystals**
10:40		Coffee
10:10		**DGKK poster award ceremony**
11:20	g)	Igor Pritula (ISC NAS, Ukraine) **Growth of Ti:Sa crystals for producing of large-size laser elements**
12:10		Workshop Closing
12:20		Lunch

Part 1: Single-crystal phosphors for high-brightness lighting
Part 2: Ultimate UV-IR Faraday rotators, CeF_3 and $(Tb_{1-x}Lu_x)_3Sc_2Al_3O_{12}$

Encarnación G. Víllora[1], Daisuke Inomata[2], Kazuyuki Iizuka[2], Akiharu Funaki[3], Kiyoshi Shimamura[1]
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In the recent years, white LED illumination is xpanding. This is based on blue LEDs plus owder phosphors (CPPs) embedded in binders. e low thermal conductivity and low irradiation of binders, as well as the decreasing conversion y of CPPs with the temperature rise, current ents are easily overheated and degraded in er applications. Therefore, all-inorganic stable phosphors are since long demanded to compact and efficient high-brightness (HB) Ds & LDs.

to obtain phosphors with the best possible roperties, we have proposed to produce these as ystal phosphors (SCPs)[1-2]. In contrast to CPPs, ve a high purity and crystalline quality, and ssess an outstanding conversion efficiency and tability (see Fig.1). Additionally, SCPs have the advantages of being binder-free & all-inorganic s having a high thermal conductivity. Therefore, eet the requirements for HB applications, in r for emerging fields such as laser projectors headlights. Furthermore, there is a demand for blue-to-green phosphors in order to bridge the ent LED 'green-gap'.

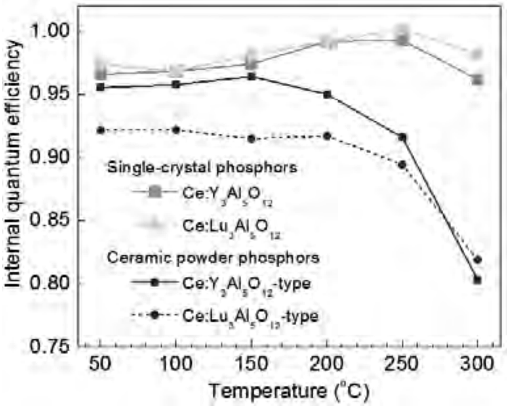

Fig. 1. Internal quantum efficiency of SCPs as a function of the temperature in comparison with equivalent CPPs of highest quality.

Optical isolators (OIs) protect lasers from ackreflections. For it, the polarization plane of has to be rotated 45 degrees by the Faraday ing a lengthy material that is highly transparent esses a high Verdet constant. $Tb_3Ga_5O_{12}$ (TGG) ystals are used for the visible and near-IR, in growth difficulties and optical losses, while 5 nm, there are only poorly performing glasses.

demonstrated for the first time the high of CeF_3 as Faraday rotator for the UV-visible th region. This crystals is highly transparent 300 nm and exhibits an outstanding Verdet in the UV (Fig.2)[3]. On the other hand, for the nd near-IR regions we have developed a new garnet, $(Tb_{1-x}Lu_x)_3Sc_2Al_3O_{12}$ (TLSAG)[4]. d with TGG (Table 1), TLSAG exhibits a ansparency, a 20% higher Verdet constant, as higher radiation resistance.

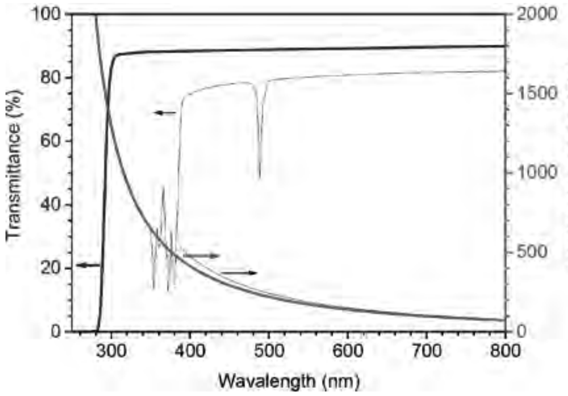

Fig. 2. Transmittance (blue) and Verdet constant (red) of CeF_3 in comparison with reference TGG (black).

Table 1. Comparison of transparency range and Verdet constant of oxides and fluorides.

Material	CeF_3	TLSAG	TGG
Trans. (nm)	> 300	> 395	> 395
Verdet const. (rad/Tm) at various wavelengths			
310 nm	1090	-	-
405 nm	397	549	455
633 nm	123	160	133
1080 nm	38	49	40

Recent development and application of nonlinear optical and scintillation crystals in China

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Functional materials play an important role in science and technology, eventually leading changes in modern life. Nonlinear optical crystal is a kind of functional crystal which can convert the laser frequency to meet ever increasing needs. Scintillation crystals can emit special light responded for the excitation of high-energy radiation. Both crystals have significant applications in many areas, including the physics, photonics, military and so on. Here, the recent development of nonlinear and scintillation crystals in China is reviewed. Growth, characterization and some application of nonlinear crystals ranged from the deep-UV to mid-infrared will be introduced, especially for self-frequency-doubling and deep-UV crystals will be highlighted. The development of representative scintillation crystals are involved, including the garnets, silicates, halides, etc., and their applications are exhibited. The future developing directions of these two kinds of crystals and their possible promising applications are discussed.

Growth of Ti:Sa Crystals for Producing of Large-Size Laser Elements

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Due to their unique lasing and thermomechanical properties, Ti:sapphire (Ti:Sa) crystals are widely used in ultrahigh power laser systems. Nowadays there exist projects aimed at creation of systems such as ELI (EU), SIOM (China), PEARL (USA), Vulcan (UK) with a power up to 10 PW and a focused intensity of ~ 10^{23} W/cm^2 for basic and applied research in high-energy physics. They imply the use of Ti:Sa large aperture gain elements with a diameter up to 150-200 mm [1]. High-quality Ti:Sa large crystals are obtained by different methods: HEM, TGT and Kyropoulos. Basic requirements for the gain elements are high optical homogeneity, that defines the spatial laser beam profile and the ability to achieve high energy density, and low content of Ti^{4+} ions, which are responsible for the formation of Ti^{3+}-Ti^{4+} pairs and residual absorption of laser generation with a maximum at 800 nm [2]. The optical homogeneity of the crystals depends on growth and annealing conditions, defects (blocks, dislocations) and activator (Ti^{3+}) distribution in the crystal bulk. Traditionally, annealing and growing under reducing conditions are used to obtain Ti:Sa with a low residual absorption.

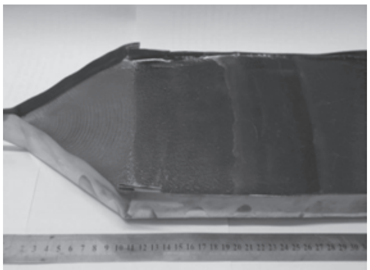

Fig. 1 Large size (170x170x35 mm^3) Ti:Sa crystal grown by new modified HDC method.

The aim of the present work was to study the conditions for the growth of large-size Ti:Sa crystals by the method of horizontally directed crystallization (HDC). The latter is one of most effective methods for the obtaining of large-size (up to 350x500x40 mm^3) sapphire crystals which can be used for producing for windows for aerospace engineering, as well as for the growth of laser and scintillation crystals [2]. A new modified HDC method for growing large size (up to 175x175x40 mm^3) Ti:Sa crystals in reducing gaseous medium ($CO+H_2$) with a high homogeneity of the activator distribution and a low ion content, was developed [3]. The structural, optical and laser characteristics of these crystals were investigated. An effective method of lowering the content of Ti^{4+} ions and residual absorption was shown to be based on the use of carbothermical treatment of the initial charge. The crystals are to be suitable for fabrication of laser gain elements with a FOM above 150 and wavefront distortion within λ/6.

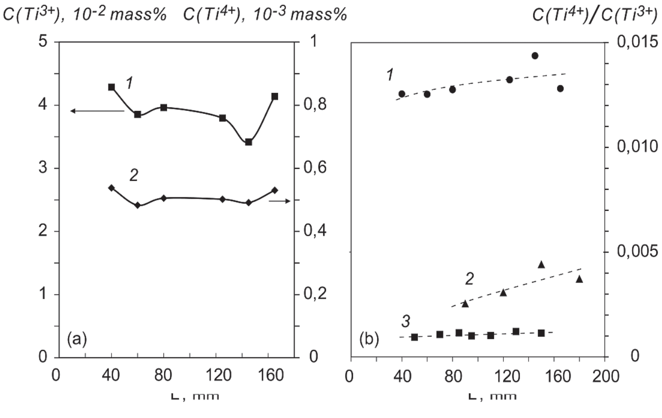

Fig.2 (a) Activator distribution in the charged states (*1*) Ti^{3+} and (*2*) Ti^{4+} over the length of the Ti:Sa crystal. (b) variation in the Ti^{4+}/ Ti^{3+} ratio over the length of the crystal grown in the CO + H_2 atmosphere (*1*), (*2*) the crystal grown in the Ar+(CO, H_2) atmosphere and (*3*) with carbothermal treatment of the initial raw material.

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LEIBNIZ-INSTITUT FÜR KRISTALLZÜCHTUNG

The Leibniz-Institut für Kristallzüchtung is a unique research institution in Europe. Our mission is to explore the scientific and technological fundamentals of crystal growth, from basic research to pre-industrial development. Our materials are of fundamental importance for modern applications in micro-, opto- and power electronics, in photovoltaics, in optics, as well as in laser and sensor technology. All these applications require crystalline materials with high perfection and specific chemical and physical properties.

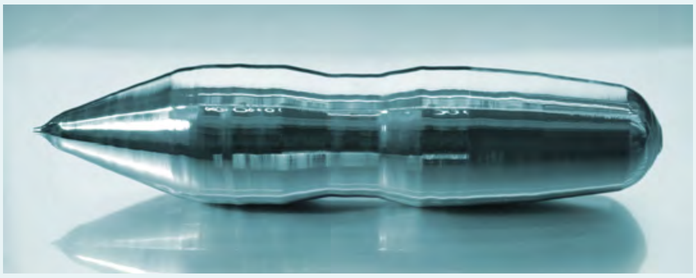
Furthermore, we provide scientific services for research institutions and industry. This includes, in particular, the growth of specific crystals for research purposes, the characterization of crystalline materials or industry-oriented technology development.

The research and service tasks include:

- development of technologies for growth, processing and characterization of bulk crystals, of crystalline structures
- supply of crystals with non-standard specifications for research and development purposes
- modelling and theoretical investigation of crystal growth processes
- experimental and theoretical investigations of the influence of process parameters on crystal growth processes and crystal quality
- development of technologies for chemo-mechanical processing of crystalline samples and scientific investigation of related processes
- physico-chemical characterisation of crystalline solids and development of suitable methods as well as investigation of the correlation between physical properties and related physical processes
- development and construction of components for growth, processing and characterization of crystals

Materials grown at the IKZ include:

- Semiconductor crystals like silicon for use in micro- and power elctronics, photovoltaics, germanium for thermolectrics or as detector material; Si/Ge layers and nanostructures for photovoltaics and thermoelectrics. Silicon layers on glass for photovoltaics
- Gallium arsenide as semiconductor for wireless communication and in microwave and high-frequency technology
- Oxide and fluoride crystals for laser-, opto- and sensor technology; transparent semiconducting oxides as wide bandgap materials for electronic applications or as substrate for epitaxial thin film growth
- Aluminium nitride as substrate material for UV-optoelectronic devices (LEDs, lasers, sensors)
- Ferroelectric and semiconducting oxide layers for micro- and power electronics, sensor applications and data storage



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	Sun, July 02	**Mon, July 03**		**Tue, July 04**		**Wed, July 05**		**Thu, July 06**	
08:50		**S1**	**Silicon & III-Vs**	**S3**	**Oxide I**	**S5**	**mc-Silicon for PV**	**S7**	**Oxide II**
09:00		a)	M. Rosch	a)	J. Frank	a)	A. K. Søiland	e)	E. G. Villora
09:50		b)	J. Kearns	b)	Z.-G. Ye	b)	G. Erfurt	f)	J. Wang
10:40			Coffee		Coffee		Coffee		Coffee
11:10		c)	L. Stockmeier	c)	C. Guguschew	c)	Z. Li		Poster award
11:20								g)	I. Pritula
11:50		d)	S. Nizhizawa	d)	G. Dosovitskiy	d)	J. Laurent		
12:20									Lunch
12.45			Lunch		Lunch		Lunch		
14:20		**S2**	**Wide Bandgap**		**Free Time**	**S6**	**Emerging Fields II**		
14:30		a)	A. Kuramata			c)	M. Schreck		
15:20		b)	M. Bockowski			d)	S. Pimputkar		
16:00	Registration								
16:10			Coffee				Coffee		
16:20				**S4**	**Emerging Fields I**				
16:30		c)	R. Bondokov	a)	K.-H. Chen	e)	C. Frank-Rotsch		
17:20		d)	T. Straubinger	b)	V. Manomenova	f)	N. Stoddard		
18:00	Dinner								
18:30			Dinner		**Workshop Barbecue**		Dinner		
19:30	Panel Discussion		Poster I				Poster II		