INVITED LECTURES

Professor CZOCHRALSKI - Distinguished Scientist and Inventor

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Prof. CZOCHRALSKI was born in Central Poland in 1835 and died 50 years ago in Poznan. In 1904 he moved from Poland to Berlin where attended university courses in chemistry. He obtained engineering degree and started to work as assistant to famous scholar Wichard von Moellendorf. Right from the beginning of his career he took interest in what can be now described as physical metallurgy. He pioneered research in plastic deformation of single crystals and contributed to crystallography. In 1929 received a honorary degree from Warsaw University of Technology and a year later accepted professorship position with the Faculty of Chemistry at this school. Soon after he organized Department and later Institute of Metallurgy and Metal Science. His major interest continued to be with processing of metals and in particular he researched crystallization. Research in this field resulted in invention of the famous CZOCHRALSKI method for growing large monocrystals, which paved the way to modern technologies of electronic materials. He also studied elastic, plastic properties of metals and their corrosion resistance. Professor CZOCHRALSKI was also a pioneer in what is now described as technology transfer. His inventions match excellence of scientific achievements. Obtained a number of patents in Germany and Poland.

Professor CZOCHRALSKI lived in turbulent times. Holding two citizenships, Polish and German, and acting successfully both within business and academia he made a great number of fans and enemies. Before the World War II was involved in much publicized legal disputes with a staff member from WUT. During the war continued with research in the unit approved by the German administration. This has been judged unfair by a group of professor who made him to retrieve from the University live. He continued with his inventions in Kcynia, his birthplace.

The scientific foundations build at WUT by CZOCHRALSKI proved to be resistant to historical misfortunes. Faculty of Materials Science and Technology, the leading materials research institution in Poland is proudly continuing tradition of metallurgy and metal science at Warsaw University of Technology. This Faculty is also one of the leaders in technology transfer taking fully with the reach achievements of its famous founder.

History, state of the art and future outlook of Silicon Czochralski crystal growth

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At present, about 99% of all semiconductor devices are made from monocrystalline silicon. 95% of silicon single crystals are grown according to the Czochralski technique.
In 1950 the first silicon single crystal were grown by CZ-technique, 2 year after the invention of transistor, which was first made from germanium. Ten years later Wacker started Silicon crystal growth by crucible pulling in small cups with charge weight between 50 and 100 g and crystal diameter of about 0.5”. The average production was 700 g per month. For economical and technological reasons the diameter increased step wise to 300 mm (12”) and the charge weight to 200 – 300 kg today. The next puller generation is equipped for 300mm crystal length up to about 3m. In 1994 Wacker Siltronic has demonstrated the growth of first 400mm crystals and in 2000 SSI has successfully grown 400 and 450 diameter crystals with charge weights up to 450kg in a research project.

Parallel to the increase of crystal diameter and weight the material properties were also improved. The first essential step was the invention to grow dislocation free crystals as developed by Dash in 1959. This property is an absolute necessity for manufacturing of highly integrated devices. The development of mechanical holding systems allow to use the dash neck technology with necks below 5 mm up to now.

In the 1970´s, the beneficial effect of oxygen delivered from the melt due to the slow dissolution of the quartz glas crucible, was detected. The homogenous incorporation of oxygen has been a challenge. Beside adjusting the growth parameters different static magnetic fields (**M**agnetic **CZ**ochralski technique) were mostly applied to reduce the oxygen content to the requested level. New developments also allow the enlargement of oxygen concentration by using alternating or travelling magnetic fields. Furthermore much R&D work was done to develop the **C**ontinuous **CZ**ochralski technique for further optimization of homogenous oxygen and dopant incorporation. Solid or liquid silicon was continuously feeded in the melt during crystal growing. Because of the high complexity only discontinuous recharging is already applied at present time.

Up to now the defect engineering during the Czochralski process is a large challenge. Different processes have been developed to deliver the requested wafer properties, i. e. OSF-ring free, vacancies free prime wafers or interstitial rich COP free monitor wafers. According to the v (pull speed)/ G (thermal gradient) law the hot zone must be optimized to get the right thermal conditions. Numerical simulation using the thermal global model and more and more convection and heat transport models support essentially the development and optimization of thermal conditions and growth parameters. Now we are able to grow “virtually” CZ crystals to study theoretically the achieved properties. By applying a very expensive uneconomical process the growth of “perfect” crystals is possible. More economical is the use of wafers which are improved by annealing in combination of N doping or by epitaxial growth after the Czochralski process.

Many alternative materials are presented for devices in the future. But in the next near future silicon will stay as the mostly used material and the Czochralski technique will stay as a technique, which is being continuously improved.

Germanium: From the first application of Czochralski growth to large diameter dislocation-free crystals

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Being the pioneer material in the history of electronics, germanium has regained a lot of interest over the last decade as a semiconductor material for opto-electronic and electronic applications. We present how developments in crystal growth and substrate production have enabled the optimal exploitation of the properties of germanium for applications in infrared optics and gamma-ray detectors, and the recent breakthrough of this material as a substrate for opto- and micro-electronic applications.

The Development of LEC technology for GaAs single crystal growth from laboratory scale to mass production

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GaAs based microelectronics has reached maturity and mass-production level during the last decade of the last century. This development was possible by transition from laboratory scale to market- oriented mass production of semi-insulating GaAs wafers. As lower specific costs per die are a main driving force in device manufacturing this transition was accompanied by the demand for an increase in wafer diameter and exactly tailored device relevant properties allowing the application of both ion implantation and epitaxy as main device manufacturing technologies. In addition, GaAs wafer manufacturers were confronted with continuous reduction of production costs as a result of decline in wafer prices. Furthermore, as the III/V compound semiconductor industry uses GaAs substrates grown by different crystal growth technologies a leading substrate supplier has to provide customer specific GaAs wafers made of crystals grown by different technologies.

State-of-the-art semi-insulating SI GaAs single crystals have a diameter of 150 mm and are grown either by the liquid encapsulated Czochralski method (LEC) or the vertical Bridgman technique (VB) and its modifications. At present the market share of LEC grown SI GaAs crystals amounts to approximately 50 % which is expected to further decrease in the future due to preference of low-epd GaAs for epitaxy. Only recently, the growth of even larger SI GaAs crystals up to 200 mm in diameter by both methods was demonstrated by FCM.

The progress made in LEC growth of SI GaAs single crystals in the last decade will be illustrated by a more detailed presentation of two key issues: furnace design by advanced computer modeling and carbon control by thermochemical analysis of the complex reaction system and the related development of an extended segregation model.

The 2D finite volume code STHAMAS which takes into account heat transfer by conduction, radiation and (turbulent) gas convection has been used for global optimization of the multiheater furnace including heat insulation and development of growth technology. It will be shown that a 3D modeling of turbulent convection in the GaAs melt is absolutely required for a realistic calculation of the shape of the solid/liquid interface. At present, 11 inch crucibles are used allowing a 28 kg process for 150 mm diameter crystals which may yield up to 160 wafers/boule. The extension to 14 inch crucibles and larger charges has been successfully demonstrated.

To ensure semi-insulating properties and fulfill customer´s resistivity specification of the crystal, the concentration of compensating carbon at nearly constant EL2 concentration has to be actively controlled in the GaAs melt during growth. It is done by controlling the chemical potentials of oxygen and carbon in the growth system. This procedure is based on a rationalization of the complicated Redox equilibria in the complex reaction system by calculating a *predominance area diagram* as suggested in the literature. The ChemSage code to minimize the total Gibbs Free Energy has been used for these calculations. Details will be given. To describe segregation behaviour a combined carbon and oxygen transport model has been developed. At present, resistivity of SI GaAs can be controlled in the range from 10^3 to 10^8 Ωcm.

Indium Phosphide crystal growth by Liquid Encapsulated Czochralski Method

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Indium Phosphide (InP) is important material for long wavelength (1,1-1,6μm) optoelectronic devices such as lasers, photo detectors, widely used in fiber optic communication. It is also promising material for high frequency HEMTs, HBTs and OEICS to be applied in 40Gbps optical networking systems, power amplifiers for 3^+G wireless handsets etc.

Development in mass production and application of these devices requires InP substrates with high quality (purity, homogeneity, structure perfection) and very low price. To decrees production costs it is necessary to grow long crystals with stable diameter. Manufacturing of such crystals is very difficult due to big convection around growth crystal and its tendency to twining.

In this presentation we report the results of the work on obtaining of [100] oriented InP crystals with diameter ≥ 2” and L > 200mm. Crystals were obtained on MARK IV puller applying of multiheater system with 6” quartz crucible. Polycrystalline InP was prepared by injection and/or HGF synthesis. 4kg charge was used for crystals growing. Two and three heaters system were investigated to optimize thermal gradients and technological parameters necessary for long single crystal growth. As the result InP crystals, S-doped with 58-60mm in diameter and max. length 300mm have been obtained.

These crystals were characterized by:

- Hall parameters measurement
- dislocation density counting and mapping,
- near infrared transmission,
- x-ray topography,
- GDMS analyses.

They showed high purity level of the material. Concentration of residual donor impurities (Si) was on the level (2-5) x 10^{15}cm^{-3} and accepters (Zn) below 1 x 10^{15}cm^{-3}. High homogeneity of electrical parameters (μ, n) was observed along crystals diameter. Dislocation density (EPD) was changing along crystal axis from 2 x 10^4 cm^{-2} at the front, up to 5 x 10^1cm^{-2} at the tail. X-ray topography of the substrates and InP epi-layers showed good quality of crystals structure.

High pressure spectroscopy of TM and RE doped oxide monocrystals obtained by Czochralski method

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The talk summarize the results on high pressure spectroscopy of the Cr^{3+}, Ti^{3+} and Ce^{3+} in different oxide crystals obtained by Czochralski method. The research has been focused on the investigations of the energetic structure electron – lattice interaction of the systems. The main effect that has been observed in all ions was pressure induced increasing of the crystal field strength, that determine the energies of the localized states, influence of pressure on energies of the conduction and valence bands. The second effect was the pressure induced changes of the electron –lattice coupling strength in the Cr^{3+} and Ce^{3+} and changes in the Jahn –Teller effect in the Ti^{3+} ions. In the case of the Cr^{3+} ions we have observed the pressure induced crossover of the $^4T_2$ and ^2E states. Thus tuning pressure we were able to analyze the inhomogeneous broadening ^2E-$^4A_2$ and $^4T_2$-$^4A_2$ transitions. In the case of Ce^{3+} the interests has been focused on influence of pressure on the energy of 5d-4f transitions in the rare earth ions and energy of the $5d^3$ with respect to the energy of valence band .

Growth of Fluoride Single Crystals by the Czochralski Technique for Laser Material and Optical Window Material

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Fig.1. 8-inch size CaF_2 single crystal grown by the Cz technique. This crystal was grown in collaboration with Tokuyama Corporation.

Because of their unique properties such as wide range transparency, fluoride single crystals have many practical applications in the UV and IR wavelength range. Recently, there has been a significant interest in using 157-nm laser sources in projection lithography as successors to the 193-nm based system. However, one of the most serious problems in realizing a 157-nm based system is the development of suitable and large-size optical materials for lenses and other optical components. At this point of view, we have been trying to grow large-size fluoride single crystals by using Czochralski (Cz) technique. The large-size CaF_2 single crystal has been grown by the Bridgman technique for the moment, however because low-stressed crystals can be grown along any crystal orientations by using suitable seed crystals in the Cz technique, we trust that the growth of high-quality and large-size fluoride single crystals with the reproducibility is achieved by using only the Cz technique. Fig.1 shows an 8-inch size colorless and transparent CaF_2 single crystal grown by the Cz technique. The birefringence of this CaF_2 crystal was less than 1.0nm/cm even before the annealing process. In the same way 8-inch size BaF_2 single crystal could be grown. Thus, the growth of 8-inch size fluoride single crystals by the Cz technique has been succeeded for the first time in the world. We have also identified colquiriite-type $LiCaAlF_6$ (LiCAF) crystal and perovskite-type $KMgF_3$ and $BaLiF_3$ crystals as a new window material. As they have superior high transparency in the VUV wavelength regions, we have grown such complex fluoride single crystals by the Cz technique. Although inclusions and cracks easily occur in the complex fluoride crystals, by modifying the crystal growth conditions, LiCAF single crystal 4-inch in diameter could be grown

Laser materials are another promising application for fluoride single crystals. Coherent optical sources in the ultraviolet (UV) wavelength region are useful for many practical applications. Recently, Ce^{3+}-doped fluoride crystal has been regarded as efficient and convenient UV solid-state laser media. We demonstrated that a coaxially pumped, large-aperture ultraviolet power-amplifier module using solid-state tunable laser medium Ce:LiCAF has 98 mJ, 290 nm output with sufficient extraction efficiency of 25%. In the IR regions, during the last few years, interest in 2 μm lasers has increased because of the availability of high power laser diodes, and the introduction of a large variety of applications that require eye-safe lasers. We have grown 1~3 inch size Tm, Ho-codoped $LiYF_4$ (YLF) and $LiLuF_4$ (LLF) single crystals by the Cz technique. We have proposed and evaluated a novel quasi-end-pumping technique using two lens ducts, which promises comparable performances. In this setup, the incident pump beams receive several reflections from the crystal faces, giving rise to uniform pumping intensity inside the crystal. The pulse repetition frequency was 1 Hz, with a current pulse length of 500 μs. Maximum output energies of 13.5 mJ (LLF) and 9.9 mJ (YLF) were obtained for 255 mJ of incident pump energy.

Acknowledgments

The author gratefully acknowledges with members of Fukuda laboratory of Tohoku University for their valuable contribution in performing the experiments. The growth experiment of large size fluoride single crystals was carried out by the continued efforts of Tokuyama Corporation. This research was partially performed as a part of Regional Consortium R&D program conducted by Ministry of Economy trade and Industry.

Progress in the Czochralski Method of Oxide Crystal Growth

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One of the main methods of crystal growth from the melt is the Czochralski method. Advantages of this method and ways of solving some of the problems arising during growth of different types of multioxides crystals are the subject of this presentation.

The main advantage of the Czochralski method is the possibility of fast growth of good quality large single crystals. Since the crystals are grown using oriented seeds they adopt required orientation.

In the typical Czochralski arrangements with the high frequency generators, the metallic crucible heats the melt and the ceramic thermal shields. The vertical temperature gradient above the melt may be optimized using active or inactive afterheater of appropriate length. The radial and vertical temperature gradients that exist during crystal growth by the Czochralski method, are relatively low; this leads to crystals with low density of defects.

Since the discovery of the method, many technical problems have been solved. The typical modern Czochralski equipment's are fully computerized. The diameter of growing crystal is continuously controlled by weighting either crystal or the crucible. The surface tension is measured at immersing the seed thus the influence of tension on the apparent weight of the crystal may be accounted for. Controlled decreasing of the crystal diameter at the end of the process may minimize thermal shock in the crystal induced by breaking contact with the melt. Monitoring of the oxygen partial pressure in the input and output gas supplies information on decomposition of the components.

The growth process always begins on a thin seed crystal with convex crystal/melt interface. When the crystal diameter increases the growth rate in the central part also increases and is higher than the actual pulling rate. At this stage of the process, the pulling rate must be reduced in order to maintain the growth rate. The crystal growth with a convex crystal/melt interface leads to crystallization on various crystallographic planes what produces core and facets regions in growing crystals. The problem was solved by adjusting the rotation rate to the flatten crystal/melt interface.

The chemical composition of crystals grown by the Czochralski method often differs from the stoichiometric composition. Such deviations were found and well documented in a few groups of materials for example in garnets. It will be shown how to determine the optimum starting composition in crystals when this deviation is not known. In order to determine the composition of the melt one should also take into account evaporation of the most volatile component that dissociates at crystal growth temperature.

There are obvious problems associated with the Czochralski method due to segregation of components in multioxides, solid solution and doped crystals that will be discussed in the lecture.

Scintillation properties of complex oxide monocrystals grown by Czochralski method

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ABSTRACT

Recent advances in modern radionuclide imaging systems for medical diagnostics in neurology, oncology and cardiology require new, more efficient and faster scintillator crystals. While older imaging systems were almost exclusively based on BGO ($Bi_4Ge_3O_{12}$) and NaI:Tl crystals the new systems, e.g. ECAT Accel, developed by Siemens/CTI are based on recently discovered and developed LSO (Lu_2SiO_5:Ce) crystals. Interestingly, despite very good properties of LSO there still is a strong drive toward a development of new scintillator crystals that would show even better performance and characteristics. Most of those crystals belong to the class of complex oxide crystals grown by the Czochralski method. .

In this presentation we shall present spectroscopic and scintillator characterization of a new complex oxide crystals, namely LSO and LuAP ($LuAlO_3$, lutetium aluminate perovskite) activated with Ce. The LSO crystals have been grown by Photonic Materials Ltd and CTI Inc, while LuAP crystals have been grown by ITME (Warsaw). All these crystals have been characterized at IF UMK (Torun). We will review and compare results of measurements of scintillation light yields, scintillation time profiles, VUV spectroscopy and low temperature thermoluminescence performed on these crystals. We will demonstrate that all the experiments clearly indicate that there is a significant room for improvement of both LSO and LuAP. While a leading position of LSO is confirmed, it is also clear that LuAP can potentially be used in systems based on a phoswich design (two different scintillator crystals) and, after a likely improvement of some parameters, it may also offer a viable alternative in single crystal machines.