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Prosperity and difficulty of bulk crystal growth of semiconductor compounds (a review)

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Semiconductor compounds are now and in future of central importance for human life. A relatively high degree of production maturity has been already achieved. GaAs holds a leading position for opto- and high-frequency microelectronics that will be continuously developed further. Single crystalline yield of InP, GaSb, CdTe and ZnO needs to increase essentially. For all these compounds the growth from melt by vertical gradient freeze is of raising relevance. High growth rates are expected for GaN and AlN. Accordingly, the mastering of the vapour-solid and flux-solid phase transitions on higher technological level is absolutely necessary. Despite of great efforts during the last decade there are some fundamental difficulties to be still solved even for the melt growth, such as overcoming of melt structuring, damping of convective perturbations, *in-situ* control of stoichiometry, minimization of precipitation, reduction of dislocation patterning, depression of twinning and installation of model-based control systems of the growth processes. The author gives an overview on possible measures being under development in his team and at Institute for Crystal Growth (Berlin) in order to meet these goals.

Полупроводниковые соединения в настоящее время имеют и в будущем сохранят первостепенное значение в жизни человечества. Уже достигнут относительно высокий уровень развития их производства. GaAs сохраняет лидирующее положение в отраслях оптоэлектроники и высокочастотной микроэлектроники, непрерывное развитие которых будет продолжаться. Необходимо существенно увеличить выход монокристаллов InP, GaSb, CdTe и ZnO. Для всех этих соединений возрастает значение выращивания из расплавов методом отверждения в вертикальном температурном градиенте. Высокие темпы развития ожидаются для GaN и AlN. Соответственно, овладение управлением фазовыми переходами газ-твердое тело и раствор/расплав-твердое тело на высоком технологическом уровне является абсолютной необходимостью. Несмотря на значительные усилия, предпринятые в течение последнего десятилетия, при выращивании из расплава также существуют некоторые принципиальные затруднения, которые нужно разрешить, например, преодоление структурирования расплава, подавление конвективных возмущений, регулирование стехиометрии *in situ*, сведение к минимуму осаждения, подавление копирования дислокаций, предотвращение двойникования и создание систем управления процессами выращивания на основе моделей. Автор представляет обзор возможных мероприятий, разрабатываемых его группой в Институте роста кристаллов (Берлин) для достижения указанных целей.

In addition to applications in light emitting optoelectronics in the narrow- (InSb, InAs, GaSb), middle- (GaAs, InP, GaP, CdTe) and wide-band regions (SiC, AlAs, GaN, AlN, ZnO, ZnSe) semiconductor compounds gain increasing importance for high-frequency microelectronics and wire-less communication (SiC, GaAs, InP, GaN),

photo- (GaAs, CdTe) and thermovoltaics (GaSb), high-power electronics (SiC, GaN, AlN), UV-, IR- and γ-radiation detection (GaN, InSb, GaAs, CdTe) etc. Nowadays the direct band gap of InN was determined to be ≤1 eV (0.7–0.85 eV) making this material also attractive for optical data transfer. Table compiles some important properties and applications of selected semiconductor compounds. For more detailed informations the just published compendiums of Capper et al. [1] and Oda [2] are recommended.

Now as before, the epitaxial processes for device production require high-quality substrate crystals. GaAs is still in a leading position. The today worldwide production capacity of semiconducting (SC) and semi-insulating (SI) GaAs wafers yields about 200 000 kcm^2 increasing by a factor of ~3 up to 2010. Due to the more complicated material parameters the share of InP wafers amounts to 5000 kcm^2 only. High growth rates are expected for GaSb used in thermovoltaic and IR-detection devices. Industrially, SI GaAs crystals with diameters up to 150 mm are grown from the melt by the Liquid Encapsulated Czochralski (LEC) and Vertical Gradient Freeze (VGF) methods. Recently, for both techniques the principal mastering of 200 mm diameter was demonstrated successfully [3]. Also InP, GaP and GaSb crystals are growing by LEC and VGF. Diameters up to 150 mm are reported for InP crystals [4]. At IKZ Berlin the vapour pressure controlled Czochralski (VCz) growth of GaAs crystals with diameters up to 150 mm even without boric oxide encapsulant was further developed. Generally, during the last ten years a replace of the LEC by VGF is running. This is due to the better control of melt convection, uniaxiality and homogeneity of the heat transfer. For instance, 2–4-inch CdTe and (Cd,Zn)Te crystals are exclusively grown by unidirectional solidification methods like vertical Bridgman (VB) and VGF [2, 5, 6].

The favourable wide-gap characteristics of SiC, GaN, AlN and ZnO make these materials of increasing interest for blue and ultra violet (UV) wave regions. However, due to the high melting points and component dissociation alternative growth techniques from vapour or solution are under development. For SiC crystals with diameters of 50–100 mm the modified Levy method of physical vapour phase deposition (PVD) was brought to industrial maturity [7]. Today, SiC holds the second place in turn out after GaAs. Worldwide nearly 8 000 kcm^2 of the 6H type and over 500 kcm^2 of the 4H type are produced. Nitrides are grown from high-pressure fluxes, low-pressure solutions or by metal halide vapour phase epitaxy (HVPE) and epitaxial layer overgrowth (ELOG) to obtain free-standing thick layers. Also the direct synthesis from vapour phase under NH_3 flow on alternative or native substrates is carried out. Recommendable overviews about the current state of the art of bulk nitride growth are given by Denis et al. [8] and by a special issue of Journal of Crystal Growth [9]. Although the low crystal growth rates from vapour and solution in five years a remarkable yield of the nitride bulk production over some hundred kcm^2 can be approximated. For GaN a share increase from today ~10 kcm^2 up to about 120 kcm^2 in 2010 is expected. About 10 kcm^2 will be the need for AlN. ZnO is mainly performed by the hydrothermal method or by the so-called pressurized melt growth. But also the vertical Bridgman growth in iridium crucibles was recently successfully demonstrated at the IKZ Berlin [10].

One can say meanwhile the bulk crystal growth of semiconductor compounds, especially of the III-Vs, reached a relatively high degree of prosperity. Most technologies are already translated from laboratory stage to industrial scale and typical economic parameters come now to the fore, such as increase of output and reduction of costs.

However, despite of great success during the last decade there are some fundamental problems to be still solved. For instance, at the melt growth the following issues must be done to the point of perfection:

— more careful consideration and overcoming of the *melt structuring*, even at materials with high ionicity (CdTe, ZnSe, InP), that may affect the growth kinetics;

— damping of *convective oscillations and turbulences* in the melt in order to improve the chemical micro-homogeneity and stability of the growing interface;

— in situ control of *stoichiometry* ensuring the minimum intrinsic point defect concentrations and precipitate contents (e.g. Te in CdTe, As in GaAs);

— control of the collective rearrangements of dislocations into *cellular structures and bundles*, driven by thermo-elastic stress and self assembling;

— prevention of *twinning* along growing {111} facets as very problematic drawback for materials with low stacking fault energy, like InP and CdTe;

Table. Selected material parameters and applications of important semiconductor compounds (* — under development at the IKZ Berlin, HF — high frequency, ME — microelectronics, OE — optoelectronics, LED — light emitting diode, LD — laser diode, UV — ultra-violet, SAW — surface acoustic waves).

Compound	Structure type	Melting point T_m [°C]	Equilibrium pressure p at T_m [MPa]	Thermal conductivity λ_T [W/cm·K]	Band gap ΔE_g at 300 K [eV]	Ionicity f_i [%]	Electron mobility μ_e at 300 K [V/cm²s]	Applications
SiC*	ZB (3C) W (4H, 6H)	> 3000	10.8	4.9	2.2 (3C) 3.3/3.0 (4H/6H)		980 (3C) 500/200(4H/6H)	High-T, high-power HF ME, blue emission
GaSb*	ZB	712	$1 \cdot 10^{-7}$	0.33	0.73	26	7700	Thermo-photovoltaics, substrate for GaInAsSb, GaAlAsSb (λ > 1.5 μm)
InP*	ZB	1070	2.75	0.7	1.35	42	6060	HF ME, fiber communication (λ = 1.3 μm), photovoltaics, OE, LEDs, LDs
GaAs*	ZB	1238	0.2	0.8	1.42	32	8500	HF ME, photovoltaics, OE, LEDs, LDs, radiation detectors
GaN*	W	2520	4500	1.4	3.44		1000	High-T, high-power HF ME, short wafelength OE, UV emission
AlN*	W	2300	10–50	3.19	6.2		300	SAW, substrate for AlGaN, blue-emitting LEDs, high-T electronics
CdTe	ZB	1092	0.07	0.01	1.48	72	1050	Substrate for HgCdTe, X- and γ-ray detectors, photovoltaics
ZnSe	ZB(W)	1520	0.1	0.19	2.71	63, 72	530	blue emitting LEDs, laser screens for projection color television set
ZnO*	W	1975	0.035	0.54	3.4	64	125	Fitted substrate for GaN epitaxy, UV light emission, SAW

— introduction of modern process *control systems* for diameter and interface stabilisation by using of model-based feed back principle.

It is the aim of the present paper to discuss these points somewhat more in detail and show possible measures being under development at IKZ Berlin. It will be seen that often the combination of two or more preconditions are required for depression of one harmful effect. For instance, twinning can be minimized only when both convection damping and careful growth rate control are established. As a result of the present study arises the question is there any hope of dislocation-free growth of semiconductor compounds in future? Finally, some newer results of GaN, AlN and ZnO bulk growth are added.

1. The "structure" of the melt

One of the most exciting questions within the framework of crystallization theory is: how does a nearly perfect crystal structure form from a non-steady disordered fluid phase? In markedly diluted mother phases, like vapour and many solutions, where the interaction between the crystal building atoms and molecules can be neglected (named completely dissociated fluids) the situation is fairly obvious. As it is considered by the theory of Burton, Cabrera and Frank (BCF) in such case the boundary between fluid phase and crystal can be treated as a localized interface. The isolated atoms or molecules arrive from the gas or solution, move along the growing crystal surface by diffusion until an energetically favoured dock (kink) position on the ordered crystal surface is reached. Otherwise, if such sites of incorporation are not delivered within the diffusion length they do leave the surface again. Close to equilibrium conditions such atomistic chronology guarantees a well-ordered phase transition and inhibits the formation of high-dimensioned defects. Of course, with increasing deviation from equilibrium the metastable incorporation probability of point defects is enhanced.

In melt growth the situation is more difficult due to the very small difference in densities between fluid and solid phases. Especially, what happens when associated melt structures are presented? As it is well known, materials with high degree of ionicity in the bond energy tend to preserve a spatial structuring within the molten state. For instance, such substances are the AII–BVI compounds like CdTe, ZnTe, ZnSe and ZnO with ionicities over 60 % (Table). Both *ab initio* molecular dynamics simulation [11] and neutron diffraction analysis [12] revealed in low superheated melts the preservation of local environments similar to the zincblende where each atom is surrounded by a distorted tetrahedron of atoms of the other type. As a result the degree of association yields more than 90 % that differs markedly from AIII–BV compounds, like GaAs, which dissociates into separated A and B atoms. Also from overheating-undercooling experiments on CdTe was found that until a critical temperature over the melting point T_m nearly no undercooling for generation of nuclei is required. Only when the melt was overheated more than 10–20 K (in ZnSe over 60–80 K [13]) the undercooling increased markedly [14–17]. One can assume that such "structured" melt does influence the growth kinetics and, therefore, enhance defect density. The danger of wrong docking of misoriented structural complexes is high.

In fact, until today the growth of AII–BVI crystals from melt with quality comparable to AIII–BV crystals is still failing. In CdTe and ZnSe Rudolph et al. [18–20] observed a correlation between the number of polycrystalline grains and degree of melt superheating. The higher the melt temperature and its holding time before the growth is started the better is the quality of the main crystal body. This dependence was also confirmed by further authors (e.g. ref. [21]). Hence, for achievement of optimum crystal quality of compounds with high ionicity a proper pre-treatment of the liquid state by temperature and time is required. Recently, the author and a cooperating team from Madrid carried out the growth of CdTe crystals by a modified Bridgman technique with a turning furnace [22] (Fig. 1). It allows the adjustment of different degrees of superheating of the melt before the crystallization process. This is achieved by separation of the overheated melt from the seed crystal. Only after the melt temperature is again reduced towards melting point the furnace is turned into growth position so that the formerly superheated melt contacts the seed and the crystallization is started. After first experiments a moderate positive effect on the structural crystal quality was observed. A reduced number of grain boundaries, precipitate content and dislocation density were achieved. The investigations will be continued.

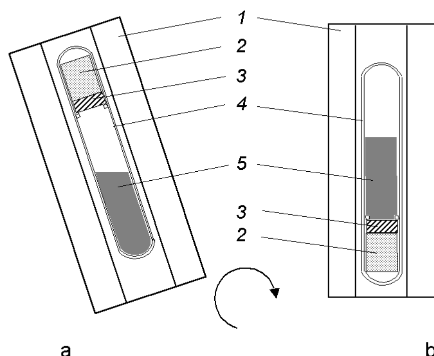

Fig. 1. Scheme of the modified Bridgman setup for growth of CdTe crystals allowing the pre-treatment of the melt [22]: a — furnace position for the superheating process, where the charge and the seed are separated in order to maintain the seed temperature lower than the melting point;. b — rotated furnace after superheating to bring in contact the melt charge with the seed and to start the crystal growth (*1* — furnace, *2* — seed support, *3* — seed, *4* — ampoule, *5* — melt).

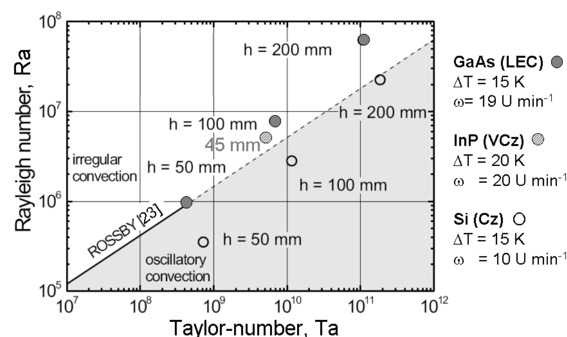

Fig. 2. Rossby stability criterion [23] between laminar and turbulent convection in semiconductor melts of given height h, crucible rotation rate ω and temperature difference ΔT. $Ra = g\beta\Delta T h^3 \nu^{-1}\kappa^{-1}$, $Ta = 4\omega^2 h^4 \nu^{-2}$, with g — gravitational acceleration, β — volumetric expansion coefficient, ν — kinematic viscosity, κ — thermal diffusivity (courtesy of A.Seidl from Schott Solar, St.Eichlern from FCM and Ch.Frank-Rotsch from IKZ).

2. Control of melt convection

Increasing melt columns as precondition for growth of longer crystals with diameters of 150–200 mm need first of all the proper control of increasing non-steady flows within the huge melt volumes. According the relation between Rayleight and Taylor numbers, i.e. between buoyancy and artificial (rotational) convection, the Rossby stability criterion [23] is not more fulfilled in III–V LEC arrangements with melt heights ≥100 mm (Fig. 2). Strong convection flow densities of some hundred N m^{-3} and temperature oscillations over ±10°C make the stable growth of single crystals very difficult. Not so critical is the situation in a VGF system with stable temperature gradient situation (lowest temperature below). However a characteristic toroidal convection pattern due to the radial temperature difference promotes undesirable concave interface morphology.

As it is well known the Lorentz force induced by a magnetic field can be used to damp natural convection and temperature oscillations or to move and mix the melt very effectively [24]. Further, a nearly flat interface shape, temperature stability and striation-free dopant distribution can be controlled by using non-steady magnetic field [25, 26]. Numerous growth experiments using magnetic fields have been reported in the literature dating back many years but has not yet been perfected. The usual method is to position a steady magnet outside of the growth chamber but this requires the generation of very high induction forces (0.1–10 T) and proves to be very expensive. Higher interaction efficiency is achieved and much lower magnetic induction (4–8 mT) is required when a non-steady longitudinal translating magnetic field (TMF) is applied [26, 27]. However, for the growth of dissociating compounds (III–V, II–VI) within thick-walled high-pressure vessels, the necessary magnetic induction forces are an order of magnitude greater when the inductor coils are placed outside. Hence, for adoption in well-established industrial growth machines, location of the coils inside the growth container is favoured. In fact, there were some attempts to arrange internal inductors around the heater since that requires additional free space around the crucible and a specific cooling set-up [28]. Compared to that, within the framework of the author's KRIST*MAG* project internal heater-magnet modules for coupled generation of temperature and translating magnetic fields, suitable for incorporation into industrial Czochralski pullers and vertical gradient freeze equipments, are under development (Fig. 3a) [29]. Amplitude, frequency and phase shift of the three-phase alternating current (AC) are all-adjustable and are combined with a direct current (DC) to control the crystallization process effectively. To that end, an universal heater-magnet con-

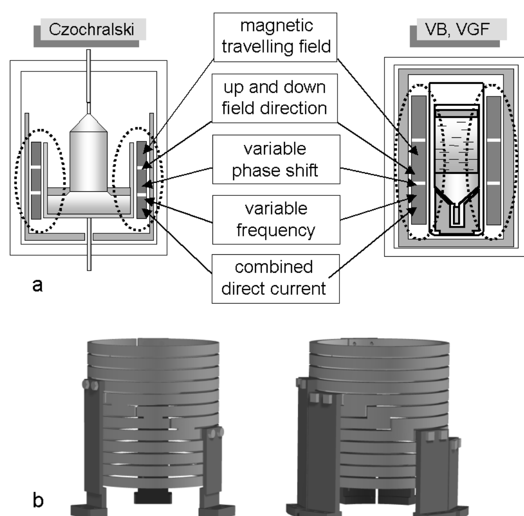

Fig. 3. a — Schemes of combined heater-magnet modules for generation of heat and traveling magnetic field replacing the conventional heaters in Czochralski and VB, VGF crystal growth equipments; b — designs of two graphite heater-magnet modules with staircase-shaped current path, subdivided in three sections for generation of travelling magnetic fields by feeding with three-phase current of given phase shift in delta (left) and star connection (right).

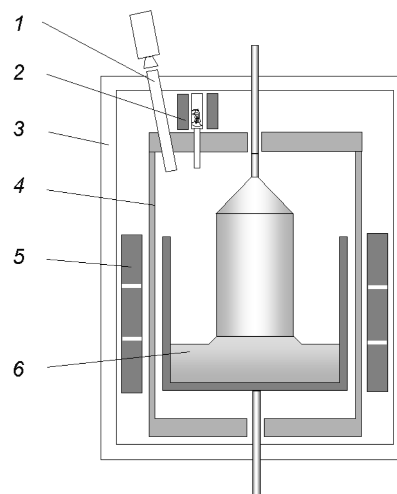

Fig. 4. Scheme of the vapour pressure controlled Czochralski (VCz) technique for growth of stoichiometric crystals (e.g. GaAs, InP) without boric oxide encapsulation: *1* — optics with camera, *2* — temperature-controlled source of volatile component (e.g. As or P), *3* — outer high-pressure vessel, *4* — inner hot-wall chamber, *5* — heater, *6* — melt without encapsulant on the surface.

troller system has been developed. Such module enables the simultaneous generation of heat for melting and of travelling magnetic fields to counter-act the violent non-steady or even turbulent convection in the melt. It replaces the conventional meander heater by a coil consisting of a spiral- or staircase-shaped current path, which is subdivided, in segments by contact points for the phase-shifted power supply (Fig. 3b). Its placement close to the melt guarantees a maximum efficiency of flow driving and low cost of adaptation.

First melt flow observations and growth experiments show very encouraging results. Nowadays at IKZ three crystal growth machines of industrial scale, i.e CI 358 for LEC, LPA "Mark 3" for VCz and "Kronos" for VGF growth, are equipped with KRIST*MAG* heater-magnet modules. The test phase is still running. However, recently, first encouraging results were obtained. Visual observations of the GaAs melt surface with floating particles in a VCz arrangement without B_2O_3 encapsulant revealed an agile reaction of the flow patterns to the variation of the TMF parameters. For instance, in contrast to the conventional mode without magnetic field a controllable outwards directed stream away from the seed could be achieved. For the first time VCz GaAs crystals were successfully grown in B_2O_3-free VCz regime under two different TMF modes operating in delta-connection with frequency $f = 50$ Hz and phase shift $\varphi = 120°$ as well as in star-connection with $f = 400$ Hz and $\varphi = 70°$. Forthcoming LEC and VGF growth experiments under TMFs will be carried out with GaAs, GaSb and Ge [29].

3. Near-stoichiometric growth

In compound crystals, such as III–Vs and II-VIs, one of the most important and complicated parameter to be controlled is the stoichiometry or a given deviation from it. Non-stoichiometric composition enhances the generation of intrinsic point defects (vacancies, interstitials, antisites) that affect the type of conductivity, carrier concentration, absorption behaviour, diffusivity, efficiency of dopant incorporation etc. It promotes the generation, multiplication and movement of dislocations. Finally, the incorporation of the excess component at the interphase in the form of inclusions and the nucleation of second phase in the form of precipitates during the cooling process of the as-grown crystal can impair the wafer and device quality markedly. Hence, the

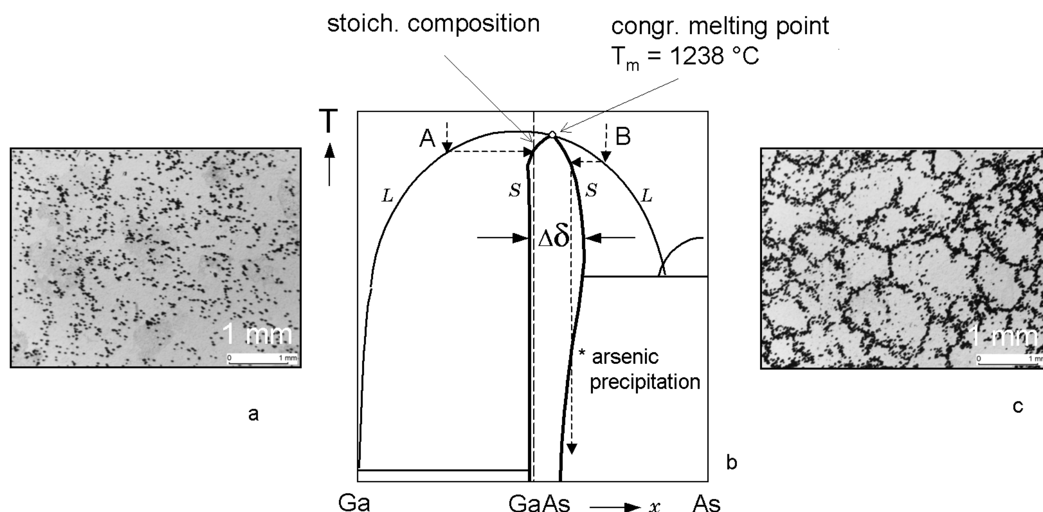

Fig. 5. Principle of growth of near-stoichiometric GaAs crystals from Ga-rich melt (crystallization path A in the phase diagram b) containing only minimal content of As precipitates and no more dislocation cells (a) which are typically for conventionally grown ingots by path B (c); a,c — dislocation etch pit images from near-stoichiometric (a) and arsenic-rich (c) crystals (courtesies of F.Kiessling and U.Juda from IKZ Berlin). In the phase diagram (b) mean: T — temperature, x — mole fraction, S — solidus, L — liquidus, $\Delta\delta$ — width of the GaAs phase extent.

maturity of in situ control of stoichiometry during growth is one of the key targets [30, 31].

The concentration of intrinsic point defects is related to the width of the compound phase extent in the phase diagram, i.e. the given deviation from stoichiometry (see Fig. 5b). In GaAs its maximum widths $\Delta\delta_{max}$ amounts at 1170°C to ~10^{-4}–10^{-3} mole fractions. The congruent melting point is located at the arsenic-rich side at ~10^{-4} excess mole fraction. Concerning newer calculations, the solidus crosses the stoichiometry at markedly Ga-rich melt with mole fractions x_L<0.40 or is even completely located on the As-rich side [32]. In InP the phase extent is studied less. One order of magnitude smaller width ($\Delta\delta_{max}\approx 1\cdot 10^{-5}$) and stoichiometry deviations towards both component sides have been calculated [33]. In CdTe the existence region is also symmetrically against stoichiometry but somewhat more deviated towards the Te-rich site [5, 34]. The maximum width is about $(1-3)\cdot 10^{-4}$. Largest compound phase extents show the IV–VIs. In PbTe and SnTe $\Delta\delta_{max}$ is $1\cdot 10^{-3}$ and $1\cdot 10^{-2}$, respectively [31].

Usually, SI GaAs crystals are grown from slightly arsenic-rich melts in order to control the As_{Ga} antisite deep donor (EL2) concentration and to compensate by controlled addition of the shallow acceptor carbon [3]. However, despite of the already achieved high industrial maturity the problems connected with non-stoichiometric growth conditions gain more and more in importance. This is due to the increasing demands to the wafer surface quality for epitaxial processes. Even precipitates and inclusions of the second phase, named crystal originated particles (COPs), are able to disturb the wafer polishing process markedly. Therefore, the in situ control of the crystal stoichiometry already during the growth process would to be a promising measure of prevention. For instance, in the author's team at IKZ Berlin the vapour pressure controlled Czochralski technique without boric oxide encapsulation [35] was developed for the growth of near-stoichiometric 3-inch GaAs crystals (Fig. 4). The related Ga-rich mole fraction of the melt (*6*) is controlled by partial arsenic pressure via the temperature of an installed As-source (*2*) communicating with an inner hot-wall chamber (*4*). Note at such growth conditions from Ga-rich melt the concentration of the deep-level defect EL2 (As_{Ga} antisite) falls below 10^{16} cm^{-3}. Therefore, the concentrations of the compensating shallow acceptor carbon and residual impurities must be also reduced in order to meet the semi-insulating precondition [EL2] > [C] + $(N_{\sigma A} - N_{\sigma D}) > 0$ with $N_{\sigma A,D}$ the total concentrations of acceptors (A) and donors (D) shallower than EL2. A proper in situ carbon control down to $1\cdot 10^{15}$ cm^{-3} could be adjusted as has been reported elsewhere [35].

For that the residual impurity content was minimized (note no more impurity gettering by the B_2O_3 encapsulant takes place as in the LEC method). Additionally, the growth rate and temperature gradient were chosen undercritically in order to prevent morphological instability due to Ga rejection at the propagating melt-solid interface. Considering all these measures perfect near-stoichiometric SI GaAs single crystals with electrical resistivity $3\cdot10^8$ Ωcm have been grown successfully. EL2 and C concentrations of $8.0\cdot10^{15}$ and $6.3\cdot10^{15}$ cm^{-3} were obtained, respectively. It was shown that such growth conditions minimize the contents of As precipitates, B_{Ga} substitutes and dislocations [35]. Such material is of high interest for Gamma ray detection [36].

Also for VGF the in situ control of stoichiometry is discussed and tested for a long time past but not yet solved on industrial scale. As a result VGF crystals show still characteristic features of non-stoichiometry such as precipitates and inclusions of the excess phase. To establish an in situ stoichiometry control the continuously decreasing height of the melt column during the normal freezing process would require a well-controlled source temperature program well fitting the real growth rate. The author studied carefully the in situ stoichiometry control during VB growth of CdTe crystals by using of a temperature controlled Cd source [5, 31]. A minimum of inclusions and precipitates could be found under stoichiometric growth conditions which must be tuned in accordance with the decreasing melt height and, therefore, changing transport regime during the whole crystallization process. Therefore, until today it is still the practice to turn the stoichiometry in wafers by post-growth annealing so far it is required for a given application (see, e.g., Oda et al. [37] for GaAs and ref. [38] for CdTe).

4. Dislocation dynamics

4.1. Dislocation cell structuring

In most as-grown crystals the stored dislocations rearrange in characteristic cell patterns (Fig. 5c), which are not desirable since physical parameter inhomogeneities are caused. For instance, across semi-insulating {100} GaAs wafers a mesoscopic resistivity variation is observed due to the accumulation of AsGa antisite defects (EL2) within the cell walls [39]. As a result a costly post-growth homogenization step by bulk annealing is required [2].

Dislocation cells are also well known from another material groups like metals, alloys, dielectrics, independently which growth method was used [40]. They are of globular type and their diameter d decreases with increasing average dislocation density ρ according $d = K\rho^{-1/2}$ with K the coefficient of proportionality ≈10 [41, 42]. Many deformation experiments below the melting point revealed their correlation with mechanical stress linking cell structure with dynamical polygonization. However, during crystal growth where much lower stress is acting, a direct experimental access to the acting stress value is not yet possible. Therefore, the author's team correlated the cell diameters d, revealed by etching and laser scattering tomography in as-grown crystals [43], with the numerically calculated thermoelastic stress τ [44]. The non-steady equation of plastic deformation was solved giving the duration period until the main dislocation interactions are completed. Coupling with the Alexander-Haasen equation [54] the history of the elastic and plastic terms along the crystal coordinates were obtained [45].

From the numeric calculations follows [45] that in growing GaAs crystals the plastic relaxation is completed after a distance of only some mm behind the interface within time period of 1–2 hours. One can expect that the prevailing part of cell formation process be transpired during that time. In fact, there are experimental proofs from real-time synchrotron X-ray topography on crystallizing Al [46] and mechanical stressed Cu crystals [47] that the appearance of cellular structures does coincide with the onset of plastic deformation. This fact substantiated the approximation to take the calculated elastic strain at the interface for correlation with the cell dimensions measured in the post-grown wafers (of course, for a more precise analysis one has to consider possible renewed increase of the elastic stress during the cooling down course of the crystal, e.g. at LEC, when it emerges from the boric oxide encapsulant and contacts the relatively cold gas atmosphere).

It was found [44, 45] that at thermoelastic stresses above 1 MPa, typically for LEC, the universal relation $d = \alpha KGb\tau^{-1}$ [48] (α — constant, G — shear modulus, b — Burgers vector) is fulfilled which has been determined by post deformation experiments

for numerous crystalline materials [49]. However, at lower stresses, typically for VGF and VCz growth, the verification of this relation proved to be more difficult. The cell ripening process is mostly not yet finished. Further, the characteristic low dislocation densities in such crystals $<10^4$ cm^{-2} are not sufficient to form completed cell walls making a scaling analysis very complicate.

Surprisingly, as-grown InP crystals do not show well-developed dislocation cell structures. We attribute this feature to the much smaller compound homogeneity region and, thus, less native point defect content. As a result the cell formation is restrained due to reduced dislocation climb [40, 50]. Further, cross glide, being also important precondition for cell formation [51], is in InP nearly impossible due to the very low stacking fault energy.

Durose and Russel [52] and Sabinina et al. [53] investigated the cell wall morphology in vapour- and melt-grown CdTe samples by transmission electron microscopy and observed that the dislocations which constitute the boundaries are nearly all parallel and most have the same Burgers vector. Such behaviour is well-known from the standard type of polygonized low-angle grain boundaries containing only the excess dislocations of similar Burgers vector after the annihilation process is completed. However, all cell patterns cannot be explained exclusively by energetically driven equilibrium thermodynamics. Even in growing crystals there are typical preconditions of irreversibility such as temperature and stress flows that allow the treatment as an open system with continuous import and export of entropy. As a result, a rate of entropy is produced within the crystal evoking self-ordering of the stored dislocations into dissipative patterns.

Cell formation is retarded at very low dislocation densities and can be prevented by doping. No cell structuring was observed in GaAs doped with In or Si at concentrations $>10^{18}$ cm^{-3}. Also in CdTe the cell formation is depressed when the mixing component Se is added [40]. Another way is the minimization of the intrinsic point defect content by in situ control of stoichiometry (Fig. 5a). Recently, the author's team demonstrated by using a modified VCz arrangement without boric oxide encapsulant (Fig. 4) that the cellular structure dissolves when GaAs crystals grow under nearly stoichiometric conditions [35] (path A in Fig. 5b). This was recently also obtained from calculations on Cu crystals [50]. Omitting the point defect driven climb no cell structure can be developed.

4.2. Is there any hope of dislocation-free compound crystals?

To grow III–V compound crystals without dislocations is a long-term vision of the crystal growers. Dislocation-free GaAs and InP wafers would to be very promising for optoelectronic devices, especially high-brightness LEDs and high-power LDs. However, the main problem making such perfectness uncertain are the unfavourable material parameters such as very low critical resolved shear stress τ_{CRSS} (~0.2–0.5 MPa near to the melting point) and high content of native point defects. So arises the question is there any chance at all?

It is well established that the density and distribution of dislocations in melt-grown crystals are due to thermoplastic relaxation of thermally induced elastic stress [54]. Therefore, the content of dislocations is determined by the (time and space dependent) stress level during growth. The level of thermal stress is related to the temperature field in the growing crystal and cooling-down procedure. The higher the temperature field nonlinearities (in first approximation correlating with temperature gradients and crystal radius), the higher the mechanical stress. This correlation together with the low natural τ_{CRSS} values make it very difficult to grow crystals of larger diameters with low dislocation density or even dislocation-free. From methodical point of view low-temperature-gradient growth techniques, like VGF and VCz, are clearly preferred in order to meet this goal. In fact, compared to LEC much lower stresses <1 MPa are acting during growth. Hence, the careful engineering of the temperature field, assisted by global computer modelling at all process stages are of essential significance. Recently, Pendurti et al. [55] reported the global numeric modelling of the non-stationary elastic stress and related dislocation development in growing LEC InP crystals by implying the history of the thermal field in the crystal as well as the convection in the melt and vapour phase. A close correlation between the calculated elastic stress history and related dislocation density evolution does exist at various crystal points. It was found out that the gas

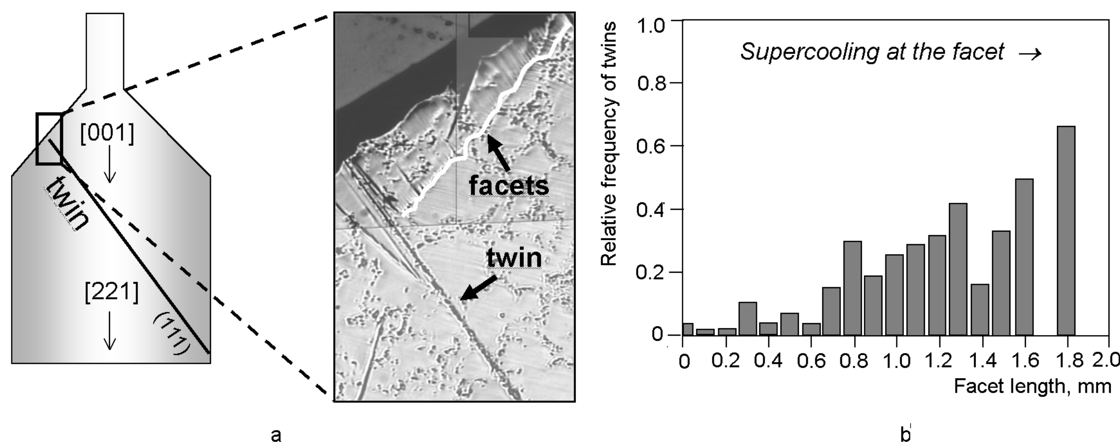

Fig. 6. a — Sketch and image of twin generation along the largest {111} facet of a facet train in the shoulder region of an InP LEC crystal. b — twinning probability vs. facet length, identically with supercooling of the facet, in LEC InP crystals [62].

convection has a significant effect on the total dislocation density — a quite important fact that was not yet considered so far.

Generally, to pave the way for dislocation-free growth of large III–V crystals the proper combination of the following conditions are required: i) use of dislocation-free seed crystals, probably, with the same diameter as the crystal to be grown [56, 57], ii) strongly uniaxial heat flow with very small temperature gradients, i.e. nearly flat isotherms at all stages of the growth process [3], iii) leave out of boric oxide encapsulant the presence of which introduces markedly thermomechanical stresses at the crystal periphery [35], iv) in-situ stoichiometry control in order to reduce the intrinsic point defect content which promotes high-temperature dislocation multiplication by climb [30, 35], v) avoidance of all parameter instabilities especially melt and gas flow fluctuations, e.g. by applying magnetic fields [24, 29] and, maybe, vi) the use of detached (dewetted) growth mode in case of directional crystallization in containers [58]. It seems that VGF (probably also further developed VCz) is the most suitable method to meet these demands in ensemble. Lowest dislocation densities of less than 100 cm^{-2} are obtained in 4" GaAs VGF crystals doped with Si [59]. Undoped crystals of the same diameter contain still around 10^3 cm^{-2}.

Despite of such noteworthy progress during the last decade today it is not yet clear of which consequence would to be a total absence of dislocations in compound crystals. As it is well known from dislocation-free silicon missing dislocations lead to higher supersaturation of native point defects and their clustering as micro voids and agglomerates (see e.g. [60]). Thus, the question arises do we really need dislocation-free compounds at all events?

5. Twinning

Growing-in twins are one of the most serious macroscopic defects the presence of which make a crystal of no use to wafer preparation because of the twin-induced growth misorientation over the whole crystal body (Fig. 6a). Up to now there is not yet an absolute reliable prevention measure due to their stochastic character of appearance. However, one can list a ranking of the most responsible material and growth parameters enhancing the twinning probability. Gottschalk et al. [61] correlated it with the stacking fault energy whereupon the highest danger of twinning exists in materials with high ionicity showing the lowest stacking fault energies. In fact, both InP and CdTe with ionicities of 42 % and 72 % and stacking fault energies of $1.8\cdot10^{-6}$ $J\cdot cm^{-2}$ and $1.1\cdot10^{-6}$ $J\cdot cm^{-2}$, respectively, show the highest twinning probability among the semiconductor compounds. Growth conditions enhancing twin appearance are — i) temperature instabilities, i.e. re-melting of the interface, ii) presence of impurities, iii) foreign particles swimming on the melt surface, iv) interface contact with wetting inner container walls, and v) morphological instability of the crystallization front. Recently at IKZ was demonstrated that there exists a clear correlation between twinning and degree of undercooling at the {111} facets [62] (Fig. 6b).

Hurle [63] has provided a possible thermodynamic description, which can explain the key features of the process. The model demonstrates that, because of the orientation dependence of interfacial energies in the presence of facets, there is a configuration of the 3-phase boundary for which, for sufficiently large supercooling, the free energy of formation of a critical nucleus is actually lowered by forming that nucleus at the 3-phase boundary in twinned orientation. This will occur only if a critical angle of conical growth presenting a portion of crystal surface normal to <111> is sampled during the growth. Such a twinned nucleus is thermodynamically favoured if the supercooling exceeds the critical value $\delta T^* = A^* (\sigma T_m/h\Delta H)$ with σ the twin plane energy, T_m melting temperature, h the nucleus height, ΔH the latent heat of fusion, and A^* the reduced work of formation of a nucleus intersecting the 3-phase boundary (its detailed derivation is given in ref. [63]).

Many LEC and Bridgman experiments have demonstrated that the twin probability is markedly reduced if the temperature fluctuations δT of the growth system, and therefore excursions of the angle of the contacting meniscus, are minimized. In fact Japanese producers succeeded in twin-free InP crystal growth with diameters up to 100 (150) mm by careful maintenance of thermal stability during growth that was achieved by applying damping magnetic fields around the melt [64, 65]. At VGF growth twinning can be reduced if flat bottom container with seed of the same diameter as the growing crystal is used [56].

In this connection well-developed control systems are of increasing importance. Recently, Neubert from IKZ Berlin [66] developed a model-based feedback controller for Czochralski processes. The basic strategy includes the use of nonlinear observers for the reconstruction of not directly measured quantities (e.g., crystal diameter and conical growth angle) and a combination of model-based and PID controllers for tracking of crystal diameter and growth velocity trajectories. The system quantities derived by means of the observer are less noisy and more accurate than those yielded by simple numerical differentiation. Furthermore, the growth velocity can be calculated from the values reconstructed by the observer. Due to the model the intricate meniscus dynamics is fully taken into account. Reconstruction by the observer and feedback control show excellent performance and the parameterization effort is remarkably reduced compared to conventional PID control. The proposed control method has been successfully used in 2" InP and GaAs growth at IKZ showing high accuracy, reproducibility, and robustness. Currently, it is tested under industrial conditions too.

6. New challenges — GaN, AlN and ZnO bulk crystals

As can be seen from Table GaN, AlN, ZnO are future materials which are of importance for blue and UV optoelectronics and high-power electronics. However, compared to the conventional compounds their material parameters, such as high melting temperature, equilibrium pressure and chemical reactivity, prove to be new challenges for the crystal grower. Several growth techniques are investigated to grow GaN bulk crystals [8]. Beside high-pressure flux growth, low-pressure solution growth (LPSG), metal halide vapour phase epitaxy (HVPE) and epitaxial layer overgrowth (ELOG) for obtainment of free-standing thick layers, the direct synthesis from vapour phase under NH_3 flow on alternative or native substrates is under development. Until now, best qualities are obtained when GaN crystals are grown from solution in liquid Ga under high pressure of nitrogen (0.8–2.0 GPa). In particular dislocation densities even lower than 100 cm^{-2} have been reported. However, their size is limited to about 1 cm^2 in area and 80–120 μm in thickness [67]. Recently, Sasaki and coworkers [68, 69] reported the growth of thick 2-inch GaN layers by liquid phase epitaxy (LPE) from Na flux under relatively low N_2 pressure of 4–5 MPa and at temperature of 850°C. First a thin GaN seed template is grown on a sapphire substrate by metal organic chemical vapour deposition (MOCVD) before the LPE process is carried out. A good flux stirring is achieved by convection due to an optimized temperature field. After the sapphire substrate is separated from the deposit free-standing GaN plates with dislocation densities ~10^4 cm^{-2} are available. GaN bulk crystals from a chlorine-free gas phase are grown at the IKZ Berlin [70]. Metallic Ga is evaporated from a heated melt and reacts with nitrogen from an ammonia and nitrogen gas mixture (Fig. 7). Pressures in the region of 10–80 kPa and moderate growth temperatures of 1000–1200°C are used. Sapphire and in house SiC and AlN are applied as substrates.

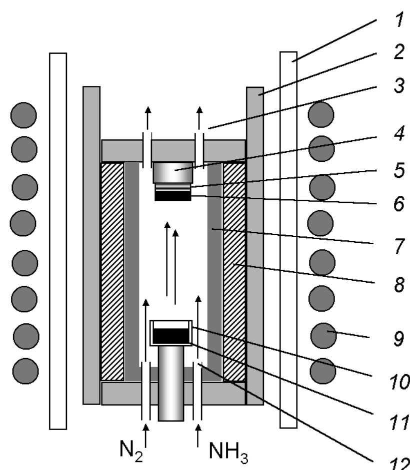

Fig. 7. Scheme of the chlorine-free vapour growth setup for GaN crystals used at the IKZ Berlin (adapted from D.Siche [70]). *1* — outer tube, *2* — insulation, *3* — gas outlet, *4* — seed holder, *5* — seed, *6* — GaN, *7* — inner chamber, *8* — heating cylinder, *9* — rf coil, *10* — source crucible, *11* — Ga source, *12* — crucible support, 13 — gas inlet.

Even AlN is more stable during heating up the system to growth temperature. The still small crystals of mm-dimension show good structural quality comparable with flux grown material.

AlN homosubstrates are the best variant for manufacturing of (Al,Ga,In)N layers for UV-LEDs. AlN bulk crystals are grown from the vapour phase. Generally, there are three approaches: i) seeded growth on non-nitride substrates, e.g. SiC, ii) growth of freestanding AlN crystals by self-seeding, and iii) crystal expansion using AlN seeds [71]. The required high growth temperatures ≥2000°C and the aggressive aluminium gas species limit the choice for crucible materials. TaC proves to be a usable candidate showing low partial pressure, high temperature and chemical stability. The successful growth of well faceted single crystalline AlN boules of 15 mm in diameter were recently reported by Herro et al. [72] using the seeded physical vapour transport method. Crystal quality increased during growth as manifested in a drop in FWHM of X-ray Rocking curves from 80 arcsec near the seed to 16 arcsec at growth surface. Also at IKZ the growth of AlN bulk crystals is under investigation [73]. Using sintered source material the undesirable oxygen content could be decreased down to 380 ppm. The self-seeding process with subsequent <0001> growth and n-doping will be optimized.

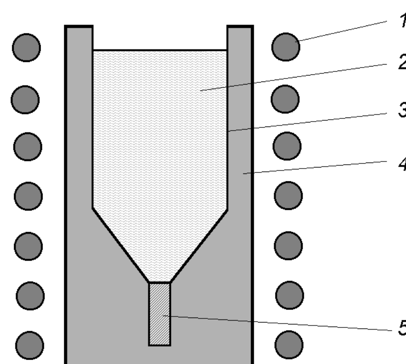

Fig. 8. Scheme of the vertical Bridgman setup for melt-growth of ZnO crystals used at the IKZ Berlin (adapted from D.Schulz et al. [10]): *1* — rf coil, *2* — melt, *3* — crucible, *4* — insulator, *5* — seed.

ZnO single crystals are of rapidly growing interest due to their potential applications as UV light emitters, green lasers, substrate for GaN epitaxy and acoustic wave devices [10]. The high melting point of $T_m = 1975°C$ and oxygen fugacity of $p_{O_2} =$ 0.35 bar make the bulk crystal growth from the melt very difficult, first of all because there is no ideal crucible material being resistant in a required oxygen overpressure. To avoid the employment of a crucible bulk crystal growth is mainly performed by the hydrothermal method [74] or by the pressurized "skull melting" [75]. However, hydrothermal grown crystals suffers from solvent incorporations and skull-melted material shows often cracks due to the characteristic high temperature gradients. Thermodynamic calculations provided at IKZ Berlin showed that iridium as crucible material is stable in the presence of an oxygen-containing atmosphere and in contact with molten zinc oxide [10]. For the first time, single crystals of 1.5 inch in diameter and up to 30 mm in length were obtained by rf-heated Bridgman method (Fig. 8). Adjusting the cooling rate during growth gives similar results like annealing with respect to optical transmission data of the crystals [76]. FWHM of X-ray Rocking curves down to 22 arcsec indicate a high structural quality of the ZnO wafers. Since occasionally mosaicity have been obtained the reproducibility of the growth technology needs to be still improved.

7. Summary

Since more than fifty years melt growth of semiconductor compound crystals the preparation of important materials, such as

GaAs, GaP, InP, CdTe, has been translated from fundamental research to industry where they became a high degree of maturity. Today, the growth of 6-inch GaAs and 4(6)-inch InP crystals by the LEC and VGF methods are already well established in production. Even the growth of 8-inch GaAs crystals was successfully tested being ready for industrial production during the next five years [3]. One can say the III–Vs, especially GaAs as the most important semiconductor after silicon, entered a prosperity market position.

However, that doesn't mean that there are no more certain difficulties to be still solved in order to complete the growth technologies towards increased gain, improved quality and lowered costs. It concerns i) the better knowledge of the influence of the melt structuring on crystallization kinetics even at materials with high ionicity (CdTe, ZnO, InP), ii) the better control of convective turbulences, e.g. with traveling magnetic fields, even when the crystal gain will be enhanced by applying larger melt charges, iii) the in situ ensuring of near stoichiometric growth conditions to control the intrinsic point defect concentration and to minimize the precipitate content even in CdTe and GaAs, iv) the prevention of dislocation patterning and bunching, and v) the damping of twinning along {111} facets as a very problematic drawback for materials with low stacking fault energy, like InP and CdTe. Even point v) is closely connected with application of modern model-based feed-back controlling systems in order to reduce temperature and meniscus fluctuations most effectively.

During the last years the optimization of growth processes for future compound materials GaN, AlN, ZnO came to the fore. The control of high process temperatures and dissociation pressures prove to be key challenges for the crystal growers during the next period. The IKZ Berlin deals actively with material engineering to complete the growth technologies of both conventional compounds (GaAs, InP, GaSb) and to work out optimal growth methods for future semiconductors (GaN, AlN, ZnO).

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References

1. Handbook of Electronic and Photonic Materials, ed. by S.Kaspar and P.Capper, Springer, Heidelberg, N.Y. (2006).
2. O.Oda, Compound Semiconductor Bulk Materials and Characterizations, World Scientific Publ., New Jersey (2007).
3. M.Jurisch, F.Borner, Th.Bunger et al., *J. Cryst. Growth*, **275**, 283 (2005).
4. K.Iwasaki, K.Sato, K.Aoyama et al., *IEEE Trans. Semicond. Manufact.*, **16**, 360 (2003).
5. P.Rudolph, *Progr. Cryst. Growth Charact.*, **29**, 275 (1994).
6. R.Hirano, H.Kurita, in: Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials, ed. by P.Capper, Wiley & Sons, West Sussex (2005), p.241.
7. T.S. Sudarshan, D.Cherednichenko, R.Yakimova, in: Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials, ed. by P.Capper, Wiley & Sons, West Sussex (2005), p.433.
8. A.Denis, G.Goglio, G.Demazeau, *Mat. Sci. Engin.*, **R 50**, 167 (2006).
9. Proc. of the 4th Int. Workshop on Bulk Nitride Semiconductors IV (IWBNS 4), *J. Cryst. Growth*, **305**, 301 (2007).
10. D.Schulz, St.Ganschow, D.Klimm et al., *J. Cryst. Growth*, **296**, 27 (2006).
11. V.V.Godlevsky, M.Jain, J.J.Derby, J.R.Chelikowsky, *Phys. Rev. B*, **60**, 8640 (1999).
12. J.Gaspard, J.Raty, R.Ceolin et al., *J. Non-Cryst. Solids*, **207**, 75 (1996).
13. P.Rudolph, N.Schafer, T.Fukuda, *Mat. Sci. Engin. R*, **15**, 85 (1995).
14. M.Muhlberg, P.Rudolph, M.Laasch, E.Treser, *J. Cryst. Growth*, **128**, 571 (1993).
15. L.Shcherbak, P.Feichouk, O.Panchouk, *J. Cryst. Growth*, **161**, 16 (1996).
16. L.Shcherbak, *J. Cryst. Growth*, **197**, 397 (1999).
17. L.Shcherbak, P.Feychuk, O.Kopach et al., *J. Alloys and Comp.*, **349**, 145 (2003).
18. P.Rudolph, M.Muhlberg, *Mat. Sci. Engin. B*, **16**, 8 (1993).
19. P.Rudolph, H.J.Koh, N.Schafer, T.Fukuda, *J. Cryst. Growth*, **166**, 578 (1996).
20. P.Rudolph, K.Umetsu, H.J.Koh, T.Fukuda, *Jpn. J. Appl. Phys.*, **33**, 1991 (1994).
21. B.W.Choi, H.N.G.Wadley, *J. Cryst. Growth*, **208**, 219 (2000).

22. E.Saucedo, P.Rudolph, E.Dieguez, in: Abstr. of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 in Salt Lake City, Electronic Release, Prod. by Omni Press, Abstract No.530 (to be published in *J.Cryst. Growth* 2007).
23. H.T.Rossby, *J.Fluid Dynamics*, **36**, 309 (1969).
24. D.T.J.Hurle, R.W.Series, in: Handbook of Crystal Growth, vol.2a, ed. by D.T.J.Hurle, Elsevier, North-Holland (1994), p.259.
25. P.Dold, K.W.Benz, *Progr.Cryst. Growth Charact.Mat.*, **38**, 7 (1999).
26. P.Schwesig, M.Hainke, J.Friedrich, G.Mueller, *J.Cryst. Growth*, **266**, 224 (2004).
27. T.P.Lyubimova, A.Croll, P.Dold, et al., *J. Cryst. Growth*, **266**, 404 (2004).
28. F.U.Bruckner, K.Schwerdtfeger, *J.Cryst. Growth*, **139**, 351 (1994).
29. P.Rudolph, in: Abstr. of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 in Salt Lake City, Electronic Release, Prod. by Omni Press, Abstract No.114 (to be published in *J. Cryst. Growth* 2007).
30. J.Nishizawa, Y.Oyama, *Mat.Sci.Engin.R*, **12**, 273 (1994).
31. P.Rudolph, *Cryst. Res.Technol.*, **38**, 542 (2003).
32. W.Dreyer, F.Duderstadt, Treatise No.995, Weierstraβ-Institute of Berlin (2004).
33. G.V.Semenova, T.P.Sushkova, A.Morozova, E.G.Goncharov, Inst. Phys. Conf. Ser., No.160, IOP Publishing Ltd. (1997), p.385.
34. J.Greenberg, Thermodynamic Basis of Crystal Growth, Phase P–T–x Equilibrium and Non-Stoichiometry, Springer, Berlin (2002).
35. P.Rudolph, F.-M.Kiessling, *J.Cryst. Growth*, **292**, 532 (2006).
36. A.V.Makarov, M.V.Mezhennyi, A.Y.Polyakov et al., *Nucl.Instr. and Meth. in Phys.Res.A*, **466**, 14 (2001).
37. S.Oda, M.Yamamoto, M.Seiwa et al., *Semicond.Sci.Technol.*, **7**, 215 (1992).
38. H.R.Vydyanath, J.A.Ellsworth, J.B.Parkinson et al., *J.Electron Mater.*, **22**, 1073 (1993).
39. J.R.Niklas, W.Siegel, M.Jurisch, U.Kretzer, *Mat.Sci.Engin.B*, **80**, 206 (2001).
40. P.Rudolph, *Cryst. Res.Technol.*, **40**, 7 (2005).
41. D.Holt, *J.Appl.Phys.*, **41**, 3197 (1970).
42. S.V.Raj, G.M.Pharr, *Mat.Sci.Engin.*, **81**, 217 (1986).
43. M.Naumann, P.Rudolph, M.Neubert, J.Donecker, *J.Cryst. Growth*, **231**, 22 (2001).
44. Ch.Frank-Rotsch, U.Juda, F.-M.Kiessling, P.Rudolph, *Mat.Sci.Technol.*, **21**, 1450 (2005).
45. P.Rudolph, Ch.Frank-Rotsch, U.Juda et al., *Phys.Stat.Sol.C*, **4**, 2934 (2007).
46. G.Grange, C.Jourdan, A.L.Coulet, J.Gastaldi, *J.Cryst. Growth*, **72**, 748 (1985).
47. B.Jacobson, H.F.Poulson, U.Lienert et al., *Science*, **312**, 889 (2006).
48. D.Kuhlmann-Wilsdorf, in: Work Hardening, ed. by D.B.Hirth, Gordon and Beach, N.Y. (1968).
49. M.Zaiser, in: Crystal Growth — from Theory to Technology, ed. by G.Muller, J.Metois and P.Rudolph, Elsevier, Amsterdam (2004), p.215.
50. B.Bako, I.Groma, G.Gyorgyi, G.Zimanyi, *Comp.Mat.Sci.*, **38**, 22 (2006).
51. R.Madec, R.Devincre, L.P.Kubin, *Scripta Mat.*, **47**, 689 (2002).
52. K.Durose, G.J.Russel, *J.Cryst. Growth*, **86**, 471 (1988).
53. I.V.Sabinina, A.K.Gutakovski, T.I.Milenov et al., *Cryst.Res.Technol.*, **26**, 967 (1991).
54. J.Volkl, in: Handbook of Crystal Growth, vol.2b, ed. by D.T.J.Hurle, Elsevier, North-Holland (1994), p.821.
55. S.Pendurti, V.Prasad, H.Zhang, *Modelling Simul.Mater.Sci.Eng.*, **13**, 249 (2005).
56. P.Rudolph, F.Matsumoto, T.Fukuda, *J.Cryst. Growth*, **158**, 43 (1996).
57. J.Amon, D.Zemke, B.Hoffmann, G.Muller, *J. Cryst. Growth*, **166**, 646 (1996).
58. T.Duffar, P.Dusserre, N.Giacometti, *J.Cryst. Growth*, **223**, 69 (2001).
59. B.Birkmann, M.Rasp, J.Stenzenberger, G.Muller, *J.Cryst. Growth*, **211**, 157 (2000).
60. T.Hibiya, K.Hoshikawa, in: Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials, ed. by P.Capper, Wiley & Sons, West Sussex (2005), p.1.
61. H.Gottschalk, G.Patzer, H.Alexander, *Phys. Stat.Sol.A*, **45**, 207 (1978).
62. M.Neubert, in: IKZ Annual Report (2005/2006) p.43 (http://www.ikz-berlin.de).
63. D.T.J.Hurle, *J.Cryst. Growth*, **147**, 239 (1995).
64. R.Pool, *Comp. Semicond.*, **8**, 4 (2002).
65. T.Kawase, S.Fujiwara, M.Matsushima et al., in : Proc. 2001 Int. Conf. on InP and Related Mat., (13th IPRM), 14–18 May 2001 in Nara, p.13.
66. M.Neubert, in: Abstr. of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 in Salt Lake City, Electronic Release, Prod. by Omni Press, Abstract No.354 (see also IKZ Annual Report 2005/06, p.82; http://www.ikz-berlin.de).
67. I.Grzegory, M.Bockowski, S.Porowski in: Bulk Cryst. Growth of Electronic, Optical and Optoelectronic Materials, ed. by P.Capper, Wiley & Sons, West Sussex (2005), p.173.
68. T.Sasaki, Y.Mori, M.Yoshimura, et al. in: Abstracts of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 in Salt Lake City, Electronic Release, Prod. by Omni Press, Abstracts No.115 and 432.
69. T.Iwahashi, Y.Kitaoka, F.Kawamura et al., *Jpn.J.Appl.Phys, Part 2, Lett. & Express Letters*, **46**, L227 (2007).
70. D.Siche, in: Abstr. of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 in Salt Lake City, Electronic Release, Prod. by Omni Press,

Abstract No.307 (see also IKZ Annual Report 2005/06, p.50; http://www.ikz-berlin.de).

71. D.Zhuang, Z.G.Herro, R.Schlesser, Z.Sitar, *J. Cryst. Growth*, **287**, 372 (2006).
72. Z.Herro, D.Zhang, R.Schlesser, Z.Sitar, in: Abstr. of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 Salt Lake City, Electronic Release, Prod. by Omni Press, Abstract No.868.
73. J.Wollweber, in: IKZ Annual Report (2005/06), p.48 (http://www.ikz-berlin.de).
74. E.Ohshima, H.Ogino, I.Niikura et al., *J.Cryst. Growth*, **260**, 166 (2004).
75. J.Nause, B.Nemeth, *Semicond. Sci. Technol.*, **20**, 45 (2005).
76. D.Schulz, St.Ganschow, D.Klimm, in: Abstr. of 15th Int. Conf. on Crystal Growth, August 12–17, 2007 in Salt Lake City, Electronic Release, Prod. by Omni Press, Abstract No. 598.

Перспективи та труднощі вирощування об'ємних кристалів напівпровідникових сполук

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Напівпровідникові сполуки мають на даний час і збережуть у майбутньому першорядне значення у житті людства. Вже досягнуто відносно високого рівня розвитку їх виробництва. GaAs зберігає лідируюче положення у галузях оптоелектроніки та високочастотної мікроелектроніки, безперервний розвиток яких буде продовжуватися. Необхідно істотно збільшити вихід монокристалів InP, GaSb, CdTe та ZnO. Для всіх цих сполук зростає значення вирощування з розплавів методом твердіння у вертикальному температурному градієнті. Високі темпи розвитку очікуються для GaN та AlN. Відповідно, оволодіння управлінням фазовими переходами газ-тверде тіло та розчин/розплав-тверде тіло на високому технологічному рівні є абсолютно необхідним.Незважаючи на значні зусилля протягом останніх десяти років, при вирощуванні з розплаву також існують деякі принципові утруднення, які треба подолати, наприклад, усунення структурування розплаву, пригнічення конвективних збурень, регулювання стехіометрії *in situ*, мінімізація осадження, пригнічення копіювання дислокацій, запобігання двійникуванню та створення систем управління процесами вирощування на основі моделей. Автор подає огляд можливих заходів, які розробляються його групою в Інституті росту кристалів (Берлін) для досягнення згаданих цілей.