THE DEVELOPMENT OF LEC TECHNOLOGY FOR GaAs SINGLE CRYSTAL GROWTH FROM LABORATORY SCALE TO MASS PRODUCTION

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1. INTRODUCTION

Despite some earlier „more stochastic" publications about III-V compounds and their properties including semiconductivity [1-2] H. Welker is commonly regarded as the „father of the III-V's". From 1951 to 1953 he thought about gallium arsenide (GaAs) and its kin from the 3rd and 5th group of the periodic system of elements and recognized that the III-V compounds could be a material to compete and/or to supplement silicon [3-5]. A period of detailed investigations of the electronic and structural properties of GaAs followed, along with the development and realization of concepts of opto- and micro-electronic devices with superior characteristics compared to silicon.

Parallel to this development considerable efforts were undertaken to create the material basis, i.e. to synthesize GaAs and to grow single crystals for manufacturing of substrates with required properties. The Czochralski method to grow GaAs single crystals was first successfully applied by Gremmelmaier using a hot wall technology in a gas-tight quartz container to suppress melt decomposition by selective arsenic evaporation [6]. But a real breakthrough was made by Mullin et al. [7] applying a liquid boron oxide encapsulation to cover the melt. This Liquid Encapsulation Czochralski (LEC) method has allowed the reproducible growth of single crystals with a circular cross section best suited for wafer manufacturing. Details can be found in [8]. The LEC method has reached maturity for market oriented mass production of GaAs single crystals during the last decade of the last century.

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As lower specific costs per die are the main driving force in device manufacturing, the transition from laboratory scale to mass production was accompanied by demand for an increase in crystal (wafer) diameter and length, and exactly tailored device-relevant properties allowing the application of both ion implantation and epitaxy as the main device technologies (Fig.1.). At the same time, the production costs were reduced by optimization and automatization of the technological flow.

Due to high thermal stress during growth and subsequent cooling, combined with a lower critical shear stress at high temperatures, LEC grown GaAs crystals contain a rather high dislocation density - in the range of (5 – 10)x10^4 cm^{-2} for 150 mm diameter crystals. Dislocations act as non radiative recombination centres and can cause degradation of devices which rely on injection of electrons from n-type region into a p-type region like luminescence and laser diodes

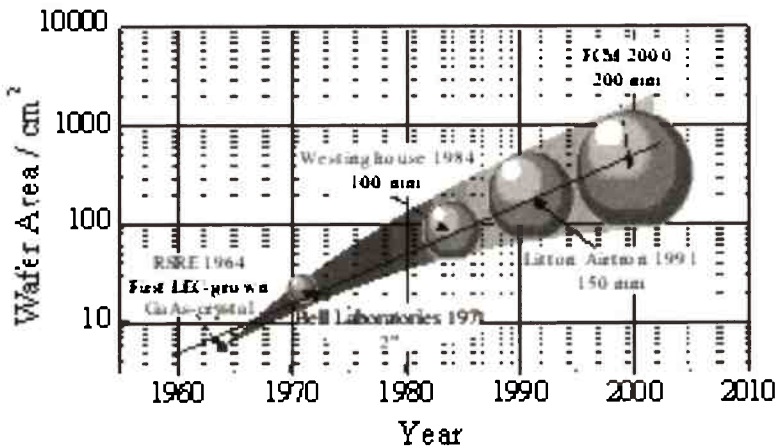

Fig.1. Diameter of SI GaAs single crystals grown by the LEC method.

and hetero-bipolar transistors, respectively. This has led to development of low thermal gradient techniques, among which the (liquid encapsulation) vertical Bridgman technique (VB) and its modifications (VGF) have reached maturity for the production of semi-conducting (SC) and semi-insulating (SI) GaAs in the last decade. In the past the market share of LEC SI GaAs crystals was greater than 50%, but it is expected to decrease due to preference of low dislocation density GaAs for epitaxy in the future.

The progress in LEC growth of SI GaAs single crystals made in the last decade was tightly related to two key issues, the development and application of a near-to-reality computer modeling for furnace design and development/ optimization of growth technology and the thermochemical analysis of the

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complex reaction system for carbon control. This will be detailed in the next chapters.

2. NUMERICAL MODELLING

It is very difficult to scale up LEC-pullers and LEC-technologies, because the mechanisms of heat transport in the growth system are highly nonlinear. The complexity of turbulent gas and melt flows makes it hard to design larger set-ups only relying on the experience of crystal growth in smaller equipment.

Here, computer simulation can help to approximate optimal growth hardware and growth processes. Two main technological topics must be optimized for the LEC-process in order to achieve a high crystal quality. Firstly, the temperature gradient in the crystal should be as low as possible under the constraint that the arsenic losses do not degrade the surface of the crystal after leaving the boron oxide melt. Secondly, the shape of the solid-liquid interface must be controlled in a manner (mainly convex from the melt) that polycrystalline growth can be avoided.

Today, many different computer codes have reached a level which is high enough to really support the development of crystal growth technologies. At FREIBERGER the codes STHAMAS and STHAMAS3D are used for development of various LEC-technologies. STHAMAS solves the Navier-Stokes equations for the 2D-axisymmetric case using a finite volume method on structured grids. In addition to the heat transfer by radiation and conduction, high-pressure gas convection is included by a buoyancy extended standard k-ε-turbulence model with wall functions [9-10]. The free crystal/melt boundary was also taken into account.

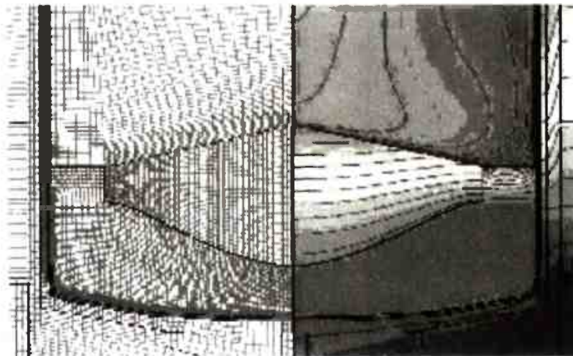

Fig.2. 2D-modeling of LEC-growth of a 200 mm GaAs crystal (left: grid, right: T-field).

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In Fig.2, typical 2D-simulation results for a 200 mm crystal growing in a 11´´ crucible are shown [11]. A block-structured numerical grid is included together with the temperature field. Apart from the fact that the calculated melt flow and the shape of the phase boundary are not yet completely refined, a temperature field with the desired main features was achieved.

But only time-dependent three-dimensional calculations with fine grids according to the real geometry of the crucible are able to predict the highly turbulent melt convection and the shape of the phase boundary in a reliable form. The software package STHAMAS 3D [10, 12] solves the Navier-Stokes equations for the 3D-case and the computational domain consists of crucible, melt and crystal. Of course, the shape of the interface is calculated, too. The thermal boundary conditions are obtained for the local 3D-simulations in form of fixed temperatures or heat fluxes e.g. at the inner or outer wall of the crucible, from the global 2D-simulations. Convection in the boron-oxide layer is not taken into account since the viscosity of the liquid boron-oxide is very high. Instead, proper boundary conditions for the velocity are applied at the surface of the GaAs melt.

The first numerical results show that, in general, a strong buoyant flow occurs due to the large melt volume [13]. In order to counteract the buoyancy driven flow, high crucible and crystal rotation rates must be applied. But, even using both high crucible and crystal rotation rates, experimental and simulation results indicate that a strong unsteady three-dimensional melt flow exists in the melt region below the crystal (Fig.3). Further, it was demonstrated that changing the maximum temperature difference inside the melt only by a few degrees has a strong influence on the stability and on the shape of the interface [13]. This sensitivity of the interface is also confirmed by experimental observations.

Fig.3. Snap shot of time dependant 3D-modelling of 150mm LEC growth in an 11″ crucible using STHAMAS3D [12]. The highly turbulent 3-dimensional melt flow below the crystal is clearly visible.

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Although the strategy of performing local 3D simulations with proper thermal boundary conditions obtained from global 2D-simulations results in a better agreement with respect to a more precise prediction of the interface shape than the pure 2D-approach, a real coupling between global 2D- and local 3D-simulations might be necessary, because the melt convection influences the thermal field not only locally in the melt. Convective heat transport in the melt might require that the heating power in the 2D-simulation has to be adapted to the new conditions. This would again result in new boundary conditions for the 3D-simulations.

3. THERMOCHEMISTRY OF CARBON DOPING

Semi-insulating behaviour of GaAs is basically connected with the intrinsic mid-gap double donor EL2, which is most probably a single arsenic antisite atom As_{Ga} [14]. The Fermi level is pinned at this state resulting in SI GaAs if the condition $N_{EL2} > [C]-(N_{\Sigma Sa} - N_{\Sigma SD}) > 0$ is fulfilled with N_{EL2} and [C] being the EL2 content and the concentration of intentionally doped carbon, respectively, and $(N_{\Sigma Sa} - N_{SSD}) \cong 10^{14}$ cm^{-3} the concentration of impurities acting as acceptors (A) and donors (D). Keeping residual impurities low and constant, the carrier concentration, and by this way electrical resisitivity, of SI GaAs is determined by the EL2- and carbon concentration.

The control procedure of carbon is based on a thermochemical analysis of the complex reaction system comprising the gas atmosphere, the boron oxide melt, solid and liquid GaAs, the crucible and the graphite heaters. Fig.4. is a schematic representation of the system under consideration.

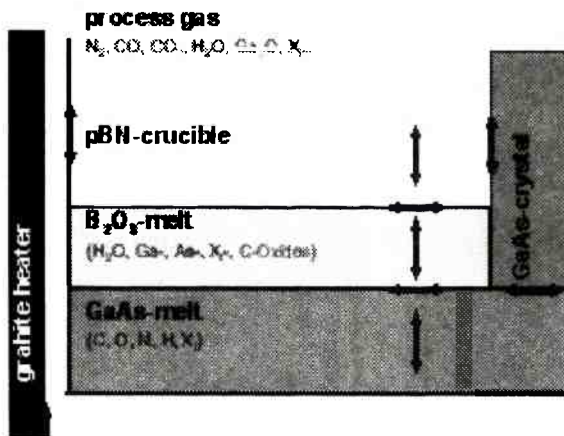

Fig. 4. Schematic representation of the complex LEC reaction system.

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Neglecting transport of reactants in the fluid phases, an equilibrium approach is studied as a first approximation. Instead of considering a complete set of describing chemical reaction equations and formulating and solving the corresponding set of mass action laws, the total Gibbs Free Energy of the system is minimized to calculate the equilibrium concentration of the given components. The commercially available ChemSage code [15] has been used. Further details are given in [16].

As mainly redox equilibria are of importance, the results of the calculations are best visualized as so-called *predominance area diagrams* [17]. It represents the stability region of the GaAs melt in the presence of the boron oxide encapsulant at the GaAs melting temperature in a plot of log a_C over log p_{O_2}, with a_C and p_{O2} the activity of carbon and the oxygen partial pressure (Fig.5). As can be seen from Fig.5, the stability region of GaAs-melt/liquid boron oxide essential for crystal growth is bounded by the dissociation of boron oxide at lower and oxidation of Ga in the GaAs-melt at higher oxygen chemical potentials. The upper boundary of the stability region is given by a_C = 1, i.e., by the solubility limit of carbon in liquid GaAs. Fixing the chemical potential of the control species carbon and oxygen in this stability region there are no degrees of freedom left in the system.

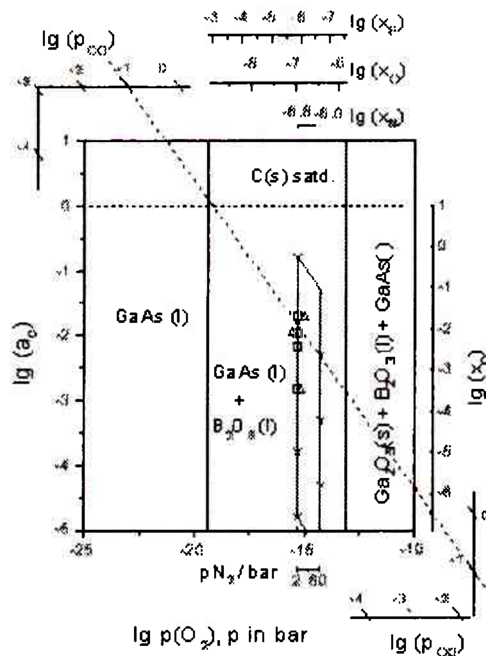

Fig.5. Predominance area diagram for LEC growth assuming oxygen control by nitrogen reaction with boron oxide.

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But not the entire stability region of GaAs/boron oxide is accessible for carbon/oxygen control during LEC growth. The working area marked in Fig.5 was calculated under the assumption that the chemical potential of carbon and oxygen will be determined by the CO and N_2 partial pressures, respectively, assuming that nitrogen reacts with boron oxide [18].

The dotted line in Fig.5 indicates a constant CO partial pressure. It is obvious that keeping the CO partial pressure constant is not sufficient to unambiguously control the carbon content in the GaAs melt, the oxygen potential must be fixed, too.

In practice, control of the oxygen potential is attempted by controlling the water content of boron oxide. But this procedure suffers from a continuous decrease of water content in boron oxide due to the evaporation/reaction of water with the other constituents of the system (graphite, gallium etc.).

Using the activity coefficient of carbon in GaAs [20], the carbon content in the melt is obtained. Correspondingly, semi-quantitative scales for oxygen, nitrogen and boron are given in Fig.5 assuming no interaction between these solutes. It is obvious that their concentration is determined by the oxygen potential alone. Finally, using the equilibrium distribution coefficients, the concentration of carbon and the other solutes in solid GaAs can be estimated.

In analogy, measured concentrations of carbon, oxygen, boron and nitrogen in solid GaAs can be used to estimate the corresponding concentrations in the melt in order to verify the calculations. The open squares in Fig.5 represent the carbon concentration at constant N_2 partial pressure and varying CO partial pressure, and demonstrate the applicability of the thermochemical approach.

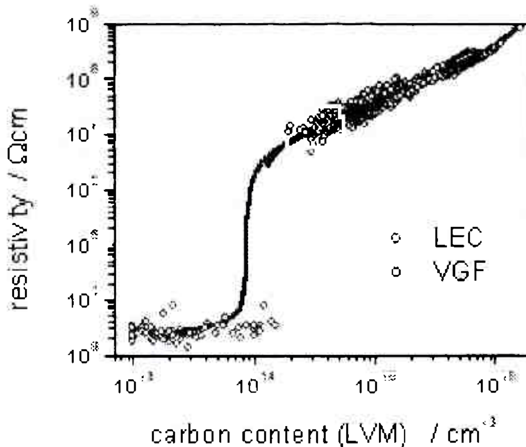

Fig. 6. Electrical resistivity versus carbon content for LEC and LEVGF grown GaAs. Solid lines were calculated using the compensation model [19].

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In the framework of the equilibrium approach there are no differences in the *predominance area diagrams* of LEC and LEVGF growth of GaAs, i.e., similar procedures are used for carbon control. This is obvious from Fig.6, representing electrical resistivity versus carbon content for state-of-the-art C-controlled LEC and LEVGF GaAs single crystals.

But the radial and axial macrosegregation of carbon observed in LEC and LEVB/VGF grown SI GaAs crystals clearly indicates that transport of reaction products in the fluid phases and/or reaction kinetics at phase boundaries can not be neglected. To demonstrate this, the axial carbon content at a constant carbon potential, and the response to a step-like increase of carbon potential is shown in Fig.7. Macrosegregation with decreasing C concentration ($k_C \cong 2$) for constant C chemical potential is followed by a transient region, where carbon content increases without reaching a new equilibrium state.

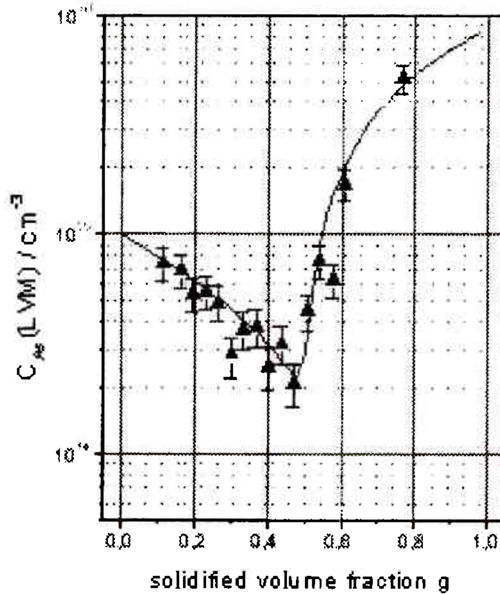

Fig.7. Axial C-concentration at constant and step-like increased chemical potentials of carbon.

Therefore, to establish a control procedure for compensation of macrosegregation a transport model is required. According to the thermochemical model it should include carbon and oxygen as control species and system-releated parameters like the area and thickness of the boron oxide layer and its transport properties. The elementary processes included in the model are illustrated in Fig.8.

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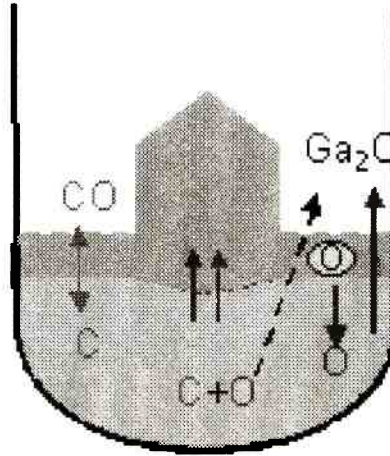

Fig. 8. Advanced transport model for liquid encapsulation growth of GaAs.

Transport in the GaAs melt is quick enough in order to neglect concentration differences in the melt. Assuming a planar solid/liquid interface the balance of carbon and oxygen in liquid GaAs can be expressed by expanding the well known SCHEIL equation as follows:

$$\frac{dN_m^C}{dt} = -\frac{dN_s^C}{dt} + \frac{dN_{B_2O_3}^C}{dt} - \frac{dN_R^C}{dt};$$

$$\frac{dN_m^O}{dt} = -\frac{dN_s^O}{dt} - \frac{dN_{B_2O_3}^O}{dt} - \frac{dN_R^O}{dt} + \frac{dN_{res}^O}{dt}.$$

The first term on the righthand side describes the incorporation of carbon and oxygen into the growing crystal (usual Scheil equation), the second, an effective transport of carbon (CO) and oxygen (Ga_2O) containing species through boron oxide including reaction kinetics at the phase boundaries, and the third, a decrease of carbon and oxygen in the melt due to a chemical reaction. The last term in the balance equation of oxygen takes into consideration that boron oxide can serve as a reservoir for oxygen due to the heterogeneous reaction of nitrogen with boron oxide. Further details can be found in [21].

The system of non-linear differential equation given above, has been numerically solved and applied to analyse the axial C-distributions in 150 mm

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crystals grown in 11 inch crucibles a charge mass of 27 kg under various CO partial pressures (Fig.9). Except for the initial concentrations of carbon and oxygen in the melt which were fitted, the experimentally obtained carbon (upper part of Fig.9) and oxygen data in a oxygen doped crystal (lower part) could be described by the C-O-model using a single set of parameters. Based on this, a control procedure has been developed using a predetermined function p_{CO} = f (g) to ensure a nearly constant axial carbon concentration.

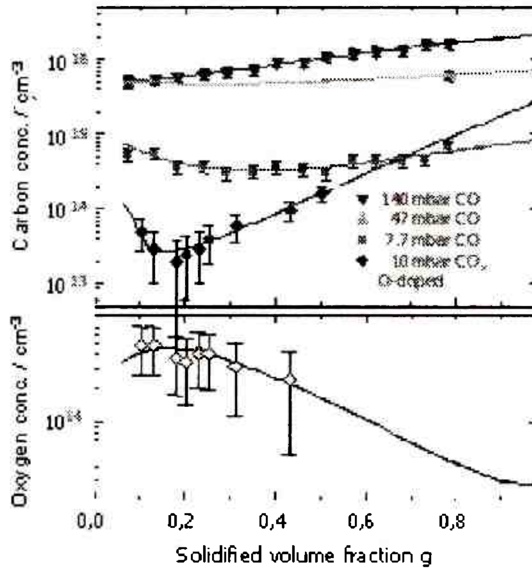

Fig.9. Comparison of measured (dots) and calculated (solid lines) axial carbon distribution in LEC crystals grown under different conditions.

4. SUMMARY

Mass production of SI GaAs single crystals based on an advanced LEC growth process has been established during the last decade of the last century. Two key issues had to be solved: Scaling up of the growth equipment and carbon control.

The progress in modelling of thermal heat transfer (radiation, conduction and turbulent convection) due to high computer power and advanced codes has made it possible to optimize the equipment and the processes in a rather short time and at lower costs.

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Based on a thermochemical analysis of the complex reaction system and an advanced C-O segregation model, a control procedure for carbon and oxygen has been developed and successfully introduced in mass production of C-controlled SI GaAs single crystals by the LEC as well as LEVGF technology.

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