Active Carbon Control During VGF Growth of Semiinsulating GaAs

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INTRODUCTION

Today 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 these different technologies. The device industry requires substrate wafers with exactly tailored properties. One main parameter of interest is the electrical resistivity of semi-insulating GaAs. The homogeneity of this parameter within a wafer (radial homogeneity) and from wafer to wafer within an ingot (axial homogeneity) is especially challenging for substrate production. State-of-the-art LEC material shows excellent electrical properties by using active carbon control during the crystal growth process [1]. However, the production process for low EPD material requires an adjusted strategy to obtain results similar to those reached in the LEC process. In this paper we report on our active carbon control during VGF crystal growth. The advantage of this new technology will be illustrated in comparison with state-of-the-art LEC material.

THERMOCHEMICAL MODELLING

To ensure semi-insulating properties and to accommodate customers' resistivity specifications for the crystal, the concentration of compensating carbon has to be actively controlled in the GaAs melt during the VGF crystal growth process. This is done by basically the same procedure as already applied in LEC growth, i.e., by controlling the chemical potentials of oxygen and carbon in the growth system. This is more difficult in the VGF process due to the lower contribution of convective flow on transport of species in the fluid phases in VGF technology. The procedure is based on a reduction of the complicated Redox equilibria in the complex reaction system by calculating a *predominance area diagram* as suggested in [2]. It represents the stability region of the GaAs melt in the presence of the encapsulant, the pBN crucible and the graphite heater in a plot of log a_C (activity coefficient of carbon) versus log p_{O2} (partial pressure of oxygen) as the

two key thermodynamic parameters (fig. 1). The ChemSage code [3] has been used in this calculation to minimize the total Gibbs Free Energy. Details are given in [4].
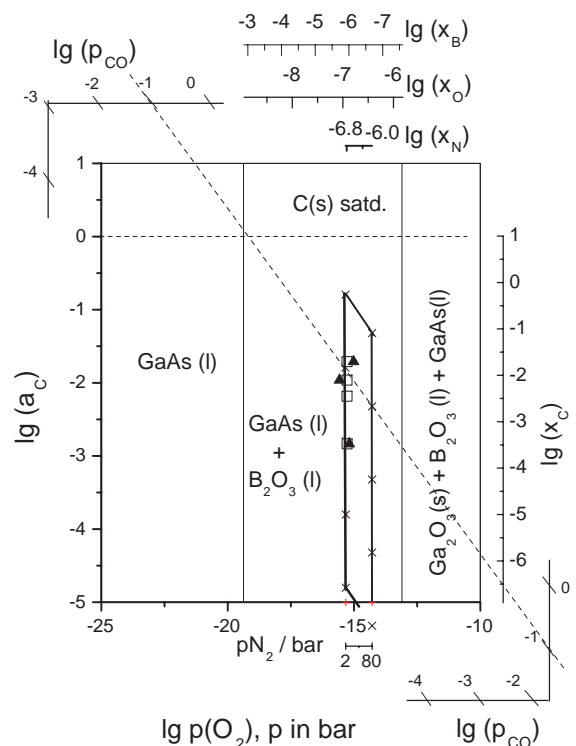

Fig. 1: Predominance area diagram for the liquid encapsulated VGF growth system

Crystal growth can be performed in the coexistence area of GaAs(l) + B_2O_3(l) which is bounded by the dissociation of boron oxide at lower and oxidation of Ga at high oxygen chemical potentials. The upper limit is given by $a_C = 1$, i.e., the carbon solubility limit in liquid GaAs. Fixing the control species C and O_2 at certain values in this region, there is no degree of freedom left in the system, as the temperature is kept constant at the melting point. An experimentally

accessible *working area* within the stability region is marked for the chemical potentials of oxygen and carbon controlled by the N_2- and CO-partial pressures in the gas phase, respectively. The dotted line indicates a constant CO partial pressure, which makes it clear that CO-control alone is not sufficient to determine the carbon content in the melt. Using the known activity coefficient of carbon in GaAs, melt the scale of carbon concentration in the melt has been obtained. Correspondingly, semiquantitative scales for oxygen, nitrogen and boron are given, assuming no interaction between these solutes.

The applicability of this procedure has been proven by analysing the C-, B- and O content in grown crystals and estimating the corresponding concentrations of the solutes in the melt using their distribution coefficients at given partial pressures of N_2 and CO. Data points in fig. 1 representing carbon concentrations at constant N_2 but variable CO partial pressure taken from the experiments described below satisfactorily agree with the calculations.

EXPERIMENTAL SETUP

For this investigation nominally undoped 100 mm and 150 mm VGF crystals were grown by the liquid encapsulated VGF technique.
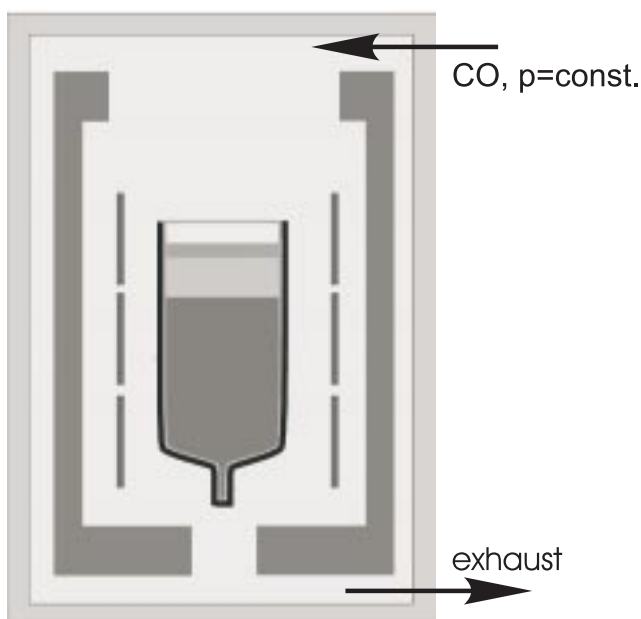

Fig.2. Schematic growth setup

For crystal growth a furnace is used which was scaled up from a design given in detail in [5,6]. The feed material used was pre-synthesized from the elements in a separate high-pressure furnace as described in detail in ref [7]. In order to define highly reproducible experimental conditions ,

the crucible preparation, furnace evacuation, heating up, melting and homogenization conditions were carefully controlled and held constant during the study. The same is true for poly material, as well as the mass and water content of the boron oxide used during growth. Oxygen potential in melt, CO-partial pressure and CO mass flow within the growth atmosphere were varied (fig. 2). After growth the crystals were annealed for homogenization of electrical properties.

The crystals were characterized by routine methods, including measurement of carrier concentration and resistivity using van der Pauw geometry. The concentrations of carbon and oxygen were determined by LVM absorption measurements using Fourier-transform infrared spectrometry at room temperature and at low temperature (77 K). Calibration factors of 1.18×10^{16} cm^{-1} for carbon and 8×10^{16} cm^{-1} for oxygen were applied. The error bars of the measurements can be estimated to be 10 %.

RESULTS AND DISCUSSION

In order to suppress the dependency of resistivity on the distribution coefficient of carbon ($k_o \approx 2$) as shown in fig. 3 independent control of carbon content is necessary to enhance the length of usable crystal with a defined resistivity. This carbon control reduces also the dependency of the resistivity of the grown crystal on the variable quality of the feed material.
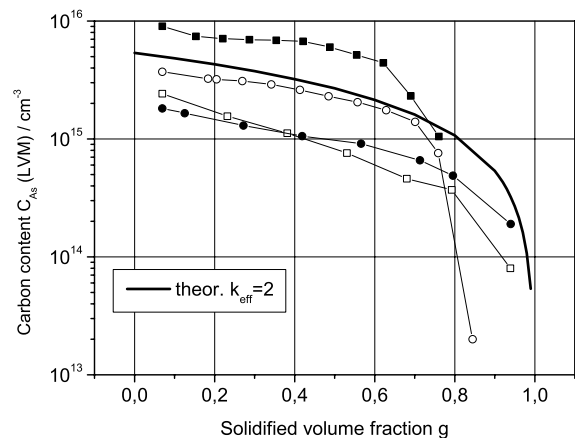

Fig.3. Carbon concentrations of several non-carbon controlled VGF grown crystals vs. solidified volume fraction

Due to the axial decrease of carbon content in crystals grown without carbon control, the resistivity drops down from the semi-insulating 1×10^7 Ωcm range to about 10^3Ωcm as illustrated in fig. 4.
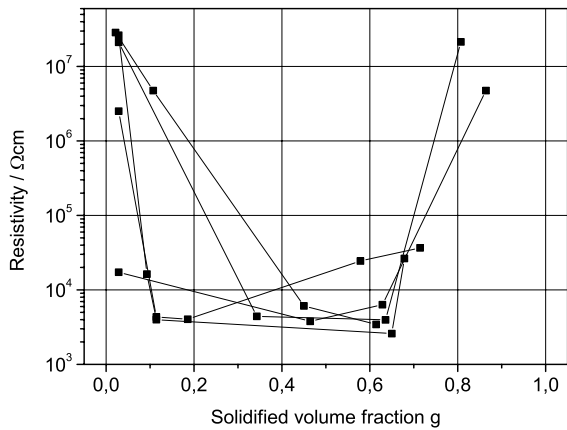
Fig. 4. Resistivity over solidified volume fraction for crystals grown without controlled carbon content

Detailed analyses show that this decrease of resistivity is not related to an additional donor. LVM measurements prove that carbon and oxygen can coexist within VGF-grown semi-insulating GaAs (fig. 5) in contrast to the well known behavior of LEC material as described e.g. in [8].
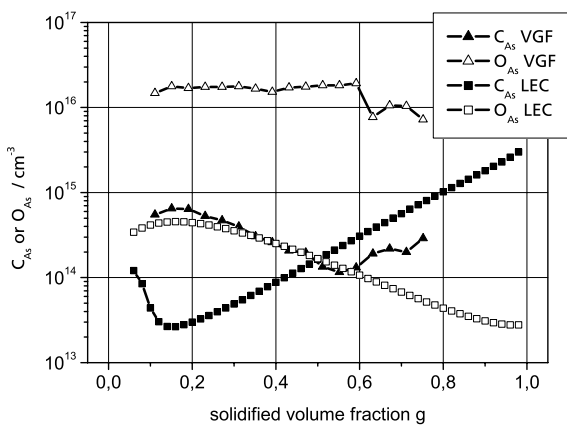

Fig. 5. Carbon and oxygen concentration as a function of solidified volume fraction for non-carbon controlled VGF grown crystals and for special LEC grown crystals

Fig. 5 illustrates the most important problem to be solved in order to allow an effective carbon control, the control of oxygen. In our experiments, the oxygen potential of the feed material was varied. Here, the mass flow of the working gas and the CO concentration were kept constant. As can be seen in fig. 6, the carbon concentration can be controlled between 10^{15} cm^{-3} and 10^{16} cm^{-3} controlling the oxygen chemical potential.
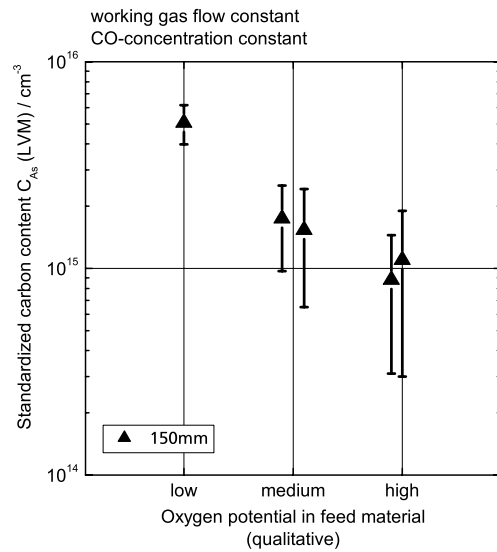

Fig.6. Carbon concentration vs. qualitative oxygen potential in feed material.

Taking into account that resistivity is a well determined function of carbon content at constant EL2-concentration, the resistivity can be varied by this way over more than two orders of magnitude from 10^7 Ωcm to 10^9 Ωcm.
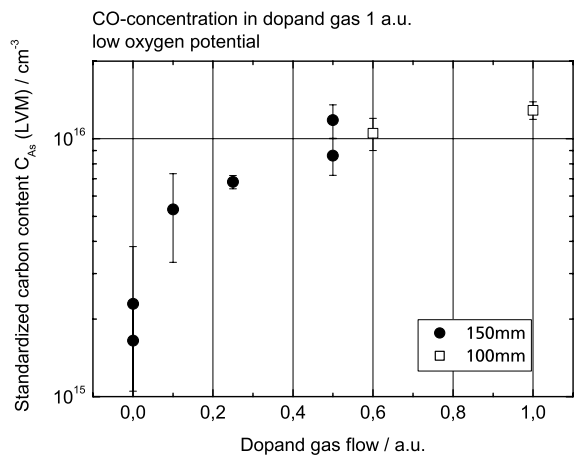

Fig.7. Standardized carbon content versus dopant gas flow

Next, the dopant gas flow was varied, while at constant CO-concentration and low oxygen potential in feed material. As shown in fig.7, even small variations of gas flow are a powerful tool to vary the carbon content in the melt and finally in the grown crystal.
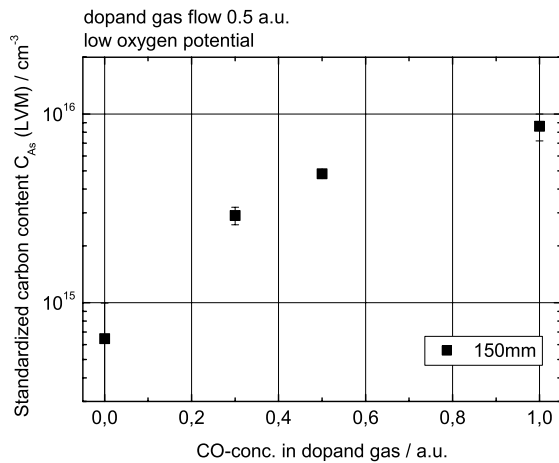
dopand gas flow 0.5 a.u.
low oxygen potential

Fig.8. Carbon content vs. CO-concentration in dopant gas flow

As shown in fig. 8, CO concentration is a more attractive parameter for regulation because carbon content depends nearly linearly on CO-concentration at low values under the chosen conditions.
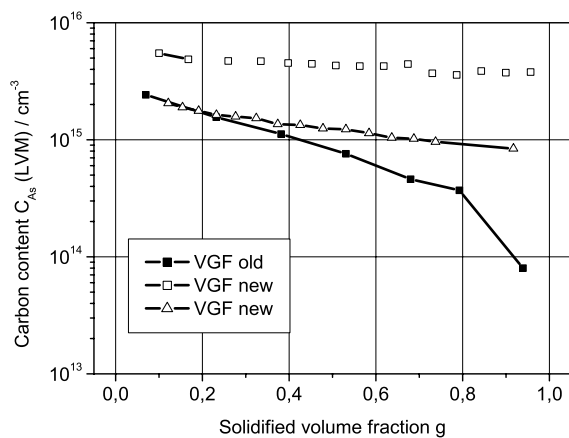

Fig.9. Carbon content vs. solidified volume fraction in comparison of old non-carbon controlled process (■) with new carbon controlled processes (Δ, □)

Fig. 9 summarizes the results of the three varied parameters. Furthermore, the first theoretical thermodynamic studies are confirmed by the experiments. The variation of carbon content for the final experiments is only weak, and further optimization is possible. As shown in fig. 10 the resulting electrical resistivity is nearly constant along the grown crystal.
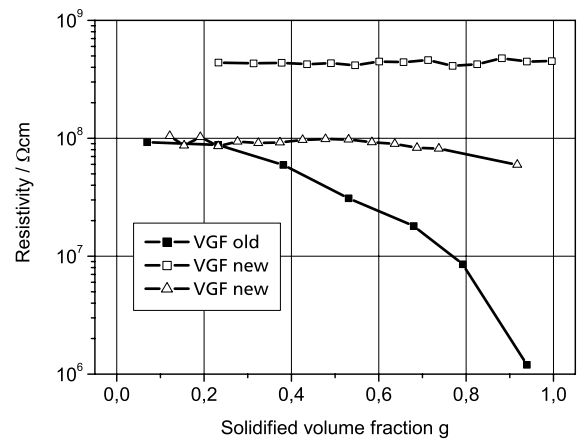

Fig.10. Resistivity vs. solidified volume fraction, comparing the old non-carbon controlled process (■) with the actively carbon controlled processes (Δ, □)

SUMMARY

The dependency of carbon concentration of semi-insulating GaAs grown by the VGF method on chemical potential of carbon and oxygen was investigated. Varying the parameters make it possible to control the carbon content from 5×10^{14} cm^{-3} to 10^{16} cm^{-3} in semi-insulating GaAs crystals and by this way, to control the resistivity from 10^7 Ωcm to 10^9 Ωcm. So, the VGF technique has reached the same level of carbon control and determination of electrical properties as well known state-of-the-art LEC grown semi-insulating GaAs crystals.

REFERENCES

[1]   T. Flade, M. Jurisch, A. Kleinwechter, A. Köhler, U. Kretzer, J. Prause, Th. Reinhold, B. Weinert, J. Crystal Growth 198/199 (1999) 336-342.

[2]   W. A. Oates, H. Wenzl, J. Cryst. Growth 191 (1998) 303 – 312.

[3]   http://gttserv.lth.rwth-aachen.de/~sp/tt/chemsage/chemsage.htm.

[4]   J. Korb, T. Flade, M. Jurisch, A. Köhler, Th. Reinhold, B. Weinert, J. Cryst. Growth 198/199 (1999) 343 – 348.

[5]   Th. Bünger, D. Behr, St. Eichler, T. Flade, W. Fliegel, M. Jurisch, A. Kleinwechter, U. Kretzer, Th. Steinegger and B. Weinert, Materials Sci. Technol. B80 (2001) 5.

[6]   K. Sonnenberg and E. Küssel, III-Vs Review 10 No.5 (1997) 30-34.

[7]   H. Immenroth, U. Lampert, E. Tomzig, J. Crystal Growth 142 (1994) 37.

[8]   S. Eichler, A. Seidl, F. Börner, U. Kretzer, B. Weinert, J. Cryst. Growth 247 (2003) 69-76.