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Semi-insulating 4-6-inch GaAs crystals grown in low temperature gradients by the VCz method

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The results of growth of semi-insulating GaAs crystals with diameters of 100-150 mm and lengths up to 200 mm from the melt with starting charges up to 25 kg by the low-temperature gradient Vapour Pressure Controlled Czochralski method (VCz) are given and compared with the state of art of LEC growth. The methodical process optimization was assisted by global numerical simulations. A slightly convex interface morphology has been found to be the most suitable for moderate EPD of ~10^4 cm^{-2} in 150-mm crystals whilst simultaneously depressing the probability of dislocation bunchings. The carbon concentration was controlled down to values below 10^{14} cm^{-3}. Electrical properties, including the EL2° content, are discussed. The first results of GaAs VCz crystals grown without B_2O_3 encapsulant are given. A reduced boron concentration but enhanced carbon and vacancy concentrations have been observed.

Key words: GaAs, VCz, Dislocation density, Electrical properties.

Introduction

As has been recently stressed [1] GaAs-based high-frequency devices are now and in the future a mainstream branch for many powerful wireless and optical communication circuits. The transition from ion-implanted field effect transistors (FET) to epitaxy-based heterostructure bipolar transistors (HBT) with higher efficiency, higher power density, lower noise and lower overall costs places an increasing demand for semi-insulating (SI) low-dislocation GaAs wafers with diameters of 100 and 150 mm (4- and 6-inch, respectively). Today, there are three methods for the growth of bulk SI GaAs crystals with all diameters desired including 6-inch - i) liquid encapsulation Czochralski method (LEC) [2], ii) vertical gradient freezing (VGF) [3, 4], and iii) vapour pressure controlled Czochralski method (VCz) [5, 6]. Whereas the LEC technique is characterized by the highest productivity, excellent controllability of the electrical parameters and dimension, the VGF method shows the best capability for low-dislocation growth. VCz is placed in between. It is distinguished by moderate dislocation density and improved homogeneity combined with relatively good productivity and variability. In particular, the possibility of the omission of the boric oxide encapsulant [6] allows an in-situ control of the melt composition. This makes the VCz technique a distinct possibility for production of precipitation- and boron-reduced material.

In order to improve the qualities of LEC GaAs crystals over the past few years the VCz method has been developed further at the Institute of Crystal Growth (IKZ) in Berlin. The present paper summarizes the results mainly of 6-inch samples.

Experimental

Figure 1 gives a schematic drawing of the VCz arrangement used. The main difference of this compared

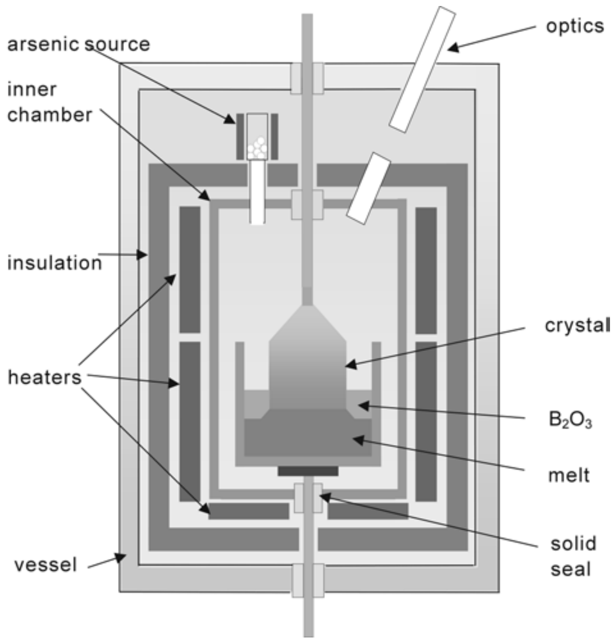

Fig. 1. Scheme of the VCz arrangement as applied at IKZ Berlin.

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to the conventional LEC technique is the presence of an inner chamber shielding the growing crystal and the hot gases from the water-cooled walls of the outer high pressure vessel. This is a precondition for growing crystals in a markedly reduced axial and radial temperature gradient compared to the conventional LEC technique. In order to prevent arsenic evaporation, and thus dissociation of the very hot crystal surface, an arsenic partial pressure is established within this chamber by a temperature-controlled source of pure arsenic. A multi-heater arrangement in a commercial puller with a fully-automated process and diameter control system was applied. Solid sealing was applied to enable the passing throughs of seed and crucible rods into the inner VCz chamber. An infinitely small out-flow of arsenic was accepted and compensated for by the arsenic source.

Starting charges of up to 25 kg were loaded in an 11-inch (~285 mm) pBN crucible to obtain 6-inch crystals with lengths up to 200 mm. Nitrogen or argon were applied as the working gases. The carbon content in the crystals was controlled by proper CO and oxygen fugacity within the VCz chamber [7]. The axial temperature gradient at the growing interface was ≈ 20 K cm^{-1} allowing only low growth velocities of 4-6 mm h^{-1}. Figure 2 shows an image of typical as-grown GaAs VCz crystals. The mirror-like lustre surfaces indicate that the crystals grew under conditions of controlled solid-gas equilibrium throughout.

To study the growth conditions and point defect content in VCz crystals under conditions without boric oxide encapsulant in a 4-inch growth arrangement the B_2O_3 layer was completely omitted and the As source temperature was varied over a wide range from 590°C (Ga-rich melt) to 630°C (As-rich melt) to maintain various melt compositions.

Generally, for the process optimization the methodical developments were assisted by global numerical simulation using the two codes CrysVUN++ and STHAMAS [8]. It was found that the temperature

Fig. 2. As-grown VCz GaAs crystals grown in the authors laboratory. On the right side: crystals with diameters 150 mm and 100 mm, respectively. On the left side: samples grown without boric oxide.

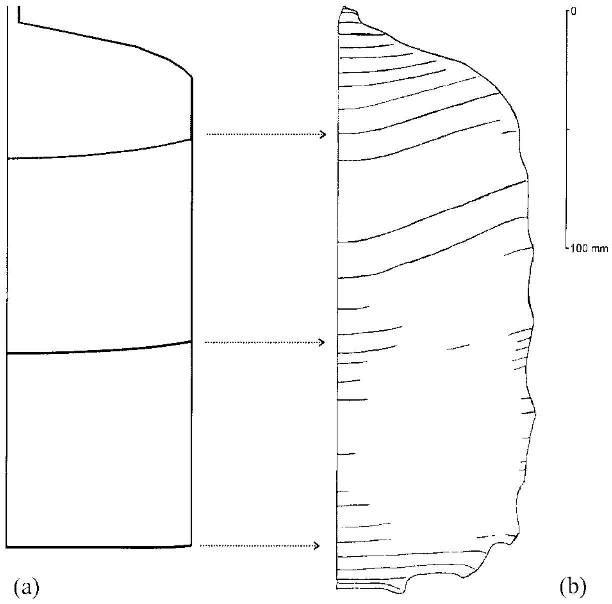

Fig. 3. Calculated shapes of the melt-solid interface of three growth positions in a 6-inch VCz crystal (a) compared with DSL (diluted Sirtl with light) - etched striations of a longitudinal cut of a 6-inch VCz crystal, grown under the same conditions as used in calculations, revealing the realistic shape of the interface (b).

differences in the convective gas phase around the growing VCz crystal are significantly lower than in the conventional LEC case due to the presence of the surrounding hot inner chamber. As a result the thermal stresses in the cooling crystal are markedly reduced. The accompanying modeling was very helpful to optimize the morphology of the interface. Figures 3a and b show calculated and experimentally revealed shapes of the growing interface in a longitudinal cut of a 6-inch VCz crystal. Although the simulation picture does not yet fit completely the experimentally-revealed curvature the tendency of the interface flattening towards the crystal end is obvious (more realistic agreement between model and experiment will be demonstrated in the future by use of 3D-simulations considering the convection in the melt). Generally, a slightly convex morphology being constant over the whole cylindrical part of the crystal proves to be the most suitable for prevention of dislocation bunching.

Results and Discussions

Figure 4 shows an etched 6-inch SI VCz GaAs wafer. The main etch pit density (EPD), determined by a dislocation mapping technique [9], yields 1×10^4 cm^{-2}. By using a ten-point analysis along the <110> and <100> directions in several 6-inch crystals the average EPD was $(1.8\text{-}2.6) \times 10^4$ and $(2\text{-}3) \times 10^4$ cm^{-2}, respectively. Minimum values of $(6\text{-}8) \times 10^3$ cm^{-2} were ascertained near the $r/2$ region (r-wafer radius). In 4-inch VCz crystals a somewhat lower average EPD of

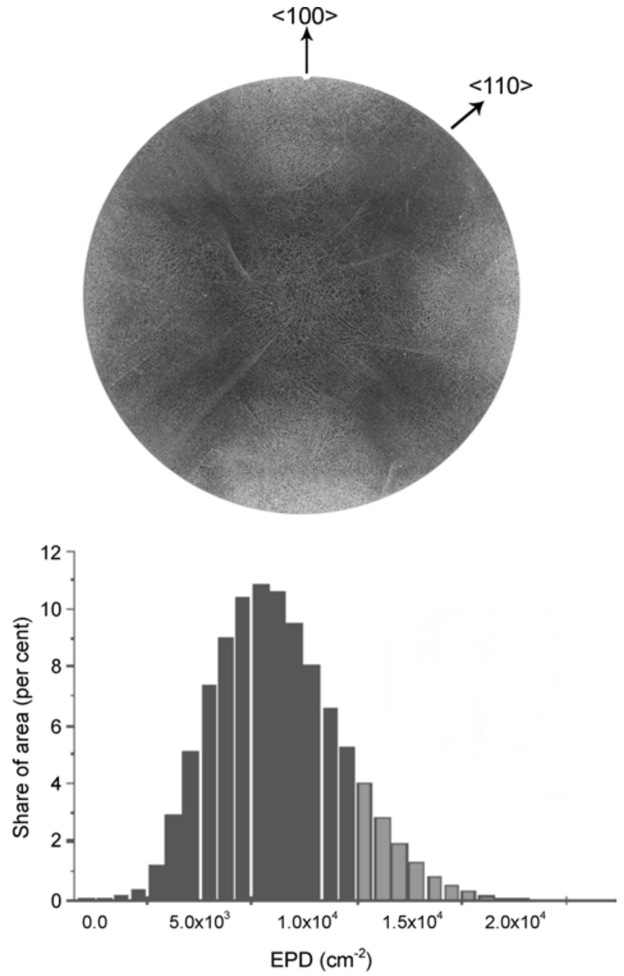

Fig. 4. KOH-etched 6-inch wafer of an as-grown VCz GaAs crystal (above) and the dislocation density histogram taken from EPD mapping over the whole wafer (below).

$(5\text{-}10) \times 10^3$ cm^{-2} was found. The full widths at half maximum (FWHM) of the double crystal rocking curve (DCRC) of representative 4- and 6-inch VCz wafers were (10 ± 2) and (13 ± 3) arc sec, respectively. Photoelastic strain maps of as-grown 6-inch (100) VCz wafers show, similarly to the 4-inch samples, very low residual strain ($\Delta\varepsilon/\varepsilon$ in the order of 10^{-6}) being about one order of magnitude lower than in as-grown LEC crystals and comparable to bulk-annealed LEC wafers. Detailed analysis of the dislocation cell structure by etching, laser scattering tomography [10] and X-ray synchrotron topography [11] were carried out. It could be shown that in both 4- and 6-inch VCz crystals the cells are of globular shape and originated from dynamic polygonization under essential participation of high-temperature dislocation climb. The cell dimensions are markedly enlarged to more than 1 mm compared to LEC crystals with cells of 100-300 μm. Several cells in VCz crystals were found not to be complete due to the reduced dislocation density.

The accidential appearance of localized dislocation bundles, elongated rod-like along the growth direction and perpendicular to the given melt-solid interface, was one of the structural problems that had to be solved. This phenomenon is well-known for GaAs LEC [12-15] and VGF growth as well [16] but its origin is still not clarified. It has been attributed to dislocation generation at incorporated foreign particles (e.g. Ga inclusions) [12], morphological instabilities of the growing interface [13] or local variations of the melt composition [14]. We found that in agreement with Shibata *et al*. [15] the probability of generation of such bundles is enhanced if concave regions at the interface are present. According to our observations even at flat interfaces such defects can be generated. Therefore, our efforts were directed at finding out the growth conditions which ensure a constant interface shape with a slightly convex curvature over the whole crystallization process. The probability of dislocation bunching was evidently reduced in both 4- and 6-inch crystals if the ratio between crystal radius r and radius of the interface cuvature r_c was $r/r_c \geq 0.25$.

The electrical parameters of the grown VCz crystals are comparable with those of LEC material. In Fig. 5 the electrical resistivities of numerous 4-inch VCz crystals as a function of the carbon concentration in comparison with LEC material [17] are shown. As can be seen from this figure for the first time low carbon contents down to values $< 10^{14}$ cm^{-3} could be achieved in VCz crystals [7]. Maximum electron mobilities in the range of 6000-7000 cm^2/Vs were found in as-grown crystals which could be enhanced up to 8000 cm^2/Vs after bulk annealing.

Generally, compared to LEC crystals as-grown VCz crystals are characterized by lower electron trap EL2° concentrations in the range of $(0.5\text{-}1) \times 10^{16}$ cm^{-3} similar to as-grown VGF material. This implies that there is obviously a correlation with the average EPD which is reduced in VCz as in VGF samples as well.

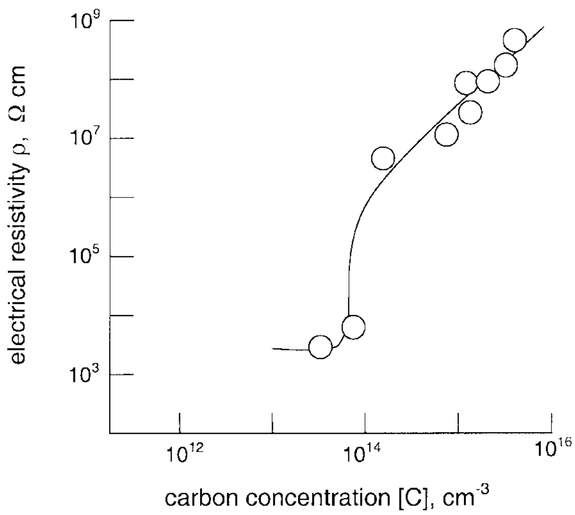

Fig. 5. The correlation between electrical resistivity ρ and carbon concentration [C] in VCz crystals (circles) in comparison with the standard curve of LEC material [17] (full line).

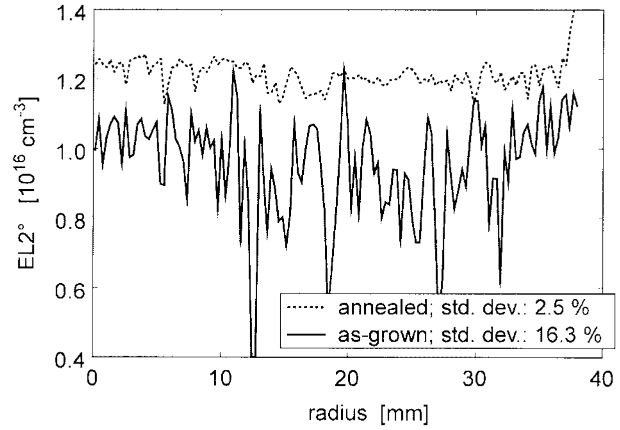

Fig. 6. Radial EL2° distribution along [110] direction in a VCz wafer taken from an annealed bulk section compared to a wafer from an adjacent as-grown section of the same crystal.

Typical scatter of the radial EL2° distribution has been found in as-grown VCz crystals due to the enrichment of antisites in the cell walls. As can be seen from Fig. 6 a marked homogenization effect can be achieved by post-growth bulk-annealing. The absolute EL2° concentration was fixed to a value of 1.25×10^{16} cm^{-3} with a residual scatter of only 2.5% along the wafer radius.

The first GaAs crystals grown in a VCz arrangement without boric oxide encapsulant have been obtained. The main radial EPD distribution was 2×10^4 cm^{-2} without a rise at the edge. This is caused by stress reduction in the absence of the B_2O_3 layer. As was expected, the boron concentration in such crystals is markedly lowered ($< 10^{15}$ cm^{-3}) compared to conventional VCz crystals ($\sim 10^{16}$ cm^{-3}). However, the carbon content is increased by about one order of magnitude up to $(1\text{-}3) \times 10^{16}$ cm^{-3} if the gas composition is not controlled (note, using the gas flow control the carbon concentration can be reduced of more than one order of magnitude). The EL2° concentration, measured by local vibration mode (LVM) IR spectroscopy, is reduced to below 2×10^{15} cm^{-3}. Hence, p-type material has been obtained in such examples due to [C] > [EL2°]. The results agree with Hot Wall Czochralski (HWC) experiments earlier described by Tomizawa *et al.* [18] demonstrating the sensitive thermo-chemical regulator role of boric oxide in the case of its presence between vapour and melt.

Positron annihilation measurements were carried out to detect negatively charged vacancies (V_{Ga}, V_{As}). The VCz samples grown without B_2O_3 with comparable melt composition as for conventional VCz crystals (slightly As-rich) show a higher average positron life time indicating a higher vacancy content. This result can possibly be attributed to the reduced boron concentration. However, further experiments are necessary to study this effect in more detail.

Conclusions

It has been shown that the structural perfection of 4 - 6-inch SI GaAs LEC crystals can be improved by use of a low-temperature gradient VCz modification. Recently, this was also very obviously demonstrated for InP [19]. For the desired dislocation densities of about 10^4 cm^{-2} without bunching in 6-inch crystals the interface shape should be slightly convex. The carbon content in VCz crystals could be controlled down to values $< 10^{14}$ cm^{-3}. No differences in the electrical properties between VCz and LEC material have been observed after bulk annealing.

The first VCz growth experiments without boric oxide encapsulant showed an improved homogeneity of the radial dislocation distribution, decreased boron and EL2° contents, and increased vacancy concentrations.

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References

1. J. Newey, Compound Semiconductor 8[6] (2002) 33-37.
2. T. Flade, M. Jurisch, A. Kleinwechter, A. Köhler, U. Kretzer, J. Prause, T. Reinhold and B. Weinert, J. Crystal Growth 198/199 (1999) 336-342.
3. X. Liu, III-Vs Review 8 (1995) 14-20.
4. Th. Bünger, D. Behr, St. Eichler, T. Flade, W. Fliegel, M. Jurisch, A. Kleinwechter, U. Kretzer, Th. Steinegger and B. Weinert, Mat. Sci. Engin. B80 (2001) 5-9.
5. M. Tatsumi, T. Kawase, Y. Iguchi, K. Fujita and M. Yamada in: Semi-insulating III-V Materials, edited by M. Godlewski (World Scientific, Singapore 1995) pp. 11-18.
6. M. Neubert and P. Rudolph, Prog. Crystal Growth Charact. Mat. 43 (2001) 119-185.
7. K. Jacob, Ch. Frank, M. Neubert, P. Rudolph, W. Ulrici and M. Jurisch, J. Korb, Cryst. Res. Technol. 35 (2001) 1163-1171.
8. Ch. Frank, K. Jacob, M. Neubert, P. Rudolph, J. Fainberg and G. Müller, J. Crystal Growth 213 (2000) 10-18.
9. J. Donecker, S. Rautenstrauch and S. Bergmann in: Proc. DRIP VII, Inst. Phys. Conf. Ser. 160 (1998) 169-172.
10. M. Naumann, P. Rudolph, M. Neubert and J. Donecker, J. Crystal Growth 231 (2001) 22-33.
11. T. Tuomi, L. Knuuttila, J. Riikonen, P.J. McNally, W.-M.

Chen, J. Kanatharana, M. Neubert and P. Rudolph, J. Crystal Growth 237 (2002) 350-355.
12. J.P. Tower, R. Tobin, P.J. Pearah and R.M. Ware, J. Crystal Growth 114 (1991) 665-675.
13. G. Frigerio, L. Zanotti, J.L. Weyher, C. Paorici, C. Mucchino and C. Bucci, Cryst. Prop. and Preparation 36 (1991) 312-317.
14. F.-Ch. Wang, M.-F. Rau, J. Kurz, M.F. Ehman, D.-D. Liao and R. Carter in: Defect Recog. and Image Proc. in III-V Comp., edited by E.R. Weber (Elsevier, Amsterdam 1987) pp. 117-124.
15. M. Shibata, T. Suzuki, S. Kuma and T. Inada, J. Crystal Growth 128 (1993) 439-443.
16. J. Stenzenberger, Thesis, Univ. Erlangen-Nürnberg 2000.
17. A. Kleinwechter, P. Bünger, T. Flade, M. Jurisch, A. Köhler, U. Kretzer, A. Seidl and B. Weinert, 2001 GaAs MANTECH, Int. Conf. Las Vegas, Nevada, May 21-24, 2001.
18. K. Tomizawa, K. Sassa, Y. Shimanuki, J. Nishizawa in: Defects and Properties of Semiconductors: Defect Engineering, edited by J. Shikawa, K. Sumino and K. Wada (KTK Scientific Publishers, Tokyo 1987) pp. 25-36.
19. R. Pool, Semiconductor Compound 8[4] (2002) 4 and 45-47.