Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Crystal Growth 292 (2006) 532–537
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Growth and characterization of GaAs crystals produced by the VCz method without boric oxide encapsulation

P. Rudolph*, F.-M. Kiessling

Institute for Crystal Growth, Max-Born-Str. 2, D-12489 Berlin, Germany

Available online 8 June 2006

Abstract

Unintentionally doped GaAs crystals grown from Ga-rich melts without B_2O_3 encapsulation by the modified vapour pressure controlled Czochralski (VCz) method are analysed. The influence of this growth technique on dislocation density and distribution is presented. The concentration of As precipitates in dependence on the melt composition is shown. Finally, the contents of residual impurities and their influence on some characteristic electrical parameters are discussed. The attention is focused on the feasibility of in situ controlled near-stoichiometric semi-insulating (SI) GaAs crystals with minimized content of As precipitates.

PACS: 81.05.Ea; 81.10.Fq; 61.50.Nw; 61.72.−y; 81.30.Mh

Keywords: A1. Defects; A1. Impurities; A1. Point defects; A1. Stoichiometry; A2. Czochralski method; B2. GaAs

1. Introduction

Since the requirements for GaAs substrates used for epitaxial circuits instead of ion-implanted ones are continuously increasing [1], the focus has changed towards improvements of the wafer surface quality. One of the most important targets is the prevention of harmful second-phase particles, so-called crystal-originated pits (COPs), affecting the surface preparation and thin film deposition process. In standard as-grown crystals obtained by the liquid encapsulation Czochralski (LEC) and vertical gradient freeze (VGF) techniques, this problem is related to the non-stoichiometry due to the growth from slightly arsenic-rich melts [2], leading to formation of As precipitates [3] and probably, inclusions. As it is well known for a long time [4] that even after post-growth annealing, there are still related residual defects forming crater-shaped pits during polishing.

Another problem related to the off-stoichiometry is the enhanced content of intrinsic point defects like As interstitials, vacancies of both types and As antisites. Especially the last one, identified as the deep-level donor EL2 (As_{Ga}) in low concentrations of $10^{16}\,cm^{-3}$, plays an important role for electrical properties. It is favourable to ensure stable semi-insulating (SI) behaviour [1], but disadvantageous for application of such crystals that are used in high-sensitivity radiation detectors [5] due to their substantial contribution to the carrier recombination and hence, to their lifetime reduction. In the present work, the efforts were directed on the growth of near-stoichiometric crystals with reduced excess of arsenic. For this, the growth from in situ controlled Ga-rich melts by the VCz method [1,2] without boric oxide encapsulant was used.

In principle, the attempts to grow GaAs by the Czochralski method without boric oxide encapsulant are very seldom, but not new, and go back to the 1950s [6] and 1960s [7]. During the 1980s, the hot-wall Czochralski (HWC) technique with controlled As atmosphere was developed [8,9], but receded somewhat into the background. Recently, we again took up this idea [10,11], however, based on our long-term experiences on VCz developments [12], and on a markedly improved structural material and construction level.

*Corresponding author. Tel.: +49 30 6392 3034; fax: +49 30 6392 3003.
E-mail address: rudolph@ikz-berlin.de (P. Rudolph).

0022-0248/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2006.04.066

2. Experimental procedure

Undoped GaAs crystals with diameters between 2 and 3 in have been grown from different Ga-rich melt compositions by the VCz method without boric oxide encapsulant, described in detail elsewhere [9,10]. Argon or nitrogen with a pressure of 0.5 MPa was used as process gas. The mole fraction of the melt y_L was controlled in situ in the range $0.45 \leqslant y_L \leqslant 0.50$ by the partial arsenic pressure between 0.02 and 2.1 MPa adjusted via the temperature of the As source from 540 to 650 °C. Experimentally, the value of y_L was estimated from the residual Ga excess in the last-to-freeze crucible charge. The carbon content in the melt, and hence in the crystal, could be controlled by CO gas streaming communicated to the inner growth chamber. The axial temperature gradient at the growing solid–liquid interface was calculated by global computer modelling to be $20\,K\,cm^{-1}$ [11]. To prevent constitutional super cooling, leading to inclusions due to the Ga enrichment in the diffusion boundary layer [11], all crystals were grown by uncritical pulling rates between 3 and $5\,mm\,h^{-1}$ depending on the melt composition. The rotation rates of seed and crucible were +6 and −(25–30) rpm, respectively. For comparison, GaAs crystals were also grown by VCz with B_2O_3 encapsulant. This method has been described in detail elsewhere [12].

The crystals grown from pBN crucibles in [0 0 1] direction were cut into some slices. For this paper, only as-grown pieces from the top region of the cylindrical crystal part were diagnosed. Precipitate analysis was provided by IR laser-scattering tomography (LST). Dislocations were revealed by KOH solution at 370 °C. The residual impurity concentrations were detected by glow discharge mass spectrometry (GDMS) and boron by secondary ion mass spectroscopy (SIMS). Additionally, the concentrations of C, O, H, N and related complexes were evaluated from their local vibrational mode (LVM) absorptions at 77 K. The $EL2^0$ content was ascertained by near-IR absorption measurements. The electrical parameters were obtained from Hall measurements at room temperature.

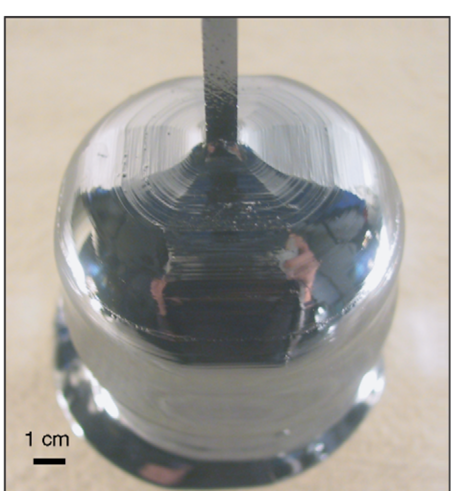
3. Results and discussions

3.1. Crystal phenotype

Fig. 1 shows images of two VCz single crystals grown from Ga-rich melts without boric oxide encapsulation. It is worth mentioning that the surfaces are mirror-like and free of any symptoms of dissociation as it is usual for LEC crystals [13]. Markedly enlarged {1 1 1} facets seen in Fig. 1a are caused by the low radial temperature gradient evolved from the absence of the B_2O_3 layer. In consequence, an enhanced twinning probability should be feared. Using highly purified and freshly synthesized starting material, and growing crystals in an optimized growth regime, we obtained twin-free crystals. As proof of the high crystallization stability, intentional variations of the crystal diameter did not provoke any twinning (Fig. 1b). This experimental fact refutes the conclusion that twin-free growth from Ga-rich melts is improbable (see e.g. [7,13,14]).

3.2. Arsenic precipitates

In order to find out the growth conditions for near-stoichiometric solid composition, we used the LST analysis. It is well known that in GaAs, the scatters can be attributed to arsenic precipitates condensing during the cooling-down process of the as-grown crystals due to the retrograde solubility of the excess As interstitials. One part decorates dislocations, while the other remains as much smaller particles in the crystal matrix [15]. It is important to note that in our present crystals, no more Ga inclusions were found ever since the morphological stability of the crystallization front was guaranteed. As we demonstrated

(a)


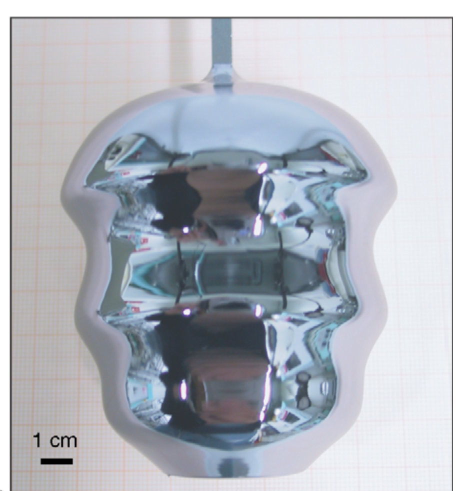
(b)


Fig. 1. GaAs VCz crystals grown without boric oxide encapsulant from Ga-rich melts. Due to the low radial temperature gradient, large {1 1 1} facets do appear.