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STRUCTURAL DEFECTS IN GALLIUM ARSENIDE

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Microscopic defects in low-dislocation LEC GaAs grown under various conditions from stoichiometric and Ga-rich melts are investigated by using eutectic etching with a molten mixture of KOH and NaOH in equal mole concentrations. Dislocations, surface roughness, tetragonally-shaped pits and raised structures are observed in In- or In+Zn-doped crystals. The size and concentration of the raised structures depend on the growth conditions, the stoichiometry of the crystal and post-crystallization cooling. The possible nature and thermal stability of the defects are discussed.

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1. Introduction

Gallium arsenide is one of the most commonly used materials in contemporary optoelectronics, and therefore single crystals grown in the melt must meet high parameter quality demands [1, 2]. High doping with impurities (Te, Si, S, In, of Zn+In) is an effective method for dislocation reduction, which however increases the formation of some specific microdefects [3-6]. The melt stoichiometry, the technological conditions of the crystal growth and high-temperature annealing also influence the structure [7, 8]. It has been determined through DSL (Diluted Sirtl-like solution with Light activation) photoetching that during the GaAs:Si growth, the deviation of stoichiometry of the melt essentially changes the density and type of dislocations and microdefects. Low dislocation density crystals can be prepared from stoichiometric or Ga-rich melts [7]. Lessoff and Gorman have observed microscopic defects, by applying hydroxide eutectic etching [9, 10]. Miyairi *et al.* investigated the relationship between growth conditions and microscopic defects, and gave an explanation of the origin of some of the defects [11]. However, crystal growth from a Ga-rich melt has not been studied with eutectic etching.

The purpose of the present research is to investigate how the stoichiometry of the melt and the grown crystals affect the dislocation density and the defects with raised structures (called “A defects”) and also to clarify the technological reasons for the appearance of the latter. In addition, the possibility for growing low-dislocation p-GaAs from a Ga-rich melt has been studied.

2. Experimental details

Wafers from (001) monocrystal GaAs doped with Zn, Zn+In, In and undoped, grown by the liquid encapsulated Czochralski (LEC) method, have been studied. One of the crystals was tested for thermo-stability by annealing at 850 ^{o}C of the whole crystal for 60 minutes and the cooling at a rate of 200^{o} per hour. The annealing was performed in a vacuum-sealed quartz ampoule, at an As vapor pressure of 10^5 Pa. The type and concentration of the doping impurities was known. The concentration and mobility of the hole carriers was measured by the Hall effect method, under

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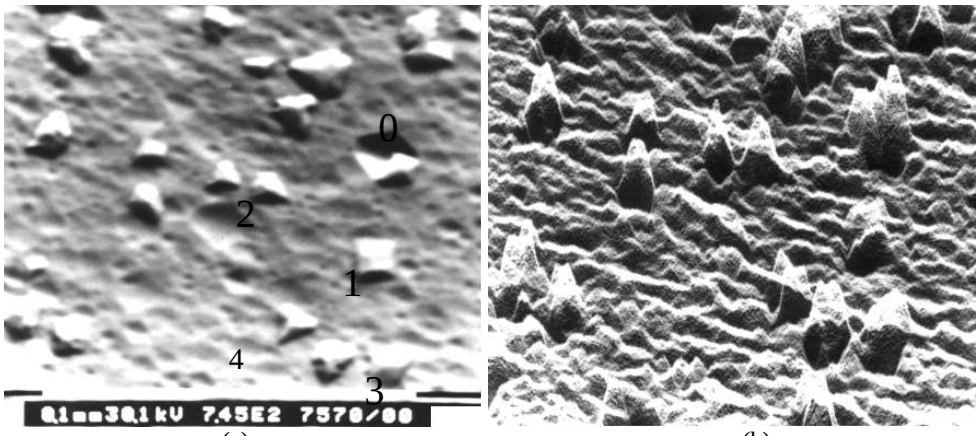
constant electrical and magnetic fields. The structural defects of the wafers were revealed through eutectic etching in an equal-mole mixture of KOH and NaOH, at a temperature of 380 ± 4 °C, for 30 minutes [12]. The preliminary preparation of the surface included mechanical polishing, chemical polishing in a mixture of $H_2SO_4 : H_2O_2 : H_2O = 3 : 1 : 1$ for 5 minutes, washing in deionized water and drying. The minimal and maximal dislocation and A-defect densities were determined using an optical microscope at x800 magnification. The data were obtained at 5 points from the low-dislocation parts of the wafers. Additionally, the radial distributions of dislocations and A-defects were measured and compared.

The stoichiometry of the polycrystal for the melt and the monocrystals used in the experiment was measured using a Philips SEM 515 scanning electron microscope operating in the energy-dispersive X-ray analysis mode (EDAX). The samples used in the experiment were cut from the low-dislocation parts of the wafers.

3. Results and discussion



(a) (b)

Fig. 1. Microdefects observed after eutectic etching, and EDAX measured amounts of Ga, As and In (at.%). (0) matrix Ga-51.71±0.45, As-48.29±0.59 / Ga-51.54±0.51%, As-48.26±0.66 Point 1 Ga–51.56±0.43%, As–48.31±0.55%, In- 0.13±54.59%; Point 2 Ga–51.61 ± 0.46 %, As–48.39 ± 0.60 %; Point 3Ga–51.54 ± 0.39 %, As–48.43 ± 0.51 %, In- 0.03±211.89%; Point 4 Ga–51.34±0.41% As–48.66±0.54%;

Wafers cut from the top and bottom parts of crystals grown from stoichiometric or Ga-rich melt have been studied. The radial distribution of the A-defects was opposite in symmetry to that of the dislocations. The density varied from 0 to 10^5 cm^{-2}, and the non-defect part was situated near the periphery of the crystal. Fig. 1 shows SEM microphotographs of GaAs:In, which were performed in (a) secondary electron image mode (SE) and (b) backscattered and secondary electron image mode (BSE). The points of EDAX measurement of the Ga, As and In concentrations are indicated numerically.

The Ga and As concentrations in the polycrystal were Ga: 51.75 ± 1.07at.%; As: 48.25 ± 1.03 at.%; and the recalculated concentrations in the melt were Ga: 50.59 at.%; As: 48.3 at.% and In: 1.11 at.%. The indium concentration in the wafer studied was 0.25 at%, as measured using atomic absorption spectroscopy. The data shown in the caption of Fig. 1 reveal that the doping element concentration was either below the instrument sensitivity threshold, or that a certain concentration is registered but the accuracy of the measurement was unsatisfactory. However, the Ga and As concentration measurement error was under 1%, and therefore the measured data can be used for stoichiometry estimation and micro-cluster registration.

The composition of the defects was similar to the composition of the matrix material. The surface was rough due to high doping and the deviation from stoichiometry. Tetragonally-shaped pits with small sizes and groove structures were also observed. The microdefects with raised

structures were of various shapes, but were clearly outlined and could be counted using an optical microscope.

Table 1 reveals the structural and electrophysical parameters which have been used to establish the effect of stoichiometry on the dislocation and A-defect density. The melt stoichiometry was recalculated in at.% and was determined by the type and proportions of the loaded materials in the melt. Stoichiometric polycrystals from direct synthesis (DS), Ga-rich polycrystals (S) and non-standard semi-insulating monocrystals were used. The data include the type of doping element (Zn, Zn_3As_2, Zn+InAs), the hole carrier concentration P and mobility μ, the specific resistivity ρ [Ωcm], the minimal and maximal surface densities of dislocations N_d, the A-defect surface concentration N_A, and the measured amounts of Ga in the material (M) and the A-defects (A).

Table 1. Electrophysical and structural parameters.

crystal	Melt Ga:As:In [at.%]	P[cm^{-3}] / ρ[Ωcm] μ[$cm^2V^{-1}s^{-1}$]	N_d [cm^{-2}] N_A [cm^{-2}]	Ga at.% M / A
1 GaAs (-)	DS 50:50	ρ=(6-7).10^7 μ=2000-3000	(1.5-4).10^4 (8-15).10^4	51.4 / 52.46
2 GaAs (-)	DS 50:50	ρ=(3-5).10^7 μ=2800	(3-5).10^4 (2-5).10^4	51.81 / 51.87
3 GaAs (-)	DS 50:50	ρ=4.10^7 μ=4200-5400	(2-7).10^4 (0-8).10^3	51.23
4 GaAs:In (InAs)	DS 50:48.91:1.08	ρ=(3-4).10^7 μ=4000-5000	(4-5.3).10^4 (2-2.8).10^5	51.93 / 51.38
5 GaAs:In (InAs)	S 50.59:48.3:1.11	ρ=5.5 μ=738	(2-4).10^4 (1-2).10^5	51.71 / 51.34-51.61
6 GaAs:Zn (Zn)	S 51.75:48.25	P=6.6.10^{18} μ=80	(2-9).10^3 0-100 +clusters(C)	52.68 C- 53.02
7 GaAs:Zn (Zn_3As_2)	50% S 51.74:48.26	P=1.3.10^{19} μ=66	(1-2).10^4 (8-10).10^4	52.89 / 52.56
8 GaAs:Zn (Zn_3As_2)	50% S 51.74:48.26	P=1.6.10^{19} μ=87	(1-2).10^4 (5-7).10^4	51.79 / 51.98
9 GaAs:Zn+In (Zn+InAs)	S 51.59:48.26:0.15	P=2.10^{19} μ=50	(3-4).10^4 0-100 +clusters	51.83
10 GaAs:Zn+In (Zn+InAs)	S 51.36:48.26:0.38	P=4.10^{18} μ=105	(1-2).10^4 (0-3).10^3	50.9
11 GaAs:Zn+In (Zn+InAs)	S 51.36:48.26:0.38	P=6.10^{18} μ=112	(4.2-7).10^3 (3-5).10^4	52.43 / 52.19
12 GaAs:Zn+In (Zn+InAs)	52%S 51.28:48.16:0.56	P=1.3.10^{19} μ=84	(9-16).10^3 (3-4).10^4	51.71 / 51.57

The data shown in Table 1 reveal that all the grown crystals were Ga-rich, with the over-stoichiometric quantity ranging from 0.9 to 2.89 at.%. The composition of the defects was similar to or slightly Ga-richer than the composition of the matrix. In GaAs:Zn, the defects had an insignificant effect on the concentration and mobility of the current carriers, from which it can be assumed that they are either neutral or p-type. The density of A-defects decreased below 10^2 cm^{-2} in wafers with Ga-rich clusters. The dislocation density was within the range $2\times10^4$to 5×10^4 cm^{-2} in GaAs doped with Zn or in Zn_3As_2 in crystals grown from a Ga-rich melt. Under the same starting conditions and doping with Zn+InAs, the dislocation density decreased to 7×10^3 cm^{-2} (sample 11). The measured stoichiometries of the undoped or In-doped crystals were up to 51.75 at% Ga and 48.25 at% As. These values can be assumed for the composition of the non-standard monocrystals. The recalculated compositions of wafers 11 and 12 are similar, as are the parameters of the grown crystals. Double Zn and In doping allows the formation of low-dislocation GaAs from a Ga-rich melt.

All studied samples were cut from the low-dislocation parts of the crystals, and the minimal and maximal values of dislocation and A-defect densities have been compared. The density of A-

defects was high (more than 10^4 cm^{-2}) with a deviation from stoichiometry above 1% and low in crystals with Ga-rich micro-clusters. Indium doping decreased the dislocation density and increased the density of A-defects (samples 4, 5, 11, 12). With deviations from stoichiometry of under 1 at%, the densities of both types of defect decreased. Thermal annealing, which was used to perform a thermo-stability test of the semi-insulating crystal, also decreased the density of A-defects (samples 2 and 3 were from the same crystal but before and after annealing respectively). The deviation from stoichiometry of the non-annealed wafer was higher than that of the annealed wafer, but the concentration of As in the defects was lower. A possible reason for this phenomenon is the presence of As-rich micro-clusters, which cannot be revealed with eutectic etching [8].

The assumption that the raised structures are anti-phase domains characteristic of crystals grown from an As-rich melt was made without measuring the crystal stoichiometry [11]. The experiments completed during the present research revealed that the A-defect concentration increased for over-stoichiometric Ga concentrations above 1 at%, and significantly decreased upon Ga-rich micro-cluster formation. The A-defects were p-type or electro-neutral, and differed in shape and size. The composition of the matrix elements in the defects was similar to that of the material, and some of them had increased amounts of In. If the defects consisted of anti-phase domains only, their composition would be As_{Ga}-Ga_{As} and low-temperature annealing would not affect them [8].

When crystals are grown under non-equilibrium conditions, micro-fluctuations of the composition and increased concentrations of impurities and point defects may appear at the crystallization front. We assume that the A-defects are structurally disordered regions of intrinsic defects, the size of which increase or decrease upon the cooling process. The variance in the shape is probably the result of the different temperature ranges of their formation and their aggregation during the cooling process.

4. Conclusions

1 The density and size of the A-defects are determined by the deviation from stoichiometry and the technological conditions of the crystallization process. The density varies from 0 to 10^5 cm^{-2}, and is changed upon thermal annealing. The A-defects are probably structurally disordered regions with higher concentrations of intrinsic point defects.

2 Low-dislocation GaAs can be grown from a Ga-rich melt with double Zn+In doping.

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