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Structural and electro-physical parameters of n-GaAs

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Samples of single crystal GaAs tellurium doped, obtained by Czochralski method from different kind of melts were tested. Preliminarily synthesized poly-crystals and, alternatively, remelts (undoped, indium doped or GaAs:Te residues) were used as input material in the experiments. A comparison was made between effect of doped impurity and thermal annealing upon carrier mobility and dislocation density. Crystals of diameters above 35 mm. pulled from synthesized material have dislocation density $(1\text{-}4)\times10^{4}$ cm^{-2} and mobility from 2000 to 3400 cm^{2}/V.s. With the same experimental set-up, low dislocation density crystals with diameters up to 30 mm and concentration of doping tellurium above 2×10^{18} cm^{-3} were pulled. Structural and electro-physical parameters of crystals obtained from remelts vary in a wider diapason, as best results are observed with crystals pulled from GaAs:In residues. The thermal annealing does not considerably influence the dislocation density and electro-physical parameters, slightly increasing carrier mobility and mechanical strength at cutting. From analysis of experimental data and literature sources a model is proposed to use remelt material and doping with InAs and Te. Combined doping improves the electro-physical and structural parameters of obtained crystals including at low concentrations of the electrically active doping element.

Key words: gallium arsenide, structural defects, electron concentration

INTRODUCTION

Gallium arsenide is one of the most popular semiconductor materials for single- and multiple-junction solar elements [1-3]. It is possible the influence of substrate on active structures to be reduced through the use of buffer layers, porous structures and the capabilities of modern epitaxial techniques [3,4]. The perspectives of a broader application of $A^{III}B^{V}$ solar cells are intended to improve effectiveness of elements and lowering the substrates price [5]. Production of cheap substrates in case of silicon is achieved using pre-crystallization of residue material or multicrystal silicon [6,7].

GaAs:Te substrates are often used in the production of heterosructures based on $A^{3}B^{5}$ compounds. Tellurium as a doping impurity is a shallow donor with high limit solubility allowing controlled manipulation of the electro-physical parameters in a wide diapason. Also it effects on critical tensions to form dislocations and tends to reduce [8]. Gallium arsenide is a decomposing compound but it allows crystals to be grown with a significant stoichiometry deviation and, respectively from remelt material. Frigerri et al. obtain undoped high resistivity GaAs, Czochralski pulled, from Ga rich melt with As content over 0.475 [9]. Through thermodynamic calculations Morozov has shown that doping with Te, Sn and Si changes the GaAs homogeneity region and supersaturated native point defect behavior occurs during crystallization and post-crystallization cooling [10]. Te-doping shifts the GaAs homogenity region to the As-rich half of the phase triangle and it is possible to obtain As rich crystals from Ga rich melt. A problem with intensive Te-doping is the occurrence of microdefects, which change their sizes and concentrations at thermal annealing [11,12] and probably impact the structural and electro-physical parameters of the substrates. Annealing of n-type substrates with over stoichiometric As leads to suppression of the dominant recombination center and increases in hole diffusion lengths [13]. Thermal annealing is a final stage of the production of undoped semi-insulated GaAs from an As-rich melt which improves significantly the structural and electro-physical parameters of crystals in the presence of As precipitates. Decoration of dislocations with arsenic or gallium is identified through etching with AB and molted KOH [8,14,15].

A problem observed in some of the tested crystals is cracking and chipping of wafers at cutting. Therefore the impact of annealing on mechanical strength is an issue of practical interest.

EXPERIMENTS

Wafers with thickness between 1 and 1.5 mm, sliced at the top and end of mono-crystalline ingots

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of LEC Czochralski GaAs:Te, were studied. All the crystals were pulled under a layer of B_2O_3 in an argon-filled chamber under pressure of 1.7 atm. and weight of the charged poly-crystal of 1 kg. The input material was divided in 4 groups. From each wafer, a small part was chipped and a sample of each was prepared for evaluation of the electro-physical parameters. The specific resistivity, Hall carrier concentration and mobility were measured.

Standard etching: all the wafers from the crystals are mechanically grinded and chemically polished with solution H_2SO_4:H_2O_2:H_2O in 3:1:1 ratio. The structural defects of all samples were developed in molted KOH in Ag crucible at temperature 470°C for 12–15 min. A resistivity furnace with thermoregulation accuracy $\pm$ 4°C was used. Dislocation density was calculated based on the method of averaging on 9 points of pits counted with metallographic microscope with 500 times magnification.

Annealing was carried out in vacuum sealed quartz ampoules, in which certain additional quantity of arsenic was loaded. Preliminary preparation of ampoules comprised of mechanical washing and acid treatment, washing with deionized water, vacuum heating at 1100°C for 4 hours and slow cooling down. The quantity of added arsenic was such as to ensure pressure of 1.5 atm. and was calculated considering the particular ampoule volume and process temperature.

RESULTS AND DISCUSSION

The results of measured carrier concentration at the top and end of the tested crystals from synthesized material (Melt I) are presented in Table 1.

The results of measured carrier concentration at the top and end of the tested crystals from remelt material are presented in Table 2. The type of the melt is indicated as follow: Melt II – from GaAs:Te residues from the beginning and the bottom part of crystals; Melt III - residues from high resistivity GaAs crystals pulled in high pressure installation; Melt IV - residues from GaAs:In crystals pulled in high pressure installation.

Table 1. Electron concentration from Hall measurements

Number of the crystal and type of the melt	Top cm^{-3}	End cm^{-3}
1 - Melt I	2.6×10^{17}	5.2×10^{17}
2 - Melt I	3×10^{17}	6.5×10^{17}
3 - Melt I	4.8×10^{17}	6.6×10^{17}
4 - Melt I	5.6×10^{17}	1.3×10^{18}
5 - Melt I	7×10^{17}	2.5×10^{18}
6 - Melt I	8.3×10^{17}	1.4×10^{18}

Table 2. Electron concentration from Hall measurements

Number of the crystal and type of the melt	Top cm^{-3}	End cm^{-3}
7 - Melt II	5×10^{17}	1×10^{18}
8 - Melt II	7.2×10^{17}	1.5×10^{18}
9 - Melt II	7.6×10^{17}	1.2×10^{18}
10 - Melt II	8.2×10^{17}	2.3×10^{18}
11 - Melt II	9.3×10^{17}	2×10^{18}
12 - Melt III	5.2×10^{17}	1×10^{18}
13 - Melt III	6×10^{17}	1×10^{18}
14 - Melt III	7.5×10^{17}	9×10^{17}
15 - Melt III	8.4×10^{17}	2.4×10^{18}
16 - Melt III	9×10^{17}	1.8×10^{18}
17 - Melt IV	7.2×10^{17}	1.5×10^{18}
18 - Melt IV	8.4×10^{17}	2×10^{18}

The results from Tables 1 and 2 show that carrier concentration of the crystals pulled from preliminary synthesized material varies in wider diapason than crystals from remelt material. Best reproducibility is observed in indium doped GaAs material (Melt-IV) and residues from high resistivity undoped crystals (Melt-III).

Fig. 1 shows the dislocation densities developed in molted KOH:

The average dislocation density of the most crystals doped only with Te varies in the range 1-3×10^4 cm^{-2} and the results are similar, irrelevant of the type of melt. The higher density of dislocations at the end of crystals No. 9 and 13 is explained with the formation of impurities defects and clusters. The surface around dislocations is rough, which is asso-

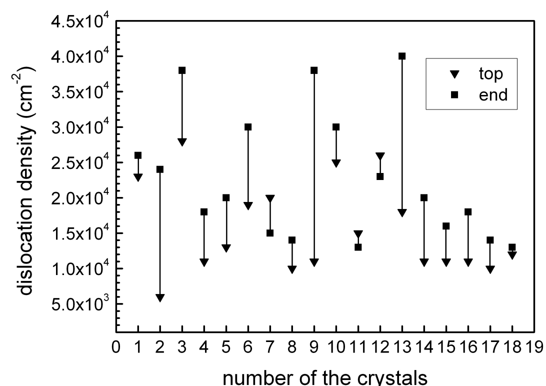

Fig. 1. Dislocation density revealed in molted KOH.

ciated with the presence of micro-defects. To illustrate capabilities of the pulling installation, two crystals with diameter 30 mm, Te concentration above 2×10^{18} cm^{-3} were pulled. The measured dislocation density is 1.9×10^{3} cm^{-2} and 4×10^{3} cm^{-2} respectively at the top and end. With impurity concentration above 3-5×10^{18} cm^{-3} dislocation density starts to decrease effectively [8], but the application of such substrates is limited. The samples with lowest dislocation density (No.17 and 18) were obtained from remelt material with In and doped with Te. Measured parameter values are comparable with the parameters which characterize crystals that are highly Te-doped, as well as with the results published by other authors for small diameter crystals pulled from synthesized material and doped with Te and In [16].

The results for carrier mobility are shown in Fig. 2.

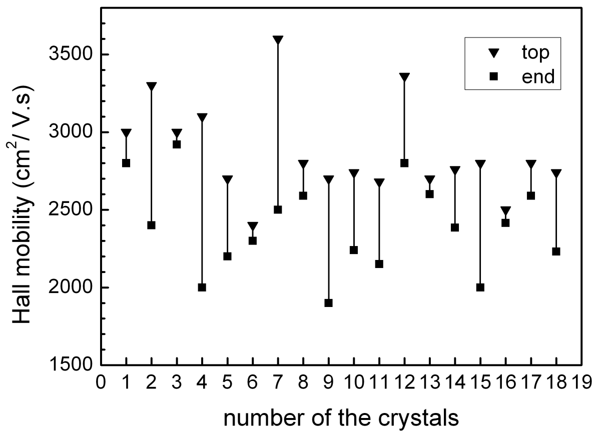

Fig. 2. Hall mobility from top and end of the crystals.

Electron mobility at the top and end of crystals is comparatively high, the values varying within (2×10^{3} – 3.4×10^{3}) cm^2/V.s for those pulled from synthesized material and (1.9×10^{3} – 3.6×10^{3}) cm^2/V.s for the rest. The presence of micro-roughness after etching in KOH, the lower concentration and high carrier mobility in crystals No. 2, 7, and 12 shows that most micro-defects are electrically neutral.

A problem in part of the crystals obtained from GaAs:Te residues is the observed cracking and chipping of wafers at mechanical slicing. Such crystals have comparatively high dislocation density, higher carrier and micro-defects concentration at the end and are obtained from a Ga-rich melt.

The stoichiometry of the same poly-crystals for the melt and mono-crystals used in the experiment was measured with a Philips SEM 515 scanning electron microscope operating in the energy-dispersive X-ray analysis mode (EDAX). The method precision error is about 1 at.%. In the preliminary synthesized poly-crystals, the ratio between components in atomic percentage is as follows: Ga (51.59) : As (48.41); in residues from undoped GaAs – Ga – (51.88 $\div$ 52.63) : As (47.33 $\div$ 48.22); in GaAs:In residues – Ga (51.14 $\div$ 52.72) : As (47.27 $\div$ 48.9), and In – (0.04); in GaAs:Te obtained from n-GaAs residues – Ga (52.43) : As (47.57).

According to other available sources, optimal annealing conditions depend on the stoichiometry of the material and the nature of micro-defects. Thermal processing of Ga-rich crystals leads to annealing of acceptors and/or generation of shallower from EL2 donors [13], but at higher temperature impurity clusters unify.

The effect from thermal annealing was studied at two temperature levels, namely: 700°C and 600°C. The experiments were carried out in vacuum sealed quartz ampoules: – 2 mono-crystals and 4 wafers obtained from different melts were loaded for the first experiment, and 1 crystal and 4 wafers for the second one. The obtained results at temperature 700°C are presented in Table 3.

The annealing at 600°C does not lead to changes in the indicated parameters, whereas some changes are observed at 700°C, which however are comparatively small. Only in crystal No. 9, a slight decreasing of carrier concentration and increasing of mobility at the end of the crystal was observed. This can be explained with non-uniform distribution of the impurities in the sample. Etching with molten KOH does not give information about the nature and magnitude of micro-defects, but it reveals clusters, twin lamellas and Ga inclusions. Such parts of the crystals which contain the aforementioned micro-defects are eliminated. It can be assumed that annealing in this temperature diapason does not impact significantly dislocation density and carrier concentration and mobility. All crystals annealed in the experiment improved their mechanical hardiness at slicing which led to a smaller number of broken wafers.

Impurity concentration in the melt is calculated with Eq. 1.

$$N = \frac{N_A m_{dop} \rho_{GaAs}}{M_{melt} A_{dop}}, \qquad (1)$$

where $N_A = 6.022\times10^{23}$ is Avogadro constant, $m_{dop.}$ – impurity mass, ρ – density of GaAs (5.317 g/cm^3), M_{melt} – mass of melt and A_{dop} – impurity atomic mass.

Table 3. Electro-physical and structural parameters on the crystals before and after thermal annealing, where: N [cm^{-3}] – Hall concentration; μ [cm^2/V.s] – Hall mobility and N_D [cm^{-2}] – dislocation density

Number of the crystal	Top			End		
and type of the melt	N	μ	N_D	N	μ	N_D
Before annealing						
3 - Melt I	4.8×10^{17}	3000	$2.8.\times10^4$	6.6×10^{17}	2920	3.8×10^4
9 - Melt II	7.10^{17}	2900	1.5×10^4	2.9×10^{18}	1900	2.8×10^4
15 - Melt III	8.4×10^{17}	2000	1.1×10^4	2.4×10^{18}	2000	1.6×10^4
19 - Melt IV	8.9×10^{17}	2333	1.1×10^4	2×10^{18}	2200	1×10^4
After annealing						
3 - Melt I	3.6×10^{17}	2960	1.8×10^4	6.7×10^{17}	2640	3.7×10^4
9 - Melt II	7×10^{17}	2990	1.8×10^4	1×10^{18}	2100	2×10^4
15 - Melt III	9×10^{17}	2070	1.3×10^4	3×10^{18}	2045	1.5×10^4
19 - Melt IV	8.4×10^{17}	2660	1.5×10^4	2×10^{18}	2580	1.8×10^4

The mass of the melt for all crystals was 1 kg and the mass of doping impurity Te is 0.7 g. Concentration of Te from Eq. 1 is equal to 1.75×10^{19} cm^{-3}.

Impurity distribution is calculated with Eq. 2:

$$C_S = C_0 k_{ef}(1-g)^{k_{ef}-1} \quad (2)$$

Where C_s is expected impurity concentration, C_0 is impurity concentration in the melt, g crystallized part and k_{ef} is effective coefficient of distribution with values from 0.016 to 0.054 [17]. The mass of the crystallized part at reaching a diameter of 35 mm and angle of growing of 45° is 29.82 g, respectively $g = 0.0298$. The expected concentration at the top is 2.8×10^{17} cm^{-3} at $k_{ef} = 0.016$ and 9.7×10^{17} cm^{-3} at k_{ef} 0.054. The measured values of carrier concentration are in the range (2.3 - 9)$\times10^{17}$ cm^{-3}, and so for the next calculations we will use $k_{ef} = 0.054$.

The expected concentration when 0.6 and 0.7 parts of the melt is crystallized are respectively 2.2×10^{18} cm^{-3} and 2.9×10^{18} cm^{-3}. We assume that the melt from GaAs:Te residues has an average impurities concentration of 2×10^{18} cm^{-3} and upon adding the doping element it rises to 1.95×10^{19} cm^{-3}. The expected carrier concentrations at crystallization levels of the melt: 0.1; 0.6 and 0.7 parts of the melt are as follows: 1.1×10^{18} cm^{-3}, 2.5×10^{18} cm^{-3} and 3.4×10^{18} cm^{-3} and they are lower than the maximum impurity solubility. The values of measured concentration at the top and end are in the range from (5-9)$\times10^{17}$ cm^{-3} to (1-2.3)$\times10^{18}$ cm^{-3}.

The expected In concentration in the melt and in the crystals at $k_{ef} = 0.13$ can be calculated likewise. The residues are cut from crystals pulled at high pressure, melt weight is 4 kg and the weight of doping compound InAs - 117 g. In concentration in the melt is 4.9×10^{20} cm^{-3} and the expected concentration when 0.1, 0.4 and 0.7 parts of the melt are crystalized is respectively 6.9×10^{19} cm^{-3}, 9.9×10^{19} cm^{-3}, 1.8×10^{20} cm^{-3} at average concentration of the residues 1×10^{20} cm^{-3}. The expected concentration of In in the crystals is 1.4×10^{19} cm^{-3} at the top and 3.3×10^{19} cm^{-3} when 50% of the melt is crystallized.

The smallest gap between expected and measured concentration was obtained with crystals doped with Te and In. The deviation of expected concentration is greater at the top of all tested crystals. The explanation is probably that the top of a crystal is exposed to high temperature for a longer time, and so phenomena occur like complex formation, evaporation of some impurity, uncontrolled residual acceptors and melt stoichiometry deviation. The main residual impurities at Czochralski process are boron, carbon and silicon. We assume that the greater deviation in carrier concentration of crystals pulled from synthesized materials is explained with the amphoteric behavior of silicon and the different levels of evaporation of doping Te. The measured stoichiometry deviation of synthesized poly-crystals is comparably small and close to the method precision error. Surely some of the synthesized poly-crystals are with stoichiometric composition. Silicon is an amphoteric impurity and depending on the prevalent own vacancies it can behave as either a donor (Si_{Ga}) or an acceptor (Si_{As}) [8].

The quantity of silicon in the other types of crystals decreases during preliminary crystallization. The

concentration of other impurities depends on humidity and graphite heater quality. Boron is an isovalent impurity, it replaces gallium vacancies but tends to increase acceptor defects Ga_{As} and $B_{Ga}V_{As}$ [18]. Carbon is an acceptor and its concentration varies in wide diapason [19]. Te doping increases the concentration of neutral and acceptor complexes [8,9,20]. Additionally, the use of Ga-rich melts may lead to formation of gallium clusters with various magnitude and effects and may form tensions [21]. That explains the deterioration of mechanical parameters of most highly doped crystals.

Double doping with Te and In decreases the dislocation density and improves significantly reproducibility of electro-physical parameters. A stronger effect can be expected with increasing the In concentration up to 2×10^{20} cm^{-3} [16]. Usually the doping impurity is added in the form of InAs compound, which increases As content in the melt.

CONCLUSIONS

The possibilities to pull GaAs:Te from residues of crystals either doped or undoped with In or Te were shown. The results for dislocation density, carrier concentration and mobility are compared to the relevant parameters of crystals pulled form preliminary synthesized poly-crystal material. Double doping with Te and In decreases the dislocation density and improves reproducibility of the parameters.

Annealing at temperatures of 600°C and 700°C for 4 hours followed by slow cooling improves mechanical parameters of crystals without any influence on basic structural and electro-physical parameters.

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СТРУКТУРНИ И ЕЛЕКТРОФИЗИЧНИ ПАРАМЕТРИ НА n-GaAs

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(Резюме)

Изследвани са образци от монокристален GaAs легиран с телур, получен по метода на Чохралски от различни видове стопилка. За изходен материал е използван предварително синтезиран поликристал или отработен материал (остатъци от нелегирани или легирани с индий кристали и остатъци от GaAs:Te). Направено е сравнение за влиянието на концентрацията на легиращия примес и температурното отгряване върху подвижността на токоносителите и плътността на дислокациите.

Получените от синтезиран материал кристали с диаметър над 35 mm са с плътност на дислокации (1-4)$\times 10^4$ cm^{-2} и подвижност от 2000 до 3600 cm^2/V.s. На същата установка са изтелени и нискодислокационни кристали с диаметър до 30 mm при концентрация на легиращия примес телур над 2×10^{18} cm^{-3}. Структурните и електрофизичните параметри на кристалите, получени от отработен материал, варират в по-широки граници, като най-добри са при използване на остатъци от GaAs:In. Температурното отгряване слабо влияе върху плътността на дислокациите и електрофизичните параметри, слабо увеличава подвижността на токоносителите и повишава механичната устойчивост на кристалите при рязане на пластини.

От анализа на експерименталните резултати и литературни данни е предложен модел за използване на отработен материал и легиране с InAs и Te. Съвместното легиране ще подобри електрофизичните и структурните параметри на получените кристали и при ниска концентрация на електрически активния примес.