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Structural defects in gallium arsenide

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Structural defects in monocrystal GaAs, obtained by Czochralski method, have been studied. Two methods of chemical etching in KOH and eutectic melt KOH- NaOH were used. The distribution of dislocations in doped with tellurium and indium, tellurium and undoped crystals were compared. Doping with tellurium and indium changes the radial distribution of dislocations, decreases its density, but increases the concentration of microdefects. The obtained results may be used for optimization of the semiconductor technological processes.

Keywords: structural defects, gallium arsenide, etching

INTRODUCTION

Gallium arsenide is a semiconductor, widely used in modern microelectronics and optoelectronics. The combination of direct energy structure, optimal band gap, high mobility of the charge carriers, well-developed technological methods for growing a single crystal, homo and hetero-epitaxial structures, make it a promising material for multijunction solar cells [1-5]. The basic requirements in terms of single crystals are orientation, diameter, dislocations density and electrophysical parameters.

In conventional production the average density of dislocations is being controlled, although most parameters of semiconductor materials are "structure-sensitive" [6]. Except dislocations in the crystals, other defects are formed like native and impurity point defects or their complexes, clusters, twins, stacking faults etc. These defects manifest themselves by the solution, offered by Abrahams and Bujocci, which is composed of 2 ml H_2O, 8 mg $AgNO_3$, 1 g CrO_3 and 1 ml HF [7]. A variant of the method is presented by the diluted modification (DS method) or diluted Sirtl - like solution with a light - DS (L) etching [8, 9]. Through these methods it has been studied the growth and multiplication of dislocations from the substrate in the epitaxial layer, the formation of misfit dislocations and the influence of point defects. This method is suitable for low density of dislocations [9].

Another method that displays both dislocations and point defects is proposed by Lessoff and Gorman and contains equal number of mols of KOH and NaOH [10, 11]. The authors consider the lower temperature and speed of the etching to be advantages of the method. Miyari and co-authors call it eutectic etching and use it to identify micro defects in undoped and In-, B- or Si-doped monocrystals [12]. This method has been used by us to study the low-dislocation parts of monocrystalline GaAs, doped with Zn, In, or Zn + In [13]. The doping with Te, In or In + Te is an effective method of reducing dislocations, but there is no evidence of their impact on the type and the distribution of microdefects, developed by eutectic etching [6, 14, 15].

The aim of this study is to compare the distribution of structural defects after development first in KOH and second in KOH-NaOH, and to study the possibilities of using eutectic etching in control of the basic parameters of monocrystalline gallium arsenide.

EXPERIMENTAL PART

Substrates were tested with orientation (001) of monocrystalline GaAs, doped with Te, In, In + Te and undoped. All crystals were prepared by the liquid encapsulated Czochralski. The information about the quantity and type of dopant are known in advance. All crystals are grown at the same temperature conditions, growth rates and crystal and crucible rotation.

The concentration and mobility of the carriers was measured by the Hall effect method under constant electrical and magnetic fields on samples with alloyed indium ohmic contacts.

The preparation of the wafers for the development of dislocations includes mechanical grinding, polishing, chemical polishing in a mixture of H_2SO_4: H_2O_2: H_2O in a ratio of 3: 1: 1 for 5 minutes, rinsing with deionized water and drying. The defects development is done in a resistivity furnace with automatic temperature control. Etching in KOH is at a temperature and time 470°C

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for 10-15 minutes and for the eutectic etching - 380°C temperature and for a 30 minutes period. Wafers in both cases are placed in a silver crucible with pre-melted base. After the process the crucible is removed, cooled and the remainder of the base was dissolved in tap water.

The morphology of the defects and the stoichiometry of a portion of the resulting crystals and of the used polycrystalline material were measured with a scanning electron microscope Philips SEM 515 in a back reflected electrons mode (BS) and energy-dispersive X-ray analysis (EDAX).

RESULTS AND DISCUSSION

The results of the electro-parameters, the type of the doping elements and the average dislocations density are shown in Table 1. The density of dislocations is determined by metallographic microscope after etching in KOH and averaging the values of nine fields.

Table 1. Electro-physical and structural parameters on the crystals where: N [cm^{-3}] is Hall concentration, μ [cm^2/V s] is Hall mobility and N_D [cm^{-2}] - dislocation density

Number of the crystal and doping element	N cm^{-3}	μ cm^2/V s	N_D cm^{-2}
1 GaAs	2 x 10^8	2850	3 x 10^4
2 GaAs : Te	5.5 x 10^{17}	3390	1 x 10^4
3 GaAs : Te	1.1 x 10^{18}	1860	3 x 10^4
4 GaAs : Te	1.2 x 10^{18}	2380	2 x 10^4
5 GaAs : Te	2.6 x 10^{18}	1730	1.6 x 10^4
6 GaAs : Te	3.1 x 10^{18}	1818	1.8 x 10^4
7 GaAs : In	4 x 10^8	4000	6,8 x 10^3
8 GaAs : Te + In	1.2 x 10^{18}	2500	4 x 10^3
9 GaAs : Te + In	2 x 10^{18}	2450	1 x 10^3

All samples except for 2 are taken from the end of the grown crystals. The concentration of the dopant in the melt of the obtained crystals is respectively: Tellurium - 1.8 x 10^{19} cm^{-3}, indium in a sample 7 – 1,28 x 10^{20} cm^{-3}, in 8 – 1,7 x 10^{20} cm^{-3} and in 9 – 5 x 10^{20} cm^{-3}. The table shows the measured concentrations of electrons and mobility of the charge carriers with the Hall effect.

The results of the table show that average density of dislocations ranges from 1 x 10^4 cm^{-2} to 3 x 10^4 cm^{-2} when doped with tellurium and is near to the dislocation density of the undoped sample. Adding In with a concentration of 1 x 10^{20} cm^{-3} in the melt slightly reduces the average density of dislocations and slightly increases the mobility of the charge carriers. The effect is enhanced in the sample 8, doped with two impurities, where the concentration of In is 1.7 x 10^{20} cm^{-3}. A significant reduction of the average dislocation density can be found in sample 9 at a concentration level of the isovalent impurity indium in the melt of 5 x 10^{20} cm^{-3}. We assume that the reduction in the average dislocation density in samples 8 and 9 is mainly due to the isovalent impurity indium. Doping with tellurium also reduces the density of dislocations, but the required concentration of the impurity in the crystal is (5 – 9) x 10^{18} cm^{-3} [6].

The dislocations distribution in the cross section of the substrates reflects the distribution of thermal stresses and provides additional information about the causes of their nucleation. Fig.1 shows the effect of doping on the radial distribution of dislocations.

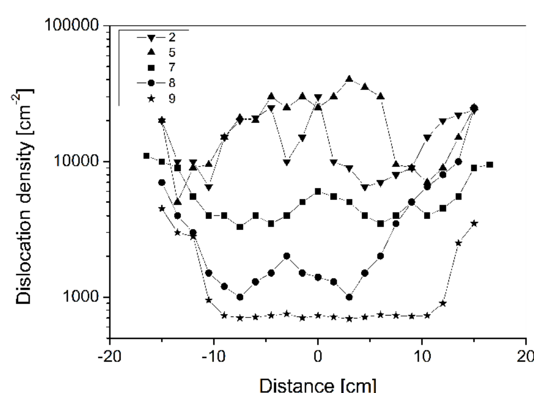

Fig.1. Radial distribution of the dislocations in the following crystals: 2 – GaAs: Te, 5 – GaAs;Te, 7 – GaAs: In, 8 – GaAs: Te+In, 9 – GaAs: Te+In

The distribution of the dislocations in samples 2 and 5 is "W" shaped with high density in the center and the periphery and lower density in the circular area between them. Increasing the concentration of indium change the macro-distribution from low "W" shaped to a "U" shape. The distributions of the dislocations depends on the distribution of thermal stresses [6].

The heat when cooling the crystal is discharged mainly through radiation from the side surface. The peripheral layers have a lower temperature than central ones and this leads to the occurrence of compressive stresses in the center, stretching stresses in the periphery and their compensation in the middle region. The influence of the electrically active impurity tellurium and the isovalent indium on the structural parameters is explained by the increase of the critical stresses for the formation of dislocations and modifying the type and concentration of the equilibrium point defects. [6, 15].

The eutectic etching develops simultaneously dislocations and various microdefects. Fig.2 reveals

SEM microphotographs of the central part of the samples of undoped and doped with tellurium and indium crystals.

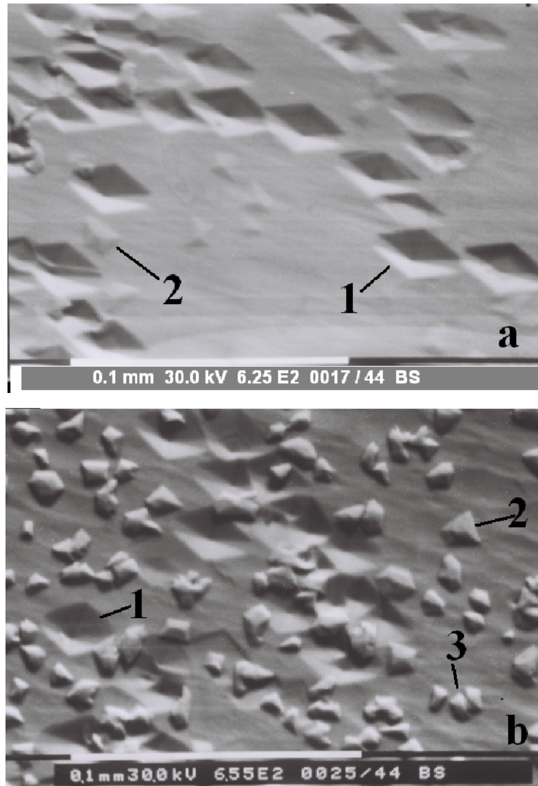

Fig.2. Microdefects observed after eutectic etching on: (a) undoped wafer 1 and (b) doped with Te + In wafer 8

To distinguish between defects the classification proposed by Tseng at al. [11] and supplemented by H. Miyairy at al [12], is used. Fig.2 shows: 1 – dislocations; 2 - raised structure and 3 - diamond shaped pit. There are also oval pits, surface roughness and rectangular pits. The dislocations are pits with a hexagonal shape and their size depends on the time of etching. The number of dislocations in the undoped sample is larger, but the concentration of microdefects is low. Alloying reduces the number of dislocations and increases the number of the microdefects. Like etching with KOH part of the dislocations have a flat bottom and are decorated with microdefects. Fig.2b shows that in the doped with In and Te crystal the prevalent types of defects are type 2 and 3, which we will call respectively A-defects, and T-defects. The size of A-defects ranges from 20 μm to 200 μm and they have an irregular shape. The T-defects have a triangular shape and relatively equal size. Part of the A and T-defects are combined in groups and form complexes with irregular shape. Alloying leads to the occurrence of surface roughness of small round pits and rectangular defects of larger size [11, 12]. In wafer 8 one can observe poorly shaped rectangular pits, which are remnants of mechanical treatment. The measured values of dislocations, A and T defects after etching in KOH and eutectic etching are shown in Table 2.

Table 2. Structural parameters after etching with KOH and KOH – NaOH

Number of the crystal	Dislocations KOH N_D cm^{-2}	Dislocations KOH-NaOH N_{DE} cm^{-2}	A-Defects N_A cm^{-2}	T-Defects N_T cm^{-2}
1	2×10^4	2.1×10^4	6.3×10^3	0
2	1×10^4	1×10^4	1×10^4	$3,1 \times 10^4$
7	9×10^3	8.5×10^3	1×10^4	1.1×10^4
8	3×10^3	2.8×10^3	2×10^4	5×10^4

The density of dislocations and microdefects is determined by counting by a metallographic microscope at a magnification of 800. The results were averaged from three measurements made in the center of the substrates. It can be seen in Table 2, that density of dislocations is not dependent on the method of etching and the dopant increases the concentration of microdefects. Fig.3 exposes the radial distribution of the dislocations, A- and T defects in sample 9 of Table 1 after eutectic etching.

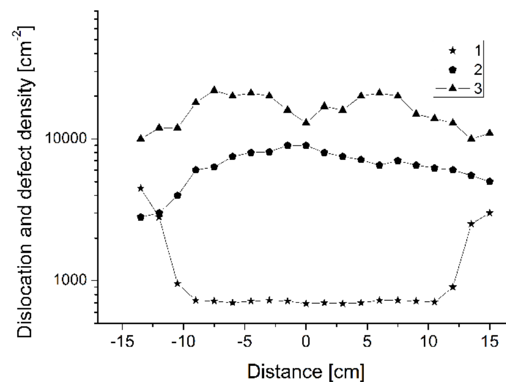

Fig.3. Radial distribution of the dislocations, A and T-microdefects (1 – dislocations, 2 – A-defects, 3 – T-defects)

The distribution of A-defects is reverse to the distribution of the dislocations and increases slightly from the periphery to the center of the crystal. A similar change is identified for the T defects, but the difference in concentrations there is much higher. The T-defects density sharply decreases around the periphery of the crystal and in the presence of Ga clusters (sample 5).

By other authors A-defects are formed with growing of As-enriched melts and the advent of T-defects is determined by the deviation of

stoichiometry to both components [12]. The origin of the A-defects is associated with antiphase domains [11]. The stoichiometry of the resulting crystals is dependent on the type of polycrystal, the growing conditions, the type and concentration of impurities and can be measured [13, 17]. Samples 1 to 7 were prepared by previously synthesized polycrystal with a composition Ga (51.59 - 51.75) at.% and As (48.05 - 48.25) at.%. The ratio between the main components when doping with Te (sample 4) is Ga (52.43 at.%) and As (47.57 at.%). The sample 8, doped with In has a composition of Ga (52.58 at.%) and As (47.42 at.%). In both cases, the stoichiometry changes, and the obtained crystals were enriched with Ga. Crystals 8 and 9 are derived from non-standard residues of semi-isolation GaAs with a residual concentration of In about $1x10^{20}$ cm^{-3} and further doped with InAs. The deviation from the stoichiometry of the resulting crystals was approximately identical to that of crystals 1-7.

The stoichiometry of the A-defects is approximately equal to that of the substrate. Part of defects in crystals 8 and 9 contain In with a concentration of less than 0.5 at.%. Similar types of defects are developed in crystals, doped with Zn or Zn + In [13]. In both cases there is no connection between the electro-parameters and the concentration of A-defects, showing that defects are electrically neutral. Both types of defects are formed by growing of crystals from a non-stoichiometric melt.

The electrically neutral anti-phase domains are complexes with a composition As_{Ga} - Ga_{As}. All crystals, examined by us, were obtained from Ga-enriched melt. The concentration of the As_{Ga} is relatively low and this hinders the formation of antiphase domains.

Samples 8 and 9, studied by us, are from the end of the formed crystals before the onset of cell growth. There is a problem with heavily doped samples, which is constitutional supercooling. This leads to termination of the crystal growth in a relatively early stage of the process.

The initiating of cells growth is determined by the following relationship:

$$g_{cell} \approx \frac{G}{R} \quad (1)$$

where the monocrystal portion is g_{cell}, G – the axial temperature gradient, and R - the growth rate [18].

Fujii et al. have shown that for an axial gradient 80°C/cm and pulling speeds of 9, 5 and 3 mm/h the values of g_{cell} are around 0.22, 0.45 and 0.7 [18].

We assume that te cause of A-defects is the high rate of crystals growth. The nonequilibrium conditions at the crystallization front lead to occurrence of microfluctuations that solidify in a defective structure. Depending on the stoichiometry and doping, it is possible that gallium or arsenic microclusters are formed, which will be impurity enriched or depleted [6,19]. The composition of the defects will be determined by the main point defects as gallium and arsenium interstials and is close to the composition of dislocation loops. It was found that the thermal annealing of the undoped crystals increases the size of the A-defects and reduces their density [13]. We assume that concentration of A and T defects can be reduced by annealing and this is the cause for the improvement of parameters in pre-epitaxial preparation of the substrates [20, 21].

CONCLUSIONS

Structural defects were examined in this study by subsequent etching with KOH and eutectic mixture of KOH and NaOH. Both methods exhibit dislocations and the measured densities are close.

Doping with tellurium and indium significantly reduces the density of dislocations, but increases the microdefects concentration.

The concentration of maximum size defects (A and T defects) depends on the stoichiometry and is close to or greater than dislocation density. The concentration increases from the periphery to the center and sharply reduced in areas with gallium clusters.

A-defects have a composition similar to the base material and in some of them there is an increased concentration of indium.

The eutectic etching can be used to improve the processing conditions for the growth of low-dislocation gallium arsenide.

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