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INFLUENCE OF BOATS TREATMENT ON THE RESIDUAL IMPURITIES IN POLYCRYSTALLINE INDIUM ARSENIDE

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Abstract. The influence of boats coated with low grain quartz crystallites on the concentration of residual impurities in indium arsenide growth was studied. The parameters of ingots obtained by two-temperature synthesis in sand blasted boats, BN coated boats and boats with surface crystallites have been compared. The results indicate that synthesis in boats with crystalline coating leads to residual impurities reduction — for instance the concentration of Si at the front and at the end of such boats are respectively 3.4×10^{15} cm^{-3} and 2.1×10^{15} cm^{-3}, while for sand blasted boat they are 8.1×10^{15} cm^{-3} and 2.7×10^{15} cm^{-3}. A model has been proposed, which relates the residual impurities not only to the type of the boat used but to the technological condition of the process.

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1. Introduction

The growing interest in narrow gap semiconductors $A^{III}B^{V}$ is determined by the advantages of these materials in the production of the emitters and detectors in the infrared region, magnetosensitive devices and the application in quantum electronics [1, 2]. It has been suggested that heterostructures based on InAs–AlSb–GaSb would be very appropriate for low dimension structures — quantum dots and quantum wires.

The polycrystalline indium arsenide is mainly used in the production of ternary and quaternary $A^{III}B^{V}$ compounds and as doping impurity for the reduction of dislocations in GaAs and GaP monocrystals. The reproducible growth of

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InGaAs layers by liquid epitaxy requires a low level of residual impurities and in particular a low level of silicon in the melt [3]. The high reactivity of some of the transient elements makes effective getters out of them. The common impurities (as examples S, Se, Si, C, Te, O and others) form stable compounds, for instance with the lanthanides Gd, Yb, Er. These compounds are not soluble in indium and can be separated during the crystallization of indium arsenide. The lowering of residual impurities in epitaxial layers by gettering has been achieved with gadolinium [4] and in bulk material with scandium [5].

A basic requirement in the synthesis of semiconductor materials is the uttermost avoidance of background impurities during the technological process. Besides, the ingot obtained should be dense, with great block structure and without micro-pores or inclusions of the second phase. It has been shown that the surface treatment of the boats greatly affects the mechanical parameters of the polycrystalline InAs [6]. The use of sand blasted boats could result in sticking of the polycrystalline material and breaking of either the boat or the ingot. The elimination of sticking is achieved through the use of boats with as grown coating of low grain quartz crystallites [7]. The characteristics of the ingots obtained depend also on the technological conditions. They are based on a phase diagram but there are not sufficient data about the arsenic condensate temperature, the crystallization rate and the saturation time [8–13]. The optimization of the technological parameters should be connected with the concentration of the residual impurities.

The purpose of this paper is to study the influence of boats on the concentration of residual impurities at indium arsenide growing. A comparison has been done between the parameters of ingots obtained by two-temperature synthesis in sand blasted boats, BN coated boats and boats with surface SiO_2 crystallites.

2. Experimental

The purity of the grown polycrystalline indium arsenide is assessed by measuring the concentration and mobility of the carriers making use of the Hall effect and by spark mass spectroscopic analysis. The samples studied were cut from the front and the end of the ingot, obtained by two-temperature synthesis and horizontal gradient freezing. The technological parameters of the processes are presented in [6]. As the metalographic analysis showed the presence of micro-inclusions in ingot No 9, the latter was additionally analyzed by scanning electron microscope SEM 515 Philips.

The electrophysical measurements were carried out using Van der Pauw method at DC 10 or 100 mA and a constant magnetic field of 0.2 T. Square samples of minimal size 4×4 mm were used, which were cut from the greatest

grains of parallel wafers from the front and the end of the ingots. The preliminary treatment involves chemical polishing and forming of ohmic contacts by high temperature soldering of indium in hydrogen flow.

3. Results and Discussion

The electrophysical parameters are an indirect indication of the residual impurities level but they are as a standard test in $A^{III}B^{V}$ compounds. The results are given in Table 1.

Table 1. The electrophysical parameters of InAs

Sample	Boat treatment	Front		End	
		N (cm^{-3})	μ (cm^2/Vs)	N (cm^{-3})	μ (cm^2/Vs)
InAs – 4	sand blasted	5.0×10^{16}	12000	6.0×10^{16}	9800
InAs – 5	sand blasted	3.2×10^{16}	14500	4.3×10^{16}	15500
InAs – 6	BN	2.5×10^{16}	19700	4.2×10^{16}	19230
InAs – 7	crystalline	3.9×10^{16}	19550	4.1×10^{16}	24509
InAs – 8	crystalline	2.6×10^{16}	23500	3.1×10^{16}	18250
InAs – 9	crystalline	2.8×10^{16}	20192	3.2×10^{16}	20540

The electrophysical parameters of experiments 1, 2, 3 have not been measured because of the small-grained polycrystalline structure, which makes the cutting of a sample impossible. All samples studied were n-type. The concentration of majority carriers increases from the front to the end of the ingots studied, which is an indication that donors prevail with a distribution coefficient less than 1. With the exception of experiment 7 the concentration of majority carriers in the front of the ingots produced in boats with crystalline coating is smaller that in ingots grown in sand blasted boats and is comparable to that of the ingot from the BN coated boat.

The results from carrier concentration and mobility measurements cannot give unambiguous information about the influence of treatment on the purity of the crystal. The reasons for that are as follows: the different size of the polycrystalline grains, the high concentration of structural defects and the precision of measurements. That is why the residual impurities concentrations at the front and at the end of 3 ingots, grown in boats, having undergone different treatment, are determined by spark mass spectroscopic analysis. The results for the front and the end of ingot No 5 (sand blasting), No 6 (BN coating) and No 7 (SiO_2 crystalline coating) are given in Figs 1 and 2.

The data in the figures are in ppb but in order to provide a better comparison with the electrophysical measurements, magnitudes in cm^{-3} have been used in the discussion.

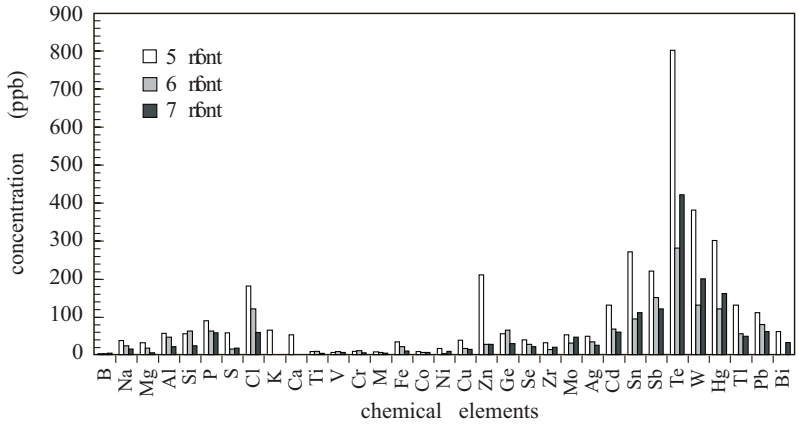

Fig. 1. Concentration of residual impurities in the ingot fronts

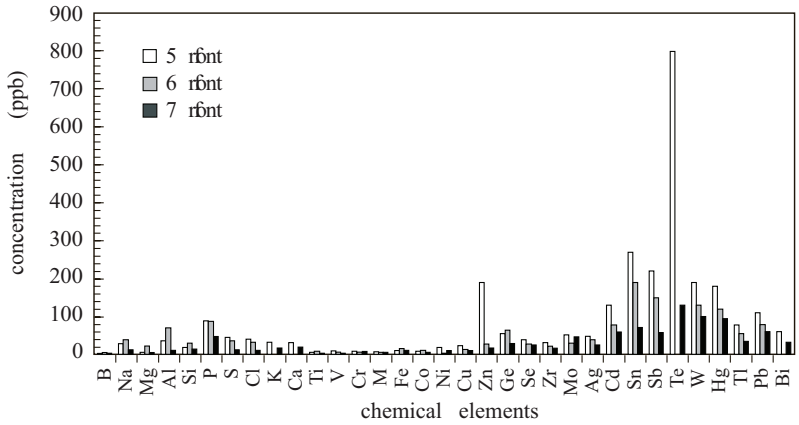

Fig. 2. Concentration of residual impurities in the ingot ends

The results of the element analysis show that the use of boats with crystallite coating leads to reduction of the concentration of all residual impurities in the ingots produced with the exception of B and Mg. Only at the front of the ingot Te with concentration above 1×10^{16} cm^{-3} has been measured. Here are the impurities with concentration exceeding 1×10^{16} cm^{-3} at the front of a sand blasted boat: P, S, Cl, Zn, Sn, Te, W and at the end: P, Zn, Te. For BN coated boat they are: Cl, Te at the front and Al, P at the end. The use of crystalline coating boats induces a decrease of Si concentration. Here are the results for the boat front and end: experiment No 5 — 8.1×10^{15} cm^{-3} and 2.7×10^{15} cm^{-3}; No 6 — 4.5×10^{15} cm^{-3} and 9.1×10^{15} cm^{-3} and No 7 — 3.4×10^{15} cm^{-3} and 2.1×10^{15} cm^{-3}. An unexpected result is the increase of that element in ingot

produced in BN coated boat. A possible cause might be the boat preparation before the deposition of the BN coating [7]. It has been shown that at high temperature some surface sputtering of the sand blasted quartz occurs, which probably causes cracking in the coating. We assume that the silicon impurity comes from the cracks in the coating, which have amorphous quartz in them.

The results from the spark mass spectroscopic analysis confirm the electrophysical measurements and prove that the use of boats with a crystalline coating is an effective way to eliminate the sticking and to reduce the residual impurities.

Besides the boat material the concentration of the residual impurities depends on technological factors. The two-temperature synthesis makes it possible to add arsenic in overstoichiometric quantities, to operate at higher pressure and to change the rate of directed crystallization. The higher vapor pressure of the volatile component reduces the saturation time of the melt. Besides it has been found that in the case of sand blasted boats the higher pressure leads to reduction of the sticking [6]. When the components are heated a vacuum distillation of a potion of the residual impurities occurs and the overstoichiometric arsenic quantity is necessary for compensation. Possible negative effects are micro-inclusions from the second phase. The preliminary metalographic analysis of all samples showed that only in experiment 9 surface micro-roughness after polishing etching occurred, which could be due to micro-inclusions from the second phase. The studies by a scanning electron microscope have proved two types of micro-inclusions with varying size and composition. Table 2 presents the results for the base and the micro-inclusions obtained by energy depressive X-ray analysis (EDAX).

Table 2. The results for the base and the micro-inclusions obtained by EDAX

	Front atomic %		End atomic %	
Upper part	In	49.39 ± 0.96	In	48.83 ± 0.84
	As	50.61 ± 1.11	As	51.17 ± 0.95
Lower part	In	48.92 ± 0.77	In	49.50 ± 1.10
	As	51.08 ± 0.87	As	50.50 ± 1.26
First type micro-inclusions	In	59.43 ± 1.25	In	52.25 ± 0.93
	As	40.57 ± 1.81	As	47.75 ± 1.15
Second type micro-inclusions	Al	83.16 ± 0.76	Al	83.72 ± 0.78
	In	9.66 ± 1.99	In	9.41 ± 2.01
	As	7.19 ± 2.74	As	6.78 ± 2.83

The results obtained indicate that the composition of the base is weakly arsenic enriched (up to 1 %), due to the added overstoichiometric arsenic quantity

and the higher pressure maintained in the ampoule. The micro-inclusions of type 1 are of greater size, irregular form and show a composition enriched by indium. The indium concentration varies from 52 to 59 % at the front and around 52 % at the end. The micro-inclusions micrographs and their distribution are shown in Fig. 3. The micro-inclusions of type 2 are of much smaller sizes; they show relatively uniform distribution and their Al heavily enriches composition. The analysis was repeated on a sample from the beginning of the same ingot, which had not undergone mechanical polishing with Al_2O_3 abrasive and it showed micro-inclusions only of type 1. That proves that the second type of micro-inclusions is the remains of the abrasive material incorporated on the surface. The indium arsenide has low hardness, which poses problems before the abrasive treatment. The preliminary treatment of the samples should include polishing with bound abrasive and/or only chemical-mechanical polishing.

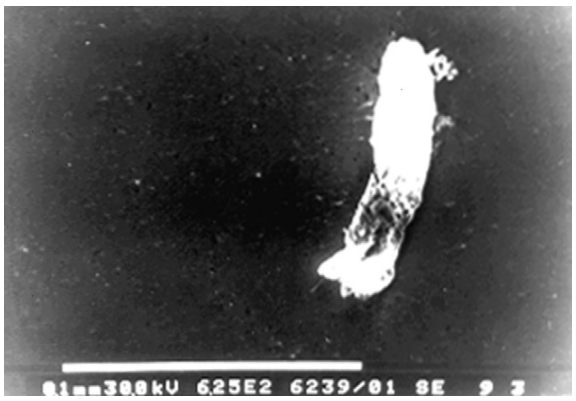

Fig. 3. Electron-microscopic research of micro-inclusions in InAs

Here are some probable causes for these defects: (1) a deviation from the stoichiometric composition, (2) insufficient time for the melt homogenization and (3) high rate of directed crystallization.

Experiment 9 has been carried out with 3.51 % additional arsenic and the measurements show overstoichiometry up to 1 %. Here arsenic enriched, but not indium-enriched micro inclusions should be expected. It means that when the melt is saturated the whole arsenic quantity is not absorbed, which proves that a vacuum distillation takes place. That is also proved by visual control during the process and the weight analysis after the ampoule has been opened.

In case 2 when the time for homogenization of the melt is not enough one should expect micro-inclusions predominantly at the front of the ingot.

The most probable cause for generation of micro-inclusions, enriched by one of the components is the relatively high rate of crystallization (case 3).

Experiment 9 was carried out with a rate of crystallization 1.7 cm/h, while this rate was lower for the other experiments (1.2 – 1.5 cm/h). Probably at the melt crystallization drops with indium were taken in, which later on formed micro-inclusions. The end of the ingot is usually cut, because it shows greater deviation in stoichiometry and residual impurities concentration. X-ray microanalysis can be used for the fast testing at polycrystalline indium arsenide growth. There is no need to grind and polish the samples, they are only cut and degreased.

Our results obtained by spark mass spectroscopic analysis and the assessment of current carrier concentration making use of the Hall effect have shown that the synthesis in crystalline coated boats leads to residual impurities decrease.

The growth of polycrystalline indium arsenide with improved mechanical parameters and reduced concentration of residual impurities could be explained by the following model. When the boats have a crystalline coating of their own, the sticking of the semiconductor to the boat is eliminated during synthesis and directed crystallization at increased pressure of the volatile component. The interaction of the boat surface layer with the semiconductor is reduced, which permits a higher crystallization rate and reducing the time of high temperature anneal. Besides at the two-temperature synthesis overstoichiometric arsenic quantities could be added vacuum distillation of arsenic occurs and part of the residual impurities is left in the ampoules cold end. The complex influence of these factors brings about residual impurities reduction in the semiconductor crystal.

4. Conclusions

- The use of boats with surface grown SiO_2 crystalline coating is an effective way to reduce the residual impurities (including Si) when indium arsenide is grown.
- The ingot parameters are influenced by the process technological conditions. Adding overstoichiometric arsenic and keeping increased pressure bring about an additional distillation of the initial components and reduction of the saturation time of the melt.
- In order to avoid generation of microdefects, the rate of the directed crystallization should not exceed 1.5 cm/h.

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