

Growth of 100 mm indium antimonide single crystals by modified Czochralski technique

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Abstract

Currently there is a worldwide trend to increase the diameter of crystals grown from elemental semiconductors and semiconductor compounds. According to literary data the diameter of 3–5 semiconductor single crystals grown nowadays is 4 to 6 inches. So far up to 75 mm indium antimonide single crystals have been grown in Russia.

Indium antimonide is the element base for the widest field of solid state electronics, i.e., optoelectronics. Indium antimonide is used for the fabrication of 3–5 mm range linear photodetectors and photodetector arrays used as light-sensitive material in heat vision systems.

Growth heat conditions have been selected and 100 mm [100] indium antimonide single crystals have been grown using the modified two-stage Czochralski technique. The graphite heating unit has been oversized to accommodate a 150 mm crucible and a 4.5–5 kg load. The results of the work have provided for a substantial increase in the yield of photodetectors.

The electrophysical properties of the as-grown single crystals have been studied using the Van der Pau method and proved to be in agreement with the standard parameters of undoped indium antimonide. Using the 9-field etch method of pit counting under an optical microscope the dislocation density in the 100 mm single crystals has been measured to be $\leq 100 \text{ cm}^{-2}$ which is similar to that for 50 mm single crystals.

Keywords

Czochralski technique, indium antimonide, 100 mm diameter, single crystal, technology, heating unit, EPD, homogeneity.

1. Introduction

Indium antimonide (**InSb**) is a special one among 3–5 semiconductor compounds due to its unique properties: the lowest melting point of these compounds, a narrow band gap, high carrier mobility and good structural perfection. These properties favor the wide use of indium antimonide as the element base for photoelectronic de-

vices and 3–5 μm range IR photodetectors. InSb based photodetector arrays exhibit high homogeneity of properties across their area, contain a large number of working cells and have a lower price as compared with similar devices fabricated on the basis of HgCdTe (**MCT**). These advantages make InSb a key material for the fabrication of large middle IR range arrays [1–5]. Figure 1 shows a sales chart of photodetector arrays fabricated on the basis of different materials.

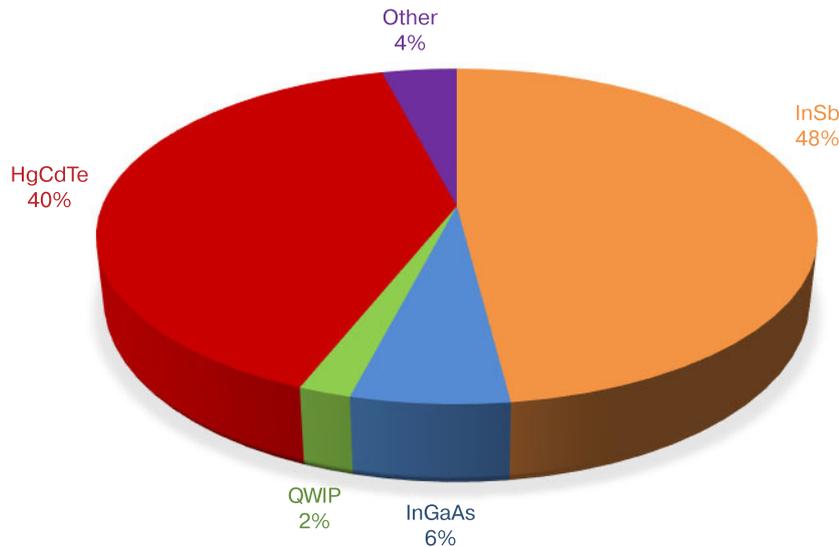


Figure 1. Sales chart of photodetector arrays fabricated on the basis of different materials (Maxtech International).

As can be seen from Fig. 1 the indium antimonide market share (48%) is far greater than those of other photodetector materials and only compares with that of MCT photodetectors (40%) which are several times more expensive than indium antimonide ones [6].

The key structural components of highly sensitive far range heat vision systems are photodetector arrays on indium antimonide substrates. The working principle of these devices is the conversion of the object's heat emission to its visible image. The heat emission of masked or hidden objects makes them visible. The application domain of heat vision systems has greatly expanded in recent years due to their increasingly deep penetration into various fields (Fig. 2).

By analogy with other 3–5 compounds, the main indium antimonide R&D trends are driven by the design of optoelectronic devices on the basis of the material [7–9]. The fabrication of photodetector arrays for high resolution recognition of full optical images and the need to increase the device yield impose new requirements to the diameter of single crystals used in the processes, their

structural perfection and homogeneity of their electro-physical properties [10–12].

Over the last 30 years Giredmet JSC has been the only Russian and former SU research organization that has developed novel technologies, including, e.g. a new polished wafer production line, and has grown indium antimonide single crystals.

The most widely used technology of single crystal semiconductor materials is the Czochralski growth technique. It is utilized for the growth of the majority market share of the key single crystal semiconductor materials, e.g. silicon, indium arsenide, gallium and indium phosphides, as well as indium and gallium antimonides. Exclusion is gallium arsenide most single crystals of which are grown by vertical directional crystallization or horizontal directional crystallization. The advantage of these techniques is the possibility to combine the synthesis, cleaning and growth of semiconductor single crystals in a single process. However these techniques are extremely labor consuming, deliver low output and require expensive equipment. The horizontal directional

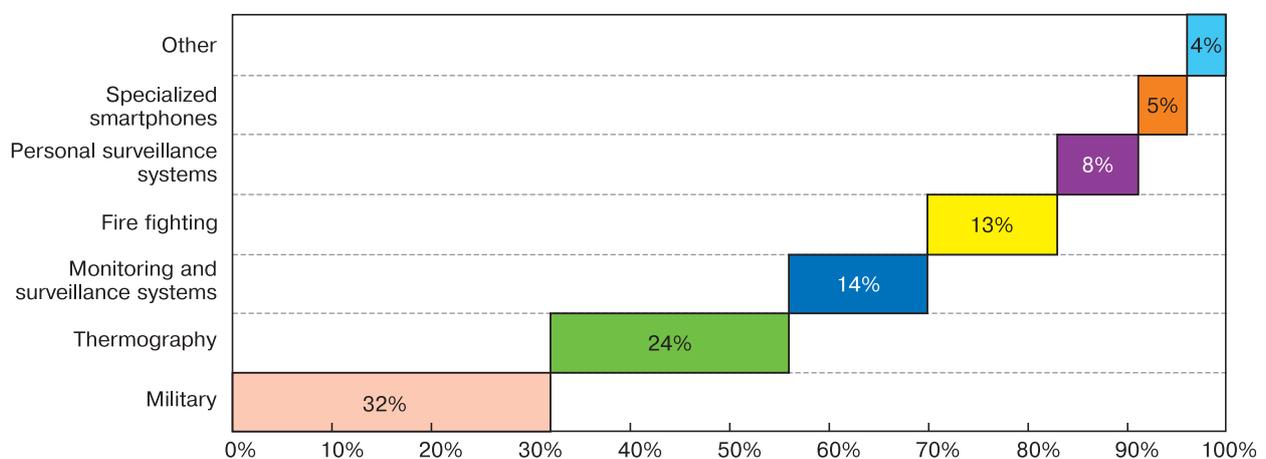


Figure 2. Application domains of heat vision systems (Yole Development, 2018).

crystallization technique was also used for the synthesis and cleaning of polycrystalline InSb from which single crystals were Cz-grown at the subsequent stage [13]. This technology also proved to be quite expensive and power consuming since it requires more than 40 passes of the melt zone at the synthesis and subsequent cleaning stages.

We therefore considered it expedient to use the advantages of the Czochralski technique as a far less power consuming and faster one as compared with vertical and horizontal directional crystallization for developing a fundamentally new resource-saving technique for the growth of large diameter (> 60 mm) indium antimonide single crystals to combine synthesis and growth in a single process cycle.

2. Modified Czochralski technique for single crystals of 3–5 semiconductor compounds

The key point of the new modified technique is to eliminate the labor and power consuming process stages of synthesis and subsequent multi-step zone melting (up to 40 zone passes) required for obtaining raw polycrystalline indium antimonide, and to implement a new combined synthesis and growth process instead. It is obvious that of special importance for this modified process are the purity of the raw materials which should be not less than 6N, special synthesis conditions and additional melt cleaning from detrimental impurities using special technology approaches. Polycrystalline indium antimonide obtained by this combined process is the raw material for subsequent single crystal growth. Thus the technique developed by us is a two-stage process, where the first stage is the synthesis of indium antimonide and growth of ultrahigh purity polycrystal for the seed and the second stage is seeding of a single crystal with the preset properties.

Figure 3 shows the heating unit used in the two-stage polycrystalline and single crystalline InSb-growth process.

The design of heating units for the synthesis and the growth of single crystals includes a filtering crucible which cleans the melt of mechanical contaminants and homogenizes the forming compound.

Comparing the existing Russian single crystal indium antimonide technology with those of the world's leading manufacturers, e.g. MTI, US, Wafer Technology Ltd., UK, and Xiamen Powerway Advanced Material Co., Ltd., China [14–16], one can trace tangible differences as are summarized in Table 1.

Table 1 shows that the Griredmet-developed process combines single crystal indium antimonide synthesis and growth in static vacuum without encapsulating flux or elevated argon pressure. Addition of small excess quantities of Sb into the melt compensates the loss of the volatile Sb component thus maintaining growing crystal

stoichiometry. As shown in Fig. 3 the melt is cleaned in the filtering crucible and the raw components have at least 6N purity. An important difference is that indium antimonide single crystals are grown on a [100] seed. The choice of this growth direction is expedient and economically justified since photodetector array designers use the (100) plane as the working surface. This greatly reduces the loss of material in comparison with [211] single crystal growth technology with further cutting of (100) wafers.

The growth of [100] indium antimonide single crystals had not yielded any results for quite a long time due to the extremely strong twinning tendency of growing crystals. The use of a heating unit with a minimum set of vertical

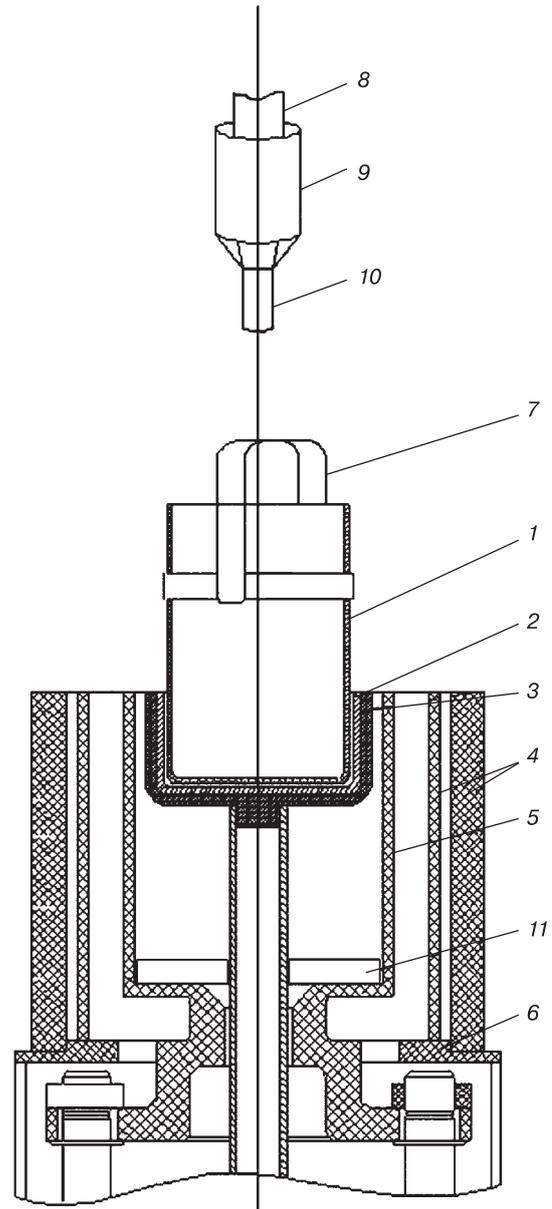


Figure 3. Schematic of heating unit for synthesis and growth of single crystal indium antimonide: (1) filtering crucible, (2) working crucible, (3) graphite support, (4) vertical screen (5) heater, (6) outer screen, (7) crossbeam, (8) rod, (9) graphite seed holder, (10) InSb single crystalline seed, (11) heat-insulating gasket.

Table 1. Key differences between Russian and foreign single crystal indium antimonide technologies

Process parameters	Manufacturers	
	Giredmet JSC	MTI, Wafer Technology Ltd., Xiamen Powerway Advanced Material Co., Ltd.
Growth technique	Modified Czochralski technique	Liquid Encapsulated Czochralski (LEC)
Atmosphere	Static vacuum, no flux	Argon, boron anhydride as flux
Synthesis	Combined synthesis and growth on seed	Separate synthesis and cleaning
Heat treatment	Stepwise post-crystallization heat treatment in growth plant	–
Crystallographic direction	<100>	<211>
Crystal diameter	>50 mm, >75 mm, >100 mm	>2”>3”, >4”, >5»

screens and a bottom/side heater (Fig. 2) coupled with experimental selection of dynamic growth conditions have allowed developing the axial temperature gradient at the crystallization front as is required for crystal growth on [100] seeds. According to earlier data [17] axial temperature gradients at the crystallization front may vary considerably during the growth of [100] and [211] single crystals, the respective figures being 35–40 and 25–30 K/cm. Furthermore the growth of indium antimonide single crystals under these conditions reduces the dislocation density in the crystals to $< 100 \text{ cm}^{-2}$ but retains large thermal stresses which play an important role in the course of further crystal treatment and cutting into wafers. Residual stress relief in as-grown single crystals is achieved with post-crystallization anneal at the end of the second process stage directly in the growth chamber by stepwise heater temperature reduction in experimentally selected mode.

3. Modified Czochralski growth and study of indium antimonide single crystals

The fabrication of >50 mm diam. indium antimonide single crystals with parameters as per customers' specifications was started following the technology developed herein. For the growth of 100 mm diam. [100] indium antimonide single crystals by the modified Czochralski technique the heating unit was optimized and growth and post-crystallization anneal modes were selected. The key properties of the so grown single crystals were then studied.

The development of 3–5 semiconductor compound technologies [18, 19] has shown that the fabrication of LSICs and VLSICs requires greater diameters and higher structural perfection of single crystal wafers for chip substrates. The fabrication of new generation indium antimonide photodetector arrays faces similar problems. For increasing the single crystal wafer diameter to 100 mm or greater the InSb growth plant space was increased from 60 to 110 litres, the heating unit was redesigned to accommodate a 150 mm working crucible, the polycrystalline

material charge was increased to 5 kg and the seed size was doubled. The growing crystal to melt diameter ratio



Figure 4. Appearance of indium antimonide single crystal: (a) 105 mm diam. single crystal and (b) facets of [100] single crystal.

Table 2. 77 K electrophysical parameters and EPD in indium antimonide specimens

Specimen code	Specimen thickness (mm)	Conductivity type	Majority carrier concentration (10^{14} cm^{-3})	Majority carrier mobility ($10^5 \text{ cm}^2/(\text{V} \cdot \text{s})$)	EPD _d (cm^{-2})
18-H1	2.35	<i>n</i>	1.6	5.3	67
18-H2	2.31	<i>n</i>	1.7	5.3	42
18-H3	2.27	<i>n</i>	2.0	5.4	56
18-H4	2.34	<i>n</i>	1.8	5.1	39
18-K1	2.37	<i>n</i>	7.7	3.4	80
18-K2	2.33	<i>n</i>	8.0	3.4	57
18-K3	2.30	<i>n</i>	7.9	3.2	79
18-K4	2.34	<i>n</i>	8.1	3.0	62

was 0.66, in agreement with the calculated range of 0.5–0.7. The thermal and dynamic conditions of >100 mm diam. indium antimonide single crystal growth were chosen experimentally and these single crystals were for the first time grown in Russia. Figure 4 shows the appearance of a >100 mm diam. [100] indium antimonide single crystal.

The key electrophysical parameters were measured for 1.5 mm thick wafers cut out perpendicularly to the growth axis from the top and bottom single crystal portions (Table 2). Each wafer was cut in 4 pieces along two perpendicular diameters for the measurements due to the measuring instrument size limitations. The Hall coefficient was measured with the Van der Pau method and the majority carrier concentration and mobility in the crystal were calculated. The measurements were made at the LN temperature (77 K).

The electrophysical properties of the indium antimonide single crystals prove to be in agreement with standard data for the undoped material: $n = 2 \cdot 10^{14} \pm 1.5 \cdot 10^{15}$ ($T = 77 \text{ K}$) [20]. It should be noted that the electrophysical properties of the wafers are quite homogeneous. The residual impurity concentration increases towards the ingot end suggesting their distribution coefficient is less than one unit.

Structural defects were studied and the dislocation density was evaluated by etch pit number counting in the wafer segments under an optical microscope. The absence of twins, lamellae or second phase nuclei in the

wafers suggests the optimum selection of thermal and dynamic single crystal growth conditions.

Table 2 shows data on the dislocation density calculated from etch pits. The data suggest that the EPD in the grown single crystals is within 100 cm^{-2} which is similar to the EPD in >50 mm diam. single crystals [20].

4. Conclusion

>100 mm diam. [100] indium antimonide single crystals were first grown in Russia using the modified Czochralski technique developed by Giredmet JSC.

Study of the electrophysical parameters of the 100 mm diam. single crystals showed that their carrier concentration and mobility agree with the standard data for the undoped material. The results suggest that the 100 mm diam. single crystals have highly homogeneous electrophysical parameters.

The structure of the single crystals was studied. The results showed that the EPD in the single crystals is within 100 cm^{-2} which is not greater than that for >50 mm single crystals. The dislocation density distribution in the crystal cross-sections was homogeneous with the density increasing slightly toward the crystal periphery. The single crystals did not contain twins, lamellae or second phase nuclei. The end parts of the crystals exhibited slight deviation from stoichiometry due to the long process time of single crystal growth.

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