

Growing of $Ga_xIn_{1-x}Sb$ single crystals by Czochralski technique

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The effective distribution coefficients for Ga in $Ga_xIn_{1-x}Sb$ single crystals ($x \le 0.2$) have been calculated according the Ostrogorsky-Mueller model taking into account the experimental data. The growing procedure of $Ga_xIn_{1-x}Sb$ single crystals using the Czochralski technique has been developed and the crystals up to 18 mm in diameter have been grown. The influence of annealing on the crack formation in $Ga_xIn_{1-x}Sb$ single crystals after cutting thereof has been studied. The crystal annealing at 170°C for 10–12 h has been found to reduce the number of cracks longer than 0.2 mm.

Определены эффективные коэффициенты распределения Ga согласно модели Острогорского-Мюллера с учетом экспериментальных данных для составов кристаллов $Ga_xIn_{1-x}Sb$ с содержанием Ga до 0,2. Разработан метод выращивания по Чохральскому, выращены монокристаллы $Ga_xIn_{1-x}Sb$ диаметром до 18 мм. Изучено влияние отжига на образование трещин после разрезания монокристаллов $Ga_xIn_{1-x}Sb$. Показано, что отжиг кристаллов при температуре 170°C в течение 10–12 часов уменьшает количество трещин длиной более 0,2 мм.

$Ga_xIn_{1-x}Sb$ solid solutions have the band gap width of 0.17 to 0.7 eV within the hole composition range from InSb to GaSb. This band gap corresponds to the IR spectrum region from 1.7 to 7 μm wavelength [1]. The crystal lattice parameter for those solid solutions varies from 0.648 to 0.610 nm. The $Ga_xIn_{1-x}Sb$ single crystals can be used in manufacturing of high-sensitivity photodetectors, light emittimg diodes, and lasers. The considerable difference in the lattice parameters, a significant distance between the liquidus and solidus in the InSb–GaSb phase diagram, and difference in the distribution coefficients of components favor the concentration overcooling that influences negatively the growth process of perfect single crystals. The Czochralski technique has some advantages over other directional crystallization methods due to the crystal rotation and absence of any contact between the crystal being pulled and the container wall. This is an important advantage in manufacturing the materials that increase the volume in the course of crystallization. To obtain the crystals of $Ga_xIn_{1-x}Sb$ solid solutions, the effective distribution coefficients for the components are to be known. Of practical importance are $Ga_xIn_{1-x}Sb$ single crystals where x amounts up to 0.2.

The equilibrium distribution coefficients for gallium have been determined from the InSb–GaSb phase diagram using the relationship [2]

$$K = C^S/C^l, \quad (1)$$

where K is the equilibrium distribution coefficient for gallium; C^S is gallium concentration in solid phase; C^l, that in liquid phase at the interface.

The effective distribution coefficient for gallium, k_e^{Ga}, was calculated in the frame of Ostrogorsky-Mueller model [3]:

$$k_e = \frac{1+\frac{4b(\omega D)^{1/2}}{f}(D/\nu)^{2n-1/2}}{1+\frac{4b(\omega D)^{1/2}}{f}(D/\nu)^{2n-1/2}\frac{1}{k}}, \quad (2)$$

Table. Melt parameters

Parameter	Value
Melt kinematic viscosity ν, m^2/s	$3.4 \cdot 10^{-7}$
Experimental K_e^{Ga} values for $Ga_xIn_{1-x}Sb$ crystals:	
at $x = 0.03$	2.625
at $x = 0.09$	2.57
Calculated diffusion coefficient D, m^2/s	$4.52 \cdot 10^{-10}$
Schmidt number, Sc	752

where n is a coefficient selected from the condition $1/2 \le n \le 1/3$ at the Schmidt number $Sc = \nu/D$ in the range $1 \le Sc \le \infty$; b, a constant varying from 1/4.6 to 1/7.2 depending on the growth surface profile. In calculations of the effective distribution coefficients for gallium, the parameters presented in Table were used. Fig. 1 shows the depencences of the equilibrium and effective distribution coefficients for Ga in the solid solutions area with Ga content up to 0.2. The effective distribution coefficient for Ga rises from 2 to 2.9 as the Ga content increases.

$Ga_xIn_{1-x}Sb$ solid solutions single crystals up to 18 mm in diameter were grown by Czochralski technique. A InSb was used as a seed for growing $Ga_xIn_{1-x}Sb$ single crystals with $x < 0.03$. $Ga_xIn_{1-x}Sb$ seed single crystals were used for growing the crystals with $x > 0.03$. These seeds had the composition $x = 0.01$ difference to these to be grown. The pulling and rotation rates of the crystals were from 2 to 3 mm/h and 10 rpm, respectively. The crucible with melt was not rotated during the growing. Special purity gallium, indium, and stibium (99.9999 mass %) were used as source materials. The crystals were grown in high-purity argon atmosphere with an excess pressure of 0.4 atm.

The crystals were cut along the pulling direction. The cut surfaces were etched in the acid mixture (HNO_3:CH_3COOH:HF, 5:3:3) for 5 to 20 s at room temperature. The etched surface was examined by optical microscopy. All the crystals have surface and inner cracks of various lengths and orientations. The number of the cracks depends on thermal conditions of the growing process and increases with rising diameter of the crystal. At the surface of a 18 mm diameter crystal, some cracks are formed in the course of growth (Fig. 2), perhaps due to a considerable difference between the axial and radial temperature gradients in the growing crystal [4]. In the crystals

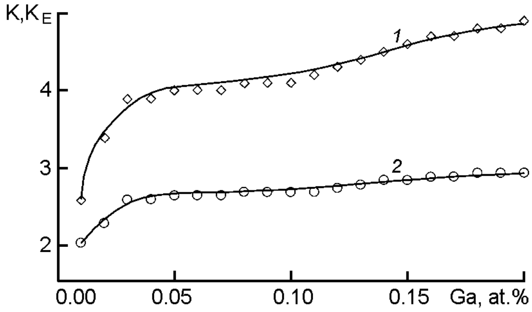

Fig. 1. Ga distribution coefficients: equilibrium (*1*) and effective according to the Ostrogorsky-Mueller model (*2*).

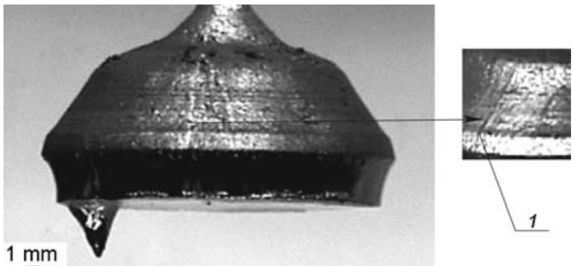

Fig. 2. A $Ga_xIn_{1-x}Sb$ crystal with $x = 0.03$. A surface crack is seen (*1*).

of less than 10 mm diameter, the cracks are smaller and not observed on the side surface.

Before, it was proposed to anneal the $Ga_xIn_{1-x}Sb$ single crystals at 150°C for 12 h [5]. This made it possible to reduce the number of cracks. In this connection, the effect of the annealing temperature and duration on the reduction of the crack number in the grown crystals has been studied in more detail. The reliability of these results has been estimated by comparing the annealed and unannealed surfaces of one and the same crystal. This estimation method where one part of the crystal is cut prior to the annealing while another thereafter provides the most reliable information, since both crystal parts have been grown in identical conditions. The $Ga_xIn_{1-x}Sb$ single crystal was cut using an electrospark lathe. The crystal cutting scheme prior to and after the annealing is shown in Fig. 3.

The crystals were annealed at 170°C for 8–12 h in air. The surface of the crystals cut prior to annealing exhibits numerous cracks up to 6 mm in length, as is seen in Fig. 4. After the crystal annealing at 170°C for 10–12 h, no the cracks longer than 1 mm were formed at an electrospark lathe cutting. Only several cracks of less than 0.2 mm have been found (Fig. 5). The annealing at the above-mentioned temperature for 8 h does not provide elimination of the cracks up to 1 mm length. Perhaps, the cracks are

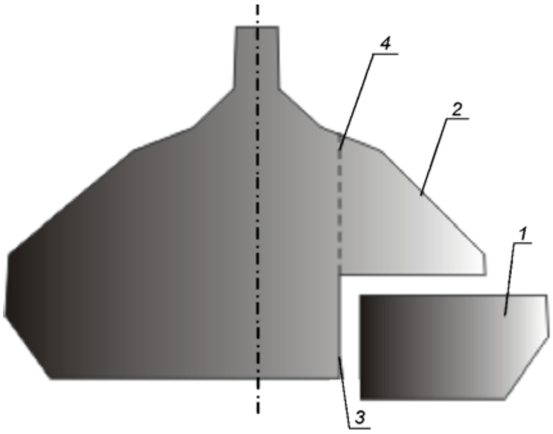

Fig. 3. Cutting scheme of $Ga_xIn_{1-x}Sb$ crystal to be annealed. *1*, the crystal part cut prior to annealing; *2*, that cut after the annealing; *3*, the surface studied prior to annealing; 4, that studied after the annealing.

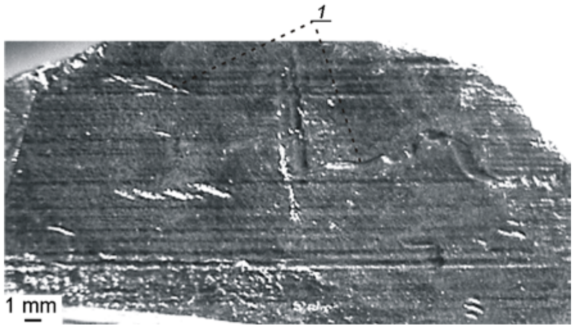

Fig. 4. A $Ga_xIn_{1-x}Sb$ crystal prior to annealing. The cracks are seen (*1*).

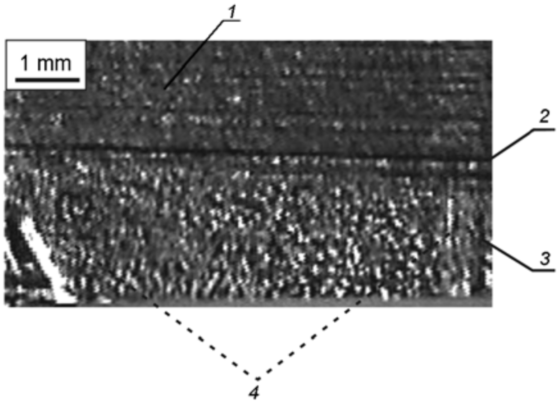

Fig. 5. $Ga_xIn_{1-x}Sb$ crystal surface prior to and after the annealing. *1*, the crystal surface after the annealing; *2*, the annealing boundary; *3*, the crystal surface prior to annealing; *4*, cracks.

due to high internal stresses caused by considerable temperature gradients in the crystals being pulled. It is to note that the cracks formed in the course of the growth and extending from the surface to the crystal depth cannot be eliminated by annealing.

Thus, the developed procedure for $Ga_xIn_{1-x}Sb$ single crystal growing by Czochralski technique has made it possible to obtain the crystals of up to 18 mm diameter. It has been established that, when $Ga_xIn_{1-x}Sb$ single crystals of a diameter larger than 10 mm are grown, the cracks may be formed on the side surface thereof. This may be due to large axial and radial temperature gradients in the solid phase. The crystal annealing at 170°C for 8–12 h provides a considerable relaxation of internal stresses and thus a reduced crack number after the crystal cutting.

References

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Вирощування монокристалів твердих розчинів $Ga_xIn_{1-x}Sb$ методом Чохральського

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Визначено ефективні коефіцієнти розподілу Ga згідно моделі Острогорського-Мюллера з урахуванням експериментальних даних для складів кристалів $Ga_xIn_{1-x}Sb$ із вмістом Ga до 0,2. Розроблено метод вирощування за Чохральським, вирощено монокристали $Ga_xIn_{1-x}Sb$ діаметром до 18 мм. Вивчено вплив відпалу на утворення тріщин після розрізання монокристалів $Ga_xIn_{1-x}Sb$. Показано, що відпал кристалів при температурі 170°C протягом 10–12 годин поменшує кількість тріщин довжиною більш ніж 0,2 мм.