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# The influence of thermal conditions on perfection in $Ga_xIn_{1-x}Sb$ single crystals

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The influence of the temperature gradient on the appearance of macro-cracks in growing $Ga_xIn_{1-x}Sb$ single crystals by Czocralski method is shown. The decrease of axial temperature gradient $dT/dz$ to 15 K/cm and radial $dT/dx$ to 5 K/cm has allowed obtaining the single crystals without the cracks. The thermal field in $Ga_{0.03}In_{0.97}Sb$ single crystal grown with use of experimental values of the temperature gradients is calculated.

Показано влияние градиента температуры в твердой фазе на трещинообразование при выращивании монокристаллов твердых растворов $Ga_xIn_{1-x}Sb$ методом Чохральского. Уменьшение осевого градиента температуры в твердой фазе $dT/dz$ до 15 K/см и радиального $dT/dx$ до 5 K/см позволило вытягивать монокристаллы без трещин. Рассчитано тепловое поле в монокристаллах твердых растворов $Ga_{0,03}In_{0,97}Sb$ в процессе роста с использованием экспериментальных значений градиентов температуры.

Single crystals of $Ga_xIn_{1-x}Sb$ solid solutions can be used to develop lasers and photodetectors in the infrared region from 1 to 7 μm [1]. The structural perfection of $Ga_xIn_{1-x}Sb$ solid solutions single crystals influences on their electronic and optic properties. It is known that with the increase of gallium content in $Ga_xIn_{1-x}Sb$ single crystals the lattice parametres essentially change [2]. This, in its turn, leads to the internal stress increase in them, which promotes the increase of dislocations density. Besides, the formation of dislocations and cracks in solid solution crystals results from the stresses appearing in the process of growth due to high temperature gradients in the solid phase [3]. The aim of our paper is study the temperature gradients influence in the solid phase on the cracks formation in the pulled $Ga_{0.03}In_{0.97}Sb$ solid solutions single crystals.

$Ga_{0.03}In_{0.97}Sb$ solid solutions, up to 7 mm in diameter were grown by Czocralski method to the InSb seed crystal in <111> direction at the pulling rate 0.05 mm/min and rotation rate up to 10 rpm. The crystal was drown from the melt mass 100 g in weight in quartz crucible 40 mm in diameter and 30 mm in height. The crucible not rotated. Indium, gallium and antimony of high purity 99.9999 % were used as source material. The crystals were pulled in high purity Ar atmosphere at 0.4 atm. overpressure. The growth plant, designed according to Czochralski pulled apparatus, allowed the regulation of axial and radial temperature gradient in the grown crystal by changing the temperature of water-cooled rod and adding more heat shields around the heater and pulled crystal. Grown single crystals were cut parallel to the growth axis and (211) plane in an electrospark lather for study of the structural perfection [4,5]. The cut surfaces were etched with a solution of $HNO_3:HF:CH_3COOH:H_2O$ = 5:3:3:11 for 10–15 seconds at room temperature.

We have determined the optimal axial and radial temperature gradients for growing of $Ga_{0.03}In_{0.97}Sb$ single crystals without any cracks. Then these optimal temperature gradients were measured experimentally. The axial and radial temperature gradients

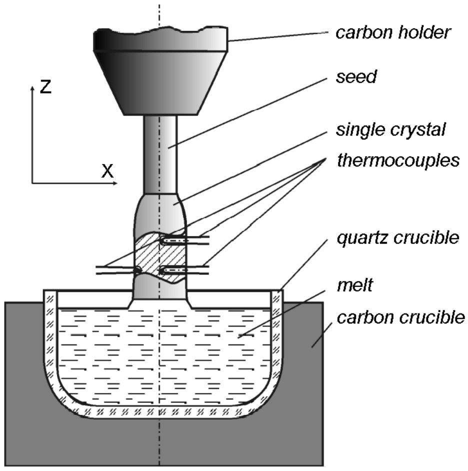


Fig. 1. The scheme of temperature gradients measurement in the crystal.

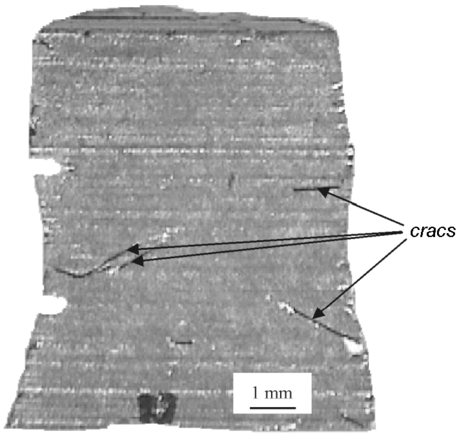


Fig. 2. The sample of $Ga_{0.03}In_{0.97}Sb$ solid solution single crystal with the most cracks.

were measured in the conditions near to those of crystal growth, according to the scheme in Fig. 1. In $Ga_{0.03}In_{0.97}Sb$ of solid solution single crystal 30 mm long and 6 mm in diameter, three holes (0.8 mm in diameter) were made in an electrospark lather. Two holes with 3 mm deep were situated along the crystal axis with 10 mm distance between them. The third hole was 0.8 mm deep and situated in the same cross-section with the lower hole. Chromel-alumel thermocouples were fixed in these three holes for the measure of the axial and radial temperature gradient in the crystal. The single crystal contacted with the melt and not rotated. The temperature gradient were measured after establishing the thermal equilibrium.

On the cut surface of crystal samples, grown at 65 K/cm axial temperature gradient and the radial one more than 100 K/cm, were found 4 cracks 3 mm in length, directed into the sample. The surface of $Ga_{0.03}In_{0.97}Sb$ solid solution single crystal sample with five cracks shown in Fig. 2. These cracks had a shape of lines and were oriented with angles from 3 to 60° to the solid-liquid interface. In Fig. 3 shown that the decrease of axial temperature gradient temperature to 20 K/cm caused the reduce of the cracks length to 1 mm. The change of radial temperature gradient to 5 K/cм at the axial temperature gradient of 47 K/cm let us the cracks length to decrease to 1 mm. The single crystals without cracks were pulled at axial temperature gradient of 15 K/cm and radial gradient temperature of 5 K/cm.

The temperature fields in grown crystals were calculated according to the known mod-

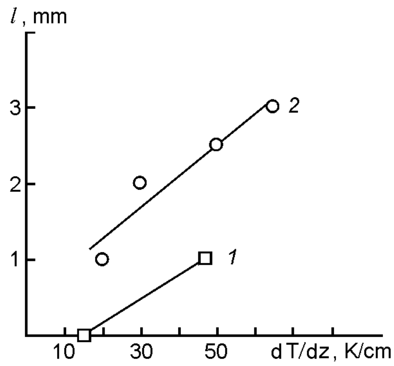


Fig. 3. The graph of cracks length dependence on axial temperature gradient $dT/dz$ in the crystals: *1* — radial temperature gradient $dT/dx$ less than 5 K/cm, *2* — radial temperature gradient $dT/dx$ more than 100 K/cm.

els which take into account the conditions for heat exchange between the growing single crystal and the environment [6–8]. The given models were used for the calculation of the thermal fields in the ingots of the materials with the melting temperature more than 1123 K. The axial and radial gradient of temperature in the solid phase were calculated according to the equation [8]:

$$T = T_C\left[1 - \frac{ah}{2}\left(\frac{r}{a}\right)^2\right]e^{-z/a\sqrt{2ah}}, \qquad (1)$$

where $r$ and $z$ are the radial and axial coordinates; $h = \alpha/\lambda$ is the relation of the crystal surface heat-transfer factor to the crystal thermal conductivity, $T_C$ is the temperature on the crystallization front, $a$ is the radius of the crystal.

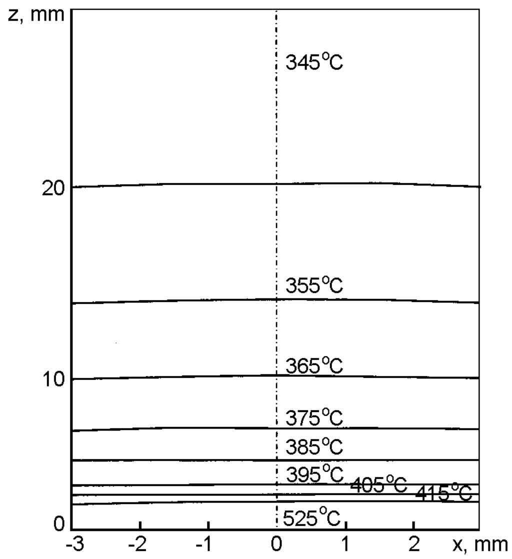


Fig. 4. Thermal field inside the growing $Ga_{0.03}In_{0.97}Sb$ single crystal.

Furthermore, the values of temperature gradient calculated by equation (1), didn't correspond to the measured gradient values. Furthermore, taking into account the experimental data, we obtained the empiric expression on its base to reflect the temperature distribution in the grown $Ga_xIn_{1-x}Sb$ single crystals:

$$T = T_0 + (T_C - T_0)\left[1 - \frac{ah}{2b}\left(\frac{r}{a}\right)^2\right]e^{-z^{1/4}/a\sqrt{2ah}}, \quad (2)$$

where $T_0$ is the ambient temperature near the crystal, $b$ is the empiric factor.

This dependence takes into account the ambient temperature near the crystal and allows one to calculate axial and radial temperature gradients in pulled $Ga_xIn_{1-x}Sb$ solid solutions single crystals. The increase of Ar gas the temperature near the crystal leads to the decrease of temperature gradients in axial and radial directions. The thermal field in grown $Ga_{0.03}In_{0.97}Sb$ solid solutions single crystals was calculated according to the given expression (Fig. 4). The Table shown the values which were used for the calculation of the thermal field in $Ga_{0.03}In_{0.97}Sb$ crystals. Fig. 4 shows that in the ingot of $Ga_xIn_{1-x}Sb$ single crystal the axial temperature gradient decreases with moving away from the crystallization front. At the same time, the influence of the radial temperature gradient increases and this leads to change of the thermal field.

Table. Calculation parameters

| | |
|---|---|
| Crystal radius $a$, mm | 3 |
| The heat-transfer factor for crystal surface *alphaБ Ata* , Wt/(cm$^2$·K) | 0.072 |
| Crystal thermal conductivity $\lambda$, Wt/(cm·K) | 0.167 |
| Temperature in the crystallization front for $Ga_{0.03}In_{0.97}Sb$ $T_C$, K | 800 |
| Ambient temperature near the crystal $T_0$, K | 533 |
| The empiric factor $b$ | 150 |

Thus in this paper we have studied the influence of axial and radial temperature gradients on the structure perfection for $Ga_{0.03}In_{0.97}Sb$ solid solution single crystals, grown by Czochralski method. The optimal thermal growth conditions are defined for the growth of $Ga_{0.03}In_{0.97}Sb$ solid solutions single crystals without cracks. Such conditions are the decrease of the axial and radial temperature gradients in the crystal to 15 K/cm and 5 K/cm, respectively.

The expression for the calculation of the thermal field in the grown $Ga_xIn_{1-x}Sb$ solid solutions single crystals is obtained.

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# Вплив теплових умов на досконалість монокристалів твердих розчинів $Ga_xIn_{1-x}Sb$

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Показано вплив градієнта температури у твердій фазі на утворення тріщин під час вирощування монокристалів твердих розчинів $Ga_xIn_{1-x}Sb$ методом Чохральського. Зменшення осьового градієнта температури у твердій фазі $dT/dz$ до 15 К/см і радіального $dT/dx$ до 5 К/см дозволило витягувати монокристали без тріщин. Розраховано теплове поле у монокристалах твердих розчинів $Ga_{0,03}In_{0,97}Sb$ у процесі росту з використанням експериментальних значень градієнтів температури.