Functional Materials 12, No.4 (2005) © 2005 — Institute for Single Crystals

# Influence of ultrasound on the growth striations in $Ga_xIn_{1-x}Sb$ single crystals

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The results of investigation experiments of the growth striations in $Ga_xIn_{1-x}Sb$ single crystals with x=0.03 grown by Czochralski method with ultrasound field at a frequency of 1.44 MHz have been presented. It was noted that ultrasound eliminate the growth striations generated by the convection in the melt in the central part of the crystals and at the crystals periphery. The experimental results have been confirmed by the modeling experiments of the convection in the liquid phase in the conditions similar to growth conditions of $Ga_{0,03}In_{0,97}Sb$ single crystals.

Приведены результаты экспериментов по исследованию слоистой неоднородности в монокристаллах твердого раствора $Ga_xIn_{1-x}Sb$ с содержанием галлия $x = 0.03$, выращенных методом Чохральского при воздействии ультразвукового поля с частотой до 1,44 МГц. Установлено, что ультразвук устраняет в центральной части и на периферии кристаллов слои, имеющие конвективную природу. Результаты данных экспериментов роста были подтверждены экспериментами моделирования конвекции в жидкой фазе в условиях, близких к условиям роста монокристаллов $Ga_{0,03}In_{0,97}Sb$.

Growth method of semiconductor single crystals in ultrasound field draws more and more attention due to its high efficiency and low energy consumption. In the several works the positive effect of ultrasound on the growth of indium antimonide, gallium arsenide, bismuth-stibium solid solutions single crystals was revealed [1-7]. So ultrasound field at a frequency of about 1 MHz provides a considerable lowering of striation that is among the main component distribution inhomogeneities in the single crystals mentioned and affects negatively the crystal electrophysical properties. However, in growth experiments of $Ga_xIn_{1-x}Sb$ crystals, the use of ultrasound at a frequency of 10 kHz and power of 120 W did not provides high-quality single crystals due to appearance of cavitation in the melt [8]. Therefore the study of influence of megahertz range ultrasonic waves on the growth striation in $Ga_xIn_{1-x}Sb$ single crystals is a new and promising field of research. Also these investigations are of practical importance, since $Ga_xIn_{1-x}Sb$ single crystals are a material of promise for optoelectronic devices due to a wide variation range of the band gap (from 0.17 to 0.7 eV [9, 10]) and the lattice parameter (from 6.48 to 6.1 nm [11]) in those crystals.

In order to obtain $Ga_xIn_{1-x}Sb$ single crystals with $x$=0.03, an experimental setup for crystal growing by Czochralski technique was used. The arrangement made it possible to introduce the ultrasound into the melt from a piezotransducer through a quartz waveguide. InSb single crystal was used as the seed and oriented so that the pulling direction was parallel to the <111>. The melt mass did not exceed 80 g. The pulling and rotation rates of crystals were 3 mm/h and from 1 to 10 rpm, respectively. The crucible was not rotated during the growing. The direction of ultrasonic waves at frequencies from 0.69 to 1.44 MHz was parallel to the pulling axis. Indium, stibium and gallium of high purity (6N) were used as source materials.The crystals were pulled in high-purity argon atmosphere with an excess pressure of 0.4 atm.

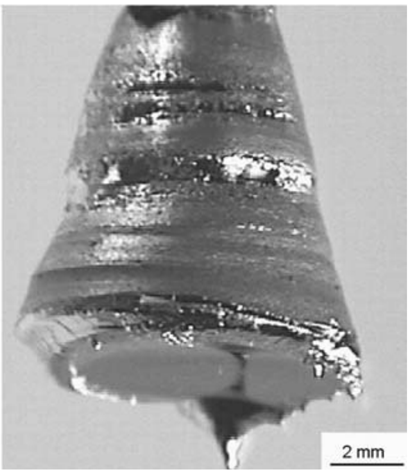

Fig. 1. Pulled single crystals of $Ga_{0.03}In_{0.97}Sb$ solid solution.

The diameter and length of grown single crystals were 12 mm and 22 mm, respectively (Fig. 1). The crystal mass was less than 4 % of the melt mass, thus providing only insignificant decrease of gallium content in the final part of the ingot. Besides, each crystal had regions of 3 to 4 mm length pulled with and without ultrasound, thus providing reliable observations of striation changes in the crystals. In order to study the striation, the grown $Ga_{0.03}In_{0.97}Sb$ single crystals were cut into 1.5 to 2 mm thick plates along the growth axis parallel to (211) plane. The plate surfaces were ground, polished, and etched with CP-4A($HNO_3$:$CH_3COOH$:HF=5:3:3) for 5 s at room temperature. The investigation of striation was carried out using a MIM-8 microscope.

In the single crystals grown without ultrasound field, there are rotational striations with period of 7-110 μm, which revealed growth interfaces (Fig. 2a). The separation between striations was increased with the decrease in rotation rate of crystal (Fig. 2b). The striation width is about 1 μm. Moreover, in $Ga_{0.03}In_{0.97}Sb$ single crystals facet was not found. One is clearly pronounced in InSb crystals pulled in the <111> direction [12]. A specific feature of gallium-enriched striations revealed in $Ga_{0.03}In_{0.97}Sb$ crystals grown under periodic switching on and switching off the ultrasound is the absence of large period (exceeding 50 μm) striations. Simultaneously, in a crystal grown in the ultrasound field at a frequency of 0.72 MHz with convex shape of S/L interface, the striations with periods of 20-27 and 12-14 μm are absent in the central part and at the periphery crystal. However, striations of about 7 μm period are observed in all crystal regions. A possible explanation of the revealed phenomenon consists in that the formation of those striations is connected not with convection in the melt assumed to be one of reasons for occurrence of the growth striation in crystals [13] but with asymmetric position of crystal to the melt surface in the laboratory setup used in this work. To confirm this assumption several $Ga_{0.03}In_{0.97}Sb$ single crystals with large deflection of the pulling axis from the vertical position were grown. In the crystal pulled with deflection of the crystal axis from the vertical of 1.7 mm period of striations decreased by a factor of 2 to 3 in the central

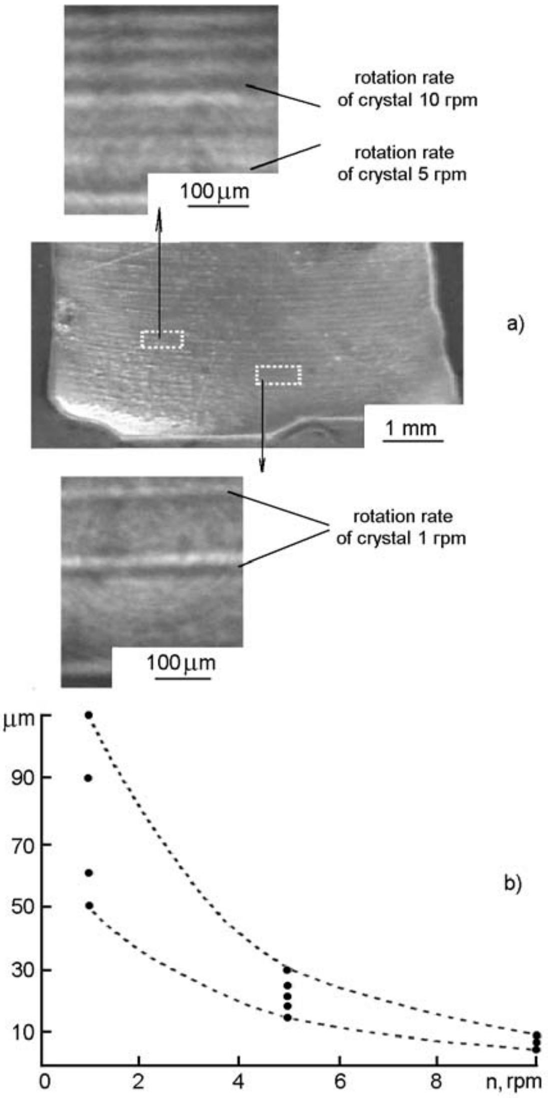

Fig. 2. Growth striation in $Ga_{0.03}In_{0.97}Sb$ single crystals grown without of ultrasound: (a), gallium-enriched striation; (b), the dependence of striations period on the crystal rotation rate.

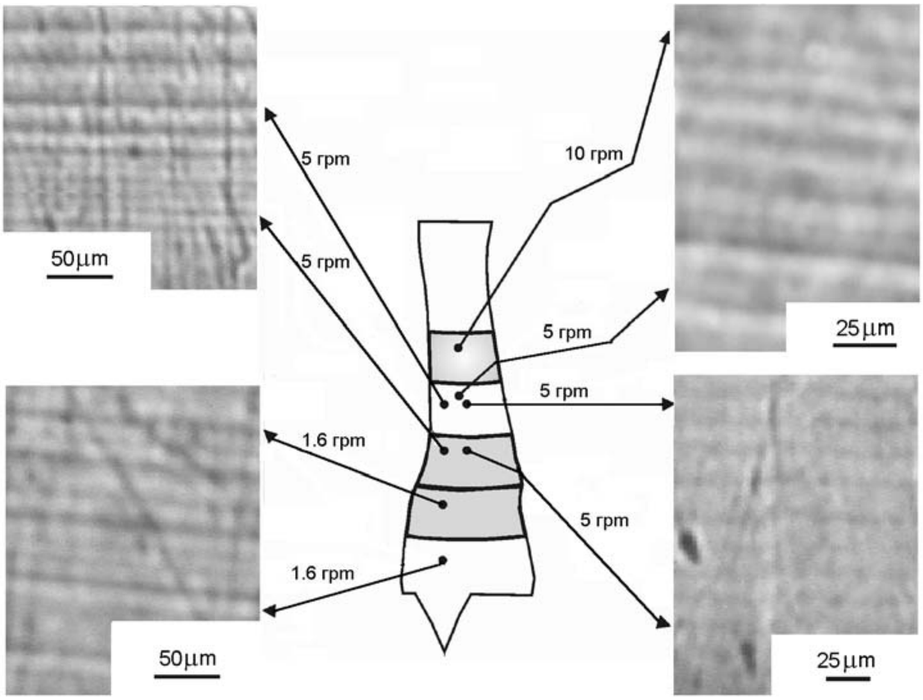

Fig. 3. $Ga_{0.03}In_{0.97}Sb$ single crystal grown with ultrasound field at a frequency of 1.42 MHz gallium-enriched striations.

part and by 1.5 times at the periphery after switching on the ultrasound at a frequency of 1.42 MHz (Fig. 3). However, in the crystal grown with deflection of the crystal axis from vertical of 1.8 mm under ultrasound at a frequency of 1.44 MHz the positive effect of the ultrasonic waves on the striation was observed only in the central part of all crystal regions and consisted in the reduction the striation period by a factor of 1.5 to 2. The striations of 7μm period have been revealed in all regions of the crystal, whereas the period of striation rises from 7 to 14 μm with increasing deflection of the crystal axis from vertical. This evidences the above assumption. In other words, the deflection of the crystal axis from vertical result in formation of striation with period from 7 to 14 μm period. This can explain also the fact that the ultrasonic field eliminates the striation with period exceeding 14 μm caused by convective flows in the melt but does not influence the striation with period of 7 to 14 μm of other origins.

These statements have been confirmed by experiments on the liquid phase convection modeling in conditions similar to those of $Ga_{0.03}In_{0.97}Sb$ single crystal growth. In the experiments, a setup was used consisted of ebonite crucible with a spherical form the bottom and two glass windows, a copper rod that servers as a crystal dummy, a circular resistance heater, and a digital video camera. Ultrasonic waves were introduced into the fluids from a piezotransducer through a fused silica waveguide in the direction parallel to the copper rod axis. The solution of water and glycerine having the Rayleigh number similar to that of the Ga-In-Sb melt as well as acetone with the mixed convectional parameter similar to that of the Ga-In-Sb melt used as transparent modeling fluids. The impurities in the solution of water and glycerine were modeled by textolite particles while in acetone, by aluminum particles of up to 50 μm maximum dimension and 5 μm thickness. In the course of experiments, the fluid depth, the temperature gradient, and the copper rod rotation rate were varied independently, thus making it possible to study the influence of those parameters on the liquid phase convection. The convection flow patterns with and without ultrasound were obtained using the digital video camera and computerized processing of the video images.

In the model experiments, axially nonsymmetric convective flows of spherical shape have been revealed without ultrasound at the vertical temperature gradient exceeding 1 K/cm (Fig. 4a) in the solution

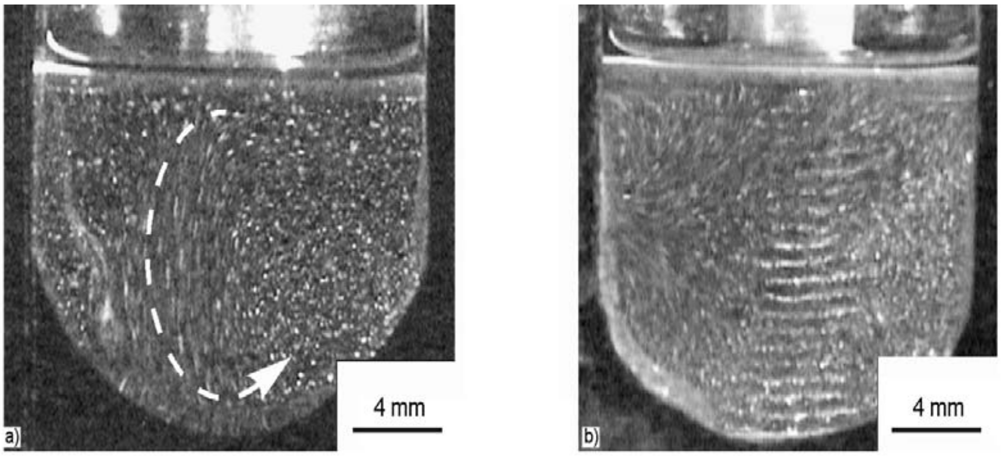

Fig. 4. Convective flows in the solution of water and glycerine mixture containing textolite particles at $h/d = 0.56$, $\Delta T/x = 1.55$ K/cm, $R_a = 0.43 \cdot 10^4$: a, without ultrasound; b, under ultrasound at frequency 0.69 MHz.

of water and glycerine and at 0.1 K/cm in acetone. The copper rod rotation and cooling generated axisymmetric flows. The flow velocity in the solution of water and glycerine did not exceed 3 mm/s while the convective flows in acetone rotated at a velocity up to 10 mm/s.

The introduction of ultrasound at a frequency of 0.69 MHz in the solution of water and glycerine resulted in stabilization of convection due to formation of ultrasonic standing waves in the central part of the crucible. The textolite particles oscillate in the wave antinodes (Fig. 4b).The standing waves were formed during 2 s after switching on ultrasound and were destroyed by the convective flows during 4 s after switching off ultrasound. The ultrasonic waves applied to acetone eliminated the convection in the central part of the crucible, but create the illusion of the disappearing aluminum particles due to the known phenomenon of Rayleigh disc. The standing waves were formed during 1 s after switching on ultrasound and were destroyed during 4-5 s after switching off ultrasound.

The ultrasonic action efficiency was reduced as the temperature gradient was increased from 0.3 to 3 K/cm and the copper rod rotation rate from 1 to 10 rpm. The fluid depth change from 19 to 14.5 mm did not influence the standing wave formation. This was revealed in experiments where acetone was evaporated under constant action of ultrasound at a frequency of 0.72 MHz. Thus, the introduction of ultrasound field in the modeling fluid provides the convection stabilization even when the fluid depth is reduced by 20 %. The experimental results obtained allow to conclude that the ultrasound eliminates the striations generated by the convection in the single crystal central part and at its periphery as well as halves the period of striations formed due to the deflection of crystal axis from vertical. Probably the reduction striation in $Ga_{0.03}In_{0.97}Sb$ single crystals is associated with the convection stabilization under ultrasound. This is confirmed by the results of modeling experiments.

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# Вплив ультразвуку на шаруватість у монокристалах $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{Sb}$

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Наведено результати експериментів дослідження шарової неоднорідності у монокристалах твердих розчинів $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{Sb}$ з вмістом галію $x = 0{,}03$, вирощених методом Чохральського при впливі ультразвукового поля з частотою до 1,44 МГц. Встановлено, що ультразвук усуває в центральної частині та на периферії кристалів шари, що мають конвективну природу. Результати вказаних експериментів вирощування підтверджено експериментами моделювання конвекції у рідкій фазі в умовах, близьких до умов росту монокристалів $\mathrm{Ga}_{0,03}\mathrm{In}_{0,97}\mathrm{Sb}$.