# SEMI-COMMERCIAL GROWTH OF HIGH-PERFORMANCE THERMOELECTRIC MATERIALS FOR ENERGY TRANSDUCERS

B.Sh. Barkhalov, A.A. Magerramov, R.Yu. Aliyev

Institute of Physics of the National Academy of Sciences of Azerbaijan, Baku, Az-1143, H. Javid prospect, 33, Baku, Azerbaijan E-mail: bbarhal@mail.ru

## ABSTRACT

Various methods of reception of single crystalline ingots of semiconductor materials for thermoelectric converters of energy have been considered. On the basis of the analysis theoretical and experimental data a number recommendations directed to increase thermoelectric efficiency factor Z of received thermoelectric materials and rise output percent of useable semiconductor material on the basis of bismuth and antimony chalcogenides under conditions of industrial production is produced.

**Keywords:** thermoelectric transducer, thermoelectric efficiency, thermoelement, crystallization, chalcogenides, zone melting.

#### **I. INTRODUCTION**

Thermoelectric efficiency factor Z of *n*- and *p*type conductivity materials used in solid-state electronic coolers is high enough and reaches values  $Z \approx (3,2\div3,4)\cdot10^{-3} \text{ K}^{-1}$ . Achievement of so high values of the efficiency factor of materials became possible thanking both to complication of their structure and reception of crystals with sufficiently perfect structure by methods of Chokhralsky or Bridgeman.

However, estimating and choosing methods of growth of the single crystals of thermoelectric materials in semi-commercial and industrial conditions it is necessary to take into account mass character of manufacture and their cost.

The majority of the Russian firms specializing in the field of full-scale production of thermoelectric modules and systems, such as "Nord" (Moscow), "Cryoterm", "Osterm" (Saint-Petersburg), "Elektronika NN" (Nizhni-Novgorod) use in their products materials with  $Z \ge (2,8-3,0 \cdot 10 \text{ K}^{-1})$ , received by a method of zone melting (floating-zone refining) [2]. Thus diameter of the received ingots of the thermoelectric material is in limits 7÷9 mm.

It is well known that  $\sigma/\chi$  ratio for solid solutions on the basis Bi<sub>2</sub>Te<sub>3</sub> is anisotropic quantity having the greatest value in a direction parallel to a cleavage plane. Therefore in the ingots received by directional crystallization the value of the thermoelectric efficiency Z is maximal in the line of their axes and comes nearer to size  $Z_{\parallel}$  for single crystals [3].

It is necessary to note that up to now there is no satisfactory theory of formation of a real crystal. It is a result first of all the big complexities, which are fraught with the real crystals containing set of the diversified defects. Arising during crystallization, defects influence this process. Therefore it is necessary to consider the theory of crystallization as particular expression of the theory of phase transitions, it is indispensable in view of all features of a crystal condition.

However such account is not carried out in one of modern theories. All of them proceed from a number of simplifying conditions of growth, preconditions that provides certain, frequently very narrow scope in practice of crystallization. Each theory explains only one side of the crystallization process. Apparently, it is possible to put under doubt an opportunity of creation of the "universal" theory of growth of the crystals, taking into account all phenomena connected to their reception [4].

It is well known that zone melting is the method used first of all for refining the materials, though it is used for growing of crystals. However, application of this method for reception of crystals is connected with difficulties of basic character. The matter is that in its basis underlies property of redistribution of components between liquid and solid phases, and as result - heterogeneity of the received crystal on composition. This method can be used for reception of homogeneous crystals provided that any segregation effects caused by moving of a zone in one direction will be eliminated by its repeated passage in the opposite direction.

In practice, at reception of substance only the material of *n*-type passes floating-zone refining in two opposite directions with the purpose of uniform distribution of an alloying impurity (Cl, Br or I) and reception of a crystal with uniform properties on length. It is considered that for a material of *p*-type

double passage of a zone not necessarily as in this material with the purpose of reception of optimum concentration of the charge carriers as a rule superfluous tellurium is added. Tellurium is entered for compensation of the action of excess antimony formed because of the stoichiometry displacement. It is not dissolved completely in a material and allocated as the second phase pushed aside at directed crystallization to the end of an ingot or allocated inside grains and on borders of grains and blocks. It results in non-uniform distribution of properties on length of the ingot and its cross-section, as well as in reduction in percent of output percent of useable semiconductor material.

One of determinatives in origin of crystals is overcooling. To provide overcooling it is necessary to heat up preliminary a liquid much above the melting temperature and remove from a solution any solid particles - mechanical inclusions, oxides of initial components, etc. which being initiators of uncontrollable crystallization, negatively influence quality of a crystal. Removal of these particles is achieved by preliminary refining of the components directly before of the substance synthesis.

Bismuth in a liquid state is transfused through a capillary and clear from oxide film and mechanical inclusions, tellurium of high purity is melted with the subsequent detach of the top part of an ingot. Antimony clear from oxide film by the mechanical way with the help of a metal brush though it is preferable to clear it by sublimation from a liquid state, having removed thus also mechanical inclusions. The selenium which is produced by the industry in ingots or granules can be not cleared, as it does not contain such quantity of oxide films and the mechanical inclusions, influencing on the process of crystallization.

Origin of the crystals is influenced by surfaces of solids adjoining with a liquid, in particular, walls of an ampoule. Separate sites of a non-uniform surface possess various activity concerning formation of a new phase. This activity is defined both the physical and chemical nature of a site, and its geometrical form and size. Such defects on walls of the ampoule as cracks and channels of almost molecular size, promote chaotic origin of crystals in a surface layer of the ingot, containing also defects and gas voids. The surface layer having the certain thickness, makes a part of mass of a crystal and its share will be the more than it is less diameter of an ingot.

As is known, quality of received crystals on the basis of bismuth and antimony chalcogenides depends on rate (v) and uniformity of moving of a heater or an ampoule with substance, stability of temperature of the furnace, a gradient of temperature (G) at front of crystallization and its form [3]. Experimental researches have shown, that the increase v and reduction G causes reduction in value of Z because of reduction on coefficients of thermo-e.m.f.  $\alpha$  and specific conductivity  $\sigma$ , and growth  $\chi$  in materials both n- and p-type conductivity. The increase in growth rate of crystals from 1.5 to 12 sm/hour for Bi<sub>2</sub> Te<sub>2.7</sub> Se<sub>0.3</sub>

entails reduction of  $\alpha^2 \sigma$  value on 5-10 % and for Bi<sub>2</sub>Te<sub>2.4</sub> Se<sub>0.3</sub> - on 20-25 %. These data have been received at value G = 200÷250 grad/s. The found experimental values  $(G/v)_{cr}$  for solid solutions Bi<sub>2</sub>Te<sub>2.7</sub> Se<sub>0.3</sub>, Bi<sub>2</sub>Te<sub>2.4</sub> Se<sub>0.6</sub> and Bi<sub>2</sub> Te<sub>2.1</sub> Se<sub>0.9</sub> are accordingly in limits  $(2\div2.5)\cdot10^5$ ,  $(1\div1.5)\cdot10^6$  and  $(2\div8)\cdot10^6$  grad·s/sm<sup>2</sup>. The analysis of other experimental data shows, that the greatest value for Z is observed at growth rates of crystals from 0,8 to 1.5 sm/hour for Bi<sub>2</sub>Te<sub>3</sub> with various contents of Bi<sub>2</sub>Se<sub>3</sub>. The more contents of Bi<sub>2</sub>Se<sub>3</sub> in an alloy, the smaller rate is necessary for growth of a crystal. Reduction of G value also causes reduction in  $\alpha^2 \sigma$  value.

Properties of anisotropic substances are influenced by a degree of crystal grains off-orientation, as well as non-uniform distribution of structure of the solid solution on length and cross-section of the crystal. Two groups of inhomogeneity are specified in the literature, distinguished on extent and the reasons of their occurrence - these are a macro-inhomogeneity and micro-inhomogeneity. The last is eliminated by homogenizing annealing. To macro-inhomogeneity relate monotonous change of structure of materials on cross-section and length of the ingots which have been prepared by a method by directed crystallization method. Change of the structure of the material on cross-section in opinion of authors [3] is connected with non-planar, concave aside solid phase, with the form of the crystallization front. Probably this distortion is connected with allocation crystallization heat and action of radial thermal streams in an ingot. Growth rate and convection conditions of the melt in various zones of non-planar crystallization front differ that results in change of effective factor of distribution and change of structure from the center to periphery of an ingot. To avoid macro-inhomogeneity in ingots a crystallization front is made flat, diameter of an ingot (at the fixed diameter and the size of a heater) and growth rate is reduced, or an axial gradient of temperature in the field of crystallization is strengthen. In conditions of industrial production of materials reduction of diameter of ingots or growth rate results in reduction make quantity, and strengthening of an axial gradient results in complication of a design of installations for crystal growth as well as increase in energy consumption. Elsewhere [5] dependence of the form, the size and stability of the fused zone on radius of the rod, density of a liquid, surface tension etc. were theoretically investigated for preparing a crystal by a method of zone melting. Experimental data allow to conclude that the basic condition of reception qualitative, uniform on length and section crystal is approximate equality of width of the molten zone to diameter of an ingot. To achieve this condition it is possible by approaching internal diameter of the furnace to diameter of an ingot, not increasing thus for its capacity selecting necessary temperature of heating.

The authors receiving chalcogenides of bismuth and antimonies by Chokhralsky method have received result, opposite to the data of the report [3]. With the purpose of increase in productivity of process they have developed technological conditions of growing of single crystals of major diameter ( $40 \div 50$  mm). Researches of Bi<sub>2</sub>Te<sub>2.85</sub>Se<sub>0.15</sub> of solid solution crystals have shown that the increase in diameter of single crystals results in increase both axial and radial uniformity [6].

Elsewhere [3] the industrial technology of the vertical zone melting is described where ampoules with growing material are bundle in a bunch, fell to furnaces, and passing a zone of heating, got in the cooled cylinder. It is interesting that the greatest value Z had ingots in diameter  $10\div15$  mm. Reduction of values Z outside of this interval and has not found an explanation within the framework of known models of growth of crystals.

## **III. CONCLUSION**

From all above-stated follows that by increase in diameter of ingots of the produced materials on the average about 8 mm to 16 mm it is possible to achieve increase of their thermoelectric efficiency in conditions of experimental-industrial production, simultaneously having increased percent of an output of usable production. On the other hand, it will allow to use as a material of *n*-type, for example,  $Bi_2Te_{2.8}Se_{0.12}$  solid solution instead of  $Bi_2Te_{2.7}Se_{0.3}$  which crystallization process does not demand creation in a heater of the big temperature gradient and reduction in growth rate.

The carried out analysis has allowed us to give the following concrete recommendations on technology of growth of single crystals of thermoelectric materials, in particular on the basis of bismuth and antimony chalcogenides, in conditions of semi-commercial production:

- initial components should be carefully cleared

from oxide layers and mechanical inclusions;

- growth rate should be about 1 cm/hour;
- diameter of ingots should be equal to ~ 16 mm;
- the width of the liquid melt zone should be equal to diameter of an ingot;
- moving a zone should occur in two directions;
- the obtained material should be exposed to homogenizing annealing.

### REFERENCES

- Svechnikova T.Ye., Konstantinov P.P. et al. Physical properties of Bi<sub>2</sub>Te<sub>2.85</sub>Se<sub>0.15</sub> monocrystals alloyed by various elements I-VI of groups of periodic system. Materials of VI Interstate Seminar, Saint-Petersburg, October, 1998, p. 30.
- Bulat L.P. Thermoelectric cooling in Russia: condition and tendencies. Materials of VIII Interstate Seminar "Thermoelectrics and their application", Saint-Petersburg, November, 2002, p. 36.
- Goltsman B.M., Kudinov V.A., Smirnov I.A. Semiconductor thermoelectric materials on the basis Bi<sub>2</sub>Te<sub>3</sub>. "Nauka" Publishing House, Moscow, 1972 (in Russian).
- 4. *Kozlova O.G.* Growth of crystals. The Moscow University Edition, 1967.
- Jones D.U. Method of growth of crystals of refractory metals. In: «Growth of crystals», "Mir" Publishing House, Moscow, 1977, p. 293.
- 6. Svechnikova T.Ye., Maksimova N.M. et al. Research of uniformity of thermoelectric properties on length and cross-section of  $Bi_2Te_{2.85}Se_{0.15}$  single crystals. Theses of reports of IV Interstate Seminar, Saint-Petersburg, November, 1994, p. 5.