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SIMULATION OF THE EFFECT OF THERMAL UNIT VELOCITY ON THE PROCESS OF GROWING Bi_2Te_3 BASED MATERIALS BY VERTICAL ZONE MELTING METHOD

The paper presents the results of computer simulation of the process of growing Bi_2Te_3 based thermoelectric materials by vertical zone melting method. It was found that, depending on the velocity of the heater and coolers, not only the curvature of the crystallization front changes, but also its shape. At temperatures of the heater and coolers T_h = 1058K, T_h = 303K for velocities greater than 1.25 cm/h, the crystallization front along the entire crystal becomes convex into the solid phase, but at lower velocities it changes its shape from convex to concave along the grown sample. Bibl. 5, Fig. 6.
Key words: simulation, vertical zone melting, thermoelectric material, bismuth telluride.

Introduction

Zone melting is one of the most commonly used methods for the production of semiconductor materials, in particular thermoelectric. However, obtaining thermoelectric materials (TEM) with the required properties is possible only under the conditions of a controlled crystallization process, since the curvature of the crystallization front, the temperature gradient at the interface between the solid and liquid phases, the geometry of the melt zone, and the velocity of zone motion have a great influence on the stability of growth and uniformity of a single crystal, etc [1, 2].

Computer simulation of TEM growing processes makes it possible to determine the growth conditions and explain possible difficulties that may arise as a result of changes in these conditions. It cannot replace, but presupposes and complements the experiment, providing information that can be experimentally obtained only indirectly. Therefore, the improvement and development of the technology for growing thermoelectric materials by means of multiparameter computer optimization of the controlled process parameters is urgent.

This study is a continuation of [3], in which the shape of the crystallization front depending on the temperature and size of the heater was studied by computer simulation.

The purpose of this work is a computer study of the effect of thermal unit velocity on the process of growing Bi_2Te_3 based materials by vertical zone melting method. In particular, the analysis of the influence of TEM growth conditions on the formation of a flat crystallization front.

Physical model of vertical zone melting

The circuit diagram of the process of growing thermoelectric materials by vertical zone melting is represented in Fig.2.

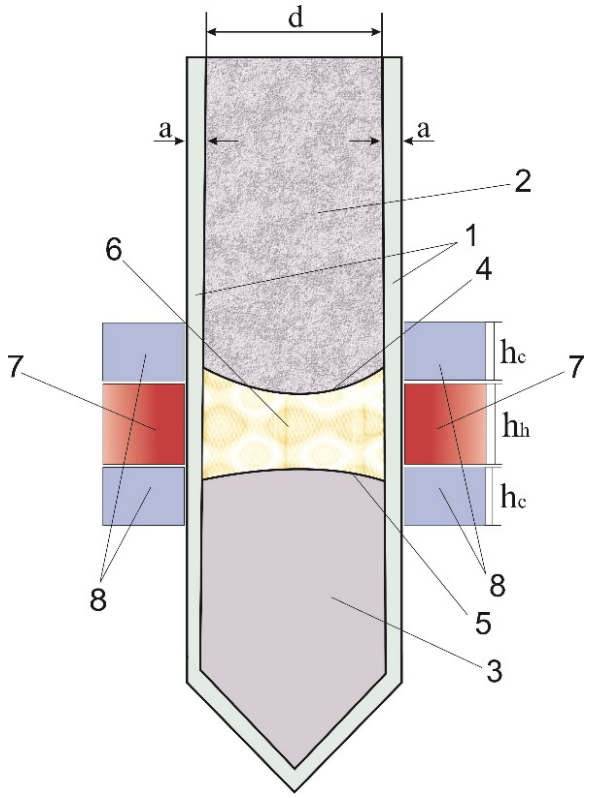

Fig.1. Physical model of installation for growing TEM by vertical zone melting method: 1 – container, 2 – material in solid phase (polycrystal), 3 – material in solid phase (single crystal), 4 – melt front, 5 – crystallization front, 6 – material in liquid phase (melt zone), 7 – heater, 8 – coolers.

The figure depicts a fragment of an ingot comprising polycrystalline material 2, a molten zone 6, and a single crystal 3. The ingot is placed in a container 1. Using a heater 7 and a system of coolers 8, a molten zone 6 is formed that moves together with the heater along the sample to provide melting of the polycrystal and crystallization of the melt below the boundary 5, which is called the crystallization front. The system which is composed of a heater 7 and coolers 8 is commonly referred to as a thermal unit.

Mathematical model of zone melting process

COMSOL Multiphysics software package was used for computer simulation of the process of growing the Bi_2Te_3 thermoelectric material, which allows simulating almost all physical processes described by algebraic and differential equations in partial derivatives. To do this, it is sufficient to use ready-made modules of the corresponding physical phenomenon. If necessary, the researcher can change the equation built into the COMSOL module, or specify his own. Numerical calculation is performed by the finite element method [5].

Simulation of the motion of the heater and coolers in the COMSOL Multiphysics system was carried out by using the Moving Mesh module, which allows changing the mesh during the calculations of unsteady processes (Fig. 2).

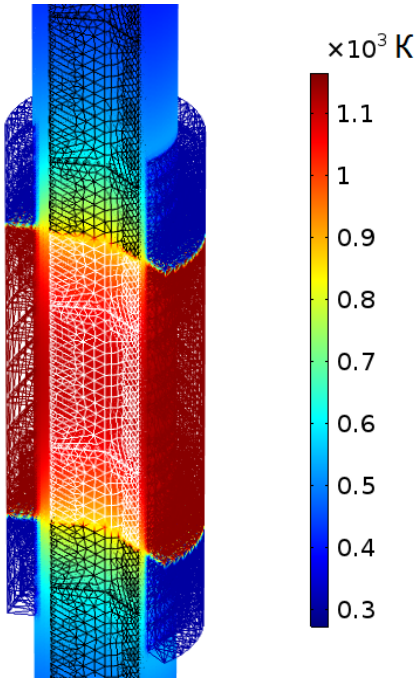

Fig.2. Image of computer model mesh of the plant for growing TEM by vertical zone melting method.

The temperature distribution in the test sample was found from solving the differential equation of thermal conductivity, supplemented by the dependences of the physical properties of the test material as a function of the phase state at a given point at a given temperature:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \nabla T + \nabla q = Q \tag{1}$$

$$q = -\kappa \nabla T, \tag{2}$$

$$\rho = \theta \rho_{phase1} + (1-\theta)\rho_{phase2}, \tag{3}$$

$$C_p = \frac{1}{2}\left(\theta \rho_{phase1} C_{p_{phase1}} + (1-\theta)\rho_{phase2} C_{p_{phase2}}\right) + L\frac{d\alpha_m}{dT}, \tag{4}$$

$$\alpha_m = \frac{1}{2} \cdot \frac{(1-\theta)\rho_{phase2} - \theta \rho_{phase1}}{\theta \rho_{phase1} + (1-\theta)\rho_{phase2}}, \tag{5}$$

$$\kappa = \theta \kappa_{phase1} + (1-\theta)\kappa_{phase2}. \tag{6}$$

where ρ is the density; C_p is the heat capacity of material; κ is thermal conductivity; u is the velocity of the medium which in the problem under study is equal to zero; T is

temperature; θ is phase ratio at a given temperature; α_m is mass ratio between phases; L is latent heat of phase transition; Q is external heat flux. The indices $phase1$ and $phase2$ indicate to which phase, solid or liquid, respectively, the properties are related.

To account for heat transfer due to radiation to the physical interface Heat Transfer in Solids in the COMSOL Multiphysics system, the boundary condition Surface-to-Surface Radiation is added, selecting the outer boundaries of the container and the thermal unit (Fig. 3). :

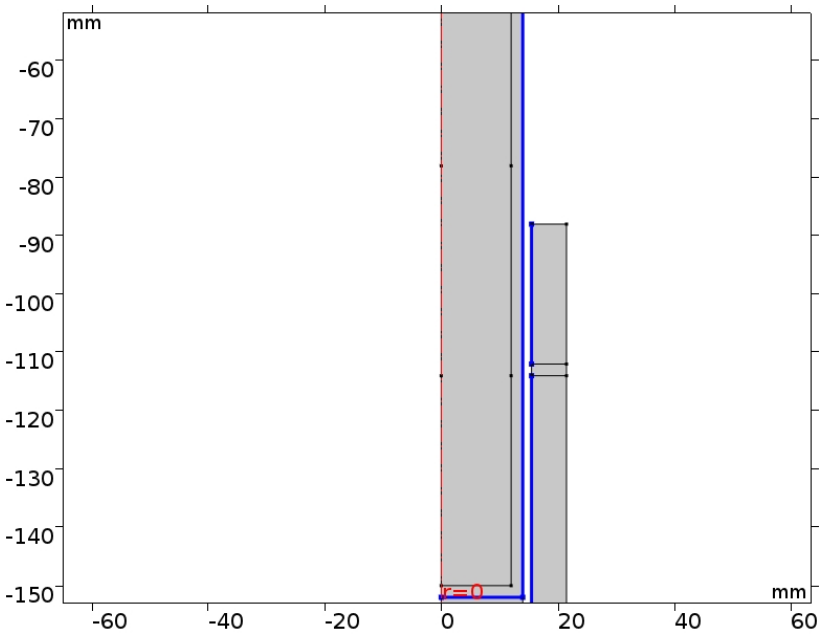

Fig.3. Radiation boundaries between the surfaces.

$$-n(-\kappa\nabla T) = \varepsilon\sigma_b(T_{ext}^4 - T^4), \tag{7}$$

where T_{ext} is temperature of thermal unit wall; T is temperature of container wall, n is vector directed along the normal to the surface of cylinder (container); $\varepsilon = \left(\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}-1\right)^{-1}$ is reduced radiation coefficient of the system; ε_1 is radiation coefficient of thermal unit, ε_2 is radiation coefficient of container; σ_b is the Stephan-Boltzmann constant.

To calculate the computer model, the geometric dimensions of the system elements, the initial temperatures of the heater and coolers, the liquidus and solidus temperatures of Bi_2Te_3 as well as the temperature dependences of the properties of the grown material are set [4]. Convection and mass transfer of molten Bi_2Te_3 are not taken into account.

Computer simulation results

With regard to the results obtained in [3], the study of the effect of thermal unit velocity on the process of growing Bi_2Te_3 was carried out with the following input parameters of the system: wall thickness of the quartz container 3 mm; the diameter d of the grown crystal was assumed to be 24 mm, its length l = 30 cm; height and temperature of the heater $h_h = 3d$, $T_h = 1058K$; height

and temperature of coolers $h_c = 1d$, $T_c = 303K$. The thermal unit velocity varied from 0.5 to 4 cm/h. The temperature of the heater was selected based on the initial simulation results such that even at high velocities, the heater had time to completely melt the crystal under study.

The change of the temperature gradient at the crystallization front depending on the velocity of the heater and coolers was studied. The simulation results are shown in Fig.4.

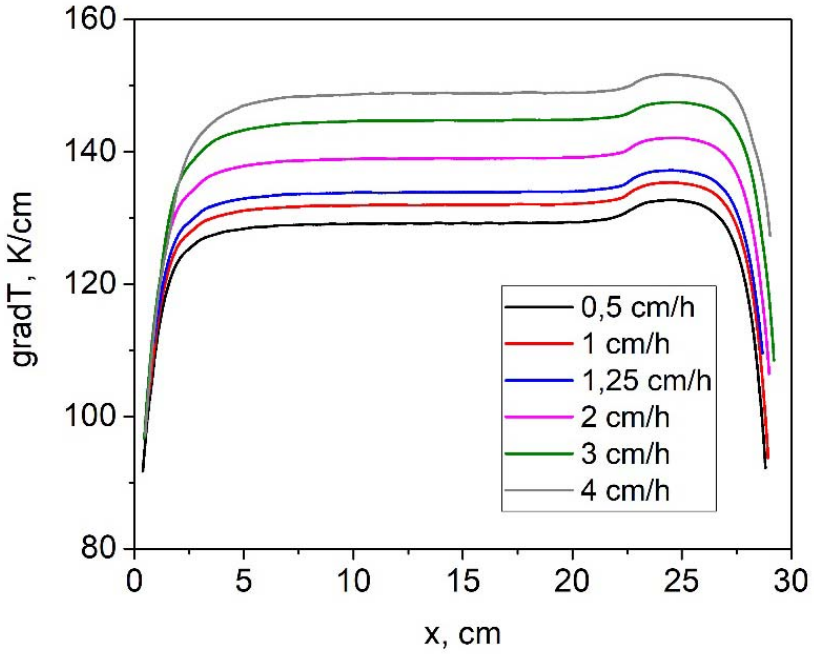

Fig.4. Change in the temperature gradient at the crystallization front along the grown crystal at thermal unit velocities v=0.5 – 4cm/h.

As can be seen from the figure, the temperature gradient at the crystallization front increases with increasing growth rate. In addition, you can see that regardless of the rate, there is a clear change in the magnitude of the gradient near the coordinate of 21 cm, which is due to the exit of the upper cooler outside the grown ingot and the violation of the thermal balance of the system.

As is known, when TEM is obtained by vertical zone melting, the curvature of the crystallization front has a great influence on the stability of the growth of a single crystal and its homogeneity [2, 3]. With directional crystallization, the cleavage planes are oriented along the normal to the crystallization front. If the front is flat, then the polycrystalline ingot consists of grains, the cleavage planes of which are oriented parallel to its axis, i.e., a directional structure is formed. Therefore, it is important to study the effect of thermal unit velocity on the nature of change in the shape of crystallization front along the crystal during its growth.

Fig. 5 shows how the shape of the crystallization front changes during the motion of the melt zone along the crystal at growth rates v = 1 cm/h and v = 4 cm/h.

It can be seen from the figure that in the lower part of the grown ingot the crystallization front is substantially convex into the solid phase for thermal unit velocity of 4 cm / h and slightly convex for a velocity of 1 cm/h. As the molten zone moves, the curvature of the front decreases in both cases, but at the end the front is again curved.

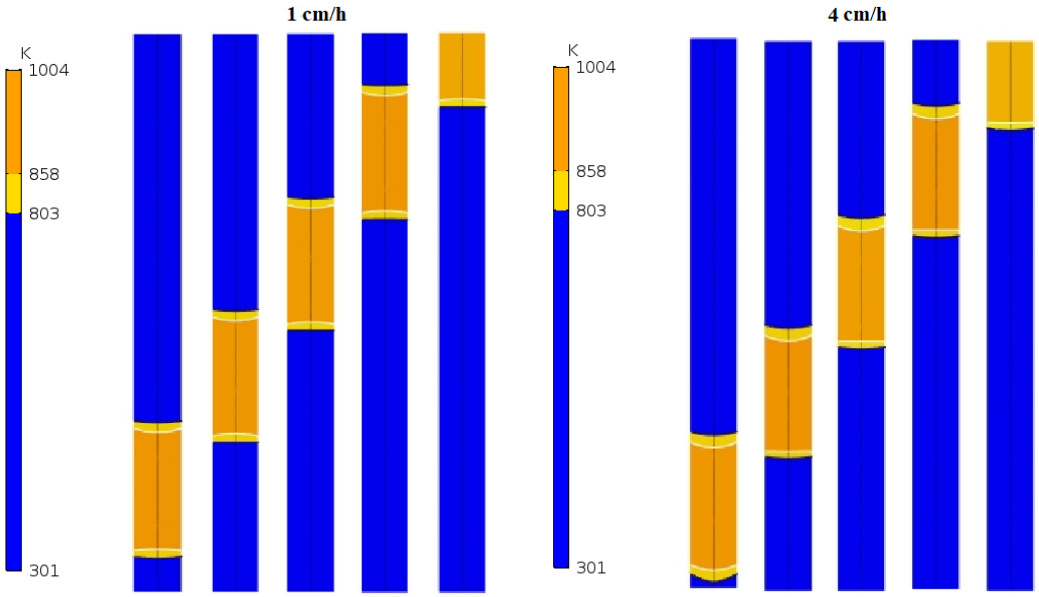

Fig.5. Image of melt zone motion along the crystal at growth rates $v = 1 cm/h$ *and* $v = 4\ cm/h$.

Fig.6 shows a dependence of the value of crystallization front curvature along the crystal at various thermal unit velocities. The curvature was calculated as a difference between the maximum and minimum points $\Delta z = z_{max} - z_{mtn}$ of the front.

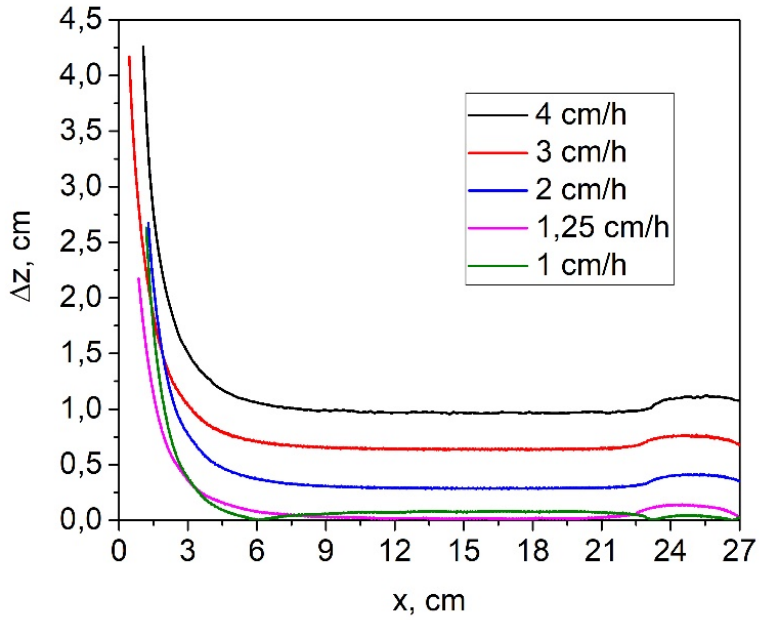

Fig.6. Dependence of the value of crystallization front curvature along the crystal on thermal unit velocity.

As can be seen from the figure, maximum flat crystallization front was achieved at a growth rate of v=1.25 cm/h. A detailed analysis of the simulation results showed that at the given temperatures of the heater and coolers (T_h = 1058 K, T_c = 303 K) for velocities greater than 1.25

cm/h the crystallization front along the whole crystal was convex into a solid phase. For velocities lower than the specified value, the front changed its shape and at the initial section of the grown crystal it was convex, then it became concave into the melt and at the end of the crystal it again became convex.

Conclusions

1. A procedure has been developed for computer simulation of the effect of the growth rate of thermoelectric materials on the crystallization process of Bi_2Te_3 based TEM by vertical zone melting method.
2. It is shown that with increasing the growth rate the temperature gradient at the crystallization front increases slightly.
3. It was established that depending on the velocity of the heater and coolers, not only the curvature of the crystallization front changes, but also its shape. At the temperatures of the heater and coolers $T_h = 1058K$, $T_c = 303K$ for velocities greater than 1.25 cm/h, the crystallization front along the entire crystal was convex into the solid phase, but at lower velocities it changed its shape from convex to concave along the grown sample.

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МОДЕЛЮВАННЯ ВПЛИВУ ШВИДКОСТІ РУХУ ТЕПЛОВОГО ВУЗЛА НА ПРОЦЕС ВИРОЩУВАННЯ МАТЕРІАЛІВ НА ОСНОВІ Bi_2Te_3 МЕТОДОМ

ВЕРТИКАЛЬНОЇ ЗОННОЇ ПЛАВКИ

У статті наведено результати комп'ютерного моделювання процесу вирощування термоелектричних матеріалів на основі Bi_2Te_3 методом вертикальної зонної плавки. Встановлено, що в залежності від швидкості руху нагрівника та охолоджувачів змінюється не лише кривизна фронту кристалізації, але й його форма. При температурах пічки та холодильників T_h=1058K, T_c=303K для швидкостей більших 1.25 см/год фронт кристалізації вздовж всього кристалу стає опуклим в тверду фазу, але при менших швидкостях він змінює свою форму від опуклого до увігнутого вздовж вирощуваного зразка. Бібл. 5, рис. 6.

Ключові слова: моделювання, вертикальна зонна плавка, термоелектричний матеріал, телурид вісмуту.

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МОДЕЛИРОВАНИЕ ВЛИЯНИЯ СКОРОСТИ ДВИЖЕНИЯ ТЕПЛОВЫХ УЗЛОВ НА ПРОЦЕСС ВЫРАЩИВАНИЯ МАТЕРИАЛОВ НА ОСНОВЕ Bi_2Te_3 МЕТОДОМ ВЕРТИКАЛЬНОЙ ЗОННОЙ ПЛАВКИ

В статье приведены результаты компьютерного моделирования процесса выращивания термоэлектрических материалов на основе Bи2Te3 методом вертикальной зонной плавки. Установлено, что в зависимости от скорости движения нагревателя и охладителей изменяется не только кривизна фронта кристаллизации, но и его форма. При температурах печи и холодильников T_h = 1058K, T_c = 303K для скоростей больших 1.25 см/ч фронт кристаллизации вдоль всего кристалла становится выпуклым в твердую фазу, но при меньших скоростях он меняет свою форму от выпуклого к вогнутого вдоль выращиваемого образца. Библ. 5, рис. 6.

Ключевые слова: моделирование, вертикальная зонная плавка, термоэлектрический материал, теллурид висмута.

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