Journal of Ovonic Research Vol. 2, No. 6, December 2006, p. 137 - 145

THE GROWTH MECHANISM OF THE LAYER-LIKE AND WIRE-LIKE CRYSTALS $A^{IV}B^{VI}$ AND $A^{IV}B_2^{VI}$ FROM GASEOUS PHASE.

D. I. Bletskan

Uzhgorod University, Uzhgorod, Ukraine

The mechanism of growth of layer-like and wire-like crystals in the system$A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ from gaseous phase is discussed

(Received December 3, 2006; accepted December 18, 2006)

Keywords: Growth mechanism, Layer-like crystals, Wire-like crystals

1. Introduction

The study of the processes related to the kinetical shift of the crystal boundary, and especially, the analysis of the elements of its relief are highly important for the accurate understanding of the mechanisms of the crystal growth [1-5]. The morphological investigation of the crystal boundary permits: a) to clearly establish the crystal growth mechanism; b) to determine the type and concentration of the dislocation in the bulk crystal, which is important for the study of their physical properties; c) to get knowledge regarding the growth conditions of given crystals [1,2].

2. Growth mechanism of the lamellar crystals.

According to modern representations, the closely packed face of the crystal can grow from gaseous phase in the presence of steps on its surface. There are known two qualitatively different mechanism of crystal growth from gaseous phase [1-3]: a) the crystal face is growing on the account of two-dimensional nuclei that are formed on it, the process takes place at significant critical saturations; b) in the presence of helical dislocations occur non-growing steps on the crystal surface that spread on the face for small saturations, not necessitating the formation of nuclei.

One of the most accessible and comparatively simple procedure for the study of the surface defects, based on the light reflection is the metallographic method [2]. Nevertheless the method is not able to evidence all the properties of the surface structure of the material even in the case when is used the interferential microscope. In particular, in this case, it is not possible to determine the difference between the polymorphous modifications of a given structure, i.e. it is not possible to identify the separate modifications. With this exception the application of the above-mentioned method is of essential help for the research and quality control of the isomorphous mono-crystals. The lamellar crystals of Ge and Sn mono- and di-chalcogenides represent, according to all their parameters, perfect materials for the study of the laws of crystal growth from gaseous phase [4-7]. They reflects excellently the light, show a good development of the faces of the habitus, large surfaces with smooth surfaces and, therefore, are convenient for the microscopic observations of the figures of growth, without any supplementary processing of the surface. For these crystals there is characteristic the presence of helical dislocations, with the Buergers vector

parallel to the axis *c*. The images of relief observed in [4-8] on the (001) faces of lamellar germanium and tin chalcogenide mono-crystals, obtained for low saturation, support the conclusion on their growth from gaseous phase, with the dislocation mechanism. It is remarkable, that with the help of an optical microscope are evidenced the helical dislocations, that gives at start a spiral growth. The spiral is formed in the place of the output of the helicoal dislocation from the fractures of orientation that differs from the direction of the close packing. In the lamellar crystals one forms, also, the so-called helical dislocations, which do not participate in the formation of the crystal and can only lead to the change of polytype at the microscopic scale if their Buergers vector is not equal to the Buergers vector of the dominant dislocation.

The form of the growth spirals both with unique or with every multiple (in different degree) Buergers vector, strongly depends on the rate of movement of the formed dislocations of atomic steps in different crystallographic directions relative to the faces. The simplest is the case when the velocity of growth of the step does not depend on the crystallographic direction. As normally, on the surface (001) of the crystals of Ge and Sn mono- and di-chalcogenides one observes multiple circular spirals. On the Fig. 5.6 a, b, e are given typical examples of such growth spirals.

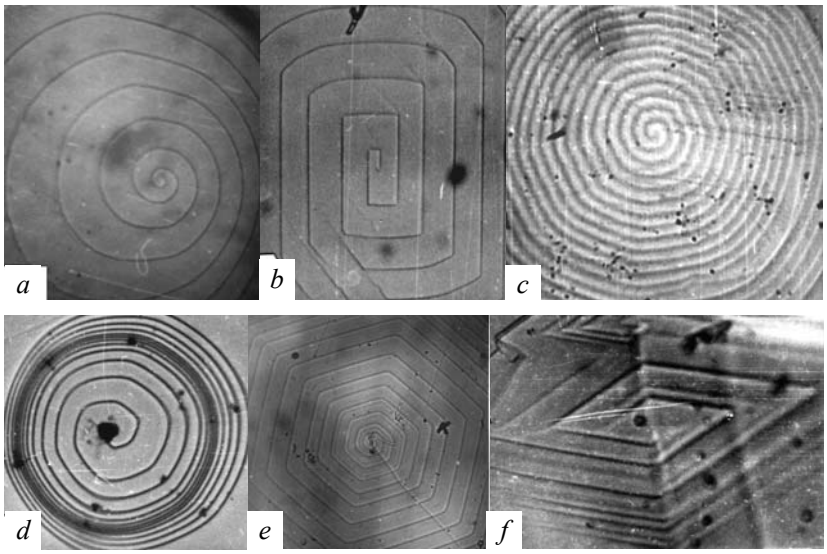

Fig. 5.6 The output of the helical dislocations on the (001) surface of single crystals: GeS (a, b), GeSe (c), $GeSe_2$ (d,e),and Sn_2S_2 (f)

Nevertheless, on the same (001) face, the multiple growth spirals exhibit not circular, but polygonal shape. On Fig. 5.6 c, d are visible four-corners (characteristic to mono-chalcogenides) and six-corners (for di-chalcogenides) growth spirals. Because the growth speed depends on the crystallographic orientation, the feature of the polygonized spirals reflects the symmetry of that face of the crystal, where is observed, and its formation are developed perpendicular to the direction of the slowest growth. When the growth conditions are not essentially convenient nor for circular, or for multi-corner spirals (on the faces (001)), it is possible to observe their intermediary type: part of the margins of such spirals are right, and part is circular (Fig. 5.6 b, c).

The peculiarities of the relief of the crystal faces are directly related with the peculiarities of growth. If on the face is spread only one good developed spiral, this means that in the formation of the crystal participated one active dislocation. But, in the process of formation of Ge and Sn crystals from the gaseous phase, in most cases participate two, three and more dislocations. As shown in Fig. 5.7 b on one and the same surface (001) of the germanium mono-chalcogenide crystals can be observed circular (Fig. 5.7 a) and polygonal (Fig. 5.7 c) dislocations. Frequently are observed crystals where the dislocation density N reaches the value $10^4 \div 10^5$ cm^{-1}. The dislocations are distributed in crystals non-uniformly (Fig. 5.7 b). The spreading of the dislocation

density in the crystal corresponds to one-two orders of magnitude. It is interesting to remark that in some parts it is characteristic the formation of left or right helical dislocations. Thus, one can conclude that in every separated part of the crystal the dislocations show essentially one sign.

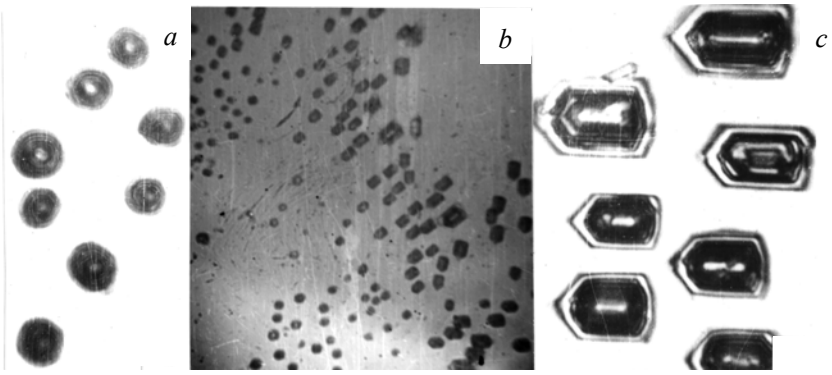

Fig. 5.7 Circular and rectangular disolocations on the face (001) of mono-crystals of GeSe: a, c – X 1500, b – X 250 [13, 7].

Because the surface of the faces (001) of the layered crystals $A^{IV}B^{VI}$ often crosses a high number of dislocations, the process of moving the faces is an extremely complicated phenomenon, which is determined by the distances between dislocations, their signs, and, also, by the vapor saturation level [2, 4]. Let look at this problem in more detail for the case of Ge and Sn chalcogenide crystals and analyze the observed growth images, starting from the known theoretical positions [1-5]. Two helical dislocations of opposite sign create closed loops, if the distance between their centers overcomes the critical diameter of the nuclei ($2r_c$, where r_c is the critical curvature radius) for given vapor saturation. This will lead to the appearance on the crystal faces of cones and pyramids, specific to growth. For the GeSe crystal the typical cones and pyramids are shown in Fig. 5.8, where is represented the unique case of two simultaneously developed dislocations of opposite sign (Frank-Reed source). Here the spiral step exhibits a circular border. The resulting shape of the growth pyramid is given by closed layers, with the exception of the center where the layer is not yet terminated because it must be created by two helical dislocations of opposite signs.

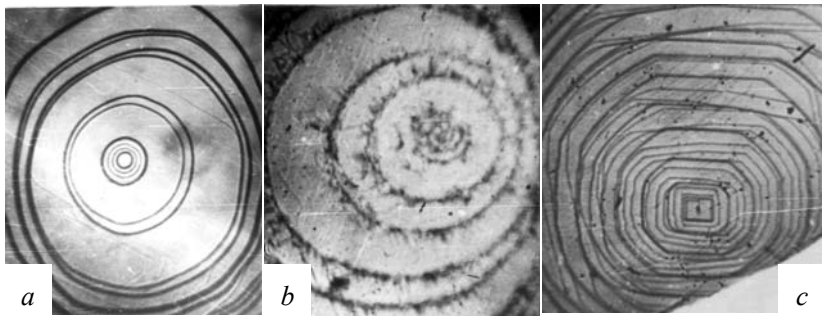

Fig. 5.8 Growth cones (a, b) and pyramids (c) that are formed from pairs of helical dislocations of opposite signs. X 400 [13, 432].

If the speed of moving of the atomic step does not depends essentially on its orientation, then on the surface of the crystal face are formed small growth cones (Fig. 5.8 a). In the opposite case the atomic steps will move mainly along the corresponding crystallographic directions and on the crystal faces forming small growth pyramids (Fig. 5.8 c). The distance between the two neighboring spires of a spiral is $y = 4\pi r_c$ [4]. For the case of very low saturations the parameter r_c

will be large so that the growth cones and pyramids will be extremely inclined. For high vapor saturations correspond small values and abruptness of the cones and, also, of the growth pyramids.

In the presence on the crystal faces of two pairs of dislocations of opposite sign, the description of its moving process becomes more complicated [4]. An example of this type of dislocation is given in Fig. 5.9. In this case, too, the speed of growth along the normal of the crystal face remains practically the same as for unique dislocation if only the distance between the components of the considered pair of dislocations is enough large.

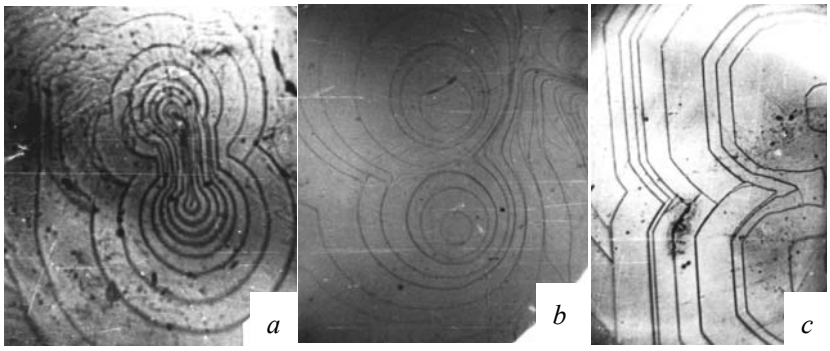

Fig. 5.9 The interaction of the growth cones (a, b) and pyramids (c) formed by two pairs of helical dislocations of opposite signs on the surfaces (001) of the GeS mono-crystals X400 [7, 13].

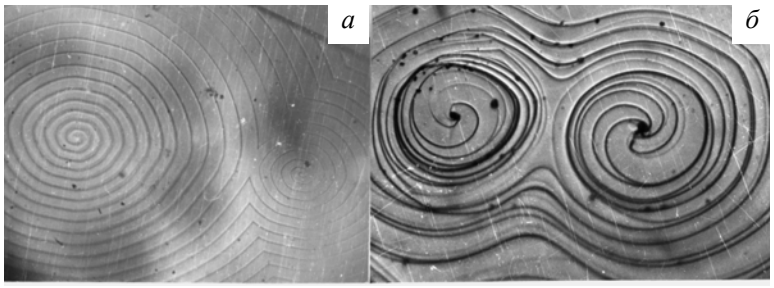

Fig. 5.10 The interaction of right and left helical dislocations on the (001) surface of the single crystals of GeS (a) and $GeSe_2$(b) X 400 [7, 9].

In the Fig. 5.10 is shown the example of two (a and b) helical dislocations of different sign that are situated at a distance higher than $2\pi r_c$. In Fig. 5.10 a is visible a spiral formed with a left helical dislocation, which extends up to the meeting of the steps of the right helical dislocation, about four spires. Beyond this margin of the atomic growth steps both dislocations will intersect. According to the properties characteristic to such steps they will "destroy" reciprocally in the intersection point. This case was theoretically studied by Warm [4].

The thickening of the elementary spirals (Fig. 5.6 and 5.10 b) lead to the formation of so-called kinematical waves of step densities [4, 10]. The appearance of such waves is conditioned by the peculiarities of the diffuse field close to the growth centers and to frontal kinematic waves.

In Fig. 5.11 a are shown two helical dislocations of the same sign, situated at a distance smaller than $2\pi r_c$ and forming a pair of non-intersecting growth spiral. The resulted spiral is formed by pairs of almost perfect parallel spires and therefore, it appears doubled. It is possible to suppose that in this case two dislocations cooperate one with another and behave similar to a multiple one [4]. Therefore, the growth rate of the crystal along the normal to the face, can, in this case, overcome many times the growth rate in the case of single dislocation.

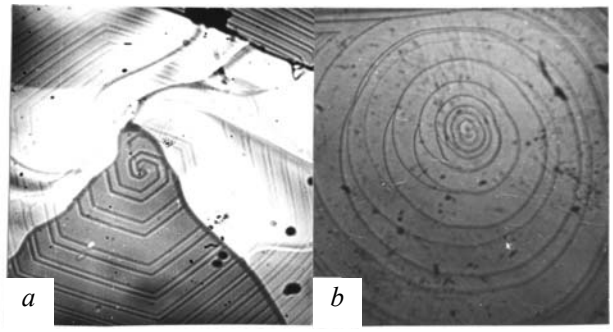

Fig. 5.11 a. The branching of the growth spiral on the surface (001) of SnS_2 crystal, formed by several dislocations of one and the same sign;
b. The interaction of the helical dislocations of the same sign, situated at at a distance higher than $2r_c$ (x 300) [7, 11].

According to [1, 3], by increasing the distance between two dislocations of the same sign up to $l>2\pi r_c$the margins of their atomic steps intersect, but as opposite to the case of the interaction of two dislocations of different sign, they will not "destroy" themselves reciprocally. The image of the crystal growth corresponding to such dislocation interaction is given in Fig. 5.11 b.

It is important to remark that a big amount of gliding dislocations determined the braking down to full stop (Fig. 5.12 a). According to [12] the main braking action on the gliding dislocation is given by other dislocations, point and surface defects, that appear in a high amount in the real crystals $A^{IV}B^{VI}$ [7]. The largest braking action is given by the fact that a large quantity of dislocations, observed by us, determines a braking, down to immobile dislocation Lommer-Cotterel, one of the most efficient barriers for gliding dislocations. Such dislocations can surround and lock all the Frank-Reed sources (Fig. 5.12 b). The Lomer-Cotterel barriers not only stop the gliding dislocations, but also can generate a source of new dislocations.

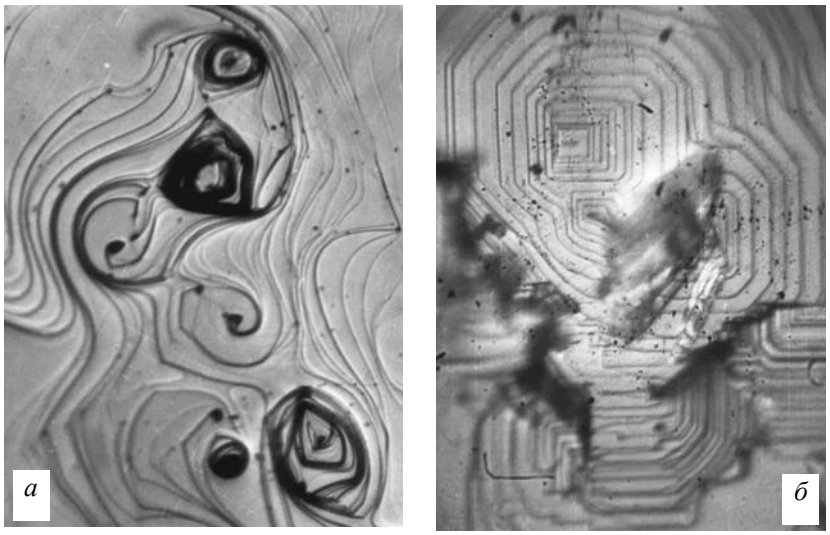

Fig. 5.12 The blocking of the helical dislocations in the single crystals $GeSe_2$ (a) and GeSe (b) x 400 [7, 13].

In single crystals, grown on seeds, always is possible to separate a coarser margin when the crystal merges with an other and from this position its growth starts. Here, in the most cases

starts the multitude of step lines, which, thereafter pass through the crystal or merge and form a front of growth.

It is also important to show that the height of the growth spirals in the single crystals of $A^{IV}B^{VI}$ an $A^{IV}B_2^{VI}$ is not monomolecular, and in most cases is higher than 1000 Å. This permits to observe them enough simply in the optical microscope [7].

It must observe that the appearance of dislocations and growth spirals in crystals is not well understood up to day. They can be triggered even in nuclei as a result of thermal fluctuations or mechanical deformations. In the latter stages of nucleus development, they can form as a result of vacancy gathering due to thermal and mechanical strains that appear when the crystal is in plastic state. Excepting this fact, the dislocation, and, also the growth spiral conditioned by them, can appear from the analogous defects on the ampoule walls and also in that case, when is produced a common growth of two differently oriented crystal germs [424, 427].

From this one can conclude that the dislocation density in crystals, can be essentially diminished if it is ensured the minimum fluctuation of the growth conditions. Therefore, the methods of crystal growth from vapor give better results because the temperature oscillation is easily maintained within up to 0.1 % accuracy, while the mechanical moving it is in general absent, i.e. its effect is totally excluded.

The stresses that appear in the crystals during their cooling can be conducted to a minimum, by diminishing the furnace temperature enough slowly. Thus, the crystals that come in close contact with the ampoule only by one of the faces (this often occurs for Ge and Sn chalcogenides) are weakly deformed. As a consequence, it is predictable that the transfer of dislocations and other defects from ampoule to the growing crystal is not significant. Apart this, it is still possible to diminish them by convenient choose of the pickling substance.

Thus, the above-described image of the growth, observed on the surface of the Ge and Sn mono-chalcogenide crystals, show that the helical dislocations play an important role in the process of their growth from gaseous phase for low saturations, because in this case they are a unique source of generation of atom steps for growth. The increase of the saturation in the ampoule by increasing the longitudinal temperature gradient $\Delta T = 100 \div 120$ K leads to the change of the mechanism of crystal growth. In this case the crystal habitus is expressed by plan-parallel platelets or dendrites (Fig. 5.13). For significant saturations, that take place during drawing of the largest parts of the crystallization of the layered compounds $A^{IV}B^{VI}$, the basic growing mechanism leads evidently to the formation and the development of two-dimensional nuclei close to the center plateau, and that leads to the formation of different growth terraces of various forms (Fig. 5.14) [13]. For this, even with the help of electron microscopy, it was not possible to get any demonstration of the fact that rapid spreading of the right angle steps appear at the output of the pairs of helical dislocations of opposite sign.

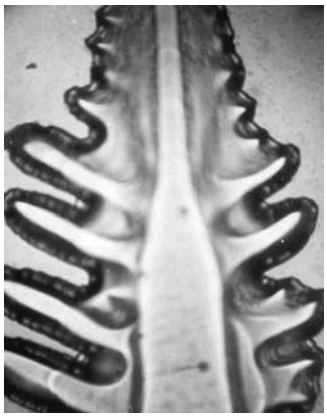

Fig. 5.13 The dendritic growth shape of the crystal GeS x5 [7, 13].

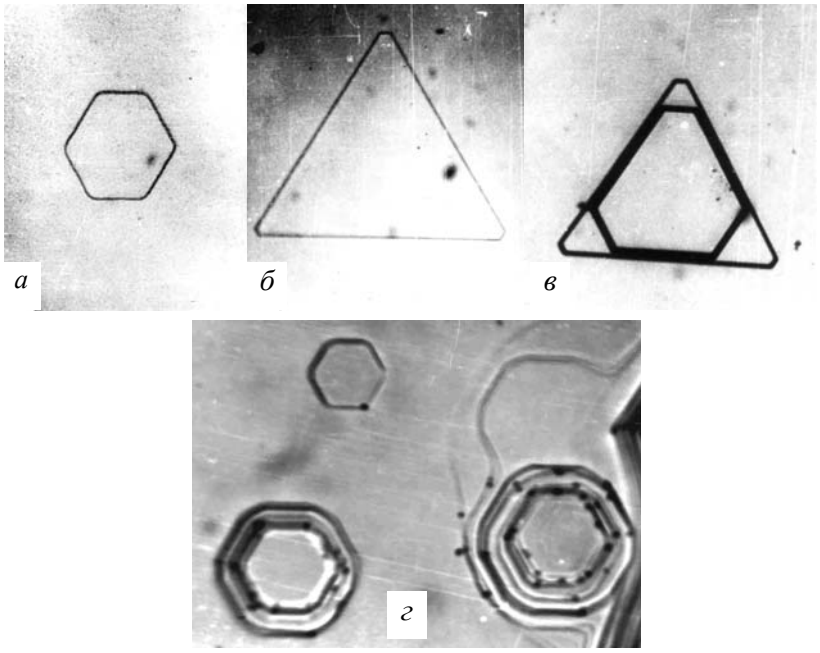

Fig. 5.14 Hills of growth formed for high saturation, on the (001) surfaces of the mono-crystals SnS_2 (a, b, c) and $GeSe_2$ (d) x150 [13].

In the GeS and GeSe crystals, grown by the CTR method, there were studied the defects with the electron microscope [13]. The fundamental planar defects are twins (110), represented by narrow bands with the width of several inter-planar distances, parallel to the plane of twining, and low angle boundaries (001), that contain dense networks of dislocations. In the paper [13] it is proposed an atomic model of twin boundary, that does not contain broken bonds, which describes the structure of the crystal by projecting the hexagonal rings and trigonal pyramids along the *c*-axis.

3. The growth of wire-like crystals of the germanium mono-sulphide

Wire-like crystals (WC) are named the mono-crystals having wire shape, that leads to important peculiarities of their properties [14, 15]. These structures can be right needles or rotated in a spiral, planar bands, formation of irregular shapes and shapes with branching. The unique geometry of the wire-like crystals raised the problem of the mechanism of their growth and stimulated in the same time the theoretical and experimental researches on the mechanisms and kinetics of growth of crystals, in general due to the simplicity of the models for one-dimensional case. Moreover, today was found the way to use the wire-like crystals in the construction materials, in electronics and measurement technique. The multitude of reports have shown that wire semiconductors and dielectrics exhibit a large number of advantages, that open the way to use them in the devices and measurement techniques etc. On their basis, have been already constructed tenso-meters, thermo-resistors, accelerometers, thermo-resistances with lateral heating, self-cathodes, pressure indicators, etc. [14, 15]. The further study of the nucleation process, the explanation of the growth mechanism, the development of the method for directional growth of new wire semiconductors with given structure and properties show without doubts a practical interest.

In the paper [16] are given the growing conditions and results of the study of the morphology of the wire-like GeS:In. The wire crystals of GeS:In have been prepared by the

method of static sublimation in two-zones furnace. The conditions for the growth of wire crystals are: the temperature of the evaporation region 900 ÷ 940 K, and for the condensation region 810 ÷821 K, the duration of the growth 10÷20 h.

The crystallization starts with the formation of a thick polycrystalline layer on the surface of the quartz ampoule in the condensation region. In the following stage from the polycrystalline substrate takes place the simultaneous growth of a large amount of wire crystals, enough close to the composition of the polycrystalline material. The wire crystals, as normally, do not nucleate on the walls of the quartz ampoule The general feature of the wire GeS:In is shown in Fig. 5.15. The wire crystals grow in the crystallographic direction [010], i.e. along the axis *b* and in cross-section the main feature is a distribution of rectangles. The wires of GeS:In have the length from 10 to 30 mm, the breadth from 0.01 to 1.0 mm, and the thickness in the range 0.005 ÷ 0.01 mm.

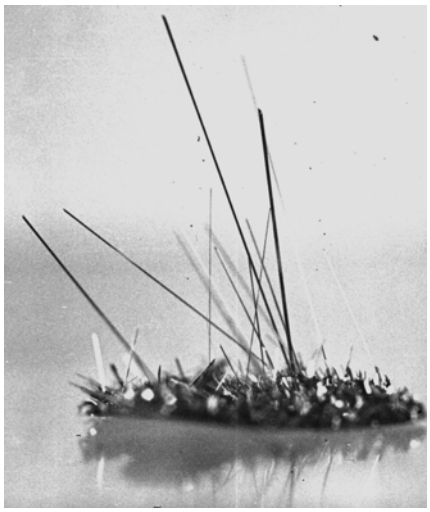

Fig. 5.15 General view on the wire GeSe:In crystals x 2 [16].

A higher attention was paid to the growth of wire crystals from the gaseous phase due to high productivity and dynamics [14]. For the explanation of single step growth of of wire crystals Sears (1953-1955) proposed a dislocation-diffusion model. He supposed that along the crystal axis passes a helical dislocation, which creates on the front a non-growing step, and thus ensures a continuous, relatively rapid growth of the crystal for small saturation. Firstly Sears considered that the most probable source of helical dislocations is the substrate, but later he postulated the appearance of dislocations during the growth of impurity particles. The Sears mechanism has not received much attention because it does not explain many important peculiarities of the wire growth: the initial and final stages of growth, the influence of the impurities during growth process, etc. These shortcomings have been partially eliminated by Wagner [15], which observed the important (activating) role played by some impurities in the growth of wires. Wagner and Ellis proposed a new model for wire growth after the scheme “vapor-liquid-crystal”. This model allowed to explain the main peculiarities of nucleation and growth of crystalline wires from the macroscopic point of view. Further development of the Wagner model was achieved by E. I. Ghivarghizova [436].

With the aim to understand the the growth mechanism of GeS:In wires Bletskan et al. [16] carried out detailed investigations of all the faces of these crystals with the help of the metallographic microscope MIM-4. It was shown that in all the investigated wires, whose breadth does not overcome 0.06 mm, the side faces are lacking any relief and growing steps and represents mirror-like, smooth surfaces. Careful analysis of the cross-section of the end of the wire did not evidenced traces of helical dislocations. On this basis Bletskan et al. [14] concluded that the growth of the GeS:In wires is described by the Wagner model [15], according to which the wire growth can be considered as a two-steps process: rapid growth of the “leader” and then the

thickening of the crystal. The growth of the "leader" of GeS:In, is produced, probably, by the mechanism " vapor-liquid-crystal", with the help of the indium impurity. For the leaders are characteristic the rectangle shape of the wire and the absence of the relief on the faces.

When the width of the GeS:In wires increases on the lateral faces (001) do appear growing steps, that generates helical dislocations that appear at the formation of the crystal. The presence of the indium impurity allows for the formation of the helical dislocations, that lead to the growth of the (001) faces. As a consequence GeS:In wires can grow as platelets. Thus indium plays an important role in the formation process of GeS:In wires and determines their electro-physical properties.

The growth of the GeS_2 wire crystals after the mechanism vapor-liquid-solid has been observed by Finkelman et al. [17] during the condensation of the gases that are formed during coal burning. The morphology, composition and structure of these wires have been studied by XRD, scanning and transmission electron microscopy. The GeS_2 wires exhibit the length of ~100 μm, diameter ~ 5 μm, with a solidified drop on the upper end and with many small wires, that grow from the main rod and develop in the directions perpendicular to the direction of the main rod. The rod is a single crystal of low temperature GeS_2 α-phase, while the hood (or drop) is amorphous and its composition is depleted in germanium.

4. Conclusions

The layer or platelet-like crystal and, also, the wire-like crystals have been grown form the gaseous phase. There were shown the special conditions to be considered for growing high quality crystals.

References

[1] G. G. Lemlein, E. D. Dukova, Kristallografia, 1(3), 352 (1956).
[2] A. Varma, Rost Kristallov i Dislokatsiia Crystal growth and dislocations (russ.) –M: IL 1958, 392 pp.
[3] A. A. Chernov, Uspehi Fiz. Nauk 73(2) 227 (1961)
[4] E. Schönherr, W. Stetter, J. Cryst. Growth, **20**(2), 158 (1973).
[5] E. Hartmann, A. Mecseki, E. Schönherr, J. Cryst. Growth, **57**(3), 616 (1982).
[6] D. I. Bletskan, V. I. Taran, M. Yu. Sichka, Ukr. Fiz. Zhurn. 21(9) 1436 (1976).
[7] D. I. Bletskan, Ukr. Fiz. Zhurn. 24(9), 1321 (1979).
[8] D. I. Bletskan, I. F. Kopinets, P. nP. Pogoretskii, E. M. Salkova, D. V. Chepur, Kristallografia, 20(5), 1008 (1975).
[9] D. I. Bletskan, Phonon spectra and electron phenomena in ordered and disordered germanium chalcogenides (Ph. D. hab. Thesis) /russ./, Kiev, 1984, 447 pages.
[10] T. G. Petrov, E. B. Treibus, A. P. Kasatkin, Viraschivanie kristallov iz rastvora –L. Nedra, 1967, 175 pp.
[11] D. I. Bletskan, I. F. Kopinets, I. M. Migolinets, S. V. Mikularinets, Preparation and investigation of the properties of the single crystals of SnS_2, determinations for germanium selenide. GeSe, Acta Crystallogr. **13**(6), 449-450 (1960).
[12] I. I. Novikov, Defecti kristalicheskoi reshetki metallov –M.: Metallurghia, 1968, 188 pp.
[13] T. H. Karakostas, J. Meter. Sci. 23(9), 3099 (1988).
[14] E. I. Ghivarghizov, Rost nitevidnih I plastinchatov kristallov iz para (russ.) –M:, Nauka, 1977, 304 pp.
[15] R. Vagner, Rost kristallov po mehanizmu PJK –M: Mir 1973 p. 42-114.
[16] D. I. Bletskan, R. Yu. Indus, Izv. Akad. Nauk SSSR, Neorg. Mat. 18(4) 544 (1982).
[17] R. B. Finkelman, R. Larson, E. J. Dwornik, J. Cryst. Growth **22**(2), 159 (1974).