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ABSTRACT

of the dissertation for the degree of Doctor of Science

**PHASE TRANSITIONS AND KINETICS
CRYSTALLIZATION IN THIN FILMS OF SOLID
SOLUTIONS BASED ON COMPOUNDS OF GROUP $A^3B^3C_2^6$**

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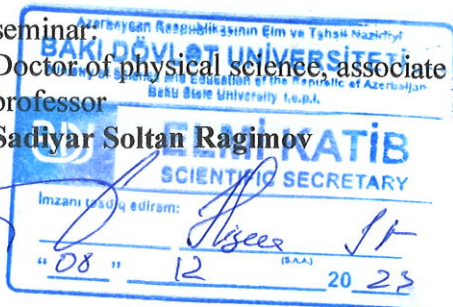
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GENERAL DESCRIPTION OF WORK

Relevance of the work and degree of study of the topic. Structural transformations, including phase transitions, have been intensively studied by scientists in world scientific centers for many years. To increase many technological parameters of strength and other characteristics of semiconductors, it is necessary to study, first of all, structural transformations. Often information about structural transformations is of a qualitative nature due to the complexity of systems, as well as due to the experimental difficulties that arise when studying such processes, including processes of practical importance. The prerequisites for their quantitative study have been created, and there is reason to expect even greater progress in this direction in the future. Essentially, structural transformations are the result of chemical and physical processes occurring in a solid.

With the creation of new functional semiconductor materials, interest in methods for producing nanostructured multicomponent semiconductor compounds has noticeably increased. Ultrathin films of such compounds belong to the so-called dimensionally limited (at least in one dimension) structures. Based on the above and a number of other reasons not mentioned here, studies of various processes in thin-film samples, which differ from bulk samples by the easier separation of various phases in their pure form, including thermodynamically stable, as well as metastable phases with intermediate-transition structures, are of general scientific importance. The results of which can subsequently be used to create multilayer heterostructures and superlattices with a perfect structure of individual nanothick layers and the interfaces between them. Such films, in their physical and optical parameters (in some cases, in structure), which have quantum properties that differ sharply from the properties of massive single-crystal samples of the corresponding composition, are of particular importance in the nanotechnology of thin-film structures, make it possible to intensify scientific and technical developments and serve as the basis for the manufacture devices of modern solid-state electronics.

The preservation or destruction of short-range order in the arrangement of atoms and the characteristics associated with it determines the preservation or loss of semiconductor properties, which are

necessary and fundamental links in the composition-structure-properties relationship. Electron diffraction study of thin amorphous films using an electrometric system for measuring intensities with possible filtering of electrons by energy occupies a special place in the range of problems solved by this method. Due to the need to comply with the temperature regime to preserve the electrical and optical properties of semiconductor layers, which is difficult and not always possible, at the stage of designing optoelectronic elements, for the corresponding calculations, knowledge of the laws of transition of a substance from one state to another, in particular from an amorphous state to a crystalline one, is required. and quantitative data on the crystallization of amorphous films.

Consequently, studies such as determining the phase composition, boundaries of phase homogeneity, phase transformations, growth mechanisms and the degree of structure perfection are of paramount importance in physicochemical studies of solids, allowing for a targeted search for new materials in film form with unique specified and reproducible properties, unattainable in bulk crystals.

Due to the above, the relevance of the problems solved in this dissertation is determined by the establishment of general laws of phase formation in the systems Tl – In (Ga) – Te (Se, S) with impurities of the chemical elements Sn and Ge. The prospects of three-component compounds, doped and undoped with impurities, which are used as highly efficient photo and thermoelements, modulators and receivers of laser radiation, nonlinear optical converters, are highlighted in the works of local and foreign scientists. The relevance lies in the search for new materials that have superperiodicity in prediction and control of the formation of superlattices of solid solutions based on superstructural phases, which makes it possible to precisely control the parameters of thin epitaxial films with new properties with the prospect of their practical application, especially in optoelectronics.

Establishment structures of short-range atomic order in amorphous thin films of $A^3B^3C_2^6$ compounds doped with chemical elements included in group IV, and the kinetic parameters of phase transitions, which are an integral part of the physics of condensed matter, can serve as a fundamental basis for a scientifically based approach in creating all kinds of technological modes, which also determines the

relevance of this work.

Object and subject of research. The object of the study was compounds $A^3B^3C_2^6$ with impurities embedded in them from group IV of the periodic table. Selection of substances of group $A^3B^3C_2^6$ as an object of study is due to the fact that compounds of this group, which differ from classical semiconductors, have a number of specific features. Compounds $TlIn_{1-x}Sn_xX_2$ (X – Te, Se, S) and $TlGa_{1-x}Ge_xX_2$ (X – Te, Se, S) ($0.01 \leq x \leq 0.09$), which crystallize in chain and layered structures and belong to the $A^3B^3C_2^6$ group. Each ternary compound doped with chemical elements included in group IV is prone to structural rearrangements and has several modifications to the point of forming defect structures in which some of the atoms occupy their positions statistically and the deficiency of atoms is filled by impurity atoms. This, under certain conditions, leads to inconstancy of properties, limiting their use, especially when such changes are not provided for. The subject of the study was the kinetics of the physical process of phase transition during isothermal heat treatment of thin films of solid solutions.

Purpose and objectives of the study. The purpose of this work is to determine the influence of impurities on the structural features of three-component compounds, study phase transitions and crystallization kinetics in chalcogen-containing thin films and establish the existence of superlattices in thin layers, study the formation of substitutional solid solutions with different substructures based on superstructural phases of compounds of the $A^3B^3C_2^6$ group using chemical elements, included in group IV of the periodic table.

In order to develop the scientific direction proposed in the dissertation and having applied significance in modern technology, existing research methods have been improved: 1) obtaining films containing highly volatile and easily oxidized components; 2) structural features and phase transformations in thin films of varying degrees of perfection, including superstructural epitaxial films, depending on the film thickness, temperature and nature of the substrates; 3) software has been developed for primary processing of data from electron diffraction studies of short-range order in amorphous films.

In accordance with the goal, it was necessary to choose the most appropriate direction of scientific research and solve the following

main tasks:

1. Taking into account a number of physical properties of chemical elements, determine the most optimal options during the preparation of thin layers containing highly volatile and easily oxidized components, establish specific for each compound of substances included in group $A^3B^3C_2^6$, interactions with elements of group IV by doping. Analyze the conditions for the formation of thin films of solid solutions, the region of existence of phases of ternary compounds related to specific structural modifications of the $Tl - In(Ga) - Te_2 (Se_2, S_2)$ systems. To generalize all aspects of the formation of phases of structurally formed and strictly stoichiometric compositions in the process of interaction of heterogeneous films with impurities embedded in them.

2. Investigate the possibility of the formation of epitaxial - single-crystal films $TlIn_{1-x}Sn_xX_2$ ($X - Te, Se, S$), $TlGa_{1-x}Ge_xX_2$ ($X - Te, Se, S$) and establish the existence of superstructures, commensurate with one or another phase. To find out the mechanism of transition of the atomic structure to long-period superstructural phases of compounds of group $A^3B^3C_2^6$, doped with elements of group IV of the periodic system, to establish orientation relationships between the superlattices of epitaxially growing films and single-crystal alkali halide substrates.

3. Determine the functions of the radial distribution of atoms in amorphous films of compositions $TlIn_{1-x}Sn_xTe_2 (Se_2, S_2)$ and $TlGa_{1-x}G_xTe_2 (Se_2, S_2)$, which establishes the number of nearest neighbors within a statistical framework. Establish the number of atoms in coordination spheres, as well as the probability of encountering an atom of one type or another located at a distance r from a given atom. Calculate interatomic interactions in amorphous films of double tellurides (selenides, sulfides) of ternary compounds $A^3B^3C_2^6$, doped with impurities of elements of group IV of the Periodic Table, which determine the probability of finding atoms oriented in space in a certain way and located at a certain distance from each other.

4. Determine the process of kinetics of phase transformations of amorphous films of compositions $TlIn_{1-x}Sn_xTe_2 (Se_2, S_2)$ and $TlGa_{1-x}G_xTe_2 (Se_2, S_2)$ ($0.01 \leq x \leq 0.09$), obtained by thermal evaporation under normal conditions – in the absence of any external influences.

5. Establish the kinetic parameters of crystallization of amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($0.01 \leq x \leq 0.09$), obtained under conditions of exposure to an external electric field parallel to the direction of deposition of the molecular beam.

6. Determine the quantitative influence of Sn and Ge atoms on the formation of various phases of thin films $\text{Tl} - \text{In}(\text{Ga}) - \text{Te}_2$ (Se_2 , S_2) on single-crystal substrates NaCl, KCl, KJ and obtaining perfect epitaxial films with extended lattice periods.

7. Determine the possibility of replacing the components of superstructural compounds with impurity atoms and establish in the films the region of solid solutions based on the superstructural phases $\text{TlIn}_{1-x}\text{Sn}_x\text{X}_2$ ($\text{X} - \text{Te}, \text{Se}, \text{S}$) and $\text{TlGa}_{1-x}\text{Ge}_x\text{X}_2$ ($\text{X} - \text{Te}, \text{Se}, \text{S}$) in the composition range $0.01 \leq x \leq 0.09$.

To achieve this goal, it is necessary to solve the following problems: determining the structural features of chalcogen-containing amorphous, polycrystalline, textured, single-crystalline (epitaxial) films doped with impurities, studying phase transitions in them and establishing the existence of superlattices in thin layers, the formation of solid solutions based on superstructural phases and studying properties of films with different substructures. The study of these processes, being the basis of the scientific direction developed in the dissertation, also has applied significance for today's technology.

Research methods. Processes of phase transformations, formation of phases with different substructures and structural changes caused by external influences and chemical reactions in ternary compounds of the $\text{Tl} - \text{In}(\text{Ga}) - \text{Te}(\text{Se}, \text{S})$ system doped with Sn and Ge impurities, as well as the formation of solid solutions on the basis of superstructural phases in epitaxial films of non-stoichiometric compositions $\text{TlIn}_{1-x}\text{Sn}_x\text{X}_2$ ($\text{X} - \text{Te}, \text{Se}, \text{S}$) and $\text{TlGa}_{1-x}\text{Ge}_x\text{X}_2$ ($\text{X} - \text{Te}, \text{Se}, \text{S}$) were studied by electron diffraction using EG electron diffraction systems and EMR – 102, the use of which in modern science has led to a more detailed study of nano-sized films of complex composition.

Structural studies of amorphous nanothick objects $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) were carried out both microphotometrically (experimental intensities of electron scattering curves were obtained using an MF-4 microphotometer) and on an EMR-102 electronograph. This electron diffraction machine is equipped with a

system for measuring the intensities of electron diffraction patterns (DK), which allows filtering out inelastically scattered electrons by scanning the DK in front of a stationary photomultiplier tube - a high-sensitivity sensor.

The crystallization process of amorphous films of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($0.01 \leq x \leq 0.09$), obtained with and without a constant electric field, was studied by kinematic electron diffraction. The thin films under study were obtained in two different vacuum universal installations (VUP – 4 and VUP – 5), the design of which was modified to create a constant external electric field using a UIP power source. The thickness of the films was controlled by a Spekord 210 plus spectrometer, and their composition was controlled by a Shimadzu atomic absorption spectrophotometer AA – 6300.”

Basic provisions submitted for defense.

1. During the condensation of the Tl – In – S system with doping with Sn impurities, the composition has a specific formation feature, depending on the method of obtaining films. In the case of sequential evaporation, regardless of the order of deposition of the components, amorphous phases are formed. After heat treatment of these films, only tetragonal and monoclinic structures of crystalline $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ ($0.01 \leq x \leq 0.09$) are formed. Thin films of the monoclinic phase $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ are dimorphic. With the simultaneous evaporation of the components of the Tl – In – S system with Sn impurities, 12 different compounds and 10 different compounds and a substitutional solid solution $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ of tetragonal, monoclinic and orthorhombic modifications are distinguished. All films formed at room temperature on NaCl, KCl, and KJ substrates are amorphous with the chosen evaporation option. Amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$, distinguished by their $S=4\pi \sin \theta/\lambda$, crystallize in three modifications – monoclinic, tetragonal and orthorhombic structures.

2. In thin films obtained by thermal sputtering of individual components, the phase equilibrium of the Tl – Ga – S system with Ge impurities depends on the initial conditions of the phase formation process and is accompanied by previously unknown patterns. The stability and reproducibility of the isolated and identified 10 compounds and solid solutions of different composition and structure are determined by the parameters of the condensation process and de-

pend on the order of deposition of the above chemical elements in the case of sequential deposition of components and on the rate of evaporation of substances. All films formed on NaCl, KCl, KJ substrates, including $\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$ films are amorphous at room temperature.

3. Phase equilibria in films obtained by sequential deposition of Tl, Ga, Se and Ge as an impurity, regardless of the order of deposition, as well as with the simultaneous evaporation of components on the above substrates at room temperature, along with the $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ phase ($0.01 \leq x \leq 0.09$) lead to the release of a number of chemical compounds of double and ternary composition in the amorphous state. The temperature range for the formation of amorphous $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ films increases (from 363 to 392 K), and they crystallize at lower temperatures compared to similar compounds without doping. It should be noted that the temperature range for the formation of amorphous phases in $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) systems increases by $6 \div 8\%$. The extent of the regions of the formed phases during simultaneous and sequential deposition of components is the same.

4. During condensation of the Tl – In (Ga) – Te system with Sn and Ge impurities, regardless of the method of preparation and the order of deposition of chemical elements during sequential deposition, the phase composition of the condensation plane is determined mainly by the state diagrams of ternary compounds of the compositions Tl_2SnTe_5 , TlInTe_2 , Tl_2GaTe_5 , TlGaTe_2 . The sequence of formation of dimorphic phases, low-temperature α and high-temperature β modifications in films of the Tl – In(Ga) – Te (Se, S) with doping with Sn and Ge impurities is determined by the rate of evaporation of elements and the temperature of the substrates.

5. In compounds of the Tl – In (Ga) – Te (Se, S) systems with an admixture of chemical elements from Group IV of the Periodic Table, substitutional solid solutions with a superstructural structure, having an average statistical order, are presumably formed. Forming structures with increased periods compared to the initial structure of atoms can lead to the formation of a new model of interatomic bonds, and as a result, to the emergence of new properties of $\text{TlGa}_{1-x}\text{Ge}_x\text{X}_2$ ($\text{X} - \text{Te, Se, S}$) and nanofilms $\text{TlIn}_{1-x}\text{Sn}_x\text{X}_2$ ($\text{X} - \text{Te, Se, S}$).

6. Short-range order of nano-sized amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$

(Se₂, S₂) and TlGa_{1-x}Ge_xTe₂ (Se₂, S₂) differs from similar compounds without impurities in the length of bonds in the immediate environment of atoms.

7. The kinetics of crystallization during heat treatment of the above amorphous films of compounds of group A³B³C₂⁶, doped with an impurity of chemical elements of group IV of the Periodic Table, obtained by vacuum evaporation under normal conditions and under the influence of an electric field, obeys the Avraami-Kolmogorov law. These films were obtained in vacuum by thermal evaporation of both pre-synthesized single-crystal solid solutions and individual chemical elements Tl, In (Ga), Te (Se, S), as well as Sn or Ge as impurities from separate sources. The effect of the electric field during the deposition of a molecular beam on a substrate affects the scatter of angles and distances in the immediate environment of atoms in amorphous films, as well as the values of crystallization activation energies, i.e. the energy of formation and growth of films is underestimated. And subsequently, the structural bonds between atoms lengthen.

8. In amorphous films of solid solutions TlIn_{1-x}Sn_xTe₂ (Se₂, S₂) and TlGa_{1-x}Ge_xTe₂ (Se₂, S₂), obtained at a constant electric field in a vacuum of ~10⁻⁵ Pa, the activation energy values for crystallization decrease compared to films formed without exposure to the field. The noted effect is associated with the influence of impurity ions during the process of atomic condensation and charge redistribution, which occurs unevenly, as well as the presence of charged point defects on the surface layers of the deposited substrates and the direction of the electric field.

9. Nano-sized films of non-stoichiometric compounds TlIn_{1-x}Sn_xX₂ (X – Te, Se, S) and TlGa_{1-x}Ge_xX₂ (X – Te, Se, S), obtained by thermal method, have peculiar advantages, controlled by dosed doping with chemical elements Sn, Ge and the formation of thin films. Tin and germanium impurities throughout the composition range 0.01 ≤ x ≤ 0.09 contribute to the formation of limited substitutional solid solutions along the superlattice structures TlGa_{1-x}Ge_xX₂ (X – Te, Se, S) and TlIn_{1-x}Sn_xX₂ (X – Te, Se, S) and allow precise control of the parameters of thin epitaxial films of superstructural phases. Local distortions of cells in superstructural epitaxial films are accompanied by statistical deviations of atoms from their occupied positions.

Scientific novelty of the research. The studies carried out allowed us to obtain the following most important results:

1. The possibility of flexible and varied formation of compositions in the required order has been proven for films of compounds of the Tl – In – Te (Se, S), Tl – Ga – Te (Se, S) systems doped with impurities - the chemical elements Sn and Ge. During the production of nano-thick films, the difficulty of which is to prevent volatilization and oxidation of highly volatile and easily oxidized components during thermal treatment of films, it was found that with the simultaneous and sequential evaporation of thallium, indium, tellurium (selenium, sulfur) and thallium, gallium, tellurium (selenium, sulfur) and, accordingly, tin and germanium as impurities, the range of formation of amorphous films is much wider than films without impurities.

2. For the first time, precision studies have proven the possibility of obtaining thin films of polymorphic $TlIn_{1-x}Sn_xS_2$ in a vacuum installation of amorphous phases, which after crystallization belong to the tetragonal, monoclinic and orthorhombic modifications. The formation of the amorphous phase does not occur at temperatures above 245K.

3. Through an electrometric system for precision measurement of intensities The short-range order structure of amorphous films $TlIn_{1-x}Sn_xTe_2$ (Se₂, S₂), $TlGa_{1-x}Ge_xTe_2$ (Se₂, S₂) has been determined. For the first time, the radial distribution of atoms has been established, i.e. radii of coordination spheres and numbers in solid solutions of the above compositions. It has been shown that amorphous films of solid solutions of tetragonal, monoclinic and orthorhombic systems and compounds without impurities have a similar short-range order structure. The differences consist mainly only in the divergence of small scatters in the lengths of interatomic bonds. When determining the coordination of atoms in amorphous films of solid solutions $TlIn_{1-x}Sn_xTe_2$ (Se₂, S₂), $TlGa_{1-x}Ge_xTe_2$ (Se₂, S₂), a mixed coordination of atoms was discovered – octahedral with tetrahedral.

4. On ionic substrates KJ and NaCl determined conditions for the formation of four superlattices with tetragonal and orthorhombic solid solutions during phase transformations in $TlIn_{1-x}Sn_xTe_2$ (Se₂) and $TlIn_{1-x}Sn_xS_2$ films, which had triple lattice parameters relative to the initial phase. The existence of two superstructural phases of the com-

position $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ has been established: a) a textured orthorhombic phase with the “c” texture axis perpendicular to the surface of the NaCl substrate; b) tetragonal modification in a single-crystalline state with superperiods that reveal good crystallographic correspondence between the mating planes of the substrate and the new phase. The unit cells of the superstructural phase were conjugated with three cells of the KJ and NaCl substrates. The mismatches between the mating lattices of the substrate and film were $\sim 3.1 \div 3.6\%$. During epitaxial growth, the films under study are oriented with the (1 00) plane parallel to the (001) KJ and NaCl substrates.

5. The conditions for the existence of superstructural phases in compounds with a tetragonal structure $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) the appearance of which was recorded in perfect single-crystalline nanothick films oriented by the plane (100) parallel to the substrates (100) NaCl and KJ, while the relative discrepancy between the mating networks is no more than 5%. The resulting superlattices with tetragonal system have double periods in relation to the initial phase.

6. The influence of tin and germanium impurities of various concentrations on the formation of solid solutions based on superstructural phases with modified compositions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) over a wide temperature range.

7. The kinetic parameters of phase transitions in thin amorphous films $\text{TlGa}_{1-x}\text{Ge}_x\text{X}_2$ ($\text{X} - \text{Te}, \text{Se}, \text{S}$), $\text{TlIn}_{1-x}\text{Sn}_x\text{X}_2$ ($\text{X} - \text{Te}, \text{Se}, \text{S}$), condensed at a constant electric field of 3000 V cm^{-1} in a vacuum of $4 \times 10^{-5} \text{ Pa}$ and without exposure to the field; isothermal curves of their crystallization kinetics were constructed.

8. It has been established that during thermal treatment of nanothick films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) with an amorphous structure, the crystallization activation energy values for these films formed without exposure to a field have higher values compared to films obtained in an electric field.

9. It has been established that when a certain dose ($0.01 \leq x \leq 0.09$) of the Sn (Ge) impurity is added to the compounds of the Tl – In (Ga) – Te_2 (Se_2 , S_2) there is a monotonic change in the lattice parameters; substitutional solid solutions are formed. But in the interval $x=0.05 \div 0.06$ impurities, a violation of the monotonicity of the change in the lattice parameter was discovered.

Theoretical and practical significance of the research. The issues of identifying local atomic environments in amorphous films, the thermal stability of substructurally different films to sudden temperature changes and to repeated cycles such as melting and solidification are of independent theoretical interest, as problems associated with certain changes in semiconductor effects. Determining the boundaries of homogeneity of the resulting phases in the form of the thinnest layers and the conditions for their production, the characteristic features of the formation of stable and reproducible thin films, obtaining information about the growth mechanism and kinetics of phase transformations, which are directly related to the issue of the temperature dependence of any semiconductor compounds, represent the practical value of this dissertation. The same applies to the possibility of using thin layers of solid solutions of substitution of superstructural phases of various compounds of the $A^3B^3C_2^6$ group, some of which were obtained in the form of two modifications with different structures. Using the large difference in the band gap and other properties, which is observed, as a rule, in substances of the same composition, which are, however, in different states – amorphous, crystalline and superstructural states, it is possible to radically change and improve the performance characteristics of devices. Options and modes for the formation of nano-sized films have been established, which affect the measurement parameters of devices developed on the basis of the above nanothick films.

Testing and application. The main results of the dissertation work were discussed and reported at Republican, International conferences and seminars: III International Conference “Amorphous and Microcrystalline Semiconductors” (St. Petersburg, July 2002); IX International Conference on Physics and Technology of Thin Films (Ukraine, Ivano-Frankivsk, May 2003); IV International Conference “Amorphous and Microcrystalline Semiconductors” (St. Petersburg, July 2004); I Me at the national scientific seminar “Li ghtinNano – Size-Solids” (Baku, September 2004); International scientific and technical conference “Information and electronic technologies in remote sensing”, dedicated to the 70th anniversary of Academician A.Sh. Mehdiyeva (Baku, December 2004); International conference “Physics – 2005”, dedicated to the 60th anniversary of the Institute of

Physics of ANAS (Baku, June 2005); V International Scientific and Technical Conference – Microelectronic converters and devices based on them – “MEPP 2005” (Baku, December 2005); V International Conference “Amorphous and Microcrystalline Semiconductors” (St. Petersburg, June 2006); IV Republican Conference “Current Problems of Physics” (Baku, June 2006); VI National Conference on the Application of X-ray, Synchrotron Radiation, Neutrons and Electrons for Materials Research – “RSNE 2007” (Moscow, November 2007); XIII National Conference on Crystal Growth – “NCRC 2008” (Moscow, October 2008); VII National Conference on the Application of X-ray, Synchrotron Radiation, Neutrons and Electrons for the Study of Nanosystems and Materials. Nano-Bio-Info-Cognitive Technologies – “RSNE – NBIC 2009” (Moscow, November 2009); International conference “CRYSTAL MATERIALS 2010” (Ukraine, Kharkov, May 31 – June 03 2010); IV International Conference “Crystal Physics of the XXI Century” and XIV National Conference on Crystal Growth “NKRK 2010” (Moscow, December 2010); VIII National Conference on the Application of X-ray, Synchrotron Radiation, Neutrons and Electrons for the Study of Nanosystems and Materials. Nano-Bio-Info-Cognitive Technologies – “RSNE – NBIC 2011” (Moscow, November 2011); International conference “Current problems of physics” dedicated to the 80th anniversary of academician. B.M. Askerov (Baku, December 2013); XXV Russian conference. by email microscopy “RKEM-2014” (Moscow region, Chernogolovka, June 2014); VIII Republican Scientific and Practical Conference “Actual problems of Physics” (Baku, December, 2015); XXIV International Scientific and Technical Conference on Photoelectronics and Night Vision Devices. "NPO "Orion" (Moscow, May 2016); XXVI Russian conference. by email microscopy “RKEM-2016” (Moscow region, Zelenograd, May – June 2016); 2nd International Forum on Electron Beam Technologies for Microelectronics – “Technounity – ELTM 2017” (Moscow region, Zelenograd, October 2017); XXV International Scientific and Technical Conference on Photoelectronics and Night Vision Devices. NPO Orion (Moscow, May 2018); XXVII Russian conference. by electron m microscopy “RKEM-2018” (Moscow region, Chernogolovka, August 2018); ISSN 2522-4352 Conference Proceedings

Modern trends in physics (Baku, may 2019); Conference with international participation “Electron beam technologies 2019”, “KELT-2019” (Moscow region, Chernogolovka, September – October, 2019); XXVIII Russian conference by email microscopy "RKEM-2020" (Moscow region, Chernogolovka, September 2020); IX International Conference “Crystal Physics and Deformation Behavior of Advanced Materials” dedicated to the 100th anniversary of the birth of Academician B.K. Weinstein (Moscow, November 2021); XXVI International Scientific and Technical Conference on Photoelectronics and Night Vision Devices. "NPO "Orion" (Moscow, Russia, May 2022); XXIX Russian Conference on Electron Microscopy “RKEM-2022” (Moscow, August 29-31, 2022); XI Eurasian scientific and practical conference “Strength of inhomogeneous structures” PROST-2023 (Moscow, April 18-20, 2023).

Publications. The main results of the dissertation are reflected in 50 scientific papers, of which 17 articles were published in journals determined by the Higher Attestation Commission of Azerbaijan (including 6 in journals included in the Clarivate database Analytics «Web of Science”), 3 articles – In collections of conference proceedings, 30 theses – In local and foreign collections of conference materials.

The name of the organization where the dissertation work was completed. The dissertation work was completed at the Institute of Physics of ANAS. The main results of research carried out during planned work are published in collections of reports of the Institute of Physics of ANAS.

Volume, structure and main content of the dissertation. The dissertation work consists of an introduction, five chapters, conclusions and a list of 327 bibliography titles – literature cited in the work. The volume of the dissertation is 359 pages, including 236 pages of computer text, 24 tables and 109 figures. The volume of the dissertation consists of 410266 characters.

SUMMARY OF THE WORK

The introduction substantiates the relevance of the topic, formulates the main goal, scientific novelty and practical significance of the dissertation work, and outlines the main provisions submitted for

defense. The approbation of the work is presented and the content of the dissertation chapters is briefly outlined.

The first chapter is devoted to a brief analytical review of the literature, which studies the thermodynamic equilibrium states of different phases of polymorphic compounds in the systems $A^3 - B^3 - C^6$: $Tl - In(Ga) - Te(Se, S)$ and solid solutions based on them. Contradictory points of view of various authors regarding the structural characteristics of these compounds, associated with errors or low accuracy in determining phases, as well as with the characteristics of chemical elements at the atomic level, have been noted.

The possibilities for obtaining new materials are significantly expanded when using solid solutions. The study of such compounds and solid solutions based on them is relevant, since they have special properties and are widely used in the field of optoelectronics. In this regard, compounds $TlIn(Ga)X_2$ ($X - Te, Se, S$), members of the $A^3B^3C^6$ group, and their solid solutions are the most promising. Based on the analysis of literature data and the identification of a number of issues that cause controversy, we have formulated the purpose and objectives of the dissertation work, which are as follows: development of scientifically based methods, technological regulations for the production of films of $TlIn_{1-x}Sn_xTe_2(Se_2, S_2)$ and $TlGa_{1-x}Ge_xTe_2(Se_2, S_2)$ ($x=0.01\div 0.09$) and their solid solutions and the formation of phase states in them.

The studied ternary thallium tellurides of gallium and indium, interacting at temperatures above $600^\circ C$, form a continuous series of solid solutions, which is shown graphically in Figure 1. Based on the analogy of the diffraction patterns of the alloys and the original ternary compounds, the lattice periods of all alloys were determined. Figure 2 shows the composition-lattice parameter relationship, according to which no deviation from Vegard's law is observed. Analysis of radiographic data shows that partial replacement of the element Ga with an element In does not disturb the structure and in this system $TlInTe_2 - TlGaTe_2$ substitution solid solutions are formed in the entire concentration range according to Rosebom type III. Therefore, the formula $TlIn_{1-x}Ga_xTe_2$ can be assigned to such solid solutions. Indexation of the powder patterns showed that they all crystallize on the basis of a tetragonal lattice.

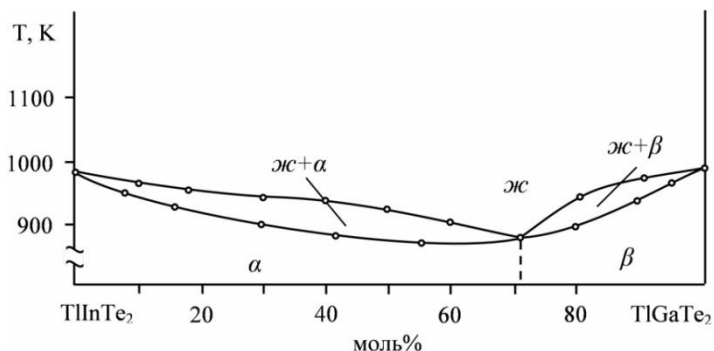


Fig. 1. Equilibrium diagram of the Tl – In – Ga – Te system

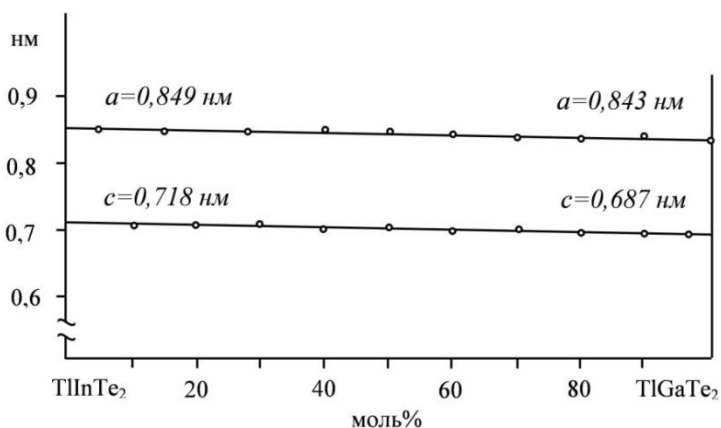


Fig. 2. Dependence of lattice parameters on composition in the TlInTe₂ – TlGaTe₂ system

As can be seen from Figure 3, the ternary compounds TlInSe₂ and TlGaSe₂ at temperatures above 980 K upon interaction form wide solubility regions with a eutectic close to the composition of TlIn_{0.49}Ga_{0.51}Se₂. When studying the microstructure, it was discovered that the structure characteristic of the initial components TlInSe₂ and TlGaSe₂ is inherent only in alloys based on these compounds, namely up to 40 mol. % on both sides. Two-phase alloys near 50 mol. %, correspond to the composition TlIn_{0.55}Ga_{0.45}Se₂.

In the composition range of 40-55 mol.% TlGaSe₂, a heterogeneous phase ($\alpha + \beta$) of solid solutions is assumed, which is confirmed by the composition-lattice parameter plot (Fig. 4). Since the initial compounds crystallize in different types of lattices, therefore, in the

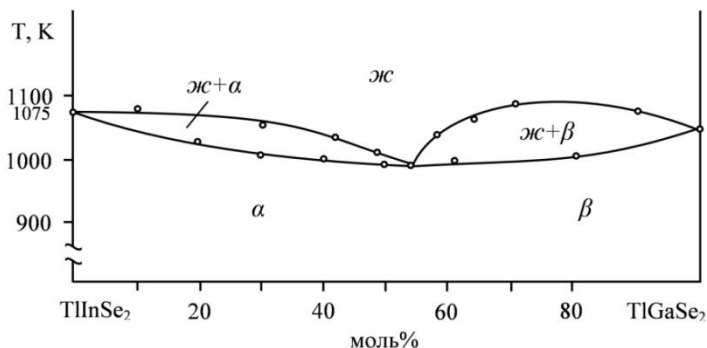


Fig. 3. Equilibrium diagram of the Tl – In – Ga – Se system ($\text{TlIn}_{0.49}\text{Ga}_{0.51}\text{Se}_2$)

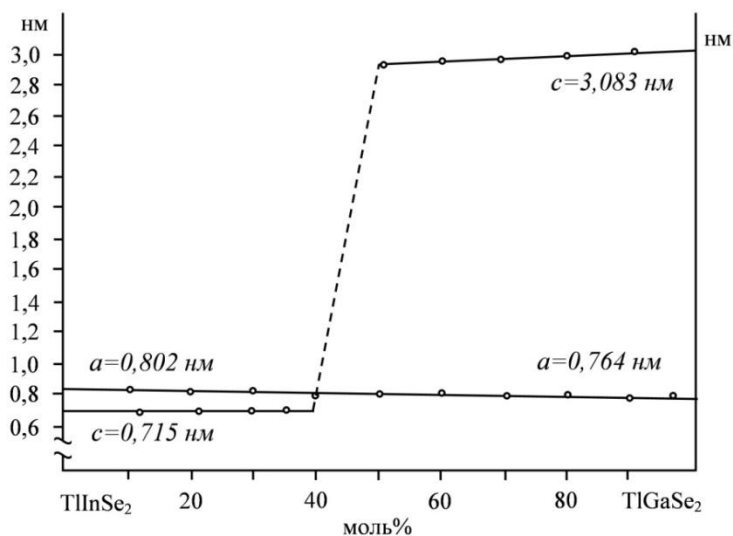


Fig. 4. Dependence of lattice parameters on composition in the $\text{TlInSe}_2 - \text{TlGaSe}_2$ system

$\text{TlInSe}_2 - \text{TlGaSe}_2$ system, some deviation from Vegard's law is observed in the «*c*» parameter. The results of thermal studies confirm that for the composition $\text{TlIn}_{0.2}\text{Ga}_{0.8}\text{Se}_2$ the crystal lattice parameters smoothly decrease to the values of the initial compositions. In the $\text{TlInSe}_2 - \text{TlGaSe}_2$ system, solid solutions crystallize in the structural types of the initial ternary compounds TlGaSe_2 with a break in the solid line at a concentration of 40-55 mol%. In $\text{TlIn}_x\text{Ga}_{1-x}\text{Se}_2$ films, a heterogeneous region is observed, and the liquidus minimum corresponds to the eutectic point.

The study of structural and phase transitions of these materials is necessary both for their practical application and for the fundamental study of their electronic energy structure. The relevance of the study of solid solutions based on $\text{TlInSe}_2 - \text{TlGaSe}_2$ is due to their capabilities in obtaining new semiconductor materials.

It is known that ternary thallium sulfides of gallium and indium crystallize in an identical structure derived from TlSe . Their crystals belong to the tetragonal system and have similar lattice parameters. The results of thermal analysis of alloys of the $\text{TlInS}_2 - \text{TlGaS}_2$ system showed the presence of a continuous series of solid solutions with a minimum of the composition $\text{TlIn}_{0.8}\text{S}_2 - \text{TlGa}_{0.2}\text{S}_2$ at temperatures above 700°C (Fig. 5). Alloys of the $\text{TlInS}_2 - \text{TlGaS}_2$ system are easily split plates and have a color that varies from yellow to green, depending on the composition.

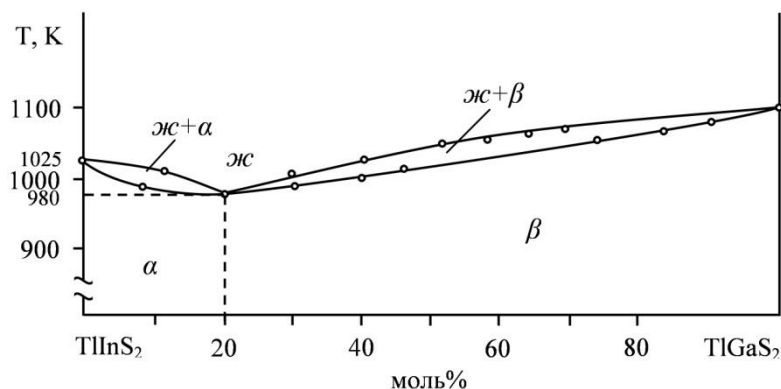


Fig. 5. System equilibrium diagram $\text{Tl} - \text{In} - \text{Ga} - \text{S}$ ($\text{TlIn}_{0.2}\text{Ga}_{0.8}\text{S}_2$).

When studying the microstructure, it was found that alloys based on TlInS_2 have a stripe structure. Only near the grains of TlGaS_2 solid solutions have a tetragonal structure. Examining the microstructure of the films, one can see that the banded structure begins in films of the composition $\text{TlIn}_{0.3}\text{Ga}_{0.7}\text{S}_2$. Consequently, the modification transition characteristic of TlInS_2 also occurs in the $\text{TlInS}_2 - \text{TlGaS}_2$ system itself and is observed up to the composition $\text{TlIn}_{0.3}\text{Ga}_{0.7}\text{S}_2$. To establish the region of homogeneity and degree of ordering of the structures of solid solutions in the $\text{TlInS}_2 - \text{TlGaS}_2$ system, an x-ray analysis of the alloys of this system was carried out (Fig. 6).

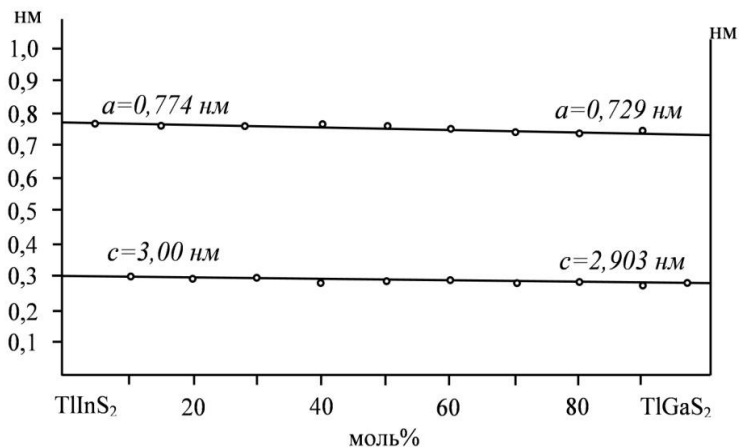


Fig. 6. Dependence of lattice parameters on composition in the TlInS₂ – TlGaS₂ system

The constancy of the structure over the entire concentration range of solid solutions is apparently associated in this case with isostructurality of the TlInS₂ and TlGaS₂ compounds. For the solid solutions studied, no deviation from Vegard's law for the composition-lattice parameter relationship was observed. Analysis of experimental data on solid solutions of the TlInS₂ – TlGaS₂ system shows that these solid solutions crystallize based on a tetragonal structure.

In the second chapter, the influence of atoms of some elements of group IV on the formation and phase formation of thin films included in the group of compounds A³B³C₂⁶ is determined. Here, experimental data on the formation of nanosized films TlIn_{1-x}Sn_xTe₂ (Se₂, S₂) and TlGa_{1-x}Ge_xTe₂ (Se₂, S₂), obtained as a result of reactions of interaction of atoms of chemical elements, and formation of crystallographic phases in the above systems. Consistently carried out various stages of the process of obtaining structurally formed films of strictly stoichiometric compositions containing easily oxidized and easily volatile components were carried out in a multi-position vacuum installation in a single cycle. When studying the processes of interaction and formation of phases in the Tl – In (Ga) – Te (Se, S) system with Sn and Ge impurities, we used generally accepted practice, which allows us to control the geometric thickness of the deposited films. The distribution of the condensate composition along the

plane of the film condensation surface was determined using the formula

$$q = \frac{Q}{4\pi h^2} \frac{1}{(1 + \alpha)^{3/2}}. \quad (1)$$

Here q is the amount of substance per unit plane of the substrate surface, Q is the amount of evaporated substance, h is the distance from the source of evaporation to any point along the condensate plane, coefficient $\alpha = x/h$, where x is the distance from the point directly under the evaporator to any point on the plane of the substrate. The thickness of films obtained by vacuum evaporation was calculated using the formula

$$q = q/\rho, \quad (2)$$

where ρ is the density of the substance in g/cm^3 . In addition, the film thickness was controlled by a Spekord-210 Plus spectrometer, and the composition was controlled by a Shimadzu atomic absorption spectrophotometer AA -6300." This allowed us to carry out electron diffraction structural analysis. Structural electron diffraction, based on the kinematic approximation of electron scattering theory, is successfully used in determining the structures of solid solutions of thin films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2(\text{Se}_2, \text{S}_2)$ and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2(\text{Se}_2, \text{S}_2)$.

Compounds $\text{TlInTe}_2(\text{Se}_2, \text{S}_2)$ and $\text{TlGaTe}_2(\text{Se}_2, \text{S}_2)$ are typical representatives of non-full-valent semiconductor compounds of the type $\text{A}^3\text{B}^3\text{C}_2^6$, which have a specific crystal lattice structure. From this point of view, it is of interest to use elements of the fourth group as impurities for the above compounds. It should be noted that comparison of the obtained results with similar films without impurities on the basis of the above theory is justified if the thin films are homogeneous, have a high degree of purity, a low concentration of structural defects and plane-parallel surfaces.

The thin films under study can be obtained using molecular beam epitaxy, metal-organic chemical vapor deposition, hybrid vapor-phase epitaxy, etc. To obtain films, we used the method of thermal evaporation from tungsten crucibles. In this work, using electron diffraction analysis, the degree of influence of small additions of Sn and Ge impurities on the crystal structure of thin films of $\text{TlInTe}_2(\text{Se}_2, \text{S}_2)$ and $\text{TlGaTe}_2(\text{Se}_2, \text{S}_2)$, and the orientation relationships ex-

isting between the epitaxial film and the substrate were established.

Films of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($x=0.01 \div 0.09$) with a thickness of 30 nm were obtained by evaporation of the synthesized substance, a ternary compound and impurities, four pure chemical elements through one, two and four tungsten furnaces, respectively, onto substrates of fresh chips of NaCl, KJ, KCl and celluloid (deposition rate ~ 5 nm/s), in a vacuum at a residual pressure above $\sim 10^{-4}$ Pa. Substrate temperature T_p varied in the temperature range $220 \div 570$ K. The resulting films were studied in an EMR-102 installation using the high-energy electron diffraction method, the accelerating voltage being 75 kV.

Films $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{0.96}\text{Ge}_{0.04}\text{Te}_2$ (Se_2 , S_2), deposited on the above substrates, had an amorphous structure with values $S=4\pi s \sin\theta/\lambda=14.66, 32.91, 40.68 \text{ nm}^{-1}$; $21.02, 34.86, 51.85 \text{ nm}^{-1}$; $27.34, 38.26, 47.81 \text{ nm}^{-1}$ and $S=4\pi s \sin\theta/\lambda=21.06, 32.88, 49.73 \text{ nm}^{-1}$; $21.51, 34.24, 45.16 \text{ nm}^{-1}$; $23.63, 36.52, 56.06 \text{ nm}^{-1}$, respectively, i.e. Three maxima are observed on the electron scattering intensity curve depending on the scattering angle (Fig. 7-9). This short-range order parameter provides certain information about the three coordination spheres. Here q is the scattering angle of the diffracted beams l and is the wavelength of the electrons. It should be noted that the figures showing the electron scattering intensities are given only for $\text{TlGa}_{0.96}\text{Ge}_{0.04}\text{Te}_2$ (Se_2 , S_2) films, since graphically these curves for $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ (Se_2 , S_2) have insignificant differences.

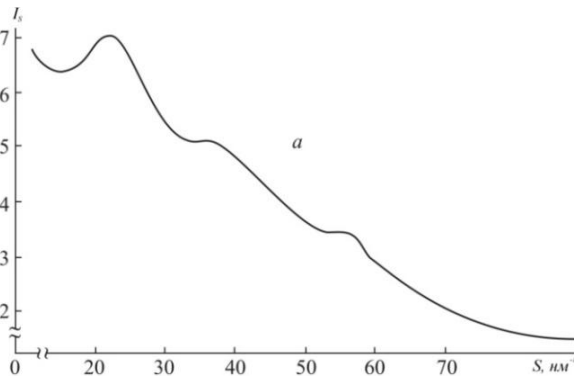


Fig. 7. Electron scattering intensity curve for an amorphous $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ film.

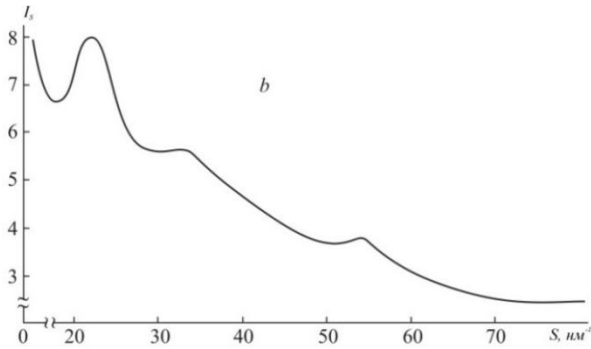


Fig. 8. Electron scattering intensity curve for an amorphous $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ film.

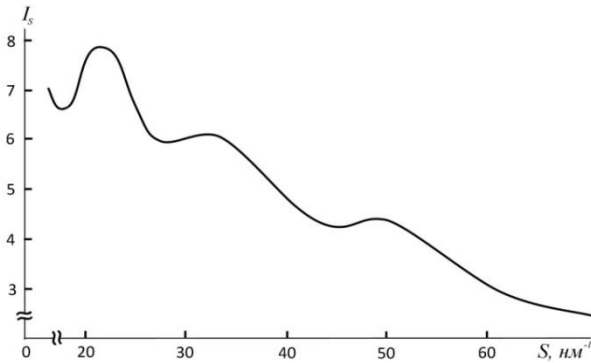


Fig. 9. Electron scattering intensity curve for an amorphous $\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$ film.

The amorphous phase of nanosized films $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ (Se_2 , S_2) is formed in vacuum on the indicated substrates located at temperatures $T_p = 220$ K, 390 K and $T_p = 313$ K, respectively. Under the same conditions for obtaining amorphous phases for $\text{TlGa}_{0.96}\text{Ge}_{0.04}\text{Se}_2$ (S_2) films, the substrate temperature is up to $T_p = 423$ (390) K, and for $\text{TlGa}_{0.96}\text{Ge}_{0.04}\text{Te}_2$ – up to $T_p = 240$ K. To prevent oxidation of $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ films were placed in a carbon capsule 3÷5 nm thick.

Crystallization of amorphous films of $\text{TlGa}_{0.96}\text{Ge}_{0.04}\text{Te}_2$ systems (Se_2 , S_2) leads to the formation of polycrystalline $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ with tetragonal lattice parameters $a = 0.8995$; $c = 0.7483$ nm, $Z = 6$, OPO I 4/mcm, $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Se}_2$ films with lattice parameters $a = 0.8355$; $c = 0.7021$ nm, $Z = 4$, OPO I 4/mcm of tetragonal system, and the $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{S}_2$ film is formed with three different lattice sys-

tems: (I.) monoclinic system – $a=0.813$; $b=0.796$; $c=2.485$ nm, OPO $P2_1/m$; (II.) rhombic system – $a=0.687$; $b=0.399$; $c=1.567$ nm, OGS D_{6h}^2 and (III.) tetragonal system $a=0.808$; $c=3.098$ nm, $Z=4$, OGS $I4/mcm$.

Crystallization of amorphous films leads to the formation of polycrystalline $TlGa_{0.96}Ge_{0.04}Te_2$ with tetragonal lattice parameters $a=0.897$; $c=0.713$ nm, $Z=4$, OPO $I4/mcm$, the $TlGa_{0.96}Ge_{0.04}Se_2$ film is formed with lattice parameters $a=1.120$; $c=1.606$ nm, $Z=4$, PGS $C_5^4 - C_c$ monoclinic system, and the $TlGa_{0.96}Ge_{0.04}S_2$ film – with lattice parameters $a=1.093$; $c=1.564$ nm, $Z=16$, PGS C_{2h}^6 monoclinic system. The values of the unit cell parameters we obtained are greater than the similar parameters of unit cells without impurities, as shown in Table 1. Here $a_{b,p}$, $c_{b,p}$ – are the parameters of the unit cells of ternary compounds without impurities. These relationships show that impurity atoms influence the formation of the crystal structure.

Table 1. Influence of impurities on unit cell parameters

Films	$a_{b,p}$ (%)	$c_{b,p}$ (%)
$TlIn_{0.96}Sn_{0.04}Te_2$	5.9	4.2
$TlIn_{0.96}Sn_{0.04}Se_2$	3.5	2.3
$TlIn_{0.96}Sn_{0.04}S_2$ (I)	4.6	3.4
$TlIn_{0.96}Sn_{0.04}S_2$ (II)	4.7	4.9
$TlIn_{0.96}Sn_{0.04}S_2$ (III)	4.4	3.2
$TlGa_{0.96}Ge_{0.04}Te_2$	6.4	3.8
$TlGa_{0.96}Ge_{0.04}Se_2$	4.0	2.7
$TlGa_{0.96}Ge_{0.04}S_2$	5.1	3.1

Polycrystalline films $TlIn_{0.96}Sn_{0.04}Te_2$, $TlIn_{0.96}Sn_{0.04}Se_2$ and $TlIn_{0.96}Sn_{0.04}S_2$ are formed on substrates (NaCl, KJ, KCl) in the temperature range $T_p=268\div468$ K, $T_p=413\div483$ K and (I) $T_p=403\div478$ K, (II) $T_p=393\div468$ K, (III) $T_p=388\div453$ K, respectively. Films with the same crystalline phase $TlGa_{0.96}Ge_{0.04}Te_2$, $TlGa_{0.96}Ge_{0.04}Se_2$ and $TlGa_{0.96}Ge_{0.04}S_2$ are obtained on the above substrates in the temperature range $T_p=365\div390$ K, $T_p=430\div453$ K and $T_p=400\div433$ K, respectively (Fig. 10-12). As the substrate temperature increases to $T_p=443$ K for $TlGa_{0.96}Ge_{0.04}S_2$ and to $T_p=463$ K for $TlGa_{0.96}Ge_xSe_2$, the monoclinic system undergoes a temperature-irreversible phase transformation and

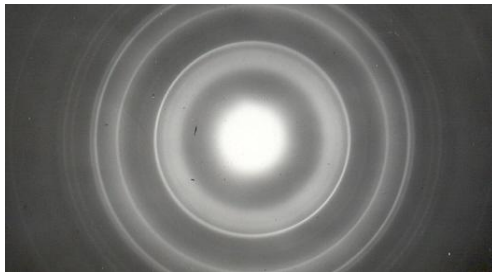


Fig. 10. Electron diffraction pattern from a $\text{TI Ga}_{1-x}\text{Ge}_x\text{Te}_2$ polycrystal

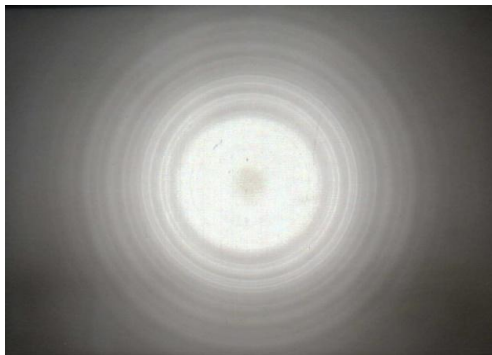


Fig. 11. Electron diffraction pattern from a $\text{TI Ga}_{1-x}\text{Ge}_x\text{Se}_2$ polycrystal

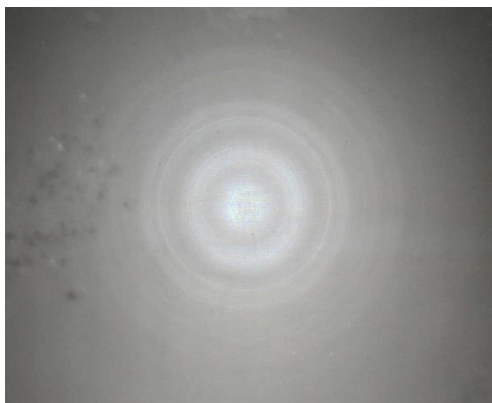


Fig. 12. Electron diffraction pattern from a $\text{TI Ga}_{1-x}\text{Ge}_x\text{S}_2$ polycrystal

transforms into a tetragonal system with crystal lattice parameters: $a=b=0.764$, $c=3.083$ nm, $Z=16$, OGS I $4/m\bar{c}m$ and $a=b=0.837$, $c=0.659$ nm, $Z=4$, ASG I $4/m\bar{c}m$. The coexistence of these two

structures, caused by the phase transition process, is apparently accompanied by a strong change in the coordination of atoms and the characteristics of the bonds between them. Electron diffraction patterns taken at an angle $\varphi=30\div 60^\circ$ relative to the incident electron beam make it possible to determine the crystal lattice period “c”.

With a further increase in the temperature of the substrates to $T_p=433$ K for the $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ condensate, for the $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Se}_2$ film to $T_p=403$ K and for $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{S}_2$ (I-III) to $T_p=463; 453; 445$ K oriented crystalline blocks are formed. The same blocks are formed in $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2, S_2) films when the substrates are heated to $T_p=413$ K ($T_p=513$ K, $T_p=453$ K). However, as the diffraction pattern shows, the resulting texture is imperfect. In addition, it was found that in the $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ (Se_2, S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2, S_2) films a textured crystalline phase is formed with the “c” axis perpendicular to the substrate (Fig. 13-15).

Single-crystal films of $\text{TlIn}_{0.96}\text{Sn}_{0.04}\text{Te}_2$ (Se_2, S_2) were formed on NaCl, KJ, KCl substrates heated to a temperature $T_p=473$ K ($T_p=451$ K, $T_p=505$ K). Subsequent increase in the temperature of the above substrates to $T_p=435$ K for $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$, to $T_p=530$ K for $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ and to $T_p=480$ K for $\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$ leads to the formation of a mosaic single crystal. With a further increase in temperature, an increase in the intensity of point reflections is observed in the electron

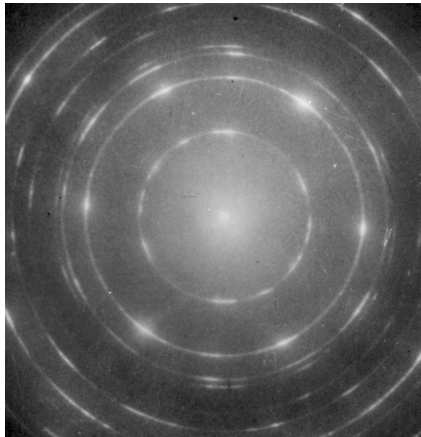


Fig. 13. Photo from textured $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ films

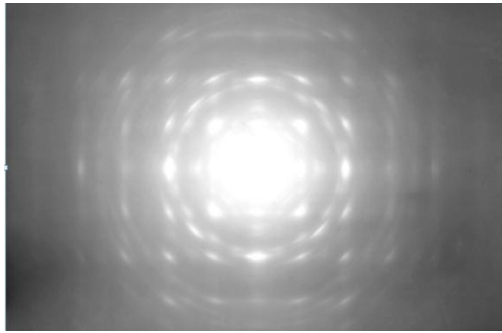


Fig. 14. Snapshot from textured $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ films

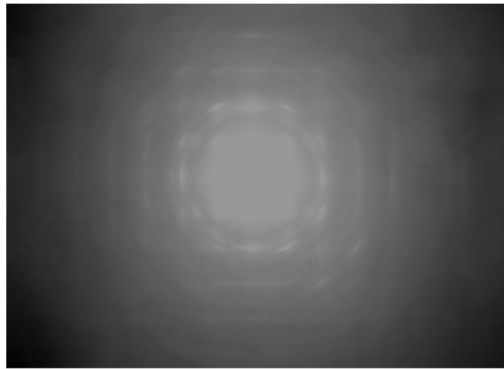


Fig. 15. Photo from textured $\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$ films

diffraction patterns, which indicates the formation of single crystal blocks with varying degrees of perfection. The intensities of reflections characteristic of a polycrystal decrease and gradually disappear. When the temperature of the NaCl, KJ, KCl substrates increases to ~ 453 K, ~ 563 K and ~ 503 K, more perfect single-crystal films $\text{TlGa}_{1-x}\text{G}_x\text{Te}_2$, $\text{TlGa}_{1-x}\text{G}_x\text{Se}_2$ and $\text{TlGa}_{1-x}\text{G}_x\text{S}_2$ are formed. The indication of the diffraction pattern from the crystalline phase, taken at right angles, is in good agreement with the parameters of the above tetragonal cell.

The resulting epitaxial films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{G}_x\text{Te}_2$ (Se_2 , S_2) are oriented by the (111) and (100) planes parallel to the (100) face of the substrate. Note that in most cases the planes of predominant segregation of impurities are the (111) planes. Thus, during the deposition of $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($x=0.01\div 0.09$) films by thermal evaporation onto substrates of single-crystalline NaCl, KJ,

KCl and amorphous celluloid at different temperatures, phases with different substructures are formed with increased parameters of the unit cells of the crystal structure, thereby changing the syngony. The addition of small amounts of impurities led to an increase in the temperature range for the formation of the amorphous phase, and for all other resulting substructures, to a change in the temperature of film formation. It has been established that one of the ways to obtain homogeneous highly oriented single crystal films with a minimum number of defects is to vary the lattice parameters.

The third chapter is devoted to research by high-energy electron diffraction of short-range order of nanothick amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2). In compounds included in the group $A^3B^3C_2^6$, it seems possible to smoothly change the parameters of the crystal lattice by introducing atoms of the chemical elements Sn and Ge. Therefore, studying the processes of formation of films with an amorphous structure and predicting their properties are of undoubted scientific and practical interest. It is known that in these compounds there is a correlation between their physical properties and structure. By changing the technological process for producing films, as well as by doping, it is possible to modify their structure. Amorphous substances, having less order, at the same temperatures and pressures are characterized by greater internal energy and entropy than substances in a crystalline state. Achieving states that correspond, at given values of temperature and pressure, to a minimum of internal energy requires the establishment of both certain distances between particles and certain configurations of their relative positions.

Amorphous films of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) with a thickness of ~ 30 nm were obtained in vacuum at a residual gas pressure of no more than $4 \cdot 10^{-5}$ Pa. In the first case, the starting materials were samples of single crystal $\text{TlIn}(\text{Ga})\text{Te}_2$ (Se_2 , S_2) and Sn (Ge), and in the second case, the single crystal $\text{TlIn}_{1-x}(\text{Ga}_{1-x})\text{Sn}_x(\text{Ge}_x)\text{Te}_2$ (Se_2 , S_2) ($x=0.01 \div 0.09$) was evaporated from tantalum, tungsten and molybdenum stoves. Fresh chips of alkali halide crystals NaCl, KCl, KJ, pre-coated with an ultrathin carbon film $3 \div 5$ nm thick, were used as substrates. The deposition rate of the substance is $\sim 5 \div 6$ nm/s. A prerequisite for the formation of amorphous

phases in the $\text{TlIn}_{1-x}(\text{Ga}_{1-x})\text{Sn}_x(\text{Ge}_x)\text{Te}_2$ system is preliminary cooling of the above substrates to a temperature of 220K.

To determine interatomic distances and coordination number (CN) of particles in amorphous films, the radial distribution functions of atoms (RADF) were calculated and the radial distribution curves of atoms (RADA) were plotted using the method of integral equations, which are based on the formula

$$4\pi r^2 \sum_m K_m U_m(r) = 4\pi r^2 U_o(r) \sum_m K_m + \frac{2r}{\pi} \int_0^\infty s \cdot i(s) \sin s r ds, \quad (3)$$

the function $i(s)$ was defined as

$$i(s) = \alpha \left[\frac{I_e(s)}{\sum_m f_m^2(s)} - \frac{I_s(s)}{\sum_m f_m^2(s)} \right] = \alpha i_i(s), \quad (4)$$

where α is the normalizing factor, $I_e(s)$ is the experimental scattering intensity, $I_s(s)$ is the average intensity. The value of the normalizing factor « α » is determined by the formula

$$\frac{1}{\alpha_{cp}} = \frac{1}{2} \left\{ \left[\frac{I_s(s)}{\sum_m f_m^2(s)} - \frac{I_e(s)}{\sum_m f_m^2(s)} \right]_{max} + \left[\frac{I_s(s)}{\sum_m f_m^2(s)} \right]_{min} \right\}. \quad (5)$$

The value of the upper limit of integration is $S=100 \text{ nm}^{-1}$. Based on the calculation of the FRRA carried out using the RADIADIS program, data on the values of short-range order parameters in the nanothick $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ film were obtained and the SRRA shown in Fig. 16 was constructed. The radius of the first coordination sphere in the amorphous film $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ is $r_1=0.292 \text{ nm}$. The sums of the covalent radii of In – Te atoms ($0.144+0.137=0.281 \text{ nm}$) are close to the corresponding values of r_1 obtained for the amorphous film $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$. The revealed value of $r_2=0.381 \text{ nm}$ corresponds to the distances between Tl-Te ions, and the third maximum, $r_3=0.475 \text{ nm}$, according to our assumption, corresponds to the distances between atoms of the same name.

The coordination number (CN) calculated from the areas under the first coordination maximum corresponds to $D_1(n_1)=4$. For the coordinating number calculated from the areas under the second and third coordination maxima, the results should be $D_2=6$ and $D_3=8$, respectively. And this indicates an octahedral environment of thallium

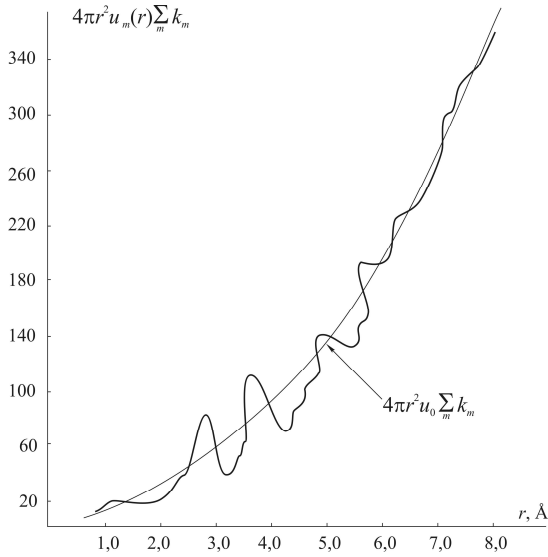


Fig. 16. Radial distribution curve of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ atoms.

atoms by tellurium ions in the first case and a tetrahedral environment by atoms of the same name in the second. However, experimental calculation of the areas of the second and third peaks under the corresponding maxima of the CRPA $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ gives overestimated CN values, $n_2=6.8$ and $n_3=8.2$. It should be assumed that in the structure of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ films the main matrix consists of octahedral and tetrahedral environments of atoms. However, in amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$, there are inhomogeneous regions enriched with Te atoms, in which a certain part of the thallium atoms has an environment consisting of eight tellurium atoms. The latter leads to a change in the shape of the structural units and the nature of their packing – a more dense packing of structural dimers.

When studying amorphous $\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$ films, the structural parameters of their short-range atomic order were determined. The CRPA of amorphous $\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$, given in Fig. 17, contains three maxima at $r_1=0.260$ nm, $r_2=0.368$ nm and $r_3=0.425$ nm. We interpret the distance $r_1=0.260$ nm as the average distance between In – Se atoms. The second and third coordination spheres with $r_2=0.368$ nm and $r_3=0.425$ nm can be interpreted as the average distances between Tl – Se and between atoms of the same name (Se – Se, Tl – Tl, In –

In), respectively. These distances are greater than the sum of the octahedral covalent radii of the Tl – Se ($r=0.313$ nm) and In – Se ($r=0.293$ nm) atoms.

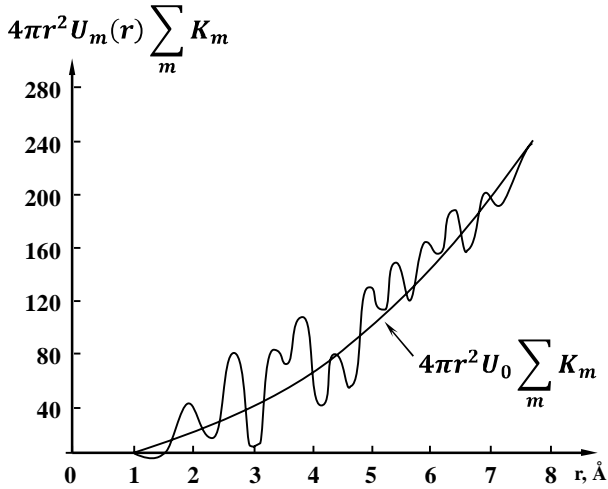


Fig. 17. CRPA of amorphous $\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$.

In the crystal lattice of $\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$ there are the same distances. Calculation of the area under the corresponding maxima of CRPA $\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$ showed that $D_1=25.9$; $D_2=39.1$ and $D_3=67.3$. The corresponding experimental values are $n_1=28.4$, $n_2=31.2$ and $n_3=67.6$, which are slightly less than the calculated values. And this can be explained by the fact that the Tl – Se distance in the second coordination sphere occurs with a higher probability than the In – Se distance, taking into account the influence of Sn atoms.

As we know, the film $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ ($x=0.01\div 0.09$) crystallizes in monoclinic, tetragonal and orthorhombic modifications, which we will further call the first, second and third amorphous forms ($\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ – I, $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ – II, $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ – III). When studying this film, covalent bonds were discovered between indium and sulfur atoms in $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ – I, $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ – III, as well as tetrahedral and octahedral surroundings of indium and thallium atoms by sulfur atoms. In $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ – II films, the main matrix consists of octahedral and tetrahedral environments of atoms with covalent bonds. Conse-

quently, one part of the thallium atoms is surrounded by six sulfur atoms, and the other by eight. And this, in turn, indicates a denser packing of structural units (dimers) compared to the first amorphous form $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$. These factors led to changes in the shape of structural units and the nature of their packaging.

Below are the results of studies of the radial distribution of atoms in thin films of $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($x=0.01\div 0.09$). The CRXA analysis of the studied amorphous films showed that the short-range order of the amorphous phases retains tetrahedral, octahedral, etc. structural motifs characteristic of crystal lattices. The coordination numbers in amorphous and crystalline nano-sized films remain unchanged.

Thus, it has been established that the difference between the crystalline and amorphous structures of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($x=0.01\div 0.09$), crystallizing in monoclinic, tetragonal and orthorhombic modifications, lies mainly in a certain spread of bond lengths in short-range orders and bond angles in tetrahedral and octahedral environments of atoms. Covalent bonds operating between atoms are preserved in both crystalline and amorphous films. Note that at large values of «x» the interaction reaction of Sn with In, Ge with Ga leads to the formation of substitutional solid solutions in a limited range in the above systems.

CRRA $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) relative to CRRA TlInTe_2 (Se_2 , S_2) and TlGaTe_2 (Se_2 , S_2) is characterized by a shift of the second maximum towards larger distances and an increase in its depth. Variations in r values of 2-4% are likely due to the influence of an atom of the chemical element tin.

The fourth chapter presents the results of studies of the kinetics of the crystallization process of nanothick amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($x=0.01\div 0.09$). The film data was obtained in a vacuum of $\sim 10^{-5}$ Pa in the absence of external influences and under the influence of a constant electric field of 3000 V cm^{-1} by condensation of the evaporated substance onto NaCl, KCl and KJ substrates. In order to prevent oxidation and changes in the composition of films, they placed in a carbon capsule.

According to the kinetic and thermodynamic criteria for the formation and growth of new phases, phase transformations over time in

all cases are thermodynamically caused by the emergence of centers of a new phase in the volume of the original phase and their subsequent growth. The kinetics of the crystallization process is determined by two interrelated parameters: 1) the rate of formation of centers of a new phase – nuclei – in the «Mother phase»; 2) linear growth rate of crystallization centers. However, this approximation does not take into account the statistical nature of the overlap of growing centers of the new phase and essentially solves the only problem of the transformation time, while the initial volume is filled with emerging and growing nuclei of the new phase.

The kinematic electron diffraction pattern shows that the diffraction lines of the crystalline phase increase with annealing time, and the diffuse lines of the amorphous phase weaken and then disappear (Fig. 18). Studying the intensity of lines characterizing the crystalline phase after certain annealing time intervals makes it possible to judge the amount of crystallized phase.

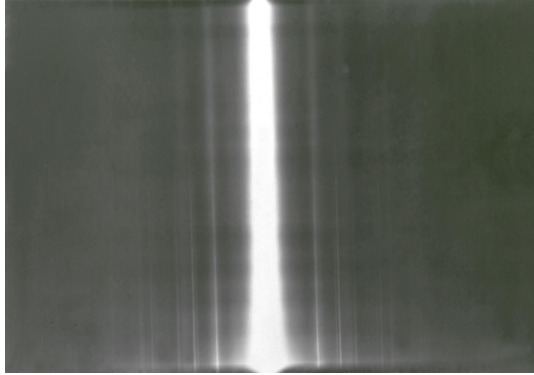


Fig. 18. Kinematic electron diffraction pattern amorphous $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$.

I_{hkl} lines was related to the irradiated volume of the crystalline substance by the relation

$$I_{hkl} = I_0 \lambda \left| \frac{\Phi_{hkl}}{\Omega} \right|^2 V \frac{d_{hkl}^2 \Delta P}{4\pi L \lambda}. \quad (6)$$

Here I_0 is the intensity of the primary radiation beam, λ is the electron wavelength, Φ is the structural amplitude of diffraction reflection, which in the kinematic approximation is calculated from atomic scattering factors, Ω is the volume of the unit cell, V is the irradiated

volume of the polycrystalline preparation, d_{hkl} and Δ interplanar distance and a small section of the Debye ring, P is the repeatability factor of the diffraction reflection amplification, $L\lambda$ is the device constant, which is determined depending on the applied voltage of the accelerating electrons. In this case, $I_{hkl} \sim V$ can be considered a good approximation.

The intensities of the lines of the growing crystalline phase of films of the above composition were determined using a microphotometer from various sections of the kinematic electron diffraction pattern. The transition from intensity values to the amount of crystallized substance is carried out by normalization: the maximum intensity value is compared with the completely crystallized volume of the substance, which makes it possible to find the volume of the crystallized part of the substance depending on the annealing time. In accordance with the above, crystallization isotherms were plotted (Fig. 19).

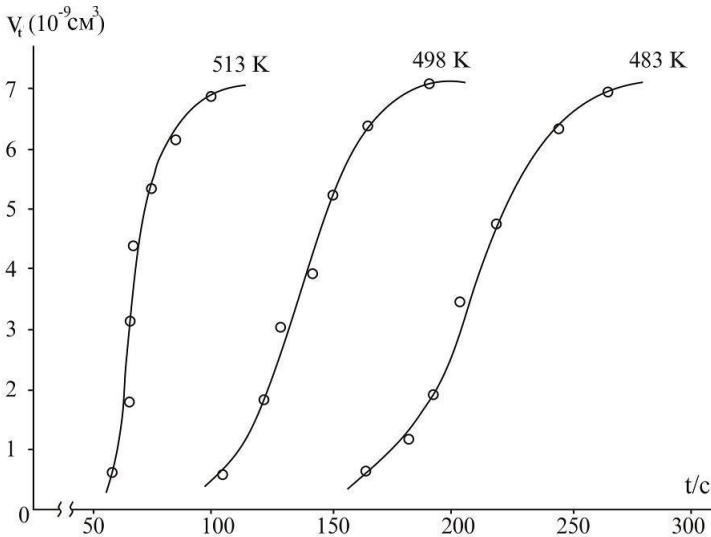


Fig. 19. Kinetic crystallization curves amorphous films $\text{TI Ga}_{1-x}\text{Ge}_x\text{Se}_2$.

As a result of the analysis of kinematic electron diffraction patterns of amorphous films crystallizing at appropriate temperatures and for a certain time, isothermal curves were obtained, which are described by the analytical expression of the kinetic curves of phase transformations established by Avrami-Kolmogorov:

$$V_t = V_0[1 - \exp(-kt^m)]. \quad (7)$$

Here V_t is the volume of the crystallized substance at time t , V_0 is the volume of the amorphous phase at the beginning of the process, where k is the reaction rate constant, and the value of m characterizes the dimension of crystal growth. Using this kinetic equation, the patterns of nucleation (v_3) and growth of crystals (v_p) at constant rates are established. It is known that the rate of emergence of nuclei of a new phase per unit of unconverted volume (v_3) and the linear growth rate of crystals (v_p) obey the Arrhenius equation, then

$$\ln K = A - \frac{1}{RT} (U_3 + 3U_p), \quad (8)$$

where U_3 – activation energy of nucleation, U_p is the activation energy for crystal growth, A is the product of the shape coefficient and the linear growth rate ($k_s \cdot v_p$) (Fig. 20).

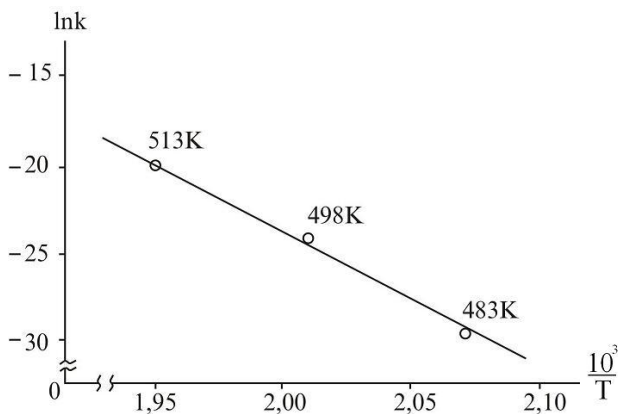


Fig. 20. Dependence of $\ln k$ on inverse temperature for crystallization of amorphous $TlGa_{1-x}Ge_xSe_2$

The distances in the immediate environment of atoms in films formed under conditions of condensate deposition in a constant electric field change. This change lies in the fact that the atoms are additionally charged and the bonds between atoms are lengthened, and as a result, crystallization parameters such as activation energies of nucleation and growth turn out to be lower compared to similar parameters of crystallizing films obtained outside the electric field (Table 2).

Table 2. Kinetic parameters of crystallization of amorphous films of solid solutions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2).

Solid solution films	Electric field strength (E), V cm^{-1}	m	Activation energy		
			U_{total} , kcal/mol	U_z , kcal/mol	U_r , kcal/mol
$\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$	0	4	74.16	26.39	15.92
	3000		62.56	19.92	14.21
$\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$	0	3	49.85	17.79	16.03
	3000		44.92	16.06	14.43
$\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2 - \text{I}$	0	4	50.2	18.1	10.7
	3000		42.7	15.4	9.1
$\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2 - \text{II}$	0	4	52.3	19.3	11.0
	3000		45.5	16.8	9.6
$\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2 - \text{III}$	0	4	53.4	20.1	11.1
	3000		47.8	18.1	9.9
$\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$	0	4	67.04	21.65	15.12
	3000		62.05	20.31	13.91
$\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$	0	4	44.1	15.3	9.6
	3000		40.9	14.4	8.8
$\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$	0	4	62.77	20.85	13.97
	3000		58.16	19.58	12.86

It was determined that for these compounds, depending on the composition of the substitutional solid solution, the effective activation energy of crystallization increases from 4% to 11 %. An increase in the crystallization temperature range of amorphous films by $60 \div 80^\circ\text{C}$ was discovered. As can be seen from the table, during the crystallization process an electric field effect is observed, which is reflected in the activation energy of crystal growth. Obtaining underestimated values of activation energies by $7 \div 16$ % for the crystallization of amorphous films of solid solutions obtained in a constant electric field, is explained by the fact that during the formation of thin films, amorphous seed molecules are additionally charged. The effect of the electric field leads to an acceleration of the crystallization process, a decrease in the temperature of phase transformations and causes a decrease in the values of activation energies. The resulting charge gradient initiates the acceleration of the crystallization process of films with nonequilibrium states. Since the electric field is of an electrostatic nature, the effect of the field on condensates

formed in the amorphous state can also be explained by its interaction with electrically charged point defects or their accumulations in thin films. But in this case, the issue of overlapping the nuclei of the new phase with each other and the resulting volume is not considered.

The fifth chapter presents the results of studies of the processes of formation of films of solid solutions of compositions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) with superstructural cells and the formation of epitaxial films. Currently, three methods are known that constitute the main directions of the search for superlattices, the emergence of which leads to the emergence of new properties of materials: 1) modulated spatial distribution of impurities in semiconductors; 2) periodic combination of both physically and chemically compatible semiconductor layers; 3) oriented crystallization, which makes it possible to grow homogeneous, highly perfect single-crystal films with a minimum number of defects. The task was to consider the influence of Sn and Ge impurities on the formation of epitaxial films of the above solid solutions obtained by the method described in previous chapters. The possibility of phase transitions from one modification to another and the formation of superstructures commensurate with one or another phase was also studied here.

$\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) solid solutions are formed on NaCl, KCl and KJ substrates located in the temperature range $T_p=508\div 563\text{K}$ and $T_p=505\div 573\text{K}$, with heat treatment duration from 10 to 40 minutes. After heat treatment, these samples were brought to room temperature in a vacuum at a speed of $7\div 21\text{K/min}$ for subsequent electron diffraction studies. Using a copper-constantan thermocouple, the temperature of the porcelain bench on which the substrates with the film were located was measured.

$\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2) films are displayed in a tetragonal cell with tripled and fivefold increased crystal lattice parameters in relation to the initial phase: $2.505\leq a\approx 3a_0\leq 2.761\text{ nm}$; $2.103\leq c\approx 3c_0\leq 2.259\text{ nm}$ and $3.831\leq a\approx 5a_0\leq 4.065\text{ nm}$; $2.584\leq c\approx 4c_0\leq 2.703\text{ nm}$, which confirms the formation of superstructural films of substitutional solid solutions. The unit cell of the superstructural phase was conjugated with two cells of the NaCl substrate. The mismatches between the mating substrate-film grids were ~ 2.3 and 2.5% . The orientation relationships

during the epitaxial growth of the solid solution films under study can be expressed as follows: (100) $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ // (001) NaCl and (110) $\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$ // (001) NaCl.

In previous chapters, the study involved the formation of monoclinic, tetragonal and orthorhombic phases $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ during the crystallization of amorphous films in an isothermal regime. As a result of heat treatment of these epitaxial films on KJ substrates at a temperature $T_p=508$ K for 10 minutes, followed by cooling to room temperature at a rate of $\sim 12\div 21$ K/min, films of the superstructural phase $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ of only the tetragonal modification were formed, which had lattice periods tripled relative to the initial phase: $2.190\leq a\approx 3a_0\leq 2.361$ nm; $8.476\leq s\approx 3s_0\leq 8.954$ nm. The unit cell of the superstructural phase was conjugated with three cells of the substrate KJ. The discrepancies between the mating substrate-film grids were $\sim 3.5\%$. The orientation relationships during the epitaxial growth of the films under study can be expressed as follows: (100) $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ // (001) KJ.

During heat treatment of the resulting epitaxial films $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ and $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ ($x=0.01\div 0.09$) on KJ and NaCl substrates at temperatures $T_p = 495\text{K}$ and $T_p = 573\text{K}$ for a duration of $20\div 30$ minutes, followed by cooling to room temperature at a speed $\sim 12\div 21$ K/min, the formation of films of the superstructural phase of solid solutions was observed. When forming $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ films on NaCl and KJ substrates, one unit cell of the superstructural phase is conjugated with three NaCl cells and two KJ cells, and the relative mismatch of the conjugating networks is $\sim 2\text{-}3\%$. The (100) plane of the films is parallel to the (100) NaCl and KJ substrates. When calculating, it was established that one unit cell of the superstructural phase $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ is conjugated with two NaCl cells, and the relative mismatch of the conjugating networks is $\sim 2.6\%$.

On KCl, KJ substrates with an epitaxial film, heated to a temperature of ~ 553 K and held in this mode for 30 minutes, followed by slow cooling, perfect single-crystal films of $\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$ solid solution with a superstructural phase were obtained.

These single-crystalline solid solutions of substitution by the superstructural phase are oriented by (100) planes parallel to the (100)

KJ faces. Each elementary cell of the superlattice is mated with three cells of the substrate, and the relative mismatch of the mating networks is about 3.2%. The superstructural phase created by impurity Ge atoms leads to statistical deviations of atoms from their positions. In this case, the superlattice $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) ($x=0.01\div 0.09$) with tetragonal system has double and triple periods in relation to the initial phases: $1.624\text{Å}\approx 2a_0$ 1.813 nm ; $1.317\text{Å}\approx 2s_0$ 1.408 nm , $1.545\text{Å}\approx 2a_0$ 1.657 nm ; $1.227\text{Å}\approx 2s_0$ 1.288 nm and $2.169\text{Å}\approx 3a_0$ 2.366 nm ; $5.903\text{Å}\approx 2s_0$ 6.236 nm .

Impurity atoms in solid solutions $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ and $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$ cause deformation of the crystal lattices of films in superstructural phases. Atoms that replace each other have different valences. Since the lattice as a whole must be neutral, the initial trivalent matrix ions $\text{Ga} (3^+)$ in ternary compounds are replaced by tetravalent Ge ions (4^+) with charge compensation by the corresponding number of holes-electronic vacancies. The formation of substitutional solid solutions based on superlattices explains the strong scatter of superlattice constants observed in electron diffraction patterns from single-crystal films of $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ and $\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$.

The superstructural phases studied in this work were formed as a result of statistical deviations of atoms from their positions under the influence of Sn and Ge impurity atoms. In this case, the periods of the superlattices of the above films of solid solutions, regardless of system, increased two, three times, or even more in relation to the initial phases. The formation of superstructural phases may be due to the structurally insensitive diffusion of impurities along the boundaries of nuclei, i.e. diffusion of impurities occurs directly through large blocks of solid solutions that make up single-crystalline superstructure films.

Thus, we were able to determine the effect of the principle of size correspondence during epitaxy and to clarify the influence of the orienting single-crystal substrate and its temperature on the epitaxial growth and formation of superstructures of nanothick films of solid solutions. We believe that Sn and Ge atoms are located at the sites of the crystal lattice. Parameters of unit cells of superstructures of solid solutions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{G}_x\text{Te}_2$ (Se_2 , S_2) linearly

depend on the concentration of impurities and obey the pattern established by Vegard. Linearity is violated only in a small composition range. The conducted electron diffraction study of the mechanisms of formation of single-crystal films is directly related to the application of superstructure films, the establishment of the conditions for the formation of which is of fundamental importance for all aspects of epitaxial films. The results obtained on superstructures, about which there is not much information, are interpreted mainly in the structural aspect and can be used in the production of instruments and other products.

CONCLUSION

1. For the first time, as a result of chemical reactions occurring in the process of establishing chemical equilibrium of heterogeneous vacuum condensates of ternary compounds of $A^3-B^3-C_2^6$ systems doped with impurities of group IV of the periodic system of chemical elements, the most general patterns of phase formation in films of nanometer thickness have been established. The conditions for the formation of complexes of amorphous and crystalline phases of solid solutions of a number of compounds included in the $A^3B^3C_2^6$ group have been identified. The metastable and thermodynamically stable phases are shown at various stages along the path to equilibrium in the indicated system.

2. Tl-In (Ga)-Te (Se, S) systems doped with Sn and Ge impurities, the formation of amorphous and crystalline phases of solid solutions occurs during thermal deposition onto single-crystalline NaCl, KCl and KJ substrates. The resulting thin films of the compositions $TlIn_{1-x}Sn_xTe_2$, $TlGa_{1-x}Ge_xTe_2$, in contrast to films of $TlIn(Ga)Se_2(S_2)$ with impurities, turn out to be crystalline at room temperature. A prerequisite for the formation of amorphous phases in the $TlIn_{1-x}(Ga_{1-x})Sn_x(Ge_x)Te_2$ system is preliminary cooling of the above substrates to a temperature of 220K.

3. Lattice periods of substitutional solid solutions $TlIn_{1-x}Sn_xTe_2$ (Se_2, S_2), $TlGa_{1-x}Ge_xTe_2$ (Se_2, S_2) depending on the concentration of impurities ($0.01 \leq x \leq 0.09$) increase from 0.7% to 11%:

$\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$	$a'=0.8619\div 0.9522;$	$c'=0.7256\div 0.7795$
$\text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2$	$a'=0.8146\div 0.8651;$	$c'=0.6890\div 0.7196$
$\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2(\text{I})$	$a'=0.7862\div 0.8581;$	$c'=2.4235\div 2.5875$
$\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2(\text{II})$	$a'=0.6637\div 0.7253;$	$c'=1.5122\div 1.6578$
$\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2(\text{III})$	$a'=0.7825\div 0.8504;$	$c'=3.0267\div 3.2163$
$\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$	$a'=0.8555\div 0.9542;$	$c'=0.6930\div 0.7408$
$\text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2$	$a'=0.8131\div 0.8721;$	$c'=0.6463\div 0.6781$
$\text{TlGa}_{1-x}\text{Ge}_x\text{S}_2$	$a'=0.7748\div 0.8451;$	$c'=3.1069\div 3.2819$

4. The conditions for the formation of epitaxial thin films of substitutional solid solutions during phase transformations in $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) as a result of heat treatment on KCl, NaCl substrates have been established. The relative discrepancy between the periods of mating networks of solid solution films and substrates is $\sim 2.5\div 3.2\%$.

5. Conditions for the epitaxial growth of films of $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) solid solutions formed on NaCl and KJ substrates heated to the required temperature have been identified, while the relative discrepancy between the periods of the unit cells of the films under study with tetragonal system and the corresponding substrates is $\sim 2.2\div 3.8\%$.

6. The radial distribution curves of atoms in amorphous films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) were constructed using the method of integral equations. The interatomic distances between like and unlike atoms have been established, the parameters of short-range atomic order have been determined, i.e. radii of coordination spheres and coordination numbers.

7. For the first time, amorphous thin layers of compositions $\text{TlIn}(\text{Ga})\text{Te}_2$ (Se_2 , S_2) doped with Sn, Ge impurities were obtained, and the patterns of their formation on single-crystal substrates were revealed. It has been established that the temperature range for the formation of amorphous films increases by 7-11% depending on the doping level of nano-sized films.

8. It was discovered for the first time that amorphous films of $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) have short-range order structures similar to the structures of bulk crystal samples. The established covalent type of bond between atoms in amorphous films

indicates that these films retain semiconductor properties in the amorphous state. Amorphous films with tin and germanium impurities introduced into them have a more dense packing of atoms. The influence of impurities on interatomic distances in amorphous films has been established, which leads to a significant lengthening of interatomic bonds.

9. For the first time, the epitaxial relationships that exist between single-crystal films and the substrates on which they grow have been established. Single crystals of superstructure films $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2) and $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) are oriented by the (100) plane parallel to the (001) faces of NaCl, KCl, KJ. At high temperatures ($\sim 513\text{K}$) of substrates, superlattices arise due to the diffusion of impurities directly through large blocks of which single-crystal superstructure films are composed.

10. It has been determined that when doping compounds of the Tl-In(Ga)-Te_2 (Se_2 , S_2) Sn(Ge) atoms ($0.01 \leq x \leq 0.09$) form substitutional solid solutions with a monotonic change in lattice parameters. But in the range $x=0.05 \div 0.06$ impurities, a violation of the monotonicity of the change in lattice parameters was discovered. The influence of impurities on the kinetic parameters of phase transitions during the crystallization of amorphous nanothick layers has been established.

11. For the first time, phase transitions have been established during isothermal heat treatment of amorphous films of solid solutions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2), obtained in a constant electric field voltage 3000 V cm^{-1} and without it.

12. For the first time, it was established that the kinetics of crystallization of amorphous films of solid solutions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2) obeys the Abraham-Kolmogorov law and is described by the analytical expression $V_t = V_0[1 - \exp(-kt^m)]$. It has been shown that during the crystallization of amorphous films of solid solutions $\text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2$ (Se_2 , S_2), $\text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2$ (Se_2 , S_2), obtained both under the influence of an electric field and without it, two-dimensional and three-dimensional growth of crystalline nuclei occurs.

13. It has been established that the application of an electric field during the formation of films causes redistribution or transfercharges

and leads to an increase in the frequency of their equilibrium distribution. A constant electric field, playing a positive role, accelerates the process of formation and further growth of nuclei, while the activation energy values decrease by 10-15%.

14. The main crystal structures of the ternary compounds $\text{TlIn}(\text{Ga})\text{Te}_2$ (Se_2 , S_2) are ordered, however, the superstructural phases of solid solutions $\text{TlIn}_{1-x}(\text{Ga})\text{Sn}_x(\text{Ge})\text{Te}_2$ (Se_2 , S_2), Based on the noted compounds, they have more ordered lattices.

15. For the first time, the conditions for the nucleation of nanoparticles with the superstructure of substitutional solid solutions in single-crystal films of compounds of the chemical group $\text{A}^3\text{B}^3\text{C}_2^6$ doped with Sn and Ge impurities were revealed. Superstructural phases during heat treatment of epitaxial films on substrates are formed only with tetragonal syngony, the unit cell parameters of which, taking into account the impurity concentration ($x=0.01\div 0.09$), are given below:

$$\begin{aligned} \text{TlIn}_{1-x}\text{Sn}_x\text{Te}_2 &- 2.505 \leq a \approx 3a_0 \leq 2.761 \text{ nm}; & 2.103 \leq c \approx 3c_0 \leq 2.259 \text{ nm}; \\ \text{TlIn}_{1-x}\text{Sn}_x\text{Se}_2 &- 3.831 \leq a \approx 5a_0 \leq 4.065 \text{ nm}; & 2.584 \leq c \approx 4c_0 \leq 2.703 \text{ nm}; \\ \text{TlIn}_{1-x}\text{Sn}_x\text{S}_2 &- 2.190 \leq a \approx 3a_0 \leq 2.361 \text{ nm}; & 8.476 \leq c \approx 3c_0 \leq 8.954 \text{ nm}; \\ \text{TlGa}_{1-x}\text{Ge}_x\text{Te}_2 &- 1.624 \text{ \AA} \approx 2a_0 \leq 1.813 \text{ nm}; & 1.317 \text{ \AA} \approx 2c_0 \leq 1.408 \text{ nm}; \\ \text{TlGa}_{1-x}\text{Ge}_x\text{Se}_2 &- 1.545 \text{ \AA} \approx 2a_0 \leq 1.657 \text{ nm}; & 1.227 \text{ \AA} \approx 2c_0 \leq 1.288 \text{ nm}; \\ \text{TlGa}_{1-x}\text{Ge}_x\text{S}_2 &- 2.169 \text{ \AA} \approx 3a_0 \leq 2.366 \text{ nm}; & 5.903 \text{ \AA} \approx 2c_0 \leq 6.236 \text{ nm}. \end{aligned}$$

It should be noted that epitaxial films of the composition $\text{TlIn}_{1-x}\text{Sn}_x\text{S}_2$ are formed in three modifications – tetragonal, orthorhombic and monoclinic. These films in the orthorhombic and monoclinic systems have only a metastable imperfect superstructural phase.

16. Unit cells of superstructural solid solutions are conjugated with several cells of substrates, and their relative mismatch is on the order of 3-4%. The lattice periods of superstructural phases differ from the initial phases from 2 to 5 times.

17. It has been shown that the mechanism of the transition of initial phases to superstructural phases is associated with the degree of ordering of atoms in crystal lattices. Superstructures have long-range periodicity of crystal lattices and are formed as a result of disordering of the ordered initial phases.

18. The temperatures of the formation of superstructural phases of substitutional solid solutions exceed the temperatures of the for-

mation of epitaxial films, which leads to the ordering of defect positions of atoms (Te, Se, S).

19. The formation of a tetragonal modification of single-crystalline superstructural phases of solid solutions is due to the structurally insensitive diffusion of impurities along the boundaries of nuclei directly through large blocks of solid solutions, as well as statistical deviations of atoms from their occupied positions under the influence of impurity atoms.

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