

## ELECTRON DIFFRACTION INVESTIGATION OF PHASE TRANSITIONS IN $A^3B^3C_2^6$ COMPOUNDS

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By electron diffraction investigations peculiarities of film formation of  $A^3B^3C_2^6$  group compounds have been established. It is shown that the interval of amorphous film compositions obtained at room temperature is much higher than the interval in massive samples. There have been determined kinetic parameters of phase transformations in amorphous films  $TlInSe_2$ ,  $TlGaSe_2$  and  $TlInS_2$  obtained under the usual conditions and the influence of external field. There have been established 3 superstructural phases of  $TlGaSe_2$  and  $TlInTe_2$  compounds, two of them are formed as a result of epitaxial growth of  $TlGaSe_2$  for NaCl and one of  $TlInTe_2$  compound for KCl.

In  $A^3B^3C_2^6$  system there have been formed a number of ternary compounds  $TlInSe_2$ ,  $TlInS_2$ ,  $TlInTe_2$ ,  $TlGaSe_2$ ,  $TlGaS_2$ ,  $TlGaTe_2$  having special physical properties which are the results of strong anisotropy of bond forces between atom groups [1]. Structural characteristics of bulk samples concerning the group of semiconductor materials with the common formula  $A^3B^3C_2^6$  are given in table 1. There are a great number of works dedicated to different properties of these compounds. On the basis of the mentioned semiconductor materials there have been created sensitive elements of photodetectors, detectors of optic radiation, strain gauges and etc.

It is known that physical properties and in some cases the structure of semiconductor films obtained by vacuum evaporation differ from the properties of the single crystals of the corresponding composition. Many problems related to the diagram of state and phase equilibrium of  $A^3B^3C_2^6$  system

compounds are unsolved so far. Therefore, the investigation of phase formation, phase transformations and features of thin films substructures of abovementioned compounds obtained by vacuum condensation are of high-priority.

### I Phase composition of Tl-In-Se system.

According to data [12-13] in Tl-In-Se system at TlSe-InSe in the 1:1 ratio there have been found Tl InSe<sub>2</sub> compound. X – ray data [14-17] of some phases formed in TlSe-InSe system are contradictory. In [14] it is noted that In<sub>2</sub>Se<sub>3</sub> has a low – symmetric structure, so author can not induce the debaegram. In [17] the possibility of In<sub>2</sub>Se<sub>3</sub> existence in two modifications has been established, in [15-16] it is stated that In<sub>2</sub>Se<sub>3</sub> has at least three different modifications:  $\alpha$ ,  $\beta$  and  $\gamma$ . They are resistant:  $\alpha$  - at room temperature,  $\beta$ - over 473 K and  $\gamma$  - 779-873K. At present determination of crystal structure of  $\alpha$ - and  $\beta$  - modifications is considered to be finished.

Table 1. Structural parameters of thallium chalcogenides.

Description	Singony	Space group	Lattice periods and angles in degrees ( nm)				Num-ber of formula units (Z)	Note	Refer-ences
			a	b	c	$\beta$			
1	2	3	4	5	6	7	8	9	10
TlGaSe <sub>2</sub>	tetra-gonal	I4/mcm	0,7620		3,0500		16		[2]
TlGaSe <sub>2</sub>	tetra-gonal	I4/mcm	0,8053		0,6417		4	Faze of high pressure	[3]
TlGaSe <sub>2</sub>	mono-clinic	$C_s^4$ or $C_{2h}^6$	1,0770	1,0770	1,5620	100°	16		[4]
TlGaSe <sub>2</sub>	mono-clinic	P2 <sub>1</sub> /m	0,7260	0,7270	1,4900	90°20'	8		[5]
TlGaSe <sub>2</sub>	mono-clinic	$C_c(C_s^4)$	1,0772	1,0771	1,5636	100°6'	16		[6]
TlGaS <sub>2</sub>	tetra-gonal	I4/mcm	0,7290		2,9900		16		[2]
TlGaS <sub>2</sub>	mono-clinic	P2 <sub>1</sub> /m	0,7000	0,7600	6,2720	90°20'	32		[7]
TlGaS <sub>2</sub>	mono-clinic	$C_s^4$ or $C_{2h}^6$	1,0400	1,0400	1,5170	100°	16		[4]
TlInS <sub>2</sub>	tetra-gonal	I4/mcm	0,7740		3,0030		16		[2]

TlInS <sub>2</sub>	tetra- gonal	I4/mcm	0,8000		0,6720		4	$\alpha$ -mod	[8]
<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
TlInS <sub>2</sub>	tetra- gonal	I4/mcm	0,7680		2,9760		16	$\beta$ -mod	[8]
TlInS <sub>2</sub>	mono- clinic	$C_{s^4}^4$ or $C_{2h}^6$	1,0950	1,0950	1,5140	100°	16		[4]
TlInS <sub>2</sub>	mono- clinic	P2 <sub>1</sub> /m	0,7760	0,7760	3,0010	90°15'	1 6	$\beta$ -mod	[9]
TlInS <sub>2</sub>	Hexa- gon	P6/mcm	0,7670		1,4980		8	$\alpha$ -mod	[9]
TlInS <sub>2</sub> – II	hexa- gon	P3m	0,3830		2,2230		3	Faze of high pressure	[10]
TlInS <sub>2</sub> –III	Hexa- gon	P6/mcm	0,3830		1,4880		2		[10]
TlInS <sub>2</sub>	Rhom- bic	$D_6^2$	0,6560	0,3810	1,4940		4		[4]
TlInSe <sub>2</sub>	tetra- gonal		0,8075		0,6847		4		[11]
TlInSe <sub>2</sub>	tetra- gonal		0,8494		0,7181		4		[11]
TlInSe <sub>2</sub>	tetra- gonal		0,8429		0,6865		4		[11]

Existence of thallium selenides have been pointed in the diagram of Tl-Se system state: Tl<sub>2</sub>Se (16,19 weight % of Se,  $T_{m(melting)} = 563K$ ); TlSe (27,28 weight % of Se;  $T_{m(melting)} = 661K$ ) and Tl<sub>2</sub>Se<sub>3</sub> (36,69 weight % of Se). Tl<sub>2</sub>Se<sub>3</sub> is melted over the temperature range 547-553 K and has two points of transformation at 445K and 465K [18-19]. Existence of TlSe and Tl<sub>2</sub>Se compounds is confirmed by X-ray analysis, however, it is not confirmed for Tl<sub>2</sub>Se [14,20]. According to electronographic data [21] TlSe is crystallized in tetragonal lattice with constants:  $a = 0,852$ ;  $c = 1,268$  nm. In Tl-Se system composition of stoichiometric composition TlSe [22] is the most resistant and of interest as semiconductor.

## II Phase composition of films Tl-In-S system.

In Tl-S [18] according to the results of thermal and X-ray investigations there have been established four stoichiometric compounds: Tl<sub>2</sub>S, Tl<sub>4</sub>S<sub>3</sub>, TlS and TlS<sub>2</sub>. Only the phase of the Tl<sub>2</sub>S composition has a congruent melting point (623K). In papers [23-24] it is established that there are intermediate phases in Tl-S system: Tl<sub>2</sub>S<sub>5</sub> (28,6 at % of Tl), Tl<sub>8</sub>S<sub>17</sub> (32,0 at % of Tl), TlS (50,0 at % of Tl), Tl<sub>4</sub>S<sub>3</sub> (57,1 at % of Tl) and Tl<sub>2</sub>S (66,7 at % of Tl). With the regard of data [23-24] in [25] there have been given specified version of diagram of Tl-S system state. Phase Tl<sub>8</sub>S<sub>17</sub> in case of long storage at room temperatures and annealing breaks down into Tl<sub>2</sub>S<sub>5</sub> and TlS phases. In [25] there have been confirmed existence of Tl<sub>2</sub>S<sub>5</sub> which was under suspicion in [18]. Phase Tl<sub>2</sub>S<sub>5</sub> is formed peritectically from Tl<sub>8</sub>S<sub>17</sub> and sulphur. In [26] there have been pointed to the production of massive amorphous samples of TlS composition. In [2,4,8-9] existence of phase of TlInS<sub>2</sub> composition of different modification has been established.

Solid phases of In-S system are investigated in sections In-In<sub>2</sub>S<sub>3</sub>. Obtained results show that In<sub>3</sub>S<sub>4</sub> does not exist independently and appears in the region of solid solution on the base of In<sub>2</sub>S<sub>3</sub>(56,3 ÷ 60,0 at % of S) at 873K and 54,5 ÷ 60,0 at % of S at 973K. In [28] there have been found In<sub>2</sub>S as a

primary component – pair being in equilibrium with In<sub>2</sub>S. Melting temperature of In<sub>2</sub>S<sub>3</sub> is 1368K [29]. In [30-31] phase  $\beta$ -In<sub>2</sub>S<sub>3</sub> with tetragonal cell period is established:  $a = 0,7620$  nm;  $c = 3,2300$  nm relating to progressive symmetry I4/amd, with 16 formula units in elementary cell and being of non-ordering modification  $\alpha$ -In<sub>2</sub>S<sub>3</sub> is.

## III Phase composition of films of Tl-In-Te system.

According to state diagram in Tl-Te system the following phases are: Tl<sub>2</sub>Te<sub>3</sub>, TlTe, Tl<sub>2</sub>Te and  $\alpha$  - phase (Tl<sub>5</sub>Te<sub>3</sub>) [14,32-36]. There have been contradictory evidence about Tl<sub>2</sub>Te. In [32-34] Tl<sub>2</sub>Te phase is not revealed, in [14] existence of Tl<sub>2</sub>Te phase on the base of X-ray analysis of Tl and Te alloys is expected. The presence of Tl<sub>2</sub>Te phase in Tl-Te system is established by thermodynamic and roentgen investigations, and microhardness [35-36]. The structure of Tl<sub>2</sub>Te compound is not coded. Contradictory data about the existence of Tl<sub>2</sub>Te phase can be explained by complexity of preventing of oxidative processes during the work with Tl and its compounds, particularly with Tl<sub>2</sub>Te. In fact, authors [35] point to the instability of Tl<sub>2</sub>Te phase in the air. According to data [37], thallium hydroxide remaining in Tl<sub>5</sub>Te<sub>3</sub> alloy as a pollution in synthesis process prevents crystal growth. Data [14,32-37] by Tl-Te system relate to massive samples with the exception of [38] where films of Tl<sub>5</sub>Te<sub>3</sub> composition are formed at evaporation of Tl<sub>2</sub>Te alloy.

By chemical and metallographic analysis of samples obtained by zone melting there have been found intermediate compounds In<sub>3</sub>Tl<sub>4</sub> and In<sub>3</sub>Tl<sub>5</sub> [39]. Formula In<sub>9</sub>Tl<sub>7</sub> is assigned to intermediate compounds of in rich content. By investigations [40] existence of In<sub>3</sub>Tl<sub>4</sub> is confirmed. Melting temperature of In<sub>3</sub>Tl<sub>4</sub> is 938K. In [41] there have been determined InTe and In<sub>2</sub>Tl<sub>3</sub> compositions; 50,8±0,1 at. % of Te and 59,7±0,1 at.% of Te, respectively. On the base of X-ray analysis it is suggested that range of homogeneity of high-temperature modification In<sub>2</sub>Tl<sub>3</sub> ( $\beta$ -In<sub>2</sub>Tl<sub>3</sub>) is more than low-

temperature modification ( $\alpha$ -In<sub>2</sub>Tl<sub>3</sub>) and inequality undergoes eutectoid decay.

Structure of ternary compound TlInTe<sub>2</sub> is determined roentgenographical [11], its melting point ( $T_m$ ) is 1045K, density ( $\rho$ ) is 9,31 g/cm<sup>3</sup> [42]. The aim of this paper is the determination of phase composition of Tl-In-Se (S,Te) systems in thin films formed at vacuum condensations of components, determination of kinetic parameters of phase transformations in TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> obtained as at normal conditions of deposition of molecular beam in electric field. There have been considered possibilities of phase transitions from one modification into another and also formation of superlattices of matching one or another phase and not found in massive samples of TlGaSe<sub>2</sub>, TlInTe<sub>2</sub> compositions.

**Experimental details.**

I. Phase composition of films of Tl-In-Se (S,Te) system is investigated at the component condensation on the substrate of NaCl crystals in vacuum  $3 \cdot 10^{-4}$  Pa. Three sources are placed along the condensation plane so that Tl and In samples are set in outer ones. Distance between samples is 13 cm from each other and they are at the height of 7 cm above condensation plane. The third source with Se (S and Te) is located at the height of 8 cm above the average point of condensation plane between Tl and In sources.

Investigation of films of Tl-In-Se system (S,Te) is of experimental difficulties connected with the oxidation of Tl in the contact with air on the one hand, and with the evaporation of Se (S and Te) by heating in vacuum on the other hand. For prevention of highly evaporating component and oxidization processes as a result of further thermal treatment of films they are placed in carbon capsules. Preliminary carbon film is applied on the substrate surface of single crystals NaCl by

the method of vacuum deposition, then investigated subject is deposited and carbon is applied above again. Maximum thickness of films with the regard of carbon ones does not exceed 50 nm. Phase composition of forming films under the condition of simultaneous and sequential deposition of Tl, In and Se (S and Tl) has been studied by electron-diffracting method for passage on devices ZG, ZGR – 102.

II. Kinetics of phase transitions in thin amorphous films TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> condensed under normal conditions and under the conditions of effect of external electric field has been studied by method of kinematical electron-diffraction examination on device ZG. Amorphous films of TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> compounds for investigation of crystallization kinetics are produced by evaporation of TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> alloy cuts in vacuum  $\sim 10^{-4}$  Pa from tungsten helical tapered furnaces. Small newly made spalls of rock salt are as substrates. The calculated thickness of films applied on crystals NaCl with the rate 1,5 nm/c is  $\sim 30$  nm.

Electric field with strength  $3000 \text{ v.cm}^{-1}$  is between parallel copper plates with the high – voltage rectifier. Substrates are arranged on the surface of the negative-charged plate. There have been hole in diameter of 5 mm in the upper plate through which molecular beam can pass and reach substrate surface.

**Results and their discussions.**

**I. Phase formation in thin films in Tl-In-Se (S,Te) systems.**

1. Electron-diffracting analysis of forming films in Tl-In-Se system showed that at simultaneous evaporation of Tl, In, Se along the condensation plane amorphous films are formed. Values of  $S=4\pi\sin\theta/\lambda$  corresponding to diffusion rings on electron-diffraction photographs are given in Table 2.

Table 2. Characteristics of phases of Tl- In- Se systems.

Description	Diffusional ring	S= $4\pi\sin\theta/\lambda$ ( nm <sup>-1</sup> )	Crystal system	Space group	Lattice periods and angles in degrees ( nm )			References
					A	b	c	
Tl <sub>2</sub> Se	1 2	21,40 32,90	tetragonal	$C_{4h}^3$ P4/n	0,8520	-	1,2680	[21]
TlSe	1 2 3 4	21,50 33,90 42,90 52,10	tetragonal	I4/mcm	0,8010	-	0,7000	[20]
TlInSe <sub>2</sub>	1 2 3	20,60 33,90 50,40	tetragonal	I4/mcm	0,8075	-	0,6847	[11]
In <sub>2</sub> S <sub>3</sub>	1 2 3 4	19,50 32,00 54,00 65,00	cubic initial	-	1,0100	-	-	[43]
InSe	1 2 3	20,00 33,20 60,00	hexagonal	R3m	0,4046	-	2,4960	[44]
In <sub>4</sub> Se <sub>3</sub>	1 2 3	22,30 40,00 51,50	rhombic	Pnmm	1,5297	1,2308	0,4081	[45]

Crystallization of amorphous films allows six differences according to phase composition and structure Tl<sub>2</sub>Se,

TlSe, TlInSe<sub>2</sub>, In<sub>2</sub>Se<sub>3</sub>, InSe and In<sub>4</sub>Se<sub>3</sub> to be established. Crystallization of Tl<sub>2</sub>Se and TlSe films are taken place at

493K and 363K, respectively. Ternary compound TlInSe<sub>2</sub> is crystallized at 443K. Obtained amorphous films are crystallized on the base of tetragonal crystal system.

By thermal heatment of amorphous phase In<sub>2</sub>Se<sub>3</sub> the latest is crystallized in cubic crystal system [43] at 473K. At 653K there have been observed phase transition into lois-symmetric phase described in [43] too. Symmetry of this modification is not revealed yet, it is kept up to 1123K. Above 1123K there have been taken place film melting in capsule. Transition temperature from amorphous into crystalline phase for compounds InSe and In<sub>4</sub>Se<sub>3</sub> is 413K and 433K, respectively. Mentioned phases are induced on the base of two crystal systems given in table 2.

Crystallization temperature of films is determined with the accuracy ±5K. We pay attention that amorphous film of Tl<sub>2</sub>Se composition is not formed at interaction of Tl and Se [46]. In this case stablization of amorphous state can be explained by the presence of In impurity. It is known that the prescuse of In in Se (up to 10 at.%) retards crystallization process [47] with the formation of rather strong bonds. As it is seen from the given data amorphous formations in films obtain compositions from Tl<sub>2</sub>Se up to Se whereas in massive samples they are limited from Tl by composition «TlSe<sub>2</sub>» [48-49].

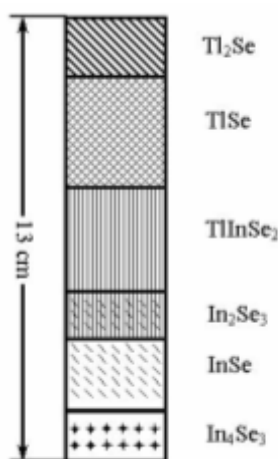


Fig. 1. Diagram of phase distribution in condensation plane for Tl-In-Se system .

At sequential deposition of Tl, In and Se in vacuum in

dependent on evaporation order of phase composition of films does not differ from the case of simultaneous deposition of components. Range extent of forming phases (fig.1) at simultaneous and subsequent depositions of components is similar.

2. There have been formed six amorphous and one crystalline phase at simultaneous evaporation of Tl, Se and In on substrates at room temperature.

Structural characteristics of crystalline phases and values of  $S=4\pi\sin\theta/\lambda$  corresponding to diffusion lines on electron – diffraction photographs of amorphous phases – 1) Tl<sub>2</sub>S, 2) Tl<sub>4</sub>S<sub>3</sub>, 3) TlS, 4) Tl<sub>2</sub>S<sub>5</sub>, 5) TlInS<sub>2</sub>, 6) In<sub>2</sub>S<sub>3</sub> are given in Table 3.

By thermal treatment of films of the first and second amorphous phases there have been formed polycrystalline Tl<sub>2</sub>S and textured Tl<sub>4</sub>S<sub>3</sub>. Annealing of correspon-ding amorphous film at 435K leads to formation of textured TlS. The fourth amorphous phase observed in region abounding in S has been realized by prolonged heating below 373K. This process causes transition of amorphous phase into crystalline with the structure of red Tl<sub>2</sub>S<sub>5</sub>. Crystallized samples as in case Tl<sub>4</sub>S<sub>3</sub> and TlS are textured. Amorphous films of ternary compound of composition TlInS<sub>2</sub> and β-In<sub>2</sub>S<sub>3</sub> are crystallized at 443 and 433K, respectively. Crystalline phase being formed at simultaneous evaporation of Tl, S and In gives textured diffraction pattern with unsharp lines. Further recrystalline annealing at 100 leads to texture perfection. The comparison of electron-diffraction photographs with powdergram for Tl<sub>8</sub>S<sub>17</sub> [24] allows to consider that crystalline phase has the same composition. Except main diffraction lines coinciding with lines given [24] on electron – diffraction photographs there have been observed weak lines (altogether 40 reflections). Diffraction pattern is induced on the base of primitive cubic lattice with elementary cell parameter  $a=1,0600$  nm.

Taking into consideration that average volume falling at one atom in elementary cell for tallium sulfides  $V = 2,6600$  nm<sup>3</sup> we find that a number of structure unity in elementary cell for Tl<sub>8</sub>S<sub>17</sub> is  $z \approx 2$ . And calculated value of density  $\rho_{calc.} = 6,0$  g/cm<sup>3</sup> is well coincided with data for TlS<sub>2</sub> ( $\rho_{calc.} = 5,8$  g/cm<sup>3</sup>) [50].

Thermal treatment of Tl<sub>8</sub>S<sub>17</sub> films showed that unlike massive samples [24] the films are stable up to 393 K. Further rise of temperature brings about mechanical destruction of films.

Table 3. The structural characteristics of crystal phases and values  $S= 4\pi\sin\theta/\lambda$  of amorphous phases of systems Tl-In-S.

Description	Diffu-sional ring	S= $4\pi\sin\theta/\lambda$ (nm <sup>-1</sup> )	Crystal system	Space group	Lattice periods and angles in degrees ( nm)				N ote	R efer-ences
					A	b	c	β		
Tl <sub>2</sub> S	1	14,22	hexa-gonal	R3	1,2200	-	1,8170			[18]
	2	22,01								
	3	34,14								
Tl <sub>4</sub> S <sub>3</sub>	1	22,03	monoclinic	P2 <sub>1</sub> /a	0,7720	1,2980	0,7960	103°50'	β- modi-fica-tion	[51]
	2	37,63								
TlS	1	17,84	tetra-gonal	14/mcm	0,7790	-	0,6800	-		[14]
	2	21,52								
	3	34,31								
	4	54,12								

**ELECTRON DIFFRACTION INVESTIGATION OF PHASE TRANSITIONS IN A<sup>3</sup>B<sup>3</sup>C<sub>2</sub><sup>6</sup> COMPOUNDS**

TlS <sub>2</sub>	-	-	tetra-gonal	P4 <sub>2</sub> /nmc	2,3200	-	5,4800	-		[50]
Tl <sub>2</sub> S <sub>5</sub> (red)	1	14,41	rhombic	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	0,6660	0,6520	1,6750	-		[14, 24]
	2	22,03								
	3	43,02								
Tl <sub>2</sub> S <sub>5</sub> (black)	-	-	rhombic	Pbcn	2,3450	0,8800	1,0570	-		[14]
TlInS <sub>2</sub>	1	20,32	monoclinic	P2 <sub>1</sub> /m	0,7760	0,7760	3,0010	90°15'	β- modi- fica- tion	[9]
	2	26,06								
	3	38,43								
In <sub>2</sub> S <sub>3</sub>	1	8,55	tetragonal	I4 <sub>1</sub> /amd	0,7620	-	3,2300	-	β- modi- fica- tion	[30, 31]
	2	27,73								
	3	40,62								

Decomposition of Tl<sub>8</sub>S<sub>17</sub> massive samples by treatment appears to be connected with partial change of composition at the expense of S (sulphur) volatility that doesn't take place in investigated films placed in coaly capsule up to 393K. Above this temperature vapour pressure of S increases highly inside the capsule and the latter is destroyed with film together.

We note that two phase regions consisting of mixture of mentioned phases are observed on the substrate. At sequential deposition of Tl and S independent on deposition order, on condensation plane by film interaction at room temperature there have been formed four amorphous phases at first: Tl<sub>4</sub>S<sub>3</sub>, TlS, TlInS<sub>2</sub> and In<sub>2</sub>S<sub>3</sub>. Sample treatment at 373-443K initiates film crystallization and besides mentioned phases another phase of Tl<sub>2</sub>S is revealed. Tl<sub>4</sub>S<sub>3</sub> and TlS composition phases are textured. Texture axis (axis C) is perpendicular to substrate surface.

3. Electron-diffractometry analysis of films deposited at simultaneous evaporation of Tl, In and Te showed that on condensation plane there have been formed phases known from state diagram of Tl-Te, In-Te and one ternary compound of TlInTe<sub>2</sub> composition. On electron-diffraction photograph of film forming in the vicinity of Tl source there have been revealed about 40 diffraction lines. Its calculation and comparison of experimentally obtained interplane distances with X-ray data [35] shows the presence of Tl<sub>2</sub>Te phase which we induce on the base of primitive cubic lattice with  $a=1,2620$  nm. Tl<sub>2</sub>Te phase is formed in a very narrow experimentally hard – established region of composition.

In region enriched in Tl (according to calculation up to 85 at.% of Tl) there have been observed phase with facecentered cubic lattice, space group F4<sub>3</sub>2  $a=1,2620$  nm which composition we do not establish. This phase is not stable and at 403K it goes over the phase with primitive cubic lattice with the same parameter of elementary cell. With the increase of Te content in the vicinity of Tl<sub>2</sub>Te phase there have been observed wide region where  $\gamma$ -phase (Tl<sub>5</sub>Te<sub>3</sub>) has been found. Electron – diffraction photograph of this phase is well induced on the base of familiar tetragonal lattice with parameters  $a=0,8920$ ;  $c=1,2630$ nm. Thus in thin films both Tl<sub>2</sub>Te phase and  $\gamma$ -phase of Tl<sub>5</sub>Te<sub>3</sub> composition are realised.

In region enriched in Te there have been observed tetragonal TlTe with parameters of elementary cell  $a=1,2950$ ;  $c=0,6180$  nm which are in agreement with data [33] and Tl<sub>2</sub>Te<sub>3</sub> phase of familiar monoclinic structure with  $a=1,3500$ ;  $b=0,6500$ ;  $c=0,7900$ nm,  $\beta=73^\circ$  [33]. On condensation plane there have been revealed presence of TlInTe<sub>2</sub> ternary compound films with constants of tetragonal lattice  $a=0,8494$ ;

$c=0,7181$ nm [11] and familiar: hexagonal In<sub>2</sub>Te<sub>5</sub> with constants of elementary lattice  $a=1,3270$ ;  $c=0,3560$ nm [40] and rhombic In<sub>2</sub>Te with  $a=0,4450$ ;  $b=1,2580$ ;  $c=1,5360$ nm [52]. At sequential deposition of Tl, In and Te substantially different results are not found. Phase composition of films on condensation plane is as in case of simultaneous deposition of components.

## II. Crystallization kinetics of amorphous films of TlInSe<sub>2</sub>, TlGaSe<sub>2</sub> and TlInS<sub>2</sub>.

Study of formation process of kinetics growth and crystallization of semiconductive material films is of great interest for semiconductive science material. The difficulty in study of these problems is that the growth mechanism is unknown. Evidence of growth mechanism and dependence of rate of crystallization on temperature can be obtained by considering temperature – time dependence of film crystallization.

Thermodynamic conditions of new phase formation are established in [53]. Common equation describing kinetics of phase transitions running with the formation of centres of new phase and their subsequent growth providing for statistical character of overlapping centres of increasing phase has been obtained in [54]. Kinetic equation [54] is the general for describing the kinetics of growth as in case of constant speed of originating as in intermediate cases (decreasing speed of originating)

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

where  $V_t$ - fraction of substance volume undergone transformations to moment  $t$ ,  $V_0$ - initial volume,  $k$  – constant of reaction rate. Value  $m$  is different for possible types of transformation and depends on measuring of growth. On the base of  $m$  exponent value one may infer about possible mechanism of transformation. However it should be noted that for production of reliable results with this theory we must have exact experimental data about value  $V_t$ .

Amorphous films TlInSe<sub>2</sub> in thickness  $\sim 30,00$  nm applied by evaporation of synthesized substance on crystals NaCl at room temperature have amorphous structures. Amorphous phase is found in the temperature range of substrate from room temperature up to  $T_s=403$ K. On electron – diffraction photographs there have been observed three diffusion rings corresponding to  $S=4\pi\sin\theta/\lambda=2,060$ ; 3,390; 5,040nm<sup>-1</sup> given in fig.1.

Crystallization of amorphous films at 423K leads to formation of polycrystalline tetragonal TlInSe<sub>2</sub> being in the agreement with the data of paper [11].

For determination of kinetic parameters of crystallization from amorphous films TlInSe<sub>2</sub> there have been obtained isothermic kinematical electron – diffraction photographs at 403K, 418K, 433K and 453K. We understand that the higher temperature the quicker transition from amorphous state to crystalline is taken place. In case of film overheating at above 453K sharp phase transition is occurred. On kinematical electron-diffraction photographs obtained at mentioned temperatures it is seen that diffusion lines of amorphous phase disappear and lines of crystalline phase TlInSe<sub>2</sub> arise. One of these electron – diffraction photographs measured at 433K is given in fig.2.

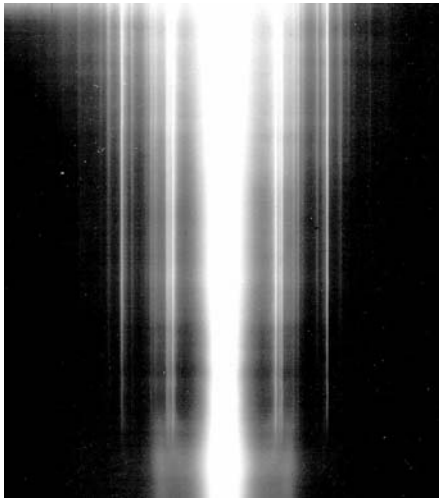


Fig. 2. Kinematical electron-diffraction photograph showing crystallization of TlInSe<sub>2</sub> at 433K.

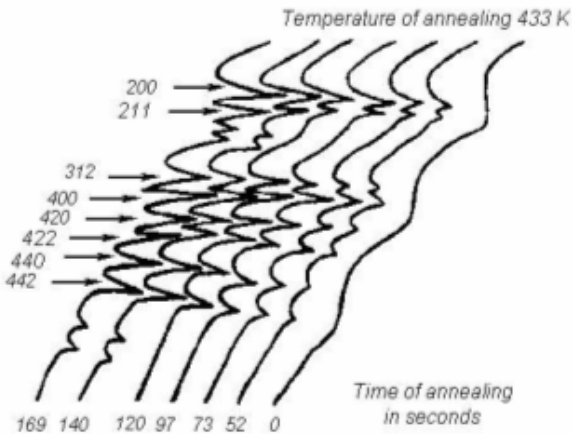


Fig. 3. Microphotographs of isothermal electron-diffraction photograph of TlInSe<sub>2</sub> at 433 K. Figures at curves annealing time (sec.)

Region of existence of both phases has been followed. Line intensities of increasing crystalline phase of TlInSe<sub>2</sub> corresponding to different time moments are microphotometrically determined. In fig.3 microphotographs of kinematical electron-diffraction photographs measured at 433K are shown. There have been determined diffraction line intensities (200), (211), (312), (400), (420), (422), (440), (442) of

crystalline TlInSe<sub>2</sub> depending on annealing time. Transition from intensity value to quantity of crystallized substance are carried out by normalization taking into account that in kinematical approximation electron scattering intensity is in proportion to the volume of scattering substance according to paper [55]. In the investigated temperature range there have been carried out kinetic curves of crystallization of amorphous TlInSe<sub>2</sub>, i.e. dependence of volume of crystallized part of TlInSe<sub>2</sub> on time at various temperatures (fig.4).

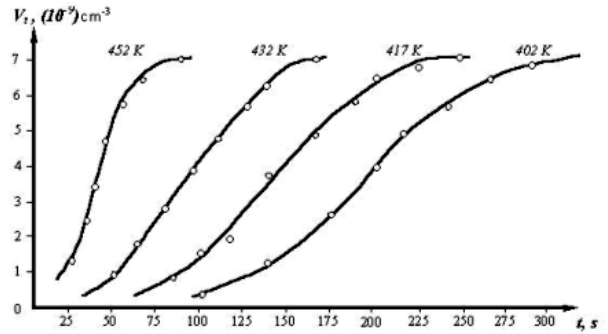


Fig. 4. Kinetic curves of TlInSe<sub>2</sub> crystallization. Values of T<sub>c</sub>. 1-403, 2-418, 3-433, 4-453K.

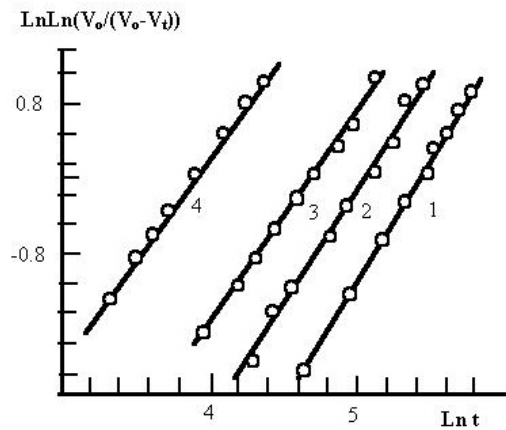


Fig. 5. Dependence of  $\ln\ln(V_0/V_0-V_t)$  on  $\ln t$

There have been carried out dependences  $\ln\ln(V_0/(V_0-V_t))$  on  $\ln t$  for 403K, 418K, 433K and 453K (fig.5). Experimental points are arranged on straight lines for all temperatures. Value of “m” exponent in equation (1) determined from shift of given straight lines appeared to be close to three points ( $m=2,68; 2,73; 2,90$  for 453K, 433K, 418K and 403K). It points out that in case of crystallization of amorphous films TlInSe<sub>2</sub> in the investigated temperature range two – dimensional growth of chips is taken place. In this case constant  $k$  appearing in formula (1) is equal to  $1/3 \pi V_n V_s^2$ . Here  $V_n$ -rate of crystallization centre formation is as amount of nucleus changing in the center into per unit of time in per unit of volume of metastable phase;  $V_s$ -linear rate of crystallization being defined as rate of change of linear sizes of increasing centers of new phase.

Values  $\ln K$  for various temperatures are the following

K	403	418	433	453
$\ln K$	-	-	-	-
	16,70	14,66	12,62	10,44

On the base of mentioned data there have been carried out chart of dependence lnk on reverse temperature which is linear. This dependence indicates that rate of nucleus formation and linear growth of chips can be described by expression of Arrhenius equation [53].

$$\ln k = A - \frac{1}{RT} (E_n + E_s) \quad (2)$$

where  $E_n$ - activation energy of nucleus formation;  $E_s$  – activation energy of chip growth;  $R$  –universal gas constant;  $A$  – constant not depending on temperature .

There have been determined total energy of crystallization activation along the shift of direct dependence lnk on 1/T, which is equal to 45,7 kkal/mol. Activation energy of nucleus formation  $E_n$  calculated along the shift of direct dependence  $1/\tau$  on lnt (where  $\tau$ -experimentally observed time for crystal-

lization start – incubation time) which is equal to 16,3kkal/mol.

Activation energy of chip growth  $E_s$  from ratio  $E_s=E_g-E_n/2$  is equal to 14,7 kkal/mol. Crystallization kinetics investigation of amorphous films TlInSe<sub>2</sub> obtained under the effect of external electric field have been made similarly for films obtained under normal conditions.

From the change of diffraction line intensities of increasing crystal phase according to above-mentioned method there have been carried out kinetic curves of crystallization and kinetic parameters of film crystallization of tetragonal TlInS<sub>2</sub> [3] and TlInSe<sub>2</sub> [2] condensed under normal conditions and under the effect electric film are determined. Values of summary activation energy of crystallization process  $E_g=E_n+2E_s$  and magnitudes of activation energy of nucleus formation ( $E_n$ ) and growth ( $E_s$ ) are determined. For comparison the obtained values are given in Table 4.

Table 4. Values of activation energy

Description	Electric field strength	m	E <sub>g</sub> kcal / mol	E <sub>n</sub> kcal / mol	E <sub>s</sub> kcal / mol
TlInSe <sub>2</sub>	E=0	3	45,7	16,3	14,7
TlInSe <sub>2</sub>	E=3000 B cm <sup>-1</sup>	3	38,0	11,0	13,5
TlGaSe <sub>2</sub>	E=0	3	61,8	17,6	22,1
TlGaSe <sub>2</sub>	E=3000 B cm <sup>-1</sup>	3	53,3	15,1	19,1
TlInS <sub>2</sub>	E=0	3	42,0	11,0	9,0
TlInS <sub>2</sub>	E=3000 B cm <sup>-1</sup>	3	36,2	9,5	7,7

From the obtained data it is seen that in all three cases there have been observed two-dimensional growth of chips: activation energy values of crystallization for films TlInSe<sub>2</sub>, TlGaSe<sub>2</sub> and TlInS<sub>2</sub> obtained under the effect of external electric field are less corresponding magnitudes for films deposited under normal conditions.

Thus with the crystallization of amorphous films TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> under the effect of electric field there have been obtained more unstable states than in case of absence of field.

Influence of electric field on crystallization of amorphous films TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> can be explained that in external electric field, in TlInSe<sub>2</sub>, TlGaSe<sub>2</sub>, TlInS<sub>2</sub> structures of chained molecules during deposition there have been formed deformations increasing the probability of chain break in short fragments, i.e. it causes increase of their mobility during subsequent thermal treatment and as a result decrease of crystallization activation energy of TlInSe<sub>2</sub>, TlGaSe<sub>2</sub> and TlInS<sub>2</sub> is taken place.

### III. Formation of superlattices of phase transformations in TlGaSe<sub>2</sub> and TlInTe<sub>2</sub>.

1. TlGaSe<sub>2</sub> structure is determined by roentgenographically and it is shown that it is isostructural with TlSe and it forms individual structural type of space group I4/mcm.

Tetragonal lattice parameters of TlGaSe<sub>2</sub> are:  $a=0,8053$ ;  $c=0,6417$ nm, molecule number in elementary cell  $z=4$ ,  $[V=41,62$ nm<sup>3</sup>] [3]. Given results in paper [6] published at the same time with [3] are not in agreement with each other. According to [4-6] TlGaSe<sub>2</sub> has monoclinic crystal system, phase with tetragonal lattice is not fixed. This circumstance makes open the discussion of possible modifications of the mentioned compound.

Below we present results of formation of the thin films TlGaSe<sub>2</sub> and TlInTe<sub>2</sub> obtained by vacuum condensation of synthesized compounds on the surface of alkali haloid compounds of crystals (NaCl, KCl). There have been studied the formation of epitaxial monocrystalline films and the influence of substrate temperature and subsequent thermal treatment on structural characteristics of forming thin films . There have been studied scope for existence of TlGaSe<sub>2</sub>, TlInTe<sub>2</sub> phases depending on films production conditions. There have been considered scope for phase transitions from one modification into another, and also superstructure formations matching one or another phase and not found in massive samples so far.

On the base of investigations we establish the following peculiarities of film formation of TlGaSe<sub>2</sub> compound: TlGaSe<sub>2</sub> films in thickness ~30,00 nm prepared by deposition of synthesized substance on NaCl, KCl crystals and celluloid at room temperature are formed at amorphous state.

On electron – diffraction photograph there have been observed three diffusion rings corresponding to values  $S=4\pi\sin\theta/\lambda=2,102; 3,445; 4,473$  Å<sup>-1</sup> . Storage of amorphous films during 4 months at room temperature does not bring about spontaneous crystallization. Amorphous phase on the surface of mentioned substrates up to  $T_s=413$  K. Crystallization of isolated amorphous films from substrate in electron – diffraction examination column at temperature and heating rate 20 deg/sec leads to formation of polycrystalline TlGaSe<sub>2</sub> with familiar monoclinic lattice.

Evaporation of TlGaSe<sub>2</sub> on heated substrates up to 443K also leads to formation of polycrystalline film. Before increasing temperature of substrates till 483K there have been formed films which electron – diffraction photographs show that observed reflections can be divided into two groups. Diffraction reflexes applies to the first group inducing in monoclinic crystal system with above mentioned parameters of

unit cells. The second group of reflexes (solid lines with arranged points on them) are induced on the base of tetragonal modification [3]. With temperature rise of substrates up to 523K the number of monoclinic phase lines is decreased.

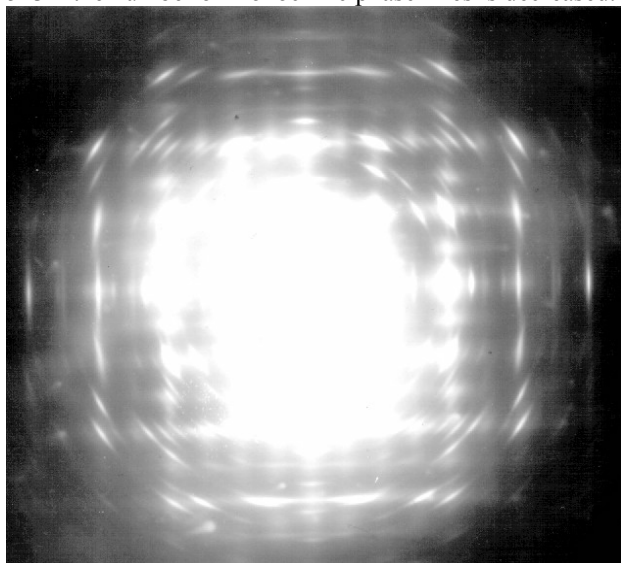


Fig. 6. Electron-diffraction photograph of TlGaSe<sub>2</sub> textured films.

Films obtained on NaCl, KCl substrates at  $T_s=543\text{K}$  with subsequent holding at given temperature over 30 minutes detect the presence of only tetragonal phase TlGaSe<sub>2</sub>. This phase is retained at room temperature. Co-existence of these two structures is due to process of phase transition accompanied by change of atom coordination and bond characteristics between them. Quite a different picture emerges during the production of films on NaCl substrates heated above. Electron-diffraction photographs of forming films under these conditions indicate about the presence of predominant orientation of chips. However formed texture is not perfect. Reflections on electron – diffraction photographs are diffused out, reflection splitting is observed. Intensity distributions in the spots do not follow any regularities. Finally at the temperature of substrates of the order of 330 we obtain samples on which electron – diffraction photographs there have been reflections arranged closely along layer lines. By electron – diffraction photographs of mentioned films (fig.6) it is established that TlGaSe<sub>2</sub> chips form texture with axis “c” being perpendicular to substrate. Parameters of tetragonal lattice with periods are determined:  $a=0,8050$ ;  $c=1,3050\text{nm}$ . Extinction system brings about space group  $I\bar{4} - S_4^2$  other than initial phase referring to group  $I4/mcm$ . Here period “a” is unchanged but there is value for period “c” which is close to the value of body diagonal of cell of initial tetragonal phase. It points to the appearance of some ordering taking place not along all the directions of cell but only along axis “c”.

TlGaSe<sub>2</sub> films grown on (NaCl) monocrystalline substrates at  $T_s=623-643\text{K}$  are monocrystalline with different degree of perfection. By point electron – diffraction photographs there have been determined lattice periods (photography with NH<sub>4</sub>Cl standard) which are equal to:  $a=1,5980$ ;  $c=1,1680\text{nm}$ . In fig.7 electron-diffraction photograph of monocrystalline film of superstructure TlGaSe<sub>2</sub> is presented. Period “c” is determined by electron-diffraction photographs measured with the angle  $\varphi=35^\circ$ . Space group  $I4/amd \left( D_{1n}^{19} \right)$  is established.

Good crystallographic agreement of conjugating substrate planes and new phase is responsible for formation of perfect monocrystalline films with superperiods. By epitaxial growth of TlGaSe<sub>2</sub> on NaCl one elementary cell of phase superstructure is conjugated with three cells of NaCl, and comparative incompatibility of conjugated lattices is 5%. Monocrystalline films TlGaSe<sub>2</sub> are orientated by the plane [001] paralleled to face [100] of NaCl. According to data [3] cell includes 4 formula units. Consequently there must be 16 formula units in cell of TlGaSe<sub>2</sub> superstructure, i.e. 16 atoms of Tl, Ga and 32 atoms of Se. Over crystallization occurs at higher temperature and compound leaning by high-volatile component is possible, as a consequence stabilization of tetragonal phase [3] is possible too. For explanation and coordination of X-ray data we suggest the following. TlGaSe<sub>2</sub> structure is laminated and is alternating packets of two opposite big tetrahedral group of (Ga<sub>4</sub>Se<sub>10</sub>) composition combined by Van- der -Waals forces [3,6].

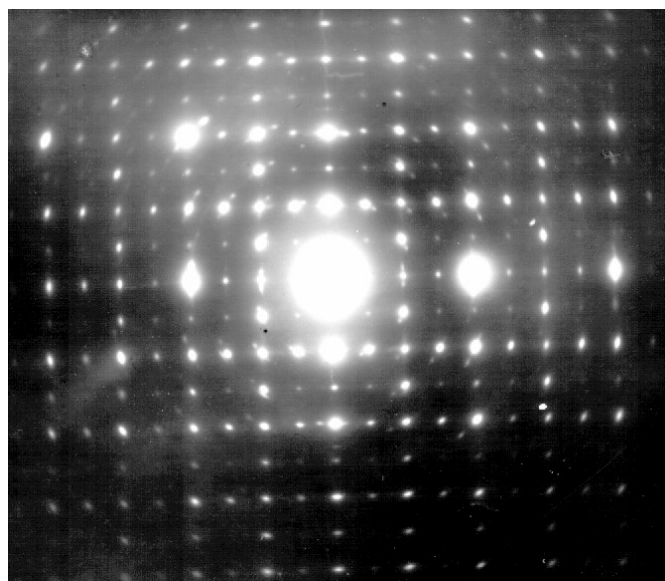


Fig. 7. Electron-diffraction photograph of TlGaSe<sub>2</sub> single crystal.

Distances between packets are 0,3 nm. We assume that the presence of such weak link while the thermal treatment undergoing deformation in dynamic conditions monoclinic laminated structure TlGaSe<sub>2</sub> falls apart into separate fragments arranging in chain tetragonal structure of TlSe – type. Thus it is shown that phase transformation connected with layer reconstruction in TlGaSe<sub>2</sub> brings about formation of its tetragonal modification. Similar processes of tetragonal phase formations are observed under investigation of phase transformations in thin films of IB subgroup chalcogenides of periodic system. In [56] it is shown that tetragonal modification is the intermediate formation and is manifested due to enrichment (leaning) of subject by one of components. It is possible that similar processes are realized for system under investigation. Period difference of revealed superlattices (in the first case it is the period “a”, in the second case both period «a» and period «c») can be connected with different degree of atom ordering and vacancies of selenium in tetragonal lattice. They are due to the change of selenium content in different positions, in consequence in structure on the whole. Superstructural phase is formed as a result of ordering of selenium atom defect positions.



2. Below we consider formation conditions of  $TlInTe_2$  thin films with different substructure and growth peculiarities of epytaxial layers.

We do not suggest that during evaporation there have been arisen substance decomposition or oxidation of this compound, films with different conditions of preparation have been obtained i.e. due to rate of evaporation and substrate temperature. With point electron-diffraction photographs of single crystal there have been obtained electron-diffraction photographs of polycrystal inducing completely on the base of tetragonal lattice with periods:  $a=0,8494$ ;  $c=0,7181$  nm space group  $I4/mcm$  ( $D_{4h}^{18}$ );  $z=4$  [11].

We obtain amorphous films under specific conditions for this compound. We establish that  $TlInTe_2$  layers can be obtained on substrate cooled tentatively up to 213K. In having films on substrates with temperature above 213K there have been observed mesophase transition into crystalline structure. On electron-diffraction photographs of amorphous films three diffusion rings with corresponding  $S=4\pi\sin\theta / \lambda=0,275$ ;  $0,335$ ;  $0,453$   $nm^{-1}$  have been observed. Later on the base of investigations there have been established the following peculiarities of film formation of  $TlInTe_2$  compound: films in thickness  $\sim 30$  nm obtained by evaporation of synthesized substance on NaCl, KCl crystals and celluloid at 223K up to room temperature and at 443K they are obtained in polycrystalline state. During sublimation of ternary alloy  $TlInTe_2$  on newly made spall of KCl single crystal heated up to 493K there have been observed film formation with mosaic crystal structure. On electron-diffraction photographs of such films there have been presented point reflections indicating the prescuse big chips in film closely oriented in an azimuth about each other however these electron-diffraction photographs cannot be induced on the base of tetragonal crystal system by relations  $c/a$ .

On all electron-diffraction photographs of monocrystalline films forming on the surface of single crystal heated up above 493K there have been observed superstructural lines which intensity rises with temperature and at 563K these lines reach good sharpness. At  $T$  close to 593K substrates form monocrystalline films with perfect structure and periods:  $a=2,500$  nm. Period “ $c$ ” is also tripled and equal to 2,185 nm. Between lattice periods  $a_0$  and  $c_0$  of initial and superstructural phases simple relationship are taken place:

$$a_{sup.stp.} = 3a_0 = 2,500 \text{ nm}; c_{sup.stp.} = 3c_0 = 2,185 \text{ nm};$$

And one elementary cell of superstructural phase is conjugated with four cells of substrate, relative incompatibility of conjugated lattice period is 4,8%. Exact extension law being in agreement with space group  $I4_1/amd$  ( $D_{4h}^{19}$ ) is established.

As base area of superstructural cell is nine times as much as base area of initial phase there must be 36 formula units in superstructural cell  $TlInTe_2$ , i.e. 36 atoms of Tl, In and 72 atoms of Te.  $TlInTe_2$  monocrystalline films is oriented by plane (001) parallel to KCl face (100).

Observed orientation relations during epytaxial growth of  $TlGaSe_2$  and  $TlInTe_2$  films as in  $TlInSe_2$  [56] are defined by relationship of atomic configuration of metal layers in crystal lattice of growing film and substrate surface. In  $TlGaSe_2$  and  $TlInTe_2$  lattices metal atoms form orthogonal lattices with distances between points equal to 0,402 and 0,421 nm, re-

spectively. Similar orthogonal lattices with distances between 0,399 and 0,444 nm point form cations or anions on NaCl and KCl crystal face (100), respectively.

However in [56] for  $TlSe$  clear epytaxial relationship is not realized in although incompatibility parameter conjugating lattices is only  $\Delta=0,5\%$  and three different crystallographic orientations is realized at which  $\Delta\approx 40\%$ . Similar phenomenon is known for the case of epytaxial growth of metals on alkalaloid crystals [57-58] and is due to the fact, that the relationship of parameters of conjugating lattices defines perfect epytaxy at initial phases of growth according to Frank-vander-Merve mechanism [59] but it does not bear the responsibility for epytaxial relationship in Folmer-Weber mechanism.

As the substances under investigation are characterized by mixed covalent and ionic links there must be Folmer-Weber mechanism characteristics for weak adhesion between crystal and substrate.

Superstructural phase formation is connected with ordering of chalcogen atom vacancies forming at temperature rise because of its volatility. Ordering of point defects can play an important role in compensation of parameter incompatibility of conjugating lattices at epytaxial growth of thin – filmed samples [60] that takes place in our experiment in  $TlGaSe_2$ ,  $TlInTe_2$  and according to [56] in  $TlInSe_2$  thin films. Nucleation and ordering of point defect vacancies in experimentally grown film appears to be brought about decrease of incompatibility stress in them and formation of more perfect monocrystalline samples. It seems that observed orientation relations for pair “film – substrate” are defined by relationship of atomic configuration  $TlGaSe_2$  – NaCl,  $TlInTe_2$  – KCl and that brings about formation of perfect monocrystalline films with super periods.

## CONCLUSIONS.

1. At sequential deposition of Tl, In and Se evaporation order and simultaneous evaporation of components there have been isolated six differences in composition and compound structure  $Tl_2Se$ ,  $TlSe$ ,  $TlInSe_2$ ,  $In_2Se_3$ ,  $InSe$ ,  $In_4Se_3$ . Formed at room temperature films are amorphous and ranges over compositions from  $Tl_2Se$  to Se, that are considerably wider than range in massive samples obtained by quick cooling of melts limiting from Tl by  $Tl_2Se$  composition. Amorphous films are stable at room temperature and are crystallized at 363-373K.

2. In case of simultaneous deposition of components in Tl-In-S system there have been observed one crystalline and six amorphous phases which are stable at room temperature and ranges over composition from  $Tl_2Se$  to  $Tl_2S_5$  much wider than the range obtained by quick cooling of melts ( $TlS$ – $Tl_2S_5$ ). For the first time there have been obtained phase  $Tl_8S_{17}$  where primitive cubic lattice with period  $a=1,060$  nm with number of structural units in elementary cell  $z=2$ .

3. At simultaneous and sequential evaporation of Tl, In and Te by interaction on the substrate there have been possible production of all phases of system  $Tl_2Te$ ,  $Tl_5Te_3$ ,  $TlTe$ ,  $Tl_2Te_3$  and ternary compound  $TlInTe_2$ . There have been established existence of metastable phase with FCC lattice and elementary cell parameter  $a=1,262$  nm, space group  $F4_32$  which changes over the phase  $Tl_2Te$  at  $\sim 403$ K crystallizing into primitive cubic lattice with the same parameter « $a$ ».

4. Values of activation energy of crystallization for  $TlInSe_2$ ,  $TlGaSe_2$  and  $TlInS_2$  films obtained under the effect

of external electric field are less corresponding values for films deposited at standard conditions. In both cases two-dimensional growth of  $\text{TlInSe}_2$ ,  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  chips are observed.

5. For the first time there have been established three superstructural phases of  $\text{TlGaSe}_2$  and  $\text{TlInTe}_2$  compounds, two

of them are formed by epitaxial growth of  $\text{TlGaSe}_2$  on NaCl and one phase of  $\text{TlInTe}_2$  composition on KCl. Good crystallographic agreement of conjugating planes of substrates and new phases is responsible for formation of perfect monocrystalline films with superperiods.

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**$A^3B^3C_2^6$  – BİRLƏŞMƏLƏRİNDƏ FAZA KEÇİDLƏRİNİN ELEKTRONOĞRAFİK TƏDQIQI**

Elektronoqrafik üsul ilə  $A^3B^3C_2^6$  qrupuna daxil olan birləşmələrin, nazik təbəqələr vəziyyətində alınma xüsusiyyətləri tədqiq edilmişdir. Göstərilmişdir, ki otaq temperaturunda formalaşan amorf təbəqələrin tərkiblərinin təşkil etdiyi interval, həcmli nümunələrinədən daha genişdir. Adi şəraitdə və xarici elektrik sahəsinin təsiri altında alınmış  $TlInSe_2$ ,  $TlGaSe_2$  və  $TlInS_2$  nazik amorf təbəqələrin faza keçidlərinin kinetik parametrləri təyin olunmuşdur. Epitaksial böyümə nəticəsində  $TlInTe_2$  təbəqələrinin  $KCl$ ,  $TlGaSe_2$  təbəqələrinin isə  $NaCl$  monokristalları üzərində böyüməsi nəticəsində uyğun olaraq 1 və 2 ədəd ifrat quruluşlu fazaların mövcudluğu müəyyən olunmuşdur.

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**ЭЛЕКТРОНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ ФАЗОВЫХ ПЕРЕХОДОВ  
В СОЕДИНЕНИЯХ  $A^3B^3C_2^6$**

Электронуqрафическими исследованиями установлены особенности формирования пленок соединений группы  $A^3B^3C_2^6$ . Показано, что интервал составов аморфных пленок при комнатной температуре значительно шире интервала в массивных образцах. Определены кинетические параметры фазовых превращений в аморфных пленках  $TlInSe_2$ ,  $TlGaSe_2$  и  $TlInS_2$  полученных в обычных условиях и в условиях воздействия внешнего электрического поля. Установлены 3 сверхструктурные фазы составов  $TlGaSe_2$  и  $TlInTe_2$ , две из которых формируются в результате эпитаксиального роста  $TlGaSe_2$  на  $NaCl$  и одна - состава  $TlInTe_2$  на  $KCl$ .

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