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SOLID SOLUTIONS IN $Cu_2Se - Ga_2Se - In_2Se_3$ NANOTHICK FILMS

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Abstract. By electron difraction method the processes of phase formation and phase transitions in $Cu_2Se - Ga_2Se - In_2Se_3$ system thin films have been investigated. By kinematic electron diffraction method it is established that as a result of polycrystalline $\alpha - \beta$ transformation of $CuIn_5Se_8$ composition ternary compound has been taken place. There have been revealed the formation conditions and phase equilibrium distributed on condensation plane of phases in the form of $CuGa_5(In_5)Se_8$ ternary compounds and $CuGa_5(In_{1-x}Ga_x)Se_8$ composition solid solutions with different ratio of components.

Keywords: phase formation, amorphous film, solid solutions, electron diffraction.
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1 Introduction

The physical properties of functional materials are formed depending on their electronic and crystalline structure. Therefore, it is important to study the structural properties of these materials. Recently, extensive research has been conducted on the study of crystals and thin layers of functional materials. The study of physical properties at the atomic level is the main direction of research in this area (Aliyev et al., 2025; Ibragimov et al., 2024; Nazarov et al., 2024; Ibrahimova et al., 2024; Ilyasly et al., 2024). Materials that retain their physical properties at small sizes and under external influences have potential for application in various fields. Therefore, extensive research is conducted on the study of size effects in materials with interesting physical properties, as well as on determining the changes that occur in these materials under the influence of temperature, pressure and radiation. The results obtained in the course of such research determine new possibilities for application in modern electronics, space technologies and nuclear technologies (Popov et al., 2024; Jabarov et al., 2021; Papailiou et al., 2010; Babayev, 2007; Huseynov, 2021; Asadullayeva et al., 2024).

Semiconductors occupy a special place among functional materials. Various physical properties can be observed in semiconductor crystals. One of such crystals is the $CuGa_5(In_5)Se_8$ system. Interest in defectively ordered $CuGa_5(In_5)Se_8$ compounds related to $A^1 - B^3 - C^6$ [A – Cu, B – (In,Ga), C – (S,Se,Te)] system is aroused by the width of their forbidden bands. For $CuGa_5Se_8$ the band gap (E_G) is 1.85 eV (Durán *et al.*, 2003). According to (Rincón *et al.*, 2001) (E_G) of hexagonal $CuIn_5Se_8$ depending on temperature (10 - 300 K) varies in the range 1.23 eV -1.13 eV. As the energy range for optimal conversion of solar energy is 1.2 – 1.4 eV, to establish the production conditions and the nature of distinct pure phases and the formation of $Cu(In_{1-x}Ga_x)_5Se_8$ - typed quaternary compounds with different ratio of components and their further growth is of particular interest and can lead to the improvement of the heterosolar cell parameters. Due to the technology of film production generally and such factors in specifically as the temperature profile and heat treatment time as film annealing, their simultaneous and sequential deposition, the ratio of chemical compounds that are compounds of double sections of the corresponding ternary systems and a number of other factors. The formation of solid solutions can be caused by substitution or preferential arrangement of gallium (indium) in the crystal lattice interstices.

There has been used high energy diffraction method to study the processes of phase formation and phase transformations in nanothick films $Cu(In,Ga)_5Se_8$ (CIGS) accepted in Ramanathan et al. (2003); Repins et al. (2008) as promising materials for creating highly efficient solar cells of new generation. Electron diffraction examination as one of the most common methods of physical and chemical analysis of thin films allows individual compounds in crystalline state to be identified: the elements of the stoichiometry of compound films formed on the condensation plane and identified by electron diffraction examination are manifested in the final solution.

2 Experimental Method

Thin film materials of Cu-In(Ga)-Se systems suitable for electron diffraction studies are obtained by thermal evaporation of Cu_2Se, Ga_2Se_3, In_2Se_3 binary compounds and in ratio of 1:5 by simultaneous and sequential evaporation. It should be noted that more common methods to obtain (CIGS) layers, differing from each other by on the method of delivering the substance to the crystallization zone are the methods of two-stage annealing of base Cu - In - Ga layers in selenium-containing atmosphere and coordinated evaporation. However the process of film production by the selenization method is a complex technological task due to the different reaction rates of Cu - In(Ga) - Se system compound formation (Marudachalam et al., 1997). In accordance with high cost of the second method it is also of little use.

To obtain films that are completely structurally formed and have strictly stoichiometric compositions when studying the processes of interaction and formation of phases in Cu_2Se – Ga_2Se_3 – In_2Se_3 system we use the practice adopted for creating a binary field of components in Tl – Fe – S systems (Asgerov et al., 2014) and phase formation in Ag - In(Ga) - S(Se) ternary systems (Ismailov & Mamedova, 2008).

The method used in the above-mentioned works allows at given substance density the geometric thickness of the deposited films with an accuracy of ˜5% to be controlled. Using profilometry and other optical methods, the accuracy of more than ˜10% has been achieved. The quantitative composition of the substance by coordinates per unit surface of the condensation plane under certain conditions of film preparation is determined by the formula

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

Here q is the amount of substance per unit surface area of the collector-substrate, Q is the amount of evaporated substance, h is the distance from the evaporation source to any point of the plane of distributed condensate $\alpha = x/h$ where x is the distance from the point located directly under the evaporator to any point of the distributed condensate over the entire area of the substrate. The thickness of the films is calculated by the formula

$$H = \frac{q}{S}, \tag{2}$$

here S - is the density of the substance in g/sm^3.

To obtain homogeneous films three evaporation sources (tungsten conically wound spirals) installed along the condensation plane are arranged as follows: the outer spirals, from which

Ga_2Se_3 and In_2Se_3 evaporation is produced are located at a distance of 200 mm and a height of 100 mm relative to the substrates as NaCl fresh spalls. The third source, from which Cu_2Se vapor condensation is performed is located exactly in the middle of substrate planes pre- degassed in a vacuum for 1.5 - 2 hours at $T = 473K$. The pressure of residual gases in a vacuum is no more than 10-5 Pa. The amount of evaporated Cu2Se, Cu_2Se and In_2Se_3 is 13.8, 2.8 and 3.0 mg, respectively the deposition rate is 0.15 nm/sec. To determine the concentration of compounds along the wedges the distribution law of the prepared substances along the substrates has been previously revealed. Eventually it is helpful to obtain uniformly distributed compounds being appropriate to Cu_2Se, Ga_2Se_3 and In_2Se_3 system compounds on the condensation plane.

Experimental studies of compound films containing easily oxidized (Cu, In) and easily volatile elements (Se) are complicated by the probability of oxidation upon contact with air and decomposition as well as the volatilization of selenium during the long-term storage especially at elevated temperatures during subsequent heat treatments. To exclude such processes the films under investigation are covered with a protective layer of amorphous carbon on both sides. For this purpose, carbon films are pre- applied on NaCl single crystal surface, by vacuum deposition method. Then the films of the objects under review are deposited, and carbon is applied on top again. Thus the samples involved are encapsulated in a peculiar way. The total thickness of the films under study with the regard of carbon ones does not exceed 5 nm. The presence of carbon films results in slight increase against background of diffraction patterns.

The phase composition and structural characteristics of amorphous and crystalline phases formed under conditions of simultaneous and sequential deposition of Cu_2Se, Ga_2Se_3, In_2Se_3 are investigated on EMR-102 electron diffraction detector in the electron beam transmission mode.

3 Results And Discussion

The phase distribution diagram constructed on the basis of electron diffraction analysis of films formed as a result of the simultaneous evaporation of binary compounds on NaCl single-crystal substrates located at a distance of 5 mm from each other at a total length of 200 mm is shown in Fig. 1.

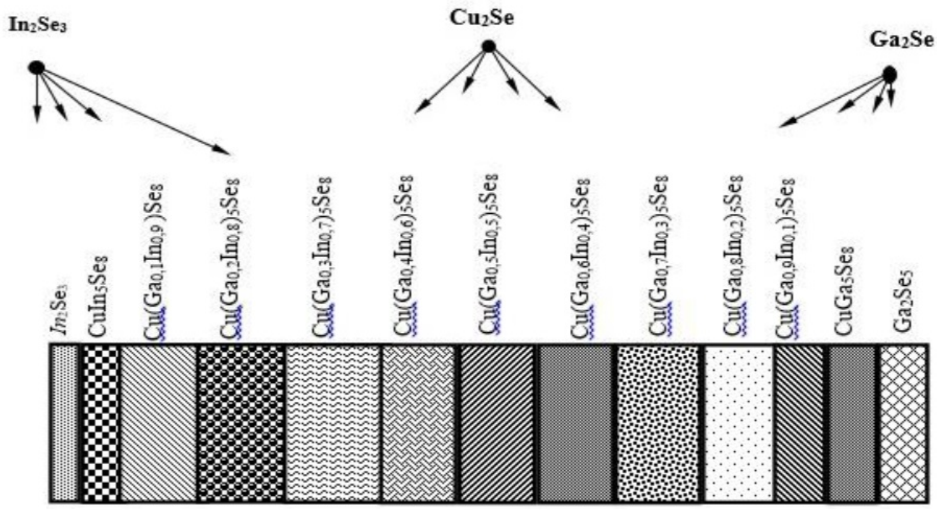

Figure 1: Diagram of solid solution composition distribution from $Cu(Ga_{0.9}In_{0.1})Se_8$ to $Cu(Ga_{0.1}In_{0.9})Se_8$

Electron diffraction study of films shows that there have been formed amorphous phases on the substrates. Using initial compound calculation the formation of Cu_2Se – Ga_2Se_3 and Cu_2Se

– In_2Se_3 systems ternary compounds would be expected with high probability.

Amorphous films formed in a very narrow region of the condensation plane directly under the evaporation sources of In_2Se_3 and Ga_2Se_3 with 19.4, 32.4, 54.0, 65.0 nm^{-1} and 20.30, 34.10, 54.30 nm^{-1} crystallize in hexagonal and cubic lattices with periods a= 1.60, c = 1.924 nm of α – modifications of In_2Se_3 and Ga_2Se_3 with zinc blende structure, respectively.

Amorphous films formed in a fairly wide region of the collector and located between the sources of Cu_2Se and In_2Se_3 (Ga_2Se_3) with values of 30.52, 40.43, 60.85 and 27.42, 35.87, 55.08 nm^{-1} (Fig. 2a,b) crystallize with structural characteristics a = 0.572, c = 1.162 nm and a = 0.5483, c = 1.094 nm being in agreement with the data for hexagonal α – $CuIn_5Se_8$ and $CuGa_5Se_8$ given in Ramanathan et al. (2003).

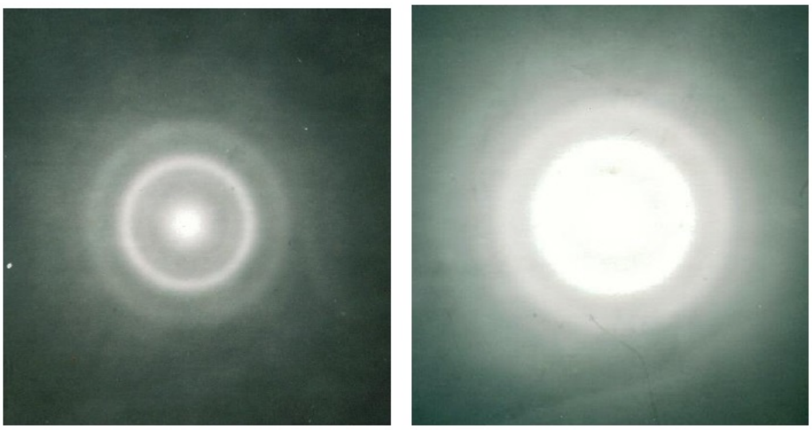

Figure 2: Electron diffraction pattern obtained from $CuIn_5Se_8$ (left) and $CuGa_5Se_8$ (right) amorphous thin films

At T = 135°–150° C $CuIn_5Se_8$ undergoes polymorphic transformation and passes into high-temperature β-modification with hexagonal lattice periods a = 0.403 nm, c = 1.637 nm.

In Fig. 3 the kinematic electron diffraction pattern obtained by the method of drawing photographic plate using continuous recording of diffraction field on it clearly demonstrates that with α - $CuIn_5Se_8$ film being heated β - $CuIn_5Se_8$ film is formed with time: per unit of time, decrease in the unit volume of α - modification accompanied by increase in the unit volume of β – phase has been in the taken place.

Thus it is established that as a result of the recrystallization of polycrystalline films formed because of heat treatment of thin layers at room temperature between sources Cu_2Se and In_2Se_3 in the amorphous state α – β transformation of ternary compound of $CuIn_5Se_8$ composition has been taken place.

The phase transition is completed within 35 seconds, after which the entire film of the compound that participated in the phase transformation process passes from α-modification to β-modification. The phase transformation process is not reversible and the reverse process does not occur when the sample is cooled. Calculation and analysis of electron diffraction patterns obtained as a result of multiple repetitions of α-β transformations of $CuIn_5Se_8$ at different temperatures reveal that while increasing the phase transformations rate the periods of β-modification crystal lattice do not change.

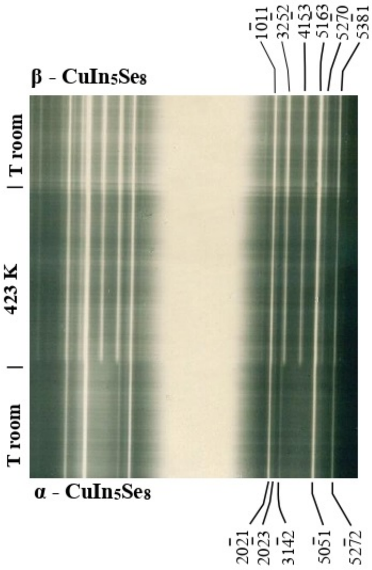

Figure 3: Kinematic electron diffraction pattern α - $CuIn_5Se_8 \to \beta - \alpha$ - $CuIn_5Se_8$ of transformation at $T = 423$ K.

Electron diffraction patterns from polycrystalline condensates obtained on substrates located at a distance of 60 mm from Cu_2Se evaporator towards In_2Se_3 and 50 mm towards Ga_2Se_3 contain diffraction lines with bigger broadenings

Condensation plane regions occupied by alloys crystallizing over hexagonal system are formed in a wide range of condensation plane and covers the composition ranges from $Cu(Ga_{0.9}In_{0.1})_5Se_8$ to $Cu(Ga_{0.1}In_{0.9})_5Se_8$. Recrystallization annealing of polycrystalline films with hexagonal structure does not bring about the change in symmetry and modification of resultant films. Electron diffraction patterns obtained by thermally activated films at $T = 473$ - 493 K show that the increase of diffraction line intensity and sharpness has been taken place.

Recrystallization of $CuGa_5Se_8$ polycrystalline films at $T = 533$ K promotes the formation of textured films (Fig. 4). Electron diffraction patterns of $CuGa_5Se_8$ texture are displayed on the basis of hexagonal lattice with the periods generated above.

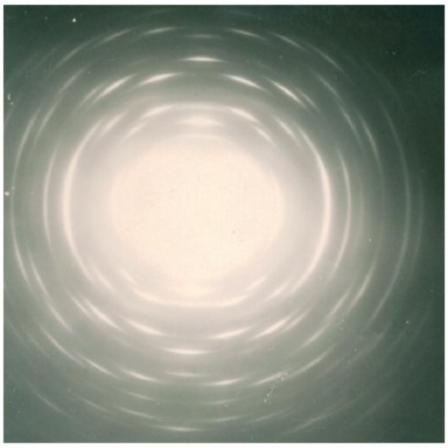

Figure 4: Electron diffraction pattern of $CuGa_5Se_8$ texture

Thus by electron diffraction analysis of alloy systems on the condensation plane with smoothly

Table 1: Structural characteristics of $CuGa_5(In_5)Se_8$ ternary compounds and solid solutions based on them

No	Solid solutions of various compositions	a, nm	c, nm
1.	$CuIn_5Se_8$	0.572	1.162
2.	$Cu(Ga_{0.1}In_{0.9})_5Se_8$	0.569	1.151
3.	$Cu(Ga_{0.2}In_{0.8})_5Se_8$	0.567	1.141
4.	$Cu(Ga_{0.3}In_{0.7})_5Se_8$	0.564	1.139
5.	$Cu(Ga_{0.4}In_{0.6})_5Se_8$	0.562	1.134
6.	$Cu(Ga_{0.5}In_{0.5})_5Se_8$	0.559	1.125
7.	$Cu(Ga_{0.6}In_{0.4})_5Se_8$	0.557	1.121
8.	$Cu(Ga_{0.7}In_{0.3})_5Se_8$	0.554	1.110
9.	$Cu(Ga_{0.8}In_{0.2})_5Se_8$	0.552	1.101
10.	$Cu(Ga_{0.8}In_{0.1})_5Se_8$	0.551	1.097
11.	$CuGa_5Se_8$	0.5483	1.094

changing composition and formed in the process of simultaneous or last evaporation of Cu_2Se, Ga_2Se_3, In_2Se_3 containing from zero up to 100% Ga_2Se_3, from 100% down to 0% In_2Se_3 and from 100% Cu_2Se in the center down to 0% at the edges of the collector the behavior of interaction and formation of phases, as well as the features of the of solid solutions distribution corresponding to compositions from $Cu(Ga_{0.9}In_{0.1})_5Se_8$ up to $Cu(Ga_{0.1}In_{0.9})_5Se_8$ have been established.

The periods of solid solution crystal lattices based on $CuGa_5(In_5)Se_8$(characteristic feature of which is the complex molecular structure of given compounds formed by direct exchange - atom places substitution) are shown in Fig. 1 or in Table 1.

Since the substitution of atoms in $CuGa_5(In_5)Se_8$ does not require compensation of charges by the corresponding number of holes - vacancies and trivalent ions of the matrix Ga(3+) exchange with In(3+) and vice versa, this makes the production of solid solutions over a wide range of compositions much easier: the implementation of mutual substitution in the state of homogeneous valence of Ga, In ions increases the range of compositions of the resulting solid solutions promotes the formation of continuous series of solid solutions in film form.

The observation of distant lines in electron diffraction patterns located at large angles in the diffraction field, i.e. the resolution of high-angle lines indicates the equilibrium of ternary compounds and the homogeneity of solid solutions formed on their basis.

By the formation of substitutional solid solutions the local distortions of the cells created by the atoms of Ga in $CuIn_5Se_8$ and In in $CuGa_5Se_8$ are such that the atoms deviating statically from their positions retain three-dimensional periodicity with averaged periods. This phenomenon can be explained by the fact that if the structure has a complex chemical formula or a large unit cell, then the requirements for the substitution of atoms for each other are somewhat relaxed. There have been more opportunities to maintain equilibrium in interatomic forces at the expense of small displacements of other atoms in the cell. In $CuGa_5(In_5)Se_8$ crystal lattices the phenomenon of solubility of Ga in $CuIn_5Se_8$ and In in $CuGa_5Se_8$ solid state with the formation of continuous series of mutually substituting solid solutions has been occurred.

4 Conclusion

During simultaneous and sequential evaporation of Cu_2Se and Ga_2Se_3, In_2Se_3 binary compounds, ternary amorphous phases have been formed on the condensation plane. Amorphous layers and solid solutions of ternary compounds containing $CuGa_5(In_5)Se_8$ are stable at room temperature and crystallize at T = 383 - 393 K. In the temperature range of T = 408 - 423 K, α-$CuIn_5Se_8$ undergoes polymorphic transformation, going into high-temperature crystalline β modification.

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