ELECTRON DIFFRACTION STUDY OF CuGaS2FILM

Abstract

In present work, the results of electron diffraction investigations of structures of amorphous thin films of $CuGaS_2$have been given and function of radial distribution of atoms (FRDA) has been calculated. Appropriate coordination number n = 4,1 we obtained from calculating the area under the first peak , also indicates tetrahedral surrounded by atoms of copper and gallium. During the deposition of this ternary compound on a substrate with T = 423-433 Kthe mixture of polycrystalline single crystal is formed. With the increase of temprature the intensivity of polycrystallines decreases and point reflections according to the monocrystal increases. Further increase of the substrate temperature to 453 K LiF leads to the formation of a perfect single crystal.

Superstructure phase $CuGaS_2$ is orientedon (100) plane parallel to the faces LiF. During epitaxial growth on LiF $CuGaS_2$ one unit cell superstructure is mated with four cells of the substrate. Between periods of lattices of the initial phase and superstructure there are simple relations common with: $a \approx 3a_0$; $c \approx 2c_0$.

Keywords. Diffraction,phase,atoms, structure,superstructure,amorphous,compositions

1.Introduction.

A number of works [1-3] were devoted to X- ray studies of crystalline structures of the compounds of group A^1-B^3-C^6. However in none of the known works

patterns of short range order structure of amorphous compositions $CuGaS_2$ were determined.

The reason for this can be found eitherby difficulties in establishing conditions for amorphous films of these compounds, or trends in amorphous films to the more dense packing.

Amorphous thin films $CuGaS_2$ of thickness 25 nm were obtained by evaporationalloys $CuGaS_2$ in the vacuum of 10^{-4} PA on the substrate *NaCl*, *KCl* and LiF located at room temperature. *NaCl*, *KCl* and LiF ion crystals have been choosen as substarte because by solving these crystals in the water thin $CuGaS_2$ layers formed on them seperating stay on the surface of water and which is kept in the metal net with diameter of 0.1-0.3 mm.

On the other hand these subtrates with cubic structure of different elementary cell parameters affect epitoxially on crystallisationin primary formation of condensate and further thermo-processing.The rate of deposition of films for all cases was the 1 1.5 nm /sec.Amorphous p hase $CuGaS_2$ is formed until T_s=383 K, crystallization, which canlead to the formation of polycrystalline with periods of a tetragonal lattice, military data [5].

Amorphous filmsformed with values $S=4\pi\sin\theta/\lambda$=24.10; 29.50; 53.70; 83,70 nm^{-1} (Fig.1)after heat treatment at T_s=380 K are crystallized in the structure of chalcopyrite tetragonal lattice $CuGaS_2$ with periods a=0,535; c=1.047 nm, CBC $I\bar{4}$ 2d [5].

2. Experiment

Parameters of short range order distances ofcoordination spheres andinteratomic distances, coordinatio

nnumbers (CN) may be determined by the functions of atom radial distribution (FARD) pr epared accordingto the retraining Fourier intensity of the coherent scattering of electrons.

$4\pi r^2 \sum_m K_{m\mathcal{P}m}\ (r) = 4\pi r^2\ U_0 \sum_m K_m\ \frac{2r}{\pi} \sum_m K_m\ \int_0^\infty St\ (s) sin(Sr) dS$ (1)[12],

Here U_0= d/Mm$_h$-average density of atoms, d-amorph object density, M -molecular mass, m_H=1.65x10^{-24} gr-hydrogen atom mass $\rho_m(r)$ - function of atom density.S = 4π $^{\sin\theta/\lambda}$ is the half of scattering angle, $K_m^2 = (Z_m/Z_l)$ (8) – scattering capability of atoms and Zm – the order number of the atom included in the content of expression,:Z_l-the order number of lighter atom of the expression in the periodical system. $I(S)=(\frac{I_h^k(S)}{\sum f_m^2}(S) - 1)$ $\sum_m$ Km (9) – interferention function .

Reliable, (FARD) can only be obtained when integrating from 0 to ∞ or before S_2, if interference functions do not feel out of oscillate that occurs in strongly disordered systems. The intensity of scattering can be determinedexperimentally with sufficient accuracy only on some interval of values S=4πsinθ/λ ,so practically the integration in (1) is over a finite interval from $S_1$to S_2.

3. Results and discussion

Intensity curve electron scattering from amorphous films $CuGaS_2$ were obtained on electr onography brand EMR-102 in the form of graphs of dependences of the intensity of scattering angles, i.e. from S=4πsinθ/λ (Fig.1).

Function $i(S)$

graphically depicted in (Fig 2.), were used to calculate (FARD) for $CuGaS_2$ (Fig. 3.) accor ding to formula (1). The calculation was carried out on the programmer"RADIADIS" on

the computer IBM. Intervals of variables accounted for $\Delta r = 0{,}01$ nm^{-1}, $\Delta S = 0{,}01$ nm^{-1}.

(FARD) $CuGaS_2$ (Fig. 3.) contains four asymmetric highs one of which is isolated and a group of false highs, emanating from the larger values of S.

The area under the respective highs, manifesting themselves in $r_1 = 0{,}234$; $r_2 = 0{,}244$; $r_3 = 0{,}282$; $r_4 = 0{,}411$nm. are equal $\Delta_1 = 16{,}0$; $\Delta_2 = 20{,}3$; $\Delta_3 = 55{,}5$ and $\Delta_4 = 80{,}0$ nm respectively.

Distance $r_1 = 0{,}234$ nm revealed on (FARD) $CuGaS_2$, is the distance between atoms Cu-S, as tetrahedral covalent radii are equal to $r_{Cu} = 0{,}135$ and $r_S = 0{,}104$ nm. Appropriate coordination number n = 4,1 obtained from calculating the area under the first peak , also indicates tetrahedral surrounded by atoms of copper and gallium.

Radius of the second coordination sphere equal to $r_2 = 0{,}244$nm which couldbe able to interpret as the distance Ga-S. The ionic radii of gallium and sulfur atoms constitute $r_{Ga} = 0{,}127$ and $r_S = 0{,}104$ nm, for which coordination number is six. Meaning coordination number equal to $n_2 = 6{,}3$ received by us from calculating the area of the second peak on (FARD) $CuGaS_2$ also indicates the octahedral environment of gallium atoms by sulfur atoms.

The bond length between the atoms equal to $r_3 = 0{,}282$ nm corresponds to the distance between the same atoms Ga-Ga. Fourth maximum detected at a distance nm can be referred to the distance between the negatively charged divalent atoms (S^{2-}).

It should be noted that on (FARD) $CuGaS_2$ arise false details too, and they may arise due to errors in the experimental intensity curve or cliff: they are mainly manifes ted in the large values of S and belong to groups with slightly blurred large coordination number equal to 8, 10 and 12.

During the deposition of this ternary compound on the substrate with T_s = 423-433 K a mixture of polycrystalline with single crystal is formed (Fig. 4.).

On the electronogramms from the shown mixture apearmore additional weaker reflexes. As a result of increase in temperature intensity polycrystalline lines are reduced but the intensity of point reflections corresponding to single crystal grow.

Further increase of the substrate temperature to 453 K LiF leads to the formation of a perfect single crystal. On electron diffraction from single crystals (Fig. 5), discontinued at right angles strong point reflexes, forming a square grid displayed on the basis of hk0 reflexes known lattice $CuGaS_2$. Indexing of all reflexes, including additional low in intensity lines is achieved with parameter a = 1.605 nm.

Period "c", established by electron diffraction, shot at an angle $\varphi = 35^o$ was found to be 2.102 nm.

Between periods of lattices of the initial phase and superstructure there are simple relations common with: $a \approx 3a_0$; $c \approx 2c_0$. In the electron derived from film on substrates formulated withhigher temperatures (T_s =473 K), dynamic effects appear (Fig. 6.) . The microstructure of single–crystal layers $CuGaS_2$ from which there is a dynamic high energy electron scattering is sho wn in Fig. 7 (X 20000).Thus, substrates can be LiF $CuGaS_2$ samples with varying substruc

ture including a super lattice phase super period.Growth mechanism of single-crystal thin - film and nano scaleepitaxial films is a model for many heterogeneous and topochemical processes.

However, the existing theory of crystallization cannot explain all of the results of a large a mount of experimental work - there is a clear discrepancy between the flow :The totality of new facts and their level of th eoretical understandingof the experimentally observed facts with a unified position cannot be considered. In existing theories of crystallization there is still no consensus on what is themain factor in orienting epitaxial.

Generally accepted explanation is not considered as such a statement and that the main fact or in orienting epitaxial is a single-crystal structure - substrates.Focused on the growth of amorphous boundary layers prepared on the surface o f the substrate crystals [6,7] , is proof that the basic structure of crystals does not determine substrate orientation effects .

Oriented crystallization on the outside boundary of polycrystalline layers [8-9] , as well as the growth of not onlyepitaxial films , but also highly perfect single crystals through the amorphous boundary layers [10] makes relate to the theory of crystallization based on the structure of single-crystal substrates seeds very carefully. Since many experimental works performed revealed aclear discrepancy between the facts and their level of theoretic al understanding,it is not yet possible to formulate some general criteria for the formation o f epitaxial films and single crystal. Therefore, conditions for the formation of single-crystal films to day, as shown in the previous chapter, are established only experimentally.

Since the bulk crystal lattice $CuGaS_2$is ordered, in order to explain the formation of super lattice phase we should assume that it is the disordered phase.Disordering ordered - structures some ofthe initial of the atoms in it are defective, resulting superstructure should have a statistical average fr equency.Regularities of similar phase transitions were first established for the phases of the chemical group of compounds $A^3B^3C^6_2$ [4].

Superstructure phase $CuGaS_2$ is oriented (100) plane parallel to the faces [11] LiF. During epitaxial growth on LiF $CuGaS_2$ one unit cell (UC) superstructure is mated with four cells of the substrate. Relative discrepancy mating crystal lattices in this case is 2,9%.

4. Conclusions.

In $CuGaS_2$ amorph layers short range order parameters have been studied and it is shown thatdistance $r_1 = 0{,}234$ nm revealed on (FARD) CuGaS2, is the distance between atoms Cu-S, as tetrahedral covalent radii are equal to $r_{Cu} = 0{,}135$ and $r_S = 0{,}104$ nm. Appropriate coordination number n = 4,1 obtained from calculating the area under the first peak , also indicates tetrahedral surrounded by atoms of copper and gallium.Radius of the second coordination sphere equal to $r_2 = 0{,}244$ nm which could be able to interpret as the distance Ga-S. The ionic radii of gallium and sulfur atoms constitute $r_{Ga} = 0{,}127$ and $r_S = 0{,}104$ nm, for which

coordination number is six. Meaning coordination number equal to $n_2 = 6{,}3$ received by us from calculatingthe area of the second peak on (FARD) CuGaS2 also i ndicates the octahedral environment of gallium atoms by sulfur atoms. It is shown that thin films on different substartes cryistalize after thermal processing. During the deposition of this ternary compound on the substrate with Ts = 423-433 K a mixture of polycrystalline with single crystal is formed.Further increase of the substrate temperature to 453 K LiF leads to the formation of a perfect single crystal.

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It is found that between periods of lattices of the initial phase and superstructure there are simple relations common with: a ≈ 3a0; c≈ 2c0.

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FiguresofELECTRON DIFFRACTION AND ELECTRON MICROSCOPYSTUDY OF FILMS $CuGaS_2$.

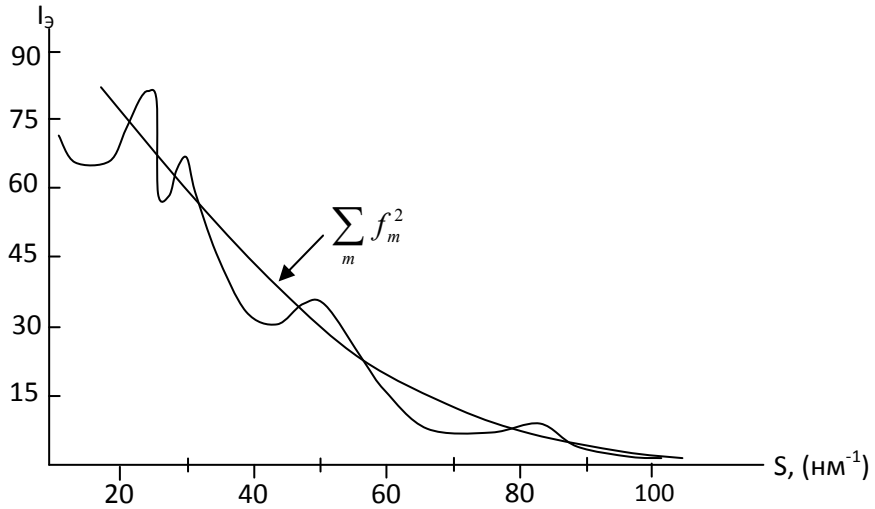

Fig.1.

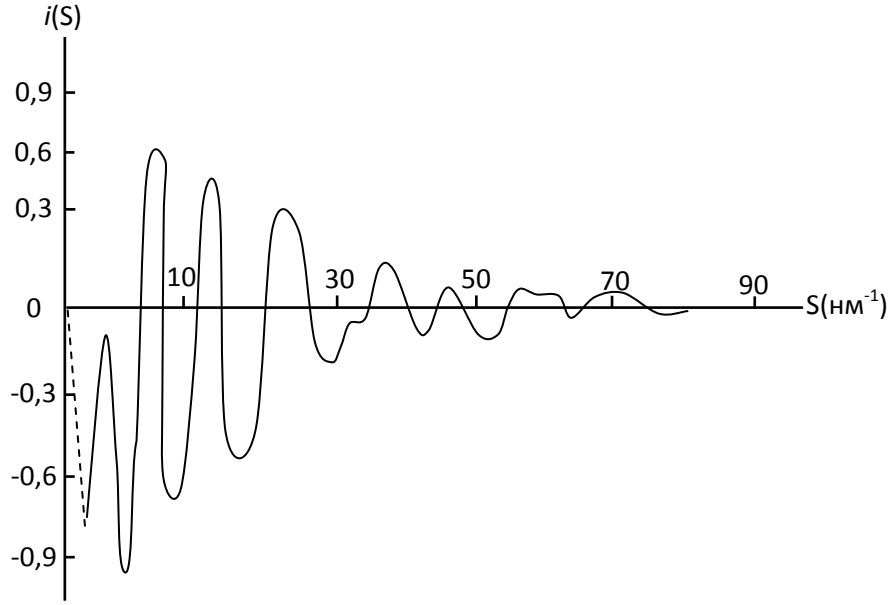

Fig.2.

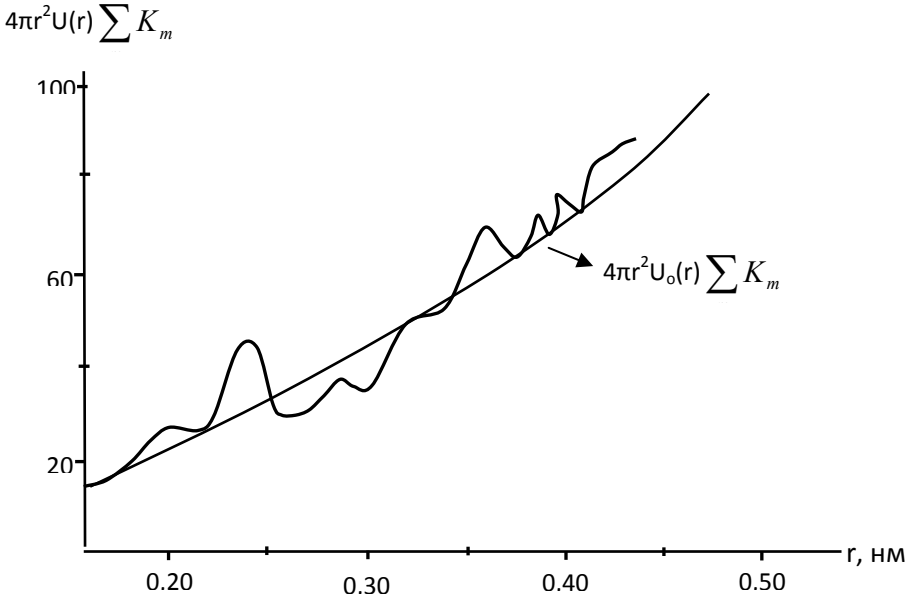

Fig. 3.

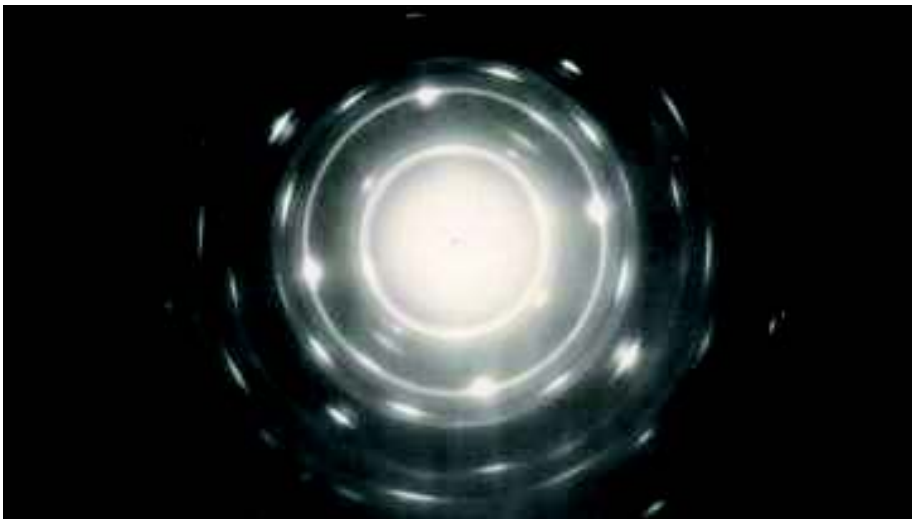

Fig. 4.

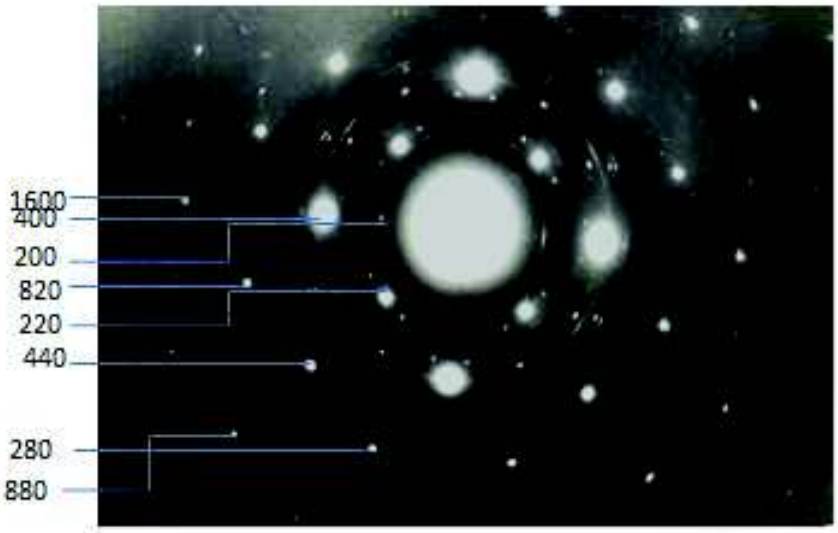

Fig.5.

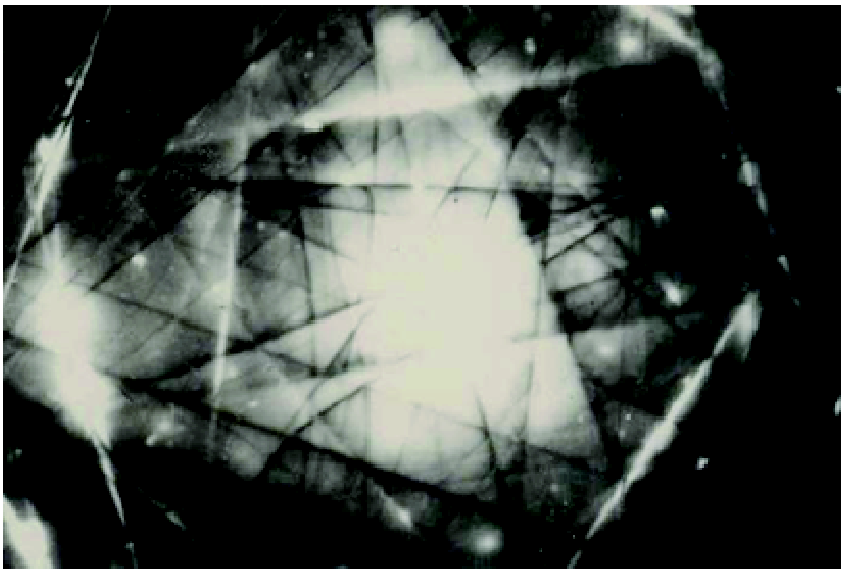

Fig.6.

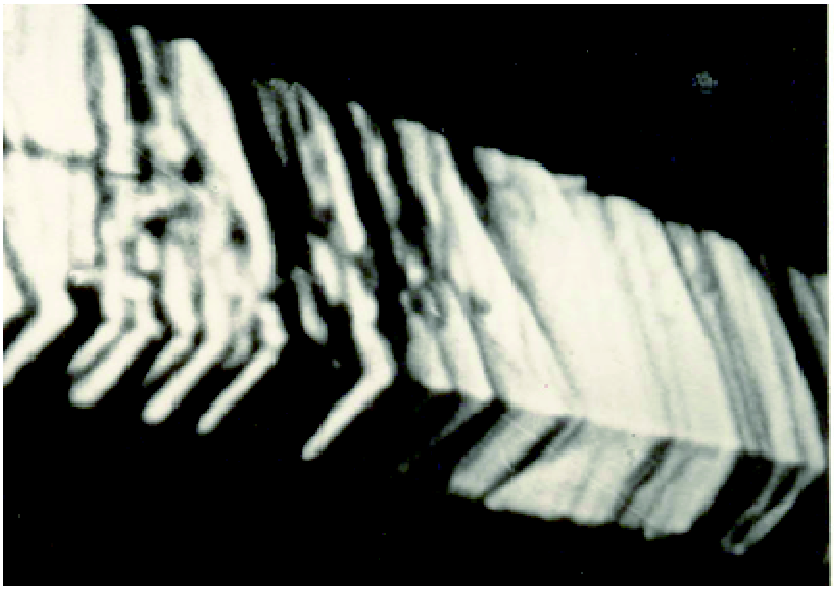

Fig. 7.

Captions to figuresof**ELECTRON DIFFRACTION AND ELECTRON MICROSCOPYSTUDY OF FILMS $CuGaS_2$.**

Fig.1. The intensity curves of amorphous $CuGaS_2$.

Fig.2. Interference scattering function of electrons of amorphous $CuGaS_2$

Fig.3. The curve of radial distribution of atoms of $CuGaS_2$

Fig. 4. Electron diffraction single crystal mixture with polycrystalline $CuGaS_2$

Fig.5. Electron diffraction from single crystal super lattic phase $CuGaS_2$

Fig.6. Electron diffraction pattern with Kikuchi lines from

single crystal $CuGaS_2$ high perfections.

Fig. 7. The microstructure of single-crystal beds of $CuGaS_2$ (H20000) .