



Electron Diffraction Study of CuGaS₂ Film

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

In present work, the results of electron diffraction investigations of structures of amorphous thin films of CuGaS₂ 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 $T = 423-433$ K the mixture of polycrystalline single crystal is formed. With the increase of temperature the intensity 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 CuGaS₂ is oriented on (100) plane parallel to the faces LiF. During epitaxial growth on LiF CuGaS₂ 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.

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1. INTRODUCTION

A number of works [1-3] were devoted to X-ray studies of crystalline structures of the compounds of group A¹-B³-C⁶. However in none of the known works patterns of short range order structure of amorphous compositions CuGaS₂ were determined. The reason for this can be found either by difficulties in establishing conditions for amorphous films of these compounds, or trends in amorphous films to the more dense packing.

Amorphous thin films CuGaS₂ of thickness 25 nm were obtained by evaporational alloys CuGaS₂ 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 chosen as substrate because by solving these crystals in the water thin CuGaS₂ layers formed on them separating 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 substrates with cubic structure of different elementary cell parameters affect epitoxially on crystallisation in primary formation of condensate and further thermo-processing.

The rate of deposition of films for all cases was the 11.5 nm/sec. Amorphous phase CuGaS₂ is formed until T_s=383 K, crystallization, which can lead to the formation of polycrystalline with periods of a tetragonal lattice, military data [4].

Amorphous films formed with values S=4πsinθ/λ=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 CuGaS₂ with periods a=0,535; c=1.047 nm, CBC I⁴ 2d [4].

2. EXPERIMENT

Parameters of short range order distances of coordination spheres and interatomic distances, coordination numbers (CN) may be determined by the functions of atom radial distribution (FARD) prepared according to the retraining Fourier intensity of the coherent scattering of electrons.

$$4\pi r^2 U_0 \sum_m K_m \rho_m(r) = 4\pi r^2 U_0 \sum_m K_m \frac{2r}{\pi} \sum_m K_m \int_0^\infty St(S) \sin(Sr) ds \quad (1) [5],$$

Here U₀ = d/Mm_H - average density of atoms, d - amorph object density, M - molecular mass, m_H=1.65x10⁻²⁴ gr - hydrogen atom mass ρ_m(r) - function of atom density. S=4πsinθ/λ is the half of scattering angle, K_m² = (Z_m/Z₁)² (2) - scattering capability of atoms and Z_m - the order number of the atom included in the content of expression, Z₁ - the order number of lighter atom of the expression in the periodical system.

I(S) = ($\frac{I_h(S)}{\sum_m K_m^2}$ (S) - 1) $\sum_m K_m$ (3) - interfeention function .

Reliable, (FARD) can only be obtained when integrating from 0 to ∞ or before S₂, if interference functions do not feel out of oscillate that occurs in strongly disordered systems. The intensity of scattering can be determined experimentally with sufficient accuracy only on some interval of values S=4πsinθ/λ, so practically the integration in (1) is over a finite interval from S₁ to S₂.

3. RESULTS AND DISCUSSION

Intensity curve electron scattering from amorphous films CuGaS₂ were obtained on electronography 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 graphically depicted in (Fig. 2.), were used to calculate (FARD) for CuGaS₂ (Fig. 3.) according to formula (1). The calculation was carried out on the programmer "RADIADIS" on the computer IBM. Intervals of variables accounted for Δr = 0,01 nm⁻¹, ΔS = 0,01 nm⁻¹.

(FARD) CuGaS₂ (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 r₁=0,234 ; r₂ = 0,244 ; r₃ = 0,282 ; r₄ = 0,411 nm. are equal Δ₁ = 16,0 ; Δ₂ = 20,3 ; Δ₃ = 55,5 and Δ₄ = 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 $r_{\text{Cu}} = 0,135$ and $r_{\text{S}} = 0,104$ 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 $r_{\text{Ga}} = 0,127$ and $r_{\text{S}} = 0,104$ 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 manifested 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 electronograms from the shown mixture appear more 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 intensity lines is achieved with parameter $a = 1.605$ nm. Period "c", established by electron diffraction, shot at an angle $\varphi = 35^\circ$ 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 with higher 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 shown in Fig. 7 (X20000). Thus, substrates can be LiF CuGaS_2 samples with varying substructure including a super lattice phase super period. Growth mechanism of single-crystal thin-film and nano scale epitaxial films is a model for many heterogeneous and topochemical processes.

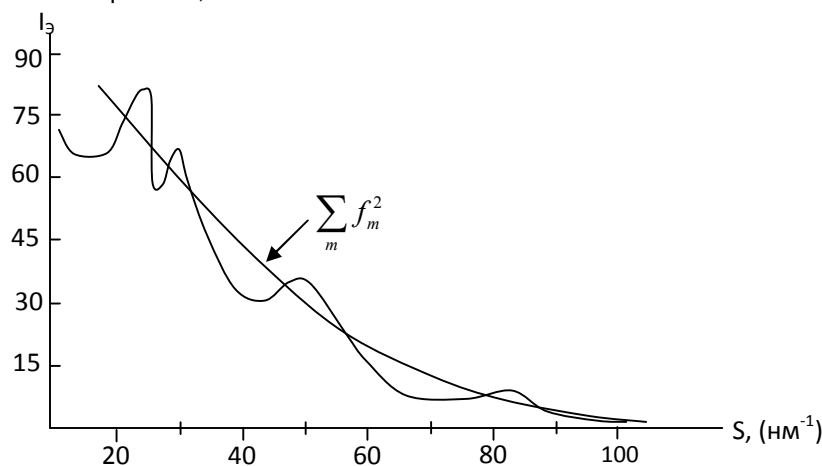


Fig. 1. The intensity curves of amorphous CuGaS_2

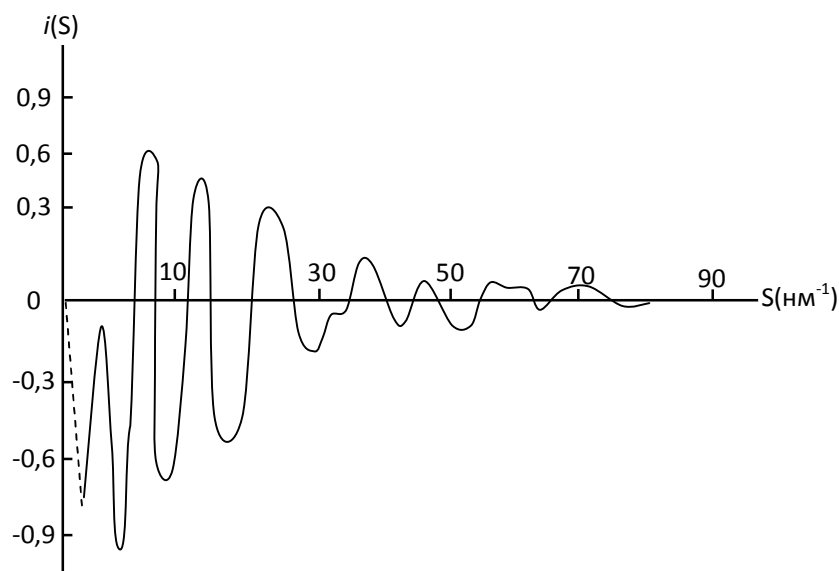


Fig. 2. Interference scattering function of electrons of amorphous CuGaS₂

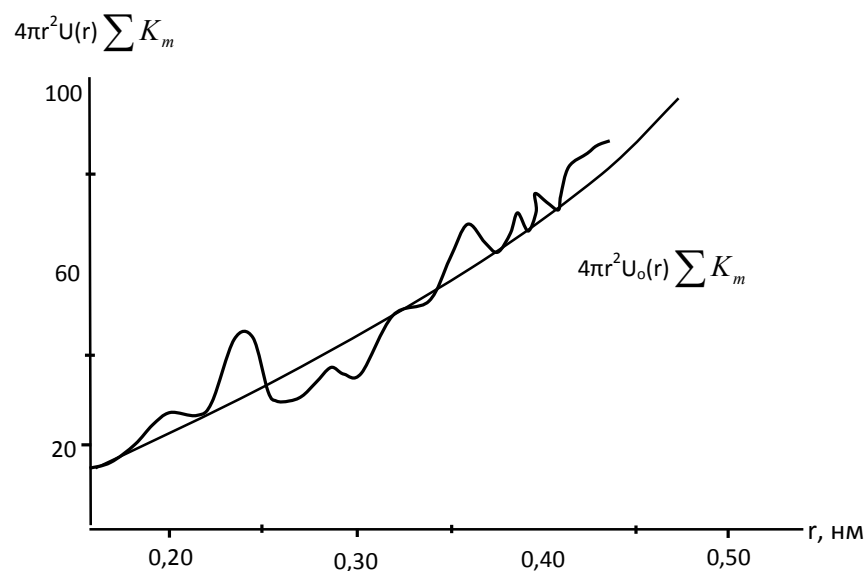


Fig. 3. The curve of radial distribution of atoms of CuGaS₂

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

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

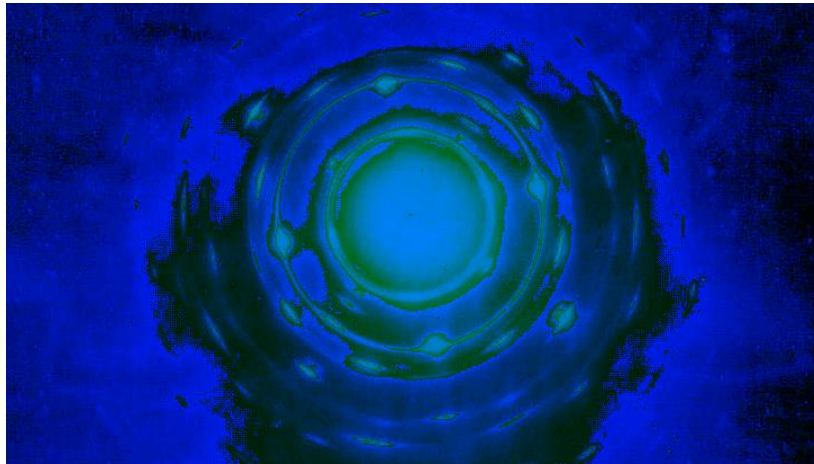


Fig. 4. Electron diffraction single crystal mixture with polycrystalline CuGaS_2

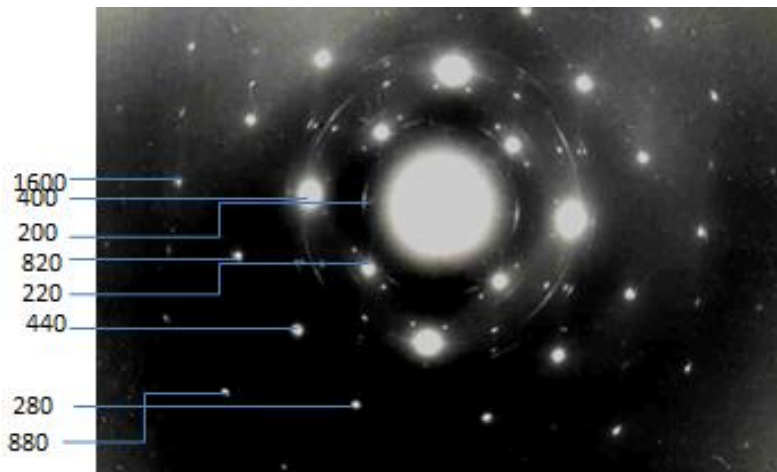


Fig. 5. Electron diffraction from single crystal super latic phase CuGaS_2

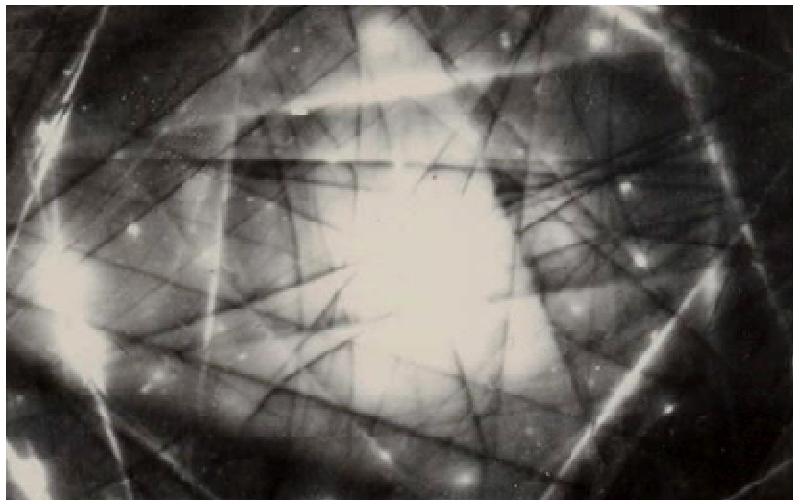


Fig. 6. Electron diffraction pattern with Kikuchi lines from single crystal CuGaS_2 high perfection

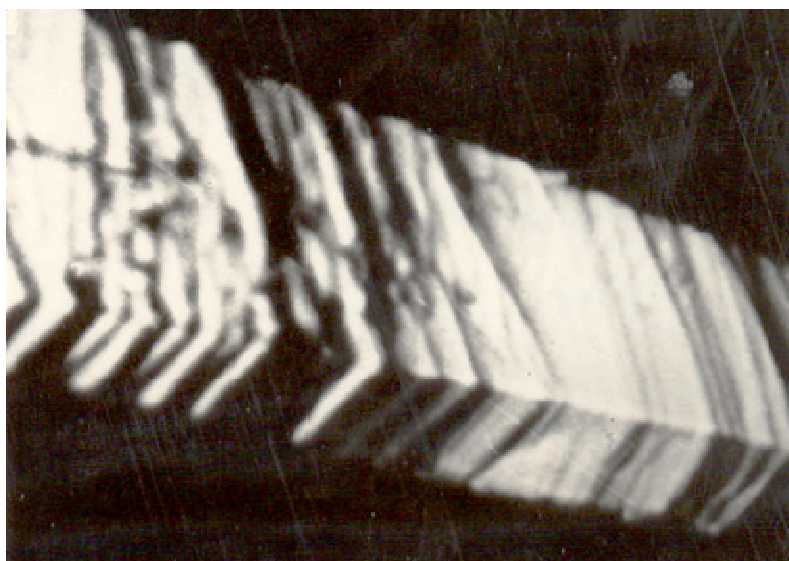


Fig. 7. The microstructure of single-crystal beds of CuGaS₂ (H20000)

Oriented crystallization on the outside boundary of polycrystalline layers [8,9], as well as the growth of not only epitaxial 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 a clear discrepancy between the facts and their level of theoretical understanding, it is not yet possible to formulate some general criteria for the formation of 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 CuGaS₂ is ordered, in order to explain the formation of super lattice phase we should assume that it is the disordered phase. Disorder of ordered – structures some of the initial of the atoms in it are defective, resulting superstructure should have a statistical average frequency. Regularities of similar phase transitions were first established for the phases of the chemical group of compounds A³B³C⁶ [11].

Superstructure phase CuGaS₂ is oriented (100) plane parallel to the faces [12] LiF. During epitaxial growth on LiF CuGaS₂ 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. CONCLUSION

In CuGaS₂ amorphous layers short range order parameters have been studied and it is shown that distance $r_1 = 0,234$ 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 calculating the area of the second peak on (FARD) CuGaS₂ also indicates the octahedral environment of gallium atoms by sulfur atoms. It is shown that thin films on different substrates crystallize after thermal processing. 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. Further increase of the substrate temperature to 453 K LiF leads to the formation of a perfect single crystal.

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%.

It is found that between periods of lattices of the initial phase and superstructure there are simple relations common with: $a \approx 3a_0$; $c \approx 2c_0$.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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