

Phase Formation in Thin Films of Cu-In-S Ternary System

M. A. Nuriyev¹

¹Faculty of Engineering, Nakhchivan State University, Azerbaijan, Nakhchivan, Russia

Correspondence: M. A. Nuriyev, Faculty of Engineering, Nakhchivan State University, Azerbaijan, Nakhchivan AZ7000, Russia. Tel: 994-50-317-0369. E-mail: mubariznuri@mail.ru

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Abstract

In this paper we present the results of studies on the interaction of thin films of Cu-In-S, which is obtained by evaporation of individual components in the plane of condensation, consisting of fresh chips NaCl. Electron-diffraction analysis shows that the length of the regions forming binary compounds and ternary compounds of CuInS₂ with simultaneous and sequential deposition of components is the same. Thus we can speak with certainty that the existence of thin film of tetragonal phase of ternary compound is present in CuInS₂.

Keywords: structural, interactions, phase, films, atoms, lattice, diffractions

1. Introduction

A^I-B^{III}-C^{VI} chemical group ternary compounds with a particular nano dimensional thin films of Cu-In-S system are promising materials to create photosensih surface barrier structures with big integral sensitivity used by changing solar energy to electric energy (Johan, 2010; Taunier, 2005; Hiroaki, 2005).

This paper deals with the investigated results on study of thin film interaction in Cu-In-S system which detailed study allows the existence of various phases of Cu-S, In-S systems and ternary compound of CuInS₂, compound in filmy state to be revealed. The first evidence for Cu-S and In-S system state diagrams being double cross-sections of Cu-In-S system is in (Djurle, 1958; Morimoto, 1962; Khansen, 1962; Zargarova, 1967) and (Hogg, 1968) respectively. By interaction between Cu and S there have been formed compounds which compositions could be in agreement with the formulae of Cu₂S, Cu_{1.8}S being known as chalcousite and dihenite according to existing minerals in nature. The phase of Cu_{1.75}S composition being known as anilite has been established in (Morimoto, 1969). In given system intermediate phases established in (Cook, 1970) are in agreement with Cu_{1.92}S and Cu_xS formulae. By In-S system component interaction In₂S, InS, In₆S₇, In₅S₆, In₄S₅, In₃S₄, In₂S₃, In₃S₅ composition compounds (Khansen, 1962; Zargarova, 1967) and (Hogg, 1968) have been formed.

2. Experimental Procedure

The comprehensive researched deals with results studied of thin films of interaction of Cu-In-S system, which shows the existence of various phases of Cu-S, In-S in the ternary system of compound CuInS₂ composition in the film state to be revealed. To produce samples with continuously changing composition and to prevent Cu and S oxidation, re evaporation of films is obtained during the process of subsequent thermal treatment in vacuum have been placed in carbon capsule. Individual components of Cu and S have been evaporated in vacuum by pressure of residual gases no more 10⁻⁴ Pa from three sources. Limiting tungsten conical helix from which Cu and In have been evaporated are at distance of 150 mm from each other at a height of 80 mm above substrates being at room temperature.

In this paper we analyze the results of studies of phase formation processes in the films of the system Cu-In-S, obtained by simultaneous deposition and stratified components of the system. In the process of obtaining thin films were realized in all phases of a single loop in the vacuum system VUP - 4. Phase analysis was performed using films formed on the ESA electronograph production brand EMR-102. In the vacuum system can be obtained films of dissimilar materials, semiconductor - metal, semiconductor-insulator interface, etc. with a certain ratio of components having different thicknesses. Structure and properties of thin films is largely determined by the conditions of condensation and compliance of its structure with the structure of the substrate. It should be noted that the degree of purity and nature of the substrate topography and the surface temperature and the degree of vacuum, the rate of evaporation, molecular beam angle of incidence to the substrate also

affects the structure and properties of the resulting films.

It should be noted that the presence of contamination greatly affects the electrical properties of the films. In Terms of growth in the film changed, if contamination located on the substrate in the form of small isolated islets from each other. Depending on whether the binding energy between the higher content of the film and contamination of materials or material between the film and the substrate-film form, or on islands or on the exposed portion of the substrate.

Therefore, before spraying had to be done, cleaning the substrate thoroughly as well as protecting them from the appearance of oil films resulting from the penetration of fluids from the vapor and primary diffusion pumps.

There have been newly used made spalls on NaCl, KCl, LiF single crystals and amorphous polyamide celluloid as substrates. The third source from S is at a height of 90 mm from condensation plane between sources Cu and In. In this case on the condensation plane the layer of continuously changing content of components are formed: alloy in this case system includes from 0 up to 100% copper, from 100 up to 0% indium and from 100% sulphur in the center up to 0% on limiting points of condensation plane, consequently all compound of Cu-In-S system.

3. Results and Discussion

Electron diffraction analysis of the layer like this allows the phase composition of component ternary field to be determined. By electron diffraction patterns obtained from the films being in close proximity to the source Cu there has been established existence of several regions: region of primarily resulting phase of chalcocite Cu_2S with rhombic cell periods $a=1.1881$ nanometers; $b=2.7323$ nanometers; $c=1.3494$ nanometers, SYS Ab2m (C^{15}_{20}), which undergoes phase transition and goes into hexagonal chalcocite with the periods $a=0.389$ nanometers; $c=0.668$ nanometers, SYS C6\mmc (Buerger, 1944); region of Cu_{2-x}S face-centered cubic phase with crystal lattice periods $a=0.560$ nanometers and Cu_7S_4 composition phase with rhombic structure periods $a=0.789$ nanometers; $b=0.784$ nanometers; $c=1.101$ nanometers, SYS Pnma (D^{16}_{2h}) (Morimoto, 1969); region of CuS hexagonal phase pure compound with lattice constants $a=0.3794$ nanometers; $c=1.6332$ nanometers, SYS $P6_3\backslash\text{mmc}$ checking with the data given in (Djurle, 1958) and also their mixtures Cu_7S_4 with CuS.

Phase composition of the films obtained at evaporation from the source In is characteristic of the presence of InS, In_6S_7 , In_2S_3 , In_3S_5 composition amorphous compounds crystallizing in rhombic crystal system with periods $a=0.394$ nanometers; $b=0.444$ nanometers; $c=1.064$ nanometers P_{mmm} (D^{16}_{2h}) (Buerger, 1944), monoclinic crystal system with periods $a=0.9090$ nanometers; $b=0.3887$ nanometers; $c=1.7705$ nanometers, SYS $P2_1\backslash\text{m}$ (Hogg, 1967), cubic crystal system with $a=0.537$ nanometers and hexagonal crystal system with $a=0.5789$ nanometers; $c=2.030$ nanometers (Aliyev, 1993), respectively.

Further films of primarily resulting phase $\alpha\text{-In}_2\text{S}_3$ have been annealed at T 313-328K. Mentioned films undergo thermal treatment within T328K for short time 3-5 min. in order significant losses of S not to be taken place. These films go irreversibly into crystal β -modification with crystallographic constants $a=1.074$ nanometers, SYS $Fd3m\text{-}0^7_h$. Amorphous film thermal treatment with $S=4\pi s \sin\theta/\lambda = 25.32$ nanometers⁻¹; 34.52 nanometers⁻¹; 58.27 nanometers⁻¹ (Figure 1) obtained on the substrates spaced 50-55mm and 55-60mm apart from Cu and In evaporator centers, in the direction of the source S is exactly in the center of condensation plane that allows polycrystalline CuInS_2 (Figure 2) with tetragonal lattice periods $a=0.552$ nanometers; $c=1.108$ nanometers, SYS I42d (D^{12}_{2b}) (Hahn, 1953) and (Novoselova, 1979) to be revealed, respectively.



Figure 1. Electron diffraction pattern of captions to the figures amorphous CuInS_2

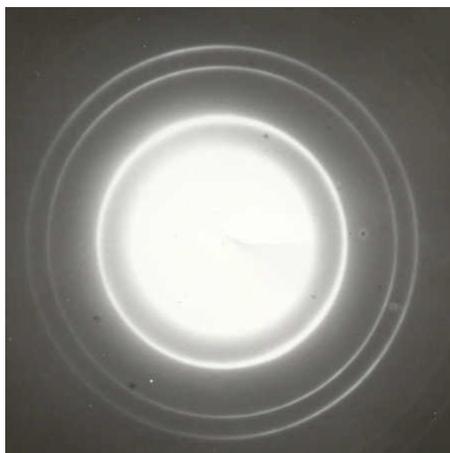


Figure 2. Electron diffraction pattern of polycrystal CuInS₂

Further annealing of CuInS₂ films at T=493K and above does not bring about any change in their structure, which electron diffraction patterns are characteristic of the presence diffraction lines of only tetragonal phase. Rate of temperature rise is 20deg/min; isothermal hold up time is 30 to 40 min.

When considering above-mentioned data on phase formation investigation in Cu-In-S system thin films one can conclude that observed amorphous phase of CuInS₂ composition is steady at room temperature. CuInS₂ crystal films do not experience transformations within T= 493K. It should be noted that at Cu, In and S deposition in vacuum one layer at a time independent of chemical element deposition order the phase composition of condensation plane (Figure 3) does nor differ from the case of their simultaneous deposition. Extension of resulting double compound regions and CuInS₂ composition ternary compound at simultaneous and subsequent depositions of components is similar. Thus one can state with assurance about the existence of only tetragonal phase of CuInS₂ composition ternary compound in filmy state.

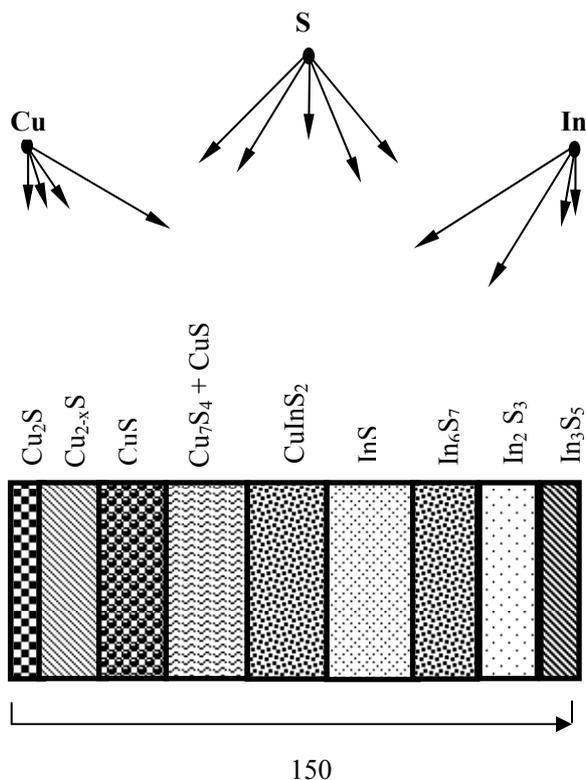


Figure 3. Diagram of phase distribution on condensation plane for Cu-In-S system

When stratified deposition Cu-In-S in a vacuum, regardless of the deposition of chemical elements; the phase composition of the condensation plane is no different from the case of simultaneous deposition. The length of the regions that form binary compounds and ternary compounds of composition CuInS_2 at the same time is sequentially deposited in components, which are identical to the phase compositions. Cu-S and In-S systems, with sections of the double triple systems Cu-In-S are characterized by crystalline compounds, Cu_2S , Cu_{2-x}S , Cu_7S_4 , CuS and mixtures of amorphous phases InS , In_6S_7 , In_2S_3 , In_3S and the presence of the compounds, respectively. Composition of the ternary compound Cu In S_2 is formed in the amorphous state with values $S = 4\pi \sin \theta / \lambda = 25,32 ; 34, 52; 58, 27$ nanometers⁻¹.

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