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SHORT – RANGE ORDER OF AGGAS$_2$(SE$_2$) AMORPHOUS COMPOUNDS AND EPITAXIALLY FILM GROWTH ON THEIR BASE WITH SUPERSTRUCTURAL CELLS

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Abstract. The short-range order parameters of AgGaS$_2$(Se$_2$) thin amorphous films have been investigated. The interatomic distances and numbers of the nearest neighbors have been determined from the atom radial distribution curves. It is shown, that the matrices of amorphous films consists from tetrahedral and octahedron surroundings of atoms. The opportunity of existence of super structural phase of AgGaS$_2$ is established and the oriental parities existing between epitaxially accruing layers of a film and a substrate.

INTRODUCTION

Determination of specific physical properties by experimental methods without studying such processes as phase formation, phase transformations, initiation and growth of single crystal films, kinetics of amorphous state crystallization and amorphous substance structure is of less information for instance it is known that perfection degree and other characteristics of the thinnest layers depend on technological conditions of film production [1,2]. On early papers [3] we describe peculiarities of phase – phase equilibrium formation in Ag – Ga – S (Se) system films.

It is established that as result of individual chemical element interaction of Ag – Ga – S (Se) system on condensation plane together with binary compounds of Ag – Ga – S (Se) system being double cross – sections of ternary compounds Ag – Ga – S (Se) amorphous films of AgGaS$_2$(Se$_2$) compounds have been formed. Being formed in rather wide plane of condensation AgGaS$_2$ and AgGaSe$_2$ amorphous films with values S = $4\pi\sin\theta\lambda$ = 23,3; 35,5; 45,2 nm^{-1} and 20,5; 22,4; 38,7 nm^{-1} are crystallized in tetragonal lattices with lattice spacings a = 0,597; c= 1,08 nm determined in [4,5] for AgGaS$_2$ and a = 0,597; c = 1,08 nm given for AgGaS$_2$ there, respectively.

This paper deals with the investigation of short – range order in AgGaS$_2$, AgGaSe$_2$ amorphous films and revealed superstructural phase of AgGaS$_2$ composition. Curves of AgGaS$_2$ amorphous phase electron scattering have been produced by 2 methods: microphotometric [6] and electric registration on installation EMR – 102 by accelerating voltage 50kV with the use of filter of in elastically scattered electrons allowing electrons in energies to be filtered out [7].

To study short-range there has been constructed radial atomic distribution curve (RADC) appropriate to equation in paper [6].

$$4\pi r^2 \sum_m K_m U_m(r) = 4\pi r^2 U_o(r) \sum_m K_m + \frac{2r}{\pi} \int_0^\infty s \cdot i(s) \sin srds \, , \qquad (1)$$

where summation goes over molecular composition, U$_m$(r) – function of substance atomic density determination, U$_o$(r) – average atomic density, K$_m$- scattering ability of atom "m" equal to $K_m = \left(\frac{Z_m}{Z_л} \right)^{0,75}$, Z$_l$- atomic number of the lightest atom included into the composition of the substance under the investigation, r- average distance between atoms, s- angle of electron beam scattering, i(s)- interference function

$$i(s) = \sum_m K_m^2 \left[\frac{I(s)}{\sum_m f_m^2(s)} - 1 \right], \qquad (2)$$

f$_m$- function of atomic scattering. i(s) has been determined by the method described in [3], according to which

$$i(s) = \alpha \left[\frac{I_{\vartheta}(s) - I_{c}(s)}{\sum\limits_{m} f_m^2(s)} \right], \qquad (3)$$

α – normalization factor $I_e(s)$ - experimental intensity of scattering, $I_{av}(s)$ - average intensity.

Value of normalization factor α is determined by the familiar formula [8]

$$\frac{1}{\alpha_{cp}} = \frac{1}{2} \left\{ \left[\frac{I_c(s)}{\sum\limits_m f_m^2(s)} - \frac{I_{\vartheta}(s)}{\sum\limits_m f_m^2(s)} \right]_{max} + \left[\frac{I_c(s)}{\sum\limits_m f_m^2(s)} \right]_{min} \right\} \qquad (4)$$

According to obtained intensities by above – mentioned methods there have been constructed RADS of $AgGaS_2$ amorphous films which are in good agreement. Upper integration limit S_{max} = 100 nm^{-1}. RADS for $AgGaS_2$ amorphous films have been constructed on the base of calculations made out on " RADIADIS" program. On fig.1 RADS for $AgGaS_2$ has the similar form.
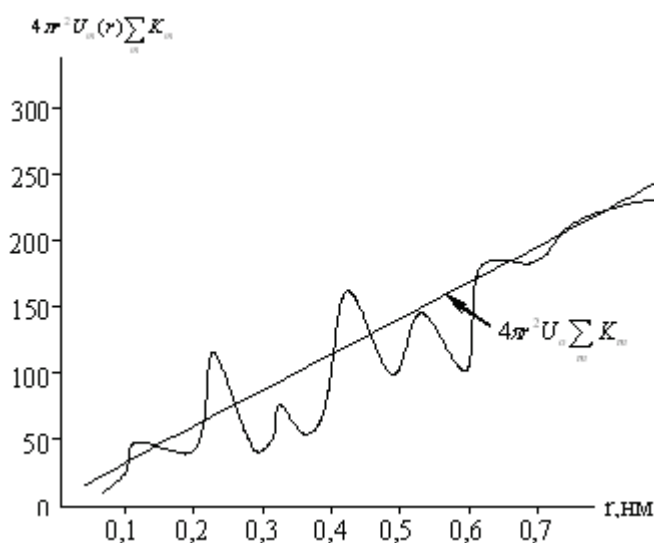

Fig.1 Curve of radial distribution of $AgGaS_2$ atoms

On RADS of $AgGaS_2$ and $AgGaS_2$ there have been false maxima at r~0,14 and r~0,18 nm respectively.

On RADS of $AgGaS_2$ there have been clearly revealed two isolated peals determinacy radia of coordination spheres. Radius of the first coordination sphere is equal to r_1 = 0,23 nm, the second one has been found at r_2 = 0,305 nm. The distance Ga – S is appropriate to the first maximum at r_1 = 0,23 nm. Covalent radii of Ga and S atoms equal to r_{Ga} = 0,124 nm r_S = 0,104 nm are really appropriate to such distance. We note that distance between Ga – Ga atoms equal to 0,248 nm has been plotted in the first $AgGaS_2$ RADC maximum but with rather less probability than probability of Ga-S distances. Coordination number for the first coordination sphere (n_1) is the number of the nearest neighbours of Ga and S atoms equal to 4 is established by the formula

$$n_{ab} = \Delta/2n_a k_a k_b, \qquad (5)$$

Where n_{ab} is the number of "b" sort neighbours around "a" atom in the corresponding coordination sphere, Δ is the area under the corresponding peak, k_a and k_b are effective scattering abilities of "a" and "b" sorts of atoms. Radius of the second coordination sphere r_2 determined from $AgGaS_2$ RADC (fig.1) is in agreement with the distance between Ag and S ions.

Value of Ag^+ and S^{2-} ion radius sums 0,116 + 0,182 = 0,298 nm is close to value r_2 (r_2=0,305). Coordination number (CN) n_2 = 6 indicates that each atom of Ag has octahedron surrounding by S atoms. It is necessary to note that radius sum of Ga and S ions equal to 0,062 + 0,182 = 0,244 nm, somewhat differs from value r_2. In this case CN has the value equal to 8,7, that is considerably more than the value obtained for Ag atom surrounding by Se atoms (n_2 = 6).

From RADC analysis of amorphous $AgGaSe_2$ constructed on the base of integrated analysis of experimental intensity curve there have been also established the shortest distances between Ga – Se and Ag – Se atoms equal to r_1 = 0,255 nm and r_2 = 0,312 nm, respectively. Ga and Ag in $AgGaSe_2$ have tetrahedral (n_1 =

4) and octahedron ($n_2 = 6$) surroundings consisting of Se atoms.

Thus we establish that amorphous film matrices of $AgGaS_2(Se_2)$ compositions consist of tetrahedral and octahedron atom surroundings, i.e. structural elements being characteristic for crystal lattices remain in amorphous layers. Covalent bonds active between atoms in crystal lattices of appropriate ternary compounds remain in $AgGaS_2$, $AgGaSe_2$ amorphous films.

We also consider initiation and formation peculiarities in single crystal epitaxial thin layers of superstructural phases of $AgGaS_2$ with super periods obtained by oriented crystallization method.

$AgGaS_2$ superthin films have been fabricated by hinge evaporation of tungsten nire in diameter 0,15 mm or conical coiled helixes. Hinges are neighted with microchemical balance to accuracy of 0,02 mg. $AgGaS_2$ minimum hinge necessary for layer fabrication in thickness 15 nm at the distance of 70 mm evaporator – substrate is equal to 4,4 mg. By sublimation of $AgGaS_2$ ternary compound alloy with the rate of evaporation and vacuum depth within $10^{-4} – 10^{-5}$ Pa on preliminary heated up to 438 K newly spalled crystals of NaCl, KCl, LiF there have been observed film formation with mosaic single crystal structure. Electron – diffraction photograph reveals point reflexes indicating the presence of different oricutatien types of $AgGaS_2$ chips when planes (100), (010) and (111) are oriented parallel to NaCl (100) plane. With temperature rise of substrates up to 453 K on NaCl surface there has been formed mixture of polycrystal – single crystal which electron – diffraction photographs besides main reflexes for $AgGaS_2$ familiar lattice include superstructural reflections. Single crystal films have been formed at substrate temperature 493 K. Indexing of all electron – diffraction photograph reflexes of $AgGaS_2$ single crystal has been made on the base of hko – reflections at the value of elementary cell period a = 1,71 nm. On electron – diffraction photographs of films obtained at bigger temperatures of substrates ($T_n = 518$ K) there have been appeared effects of dynamic electron scattering (fig.2b) pointing to a bigger perfection formicy in $AgGaS_2$ thin layers.

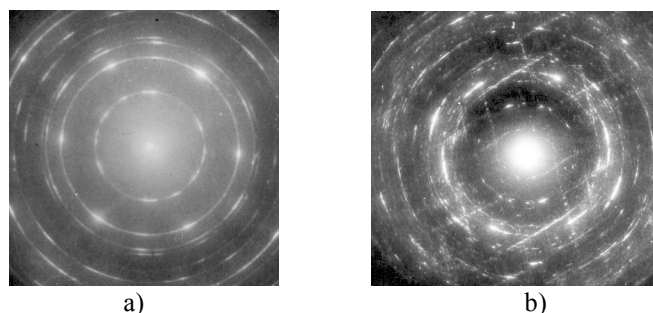a)   b)

Fig.2 Electron – diffraction photographs of samples obtained at different temperatures of substrates a) electron – diffraction photograph of mosaic single crystal with $AgGaS_2$ superstructural phase, $T_s = 493$ K; b) electron – diffraction photograph with display of dynamic effects of $AgGaS_2$ single crystal.

Period "c" equal to 2,023 nm has been determined by electron – diffraction photographs taken with an angle of 30°. Thus the set of reflections observed on electron – diffraction photographs of $AgGaS_2$ superstructural phase can be indexed at triple and double periods "a" and "c", $a_{sup.str.} \approx 3a_o$; $c_{sup.str.} \approx 2 c_o$ respectively.

Presence of 00l c l = 2n – typed reflections allows unambiguously the observed superstructure to space group of crystal symmetry $P4_2 – C_4^8$ to be referred. Chips of $AgGaS_2$ superstructrural films are arranged on the planes (100) oriented parallel to NaCl faces (100). One elementary cell of superstructural $AgGaS_2$ has been integrated with 3 cells of NaCl, where relative incompability is $\sim 1,9 \div 2\%$.

As crystal structure of $AgGaS_2$ initial phase is ordered in this case superstructural phase must be considered as disordered one and have only average statistic periodicity of crystal lattice.

CONCLUSIONS

By method of integral equations on the base of experimental data structures of short – range atomic order in $AgGaS_2$ and $AgGaSe_2$ amorphous films have been determined.

It is shown that main structural elements tetrahedral and octahedron coordinations characteristic for crystal lattices of appropriate compounds remain in amorphous films. The difference is mainly in certain spread of bond lengths in local short – range orders.

There has been established possibility of $AgGaS_2$ composition superstructural phase existence with tetragonal lattice periods a = 1,710 nm; c = 2, 023 nm. Superstructural phase of $AgGaS_2$ is disordered and has only average statistical periodicity of crystal lattice.

REFERENCES

1. Phillips D. Zh. Thin Films Mutual diffusion and reactions. M. Mir., 1982 pp.576.

2. Skakov Yu. A., Ednereal N. N., Mazorra Ch. A., Kraposhin V. C. Amorphous metal alloys. Scientific papers №147. M.: Metallurgu, 1983, pp.8

3. Ismailov D. I., Mamedova A. Ch. Electron- diffraction investigation of kinetics of $AgGaS_2(Se_2)$ amorphous film crystallization. Fizika, 2007, №1-2, pp.214 -216

4. Hann H. Frank G., Klingler W., et al. //Zetisch fur anorg. Und allgem. Chemie, 1953, v.271, №3 – 4, p.153 – 170

5. Novoselova A.V., Lazareva V.B. Physico – Chemical properties of semiconductive substances.- M Nauka, 1979, pp.340

6. Tatarinova L.I. Electron – diffraction examination of amorphous substances. M. Nauke. 1972., p.102

7. Aliyev F.I., Ismailov D.I., Shafizade R.B. Electron – diffraction investigation of TlS AMORPHOUS FILMS. //Crystallography, 1982, V.27, №6, pp.1168 -1170

8. Nabitovich I.D., Stetsiv Ya. I., Volushik Ya.B. Determination of coherent intensity and background intensity on experimental curve of electron scattering.// Crystallography, 1967, .12, №4, pp.584 – 590.

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