THE ATOMIC SHORT-RANGE ORDER PARAMETERS IN THE FILMS OF TRIPLE COMPOUNDS OF Cu – In – S(Te) SYSTEM

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The structural characteristics of short-range order parameters in amorphous films $CuInS_2$ (Te₂ were discussed on the base of electron diffraction method.

The values of nearest atomic spacings, the radii of coordination spheres and coordination numbers have been established.

Earlier it has been established by us, that at the thin film interactions of Cu-In-S(Te) obtained by the simultaneous and serial evaporation of individual chemical elements the film phase composition is also characterized by triple compounds of CuInS₂, CuInTe₂ compositions along with double compounds with Cu(In) – S(Te) system, being double cross-sections of triple systems [1-2].

It is experimentally established by our investigations, that thin films of any composition and any phase compounds of Cu–In–S(Te) systems in the difference from the massive sample can be created in the form of amorphous and polycrystalline, monocrystalline and textured layers. Using the possibilities of oriented crystallization the obtaining of thin films of CuInS₂(Te₂) compounds, having long-period superlattices is possible. It is also shown, that amorphous films CuInS₂ and CuInTe₂ with $s=4\pi sin\pi/\lambda=25,32$; 34,52; 58,27 and 15,78; 32,37; 56,07nm⁻¹ correspondingly, are crystallized with periods of elementary cells of tetragonal lattice CuInS₂ a=0,552; c=1,108 and crystal lattice CuInTe₂ a=0,168; c=1,234nm. The both crystal structures are described by space symmetry group of $I\overline{4}2d$ (D_{2d}^{12}) crystal [3].

The temperature-time dependencies of crystallization are defined: kinetic parameters of amorphous film crystallization of $CuInS_2(Te_2)$ compounds and quantitative values of activation energies are established.

Moreover, the question of atomic short-range order parameters in amorphous films of $CuInS_2(Te_2)$, the structures of which are quite indefinite and are totally absent in scientific literature is not quite investigated. This question is present as quite important one, as physical properties of any materials are defined by atomic short-range order parameters on concept, existing now.

The films with width ~ 30 nm, coated by evaporation of synthesized substances CuInS₂(Te₂), and films, obtained both at simultaneous and serial precipitation of individual components of the given systems were used as investigation objects.

The functions of atom radial distribution (FARD) are

calculated by us by method of integral equations, in the foundation of which lies the formula:

$$\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2r}{\pi} \int_o^\infty si(s) sin(sr) ds, \quad (1)$$

defining the curve of atom radial distribution for amorphous substances, consisting of atoms of different types. The structural characteristics of amorphous films were defined on the results of electrometer measurement system of diffraction maximums, allowing one to filter the electrons on the energies.

The dependence of intensity of electron beam I on $S=4\pi \sin\theta/\lambda$ was written in the mode of direct registration of electron current. At the construction of $I(s)/\Sigma f^2(s)$ function we graphically define the graded curve $\langle I(s) \rangle \Sigma f^2(s)$, near which the given function oscillates by the following way

$$\int_{s_1}^{s_2} \left[\frac{I(s)}{\sum f^2(s)} - \frac{\langle f(s)}{\sum f(s)} \right] ds \approx 0$$

where s_1 , s_2 are lower and upper integration limits, $\sum f^2(s) = \sum_{l=1}^{N} aif_i^2(s), N=3 \text{ is number of atom types, being}$

part of composition of considered CuInS₂,CuInTe₂; *ai* - falling to the share of formula unit of different type atoms, $f_i(s)$ is atom scattering factors.

The calculated interferential function

$$i(s) = I(s) / \sum f^2(s) - \langle I(s) \rangle / \sum f^2(s)$$

was transformed into FARD.

$$W = \sum_{i=1}^{N} \sum_{j=1}^{N} a_{i} k_{i} k_{j} 4\pi r^{2} \rho_{ij}(r) = 4\pi r^{2} \rho \left(\sum_{i=1}^{N} a_{i} k_{i} \right)^{2} + \frac{2r\alpha}{\pi} \left(\sum_{i=1}^{N} a_{i} k_{i} \right)^{s_{2}} i(s) sr \sin ds.$$
(2)

here k_i is relative atom scattering power of *i* type, which is equal to $f_i(s)/\sum f^2(s)$, $\rho_{ij}(r)$ is atom partial radial densities, ρ is average atom density.

The density of amorphous films $CuInS_2(Te_2)$ was chosen on 10% less, than density of corresponding crystal substances.

The normalization factor α was defined as average values of following ones:

$$\alpha_{\min}^{-1} |i(s)_{max}| \quad \text{and} \quad \alpha_{\max}^{-1} |< I(s) > /\sum f^{2}(s)|_{\min},$$
$$\frac{1}{\alpha_{av}} = \frac{1}{2} \left[\left(\frac{I_{c}(s)}{f^{2}(s)} - \frac{I_{3}(s)}{f^{2}(s)} \right)_{max} + \left(\frac{I_{c}(s)}{f^{2}(s)} \right)_{\min} \right] = 0,0426;$$

 $\alpha_{av} = 23,47$

The curve of atom radial distribution (CARD) of amorphous CuInS₂ and CuInTe₂, constructed on the base of experimental intensity curves have quit expressed three maximums at r_1 =0,250; r_2 =0,262; r_3 =0,380 and r_1 =0,285; r_2 =0,293; r_3 =0,418 nm correspondingly. The areas under the corresponding maximums are equal: Δ =25,7; 39,5; 55,6 and 33,0; 46,6; 70,2 correspondingly. CARD of amorphous CuInS₂ is given on the fig.1.



Fig.1. The curve of radial distribution of CuInS₂ atoms.

The distances r_1 =0,250; 2,80 on FRDA of CuInS₂(Te₂) are interpreted as the average from of atomic spacings Cu – S and Cu – Te. The average tetrahedral covalent radii Cu – S(Te)=0,256(0,285)nm.

The calculations of area values under first peaks give the values 22,9 for CuInS₂ and 31,2 for CuInTe₂, well coinciding with experimentally obtained atomic spacings in CuInS₂(Te₂). The second coordination spheres with radii

 Fazoobrazovaniye pri vzimodeystvii stekhiometricheskikh kolichestv elementarnikh sostavlyayushshikh sistemi Cu–In–S(Te). Trudi Nacionaloy konerencii po rostu kristallov, «NKRK – 2006». Moskow, 2006, s.428. (In Russian). $r_2=0,262$ in CARD of CuInS₂ and $r_2=0,293$ nm in CARD of CuInTe₂ can be interpreted as the average atomic spacings Cu(In) – S(Te). These atomic spacings are bigger, than sum of covalent octahedral radii of Cu(In) and sulfur atoms, and also Cu(In) and tellurium. The calculation of area values under second maximum CARD of CuInS₂ gives the value $\Delta_2=43,1$. This can be explained by the supposition that atomic spacings In–S in second coordination sphere meet with bigger probability, than ones Cu – S.

The atomic spacings $r_3=0,380$; 0,418 nm correspond to ones between same atoms S–S in CuInS₂ and Te–Te in CuInTe₂.

Based on these data, note, that structure of amorphous films of CuInS₂(Te₂), the matrixes of which consist of tetrahedral and octahedral atom surroundings (n_1 =4; n_2 =6), i.e. atoms Cu and In, having surroundings, which consist of four and six sulfur (tellurium) atoms, well agree with grid model, consisting mainly of structural fragments.



If we will take the values of atomic distances, which are character for CuInS₂ and CuInTe₂ crystals and are equal to 0,255 and 0,290nm correspondingly, then in this model the radii of first coordination spheres would be r_1 =0,250 nm for CuInS₂ and 0,285nm for CuInTe₂. They are bigger, than experimental values, obtained by us, showing, that covalent bonds, acting between atoms remain in crystal lattices and even amplify in amorphous films of CuInS₂(Te₂) compounds.

Thus, it is revealed, that matrix of amorphous films consists of tetrahedral and octahedral atom surroundings, i.e. structural motives, character for crystal lattice of corresponding triple compound are saved in amorphous films by the same way as in amorphous layers, established by us in [4].

However from CARD, constructed by us for amorphous films of CuInTe₂ compound, it is established, that there are inhomogeneous regions, enriched by tellurium atoms in the structure of this compound along with tetrahedral and octahedral atom surroundings. As the calculation of Cu coordination number gives the value, which is equal to seven $(n_2=7)$, it is followed to suppose, that defined part of cuprum atoms in CuInTe₂ has the surrounding, consisting of eight tellurium atoms. By this fact it is established, that the change of structural unit forms and character of their packing take place in the region of second coordination sphere that leads to more solid packing of structural dimmers in CuInTe₂.

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Cu – In – S(Te) SİSTEMLƏRİNİN ÜÇLÜ BİRLƏŞMƏLƏR TƏBƏQƏLƏRİNDƏ YAXIN ATOM MƏSAFƏLƏRİ

Elektronoqrafik tədqiqatlar əsasında CuInS₂(Te₂) amorf təbəqələrində yaxın atom məsafələrinin struktur xarakteristikaları müzakirə edilmişdir.

Ən yaxın atomlararası məsafələrin kəmiyyətləri, koordinasiya dairələrinin radiusları və birinci seçilən bu və ya digər atom ətrafında ən yaxın qonşuların sayı müəyyən edilmişdir.

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БЛИЖНИЙ АТОМНЫЙ ПОРЯДОК В ПЛЕНКАХ ТРОЙНЫХ СОЕДИНЕНИЙ СИСТЕМ Cu – In – S(Te)

На основе электронографического исследования обсуждены структурные характеристики ближнего атомного порядка в аморфных пленках CuInS₂(Te₂).

Установлены величины ближайших межатомных расстояний, радиусы координационных сфер и число ближайших соседей вокруг того или иного атома выбранного за начальный.

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