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MODIFICATION OF AMORPHOUS FILM STRUCTURE OF CHALCOGENIDE GLASS-LIKE SEMICONDUCTORS DUE TO THE CHANGE OF THEIR CHEMICAL COMPOSITION

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By X-ray diffraction method the structure of chalcogenide glass-like semiconductors As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$, As-Se-S and As-Se-Te has been investigated. Data analysis obtained from the first sharp diffraction peak shows that the degree of disorder for glasses of nonstoichiometric composition is higher than for stoichiometric one. It is also shown that tellurium containing samples are more disorder.

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1. Introduction

Chalcogenide glass-like semiconductors (CGS) as promising materials for electronics and optoelectronics are the subject of numerous investigations. Search of control possibilities of material properties to reveal news potentialities of their using is one of the high-priority aspects of investigations like these. Investigations shows[1-4] that in CGS materials the correlation between physical properties and structure has been existed.

By changing the production process regime, chemical composition as well by doping one can modify the structure [1-11] and hence affect electron and optoelectronic properties.

CGS materials by structure are distinguished from corresponding crystals by existing free volumes being an integral part of the material and voids in atomic scale or even of less sizes [5]. Therefore, when establishing the structural origin of CGS physical properties one should take into consideration not only atomic structure but the void one too. Authors of paper [12] show that for CGS of As-Se-S and As-Se-Te systems the model of chemically ordered network (CON) which fulfils Rule 8-N and presents the distribution of bond types in covalent network with several elements. In CON model the stronger heteropolar bonds are preferable but not homopolar ones.

According to this model in CGS of stoichiometric composition the concentration of homopolar bonds does not exceed 1% and they can be considered as structural defects [4]. As a result of deviation from stoichiometry, i.e. when the chalcogenid atom concentration exceeds the values appropriate to the stoichiometric composition the part of homopolar bonds among the chalcogen atoms rises. At the same time the individual fragments of chalcogen atoms having on influence on structure disorder have been formed. Thus by changing composition of As-Se-S and As-Se-Te systems one can achieve the modification of CGS local structure and degree of disorder that allows their properties to be controlled.

The present paper deals with the investigation of structural peculiarities of CGS materials As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$, As-Se-S and As-Se-Te has been carried out in the following sequence: specially pure elementary elements in appropriate atomic percentauges are filled into the quartz ampoules and after evacuating the air down to the pressure 10^{-4} mm Hg they are heated for 3 hours up to T 900-950^0 C and kept for about 12 hours at this temperature. To

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maintain the homogeneity of samples the synthesis is conducted in Furnace off. The films 10 mkm in thickness used in the investigations have been obtained by thermal evaporation with the rate 0,4÷0,5 mkm/sec on the glass substrates in vacuum at the pressure 10^{-4} mm Hg. Investigations of aggregate state and structure of synthesized materials and deposited films have been made out by X-ray diffraction analysis on the powder diffractometer D8 ADVANCE, of Bruker (Germany) within the regime 40 kV, 40 mA, Cu Ka-radiation, λ=1,5406 A°, $0<2\theta<80^0$. Diffraction patterns have been analyzed using special program Evaluation determine such parameters of diffraction peak as their area, amplitude, position (2θ) and full width at half maximum (FWHM).

2. Results and their discussion

In figure there have been shown the curves of X-ray diffraction intensity in thermally evaporated films of materials under the investigation.

Observation of wide maxima in diffraction pattern shows their amorphism. As it is seen from the pattern appropriate to X-ray diffraction intensity of CGS under the investigation as in most other glasses [4, 7, 13-18] there has been observed the narrow maximum designated as the first sharp diffraction peak (FSDP) which is different from others by anomalous dependence on temperature and pressure [13-14].

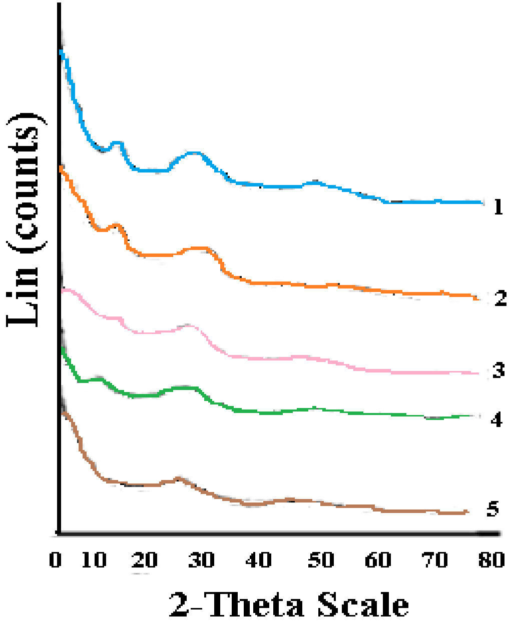

Fig.1. Curves of X-ray diffraction intensity in thermally evaporated films: 1-As_2Se_3; 2-$As_{40}Se_{30}S_{30}$; 3-$As_{40}Se_{30}Te_{30}$; 4-As-Se-S; 5-As-Se-Te.

As a rule FSDP on the curves of X-ray diffraction intensity in CGS relates to the existence of ordering in medium-range order scales. In Table FSDP characteristics concerning the films under the investigation have been shown.

Parameters	Area	amplituda	2Θ°	β°(FWHM)	L(A°)	d/ Å	L/d
As_2Se_3	7.12	23.6	15.95	2.051	39.05	5.55	7.04
$As_{40}Se_{30}S_{30}$	11.06	27.7	15.715	1.98	40.50	5.63	7.19
As-Se-S	11.17	23.7	16.732	2.367	33.92	5.29	6.41
$As_{40}Se_{30}Te_{30}$	29.43	19.5	29.168	4.014	20.45	3.06	6.68
As-Se-Te	26.35	15.7	28.483	5.118	16.01	3.13	5.11

Using the data given in Table there have been estimated the magnitudes of R and L which results are presented in Table.

Where R is the "quasi-period" of structure or fluctuation of atom density [19-21] which repetition in certain region of correlation can be due to the FSDP appereance; L is the correlation length, i.e. which size of region is kept by periodicity of atom fluctuation [22]. The values of mentioned parameters are calculated by Sherer formula [23-24].

$$\mathrm{L} = \{\mathrm{K}\lambda/\beta(\mathrm{FWHM})\cos\Theta(\mathrm{FSDP})\}.\{360/2\pi\}\,,$$

K=0.9 is the Debyae-Sherer constant, λ is the wavelength of X-ray.

$$\mathrm{R} = \lambda/2\sin\Theta(\mathrm{FSDP}),$$

$\beta(FWHM)$-is the full width at half maximum (FWHM). As it is seen from Figure and Table the form of X-ray diffraction intensity curves as well numerical values of parameters characterizing CGS structures depend on the chemical composition. Numerical values of parameter R and correlation length L for As_2Se_3 are 5,55 A° and 39,05 A°, but coefficient of structural units packing is determined by relationship L/R=7,04. For $As_{40}Se_{30}S_{30}$ the values of mentioned magnitudes are slightly more but for nonstoichiometric composition for As-Se-S is substantially less than for As_2Se_3. It is also seen from Table that FWHM for $As_{40}Se_{30}S_{30}$ is slightly lees but for As-Se-S is markedly more than for As_2Se_3. From given date one can make a conclusion that in As_2Se_3 by substituting half of Se atoms by S the degree of disorder increases that appears to be related to S chemical activity.

According to CON model in nonstoichiometric composition for As-Se-S one should expect the presence of pyramidal structural elements $AsSe_3$ and AsS_3 and "mixed" pyramids $AsSeS_2$ and $AsSSe_2$, also arranged chains in disorder involving Se atoms, S atoms, Se_8 rings, S rings and Se_xS_{8-x} "mixed" rings. The presence of As atoms in CGS of As-Se-S system brings about the fact that the part of ringed molecules breaks down and changes to the chain macromolecules and in this case As atoms play the role of bridges among structural units. By this means there have been formed bonds among the chains involving Se and S atoms, i.e. the number of chain and ringed macromolecules decreases, net-chain structure has been established. However As concentration is deficient to form perfect net-chain structure and also ringed and chain molecules in major amount in materials have been assisted. Besides in mentioned material the defects in the form of molecular fragments of $As_4S(Se)_4$, S(Se) and in the form of pores, voids, broken bonds can be existed. Mentioned peculiarities of the structure leads to the growth of disorder degree caused by the breakage of stoichiometry that is confirmed by the data given in Table. It is also seen from Table that structural parameters of $As_{40}Se_{30}Te_{30}$ and As-Se-Te are highly different from like these ones for As_2Se_3, $As_{40}Se_{30}S_{30}$ and As-Se-S. Big value of FWHM and low value values of R, L and L/R are indicative of disorder high degree of structures $As_{40}Se_{30}Te_{30}$ and As-Se-Te comparing with As_2Se_3, $As_{40}Se_{30}S_{30}$ and As-Se-S. As it is known [23] amorphous selenium is basically involved mixture of two structural elements: chain –Se-Se-Se-… arranged chaotically and ringed molecules Se_8. By adding telluride to amorphous selenium Te atoms being included in selenium chains facilitate their breakage, i.e. promote the decrease of chain molecule sizes. When introducing arsenide to amorphous systems Se-Te there have been formed bonds between chains involving Se and Te atoms, i.e. the number of chain and ringed macromolecules are reduced. However for low concentration of As as well the ability of Te to break chain molecules the imperfect net-chain structure has been established. In $As_{40}Se_{30}Te_{30}$ and especially in As-Se-Te as compared with As_2Se_3, $As_{40}Se_{30}S_{30}$ and As-Se-S the macromolecules have a small sizer and great many microinclusions are existed involving molecular fragments $As_4Te(Se)_4$, Te(Se) and etc. also defects in the form of broken bonds and voids. Peculiarities of $As_{40}Se_{30}Te_{30}$ and As-Se-Te bring about the substantial change of structure parameters at the level medium-range order and short-range order (see Table).

3. Conclusions

It is shown that forms of X-ray diffraction intensity curves as well numerous values of parameters of CGS structures under investigation depend on their chemical composition. Numerous values of (R) structure "quasi-period", correlation length (L) and coefficient of structural unit packing (L/R) for As_2Se_3 are 5,55 A° and 39,05 A°, 7,04 A°. Substitution of half Se atoms by S ones in ($As_{40}Se_{30}S_{30}$) leads to the weak growth of mentioned parameter values and when chalcogen concentration is superior to the stoichiometry in (As-Se-S), it leads to the marked decrease. Full width at half maximum (FWHM) for $As_{40}Se_{30}S_{30}$ is slightly less but for As-Se-S is appreciated more than for As_2Se_3. Structural parameters of $As_{40}Se_{30}Te_{30}$ and As-Se-Te are highly different from like these ones for As_2Se_3, $As_{40}Se_{30}S_{30}$ and As-Se-S. Their values of FWHM are more but the values of R, L and L/R are less than for telluride-free glasses. The modification like of structural parameters relates to the change of disorder degree due to the chemical composition. The samples of nonstoichiometric composition (As-Se-S and As-Se-Te) have a more disordered structure. Distinctions in parameters of sulphur and tellurium containing samples relate to their chemical properties.

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