PHASE TRANSITION AT TERMAL TREATMENT OF $TlIn_{1-x}Sn_xSe_2$ AMORPHOUS FILMS

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The crystallization process of $TlInSe_2$ amorphous films doped by tin impurity is investigated by method of high-energy electron diffraction. It is shown that crystallization of amorphous films by width 30nm obtained in high vacuum by thermal method takes place by regularities established by Abraham-Kolmogorov and it is described by analytical expression $V_t = V_o[1 - \exp(-kt^m)]$. The influence of tin impurity on values of nucleation activation energies and their further growth is defined by kinematic electron diffraction pattern of $TlIn_{1-x}Sn_xSe_2$ films.

Keywords: electrography, doping, structure, amorphous phase, kinetics, crystallization.
PACS: 61.66.Fn

INTRODUCTION

The investigation of structural characteristics of nanothickness semiconductor films of $A^{III}B^{III}C$ type with different impurities and solid solutions on their base becomes more actual one day by day. The compounds including in the given group, belong to the wide-band-gap semiconductors in which the forbidden band width can be gradually changed. Their structure can be modified by change of technological process of film obtaining and also by doping [1 – 4]. These complex semiconductor compounds are anisotropic ones and they are of interest for modern optoelectronics [5 -8].

$TlInSe_2$ compound is the one of the representatives of incomplete valence semiconductor compounds with chain structure having the specific structure of crystal lattice. The crystallization kinetic parameters of $TlInSe_2$ nano-dimensional films are investigated and established in [9]. The experimental data on atom interactions in solid substances, valence electrons in atoms can be obtained by methods of electron diffraction [10, 11] from which the electron diffraction method is the more suitable for the investigations in the given direction. Using this method the influence of Sn chemical element doping on phase transition kinetics of $TlInSe_2$ amorphous films crystallizing in structure with tetragonal volume-centered lattice corresponding to symmetry group D_{4h}^{18}–I4/mcm were investigated [12]. The experiments on semiconductor study doped by impurities can be divided on two groups. The works in which the band structure change is studied caused mainly by distortion of semiconductor crystal lattice, belong to the first group. The investigation of state density tail spreading deep into the forbidden band belong to the second group.

The study difficulty of these questions is in the fact that the film growth mechanism is often unknown. The investigation of temperature-time dependence of film crystallization promotes the explanation of their growth mechanism.

EXPERIMENTAL PART

The investigated thin films are obtained by different methods the one of which is the thermal evaporation in vacuum installation. In the given work $TlIn_{1-x}Sn_xSe_2$ (x=0.02÷0.09) amorphous films of width ~30 nm are obtained in vacuum $3x10^{-5}$ Pa in installation ВУП-5 by thermal method and simultaneous deposition of $TlInSe_2$ and Sn from two molybdenum furnaces on the substrate consisting of fresh cleavages of KCl, NaCl and KJ being lower than 403K and previously covered by carbonic film. The deposition time is 5-10 sec. The value of substance separation coefficient is taken under consideration for obtaining of films with impurity uniform distribution. The carbonic film by width 2-3 nm is marked again on obtained films for prevention of evaporation of easily volatile component and oxidation processes in the result of further thermal treatment of films. Dissolving the substrate, the investigated film is transferred on tungsten furnace-substrate where it is subjected by thermal treatment.

The distribution of condensate composition on coordinates on condensation plane is defined with the help of known formula in crystallography [10]:

$$q = \frac{Q}{4\pi h^2}\frac{1}{(1+\alpha)^{3/2}} \qquad (1).$$

Here q is amount of substance per unit of substrate surface plane, Q is amount of evaporated substance, h is distance from evaporation source to any point on condensate plane, coefficient α = x/h, where x is distance from the point being directly under evaporator to any point on substrate plane. The film thickness obtained by vacuum evaporation is calculated by following formula:

$$H = \frac{q}{\rho} \qquad (2),$$

where ρ is substance density. Besides, the film thickness is controlled by spectrometer «Spekor-250»,

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and fill composition is controlled by atomic-adsorption spectrophotometer «ShimadzuAA-6300».

The crystallization kinetics of $TlIn_{1-x}Sn_xSe_2$ amorphous films is investigated on electron diffractometer of ЭМР-102 type using the energy filter for separation of inelastically scattered electrons and electric registration of diffraction line intensity appearing as a result of amorphous phase crystallization. The size of intensity electronic pickup slot at electric registration of chosen line intensity of crystal phase is defined from ratio $2/3d=l$, where d is slot width, l is half-width of registered line. The recording maximum level of chosen line intensity can be achieved by regulation of signal amplification. The investigated film is heated at constant temperature in region of phase transformation, i.e. crystallization on this recording level. The crystallization temperature of $TlIn_{1-x}Sn_xSe_2$ amorphous films is 420 – 480K. The thermal treatment of amorphous films at the given temperature leads to the fact that phase transformation begins. The investigated film being in the original carbonic capsule, is totally defend from oxidation and evaporation at transfer in electron diffractometer and further thermal treatment. The high quality of electron diffraction patterns obtained from the films deposited on KCl is observed. But not all obtained samples are seemed applicable for the investigation as substrate roughness on atomic level and stress on interface film-substrate influence the destructive action on the films during their separation from the substrates that is confirmed in [13].

The kinematic electron diffraction patterns in which the isothermal phase transformation is observed, i.e. the changes of the quantity and intensities of increasing crystal phase lines corresponding to different time moments are observed, are obtained at temperatures 420, 450 and 480K.

RESULTS AND THEIR DISCUSSION

$TlIn_{0.93}Sn_{0.07}Se_2$ films are chosen from obtained $TlIn_{1-x}Sn_xSe_2$ (x=0.02÷0.09) films by the way of change of phase composition. Three diffusion lines: $S=4\pi\sin\theta/\lambda$ = 0.212; 0.349; 0.519 nm^{-1} are observed in the beginning on kinematic electron diffraction pattern obtained at 450K (Fig.1) showing the process phase transformation.

Fig. 1. Kinematic electron diffraction pattern showing $TlIn_{0.93}Sn_{0.07}Se_2$ crystallization at temperature 450K.

The threshold temperature at which the instantaneous crystallization of amorphous film not allowing us to observe the whole dynamics of phase transformation process takes place, is 483K. The diffraction lines from polycrystal on kinematic electron diffraction pattern are indicated on the base of parameters of tetragonal cell $TlInSe_2$ with values a=b=0.8075, c=0.6847 nm [12].

The measurements of intensity, reflex radius and others are carried out for interpretation of electron diffraction pattern. As it is known [10], I_{hkl} line intensity is connected with irradiated volume of crystalline substance by following expression:

$$I_{hkl} = I_o\lambda\left|\frac{\Phi_{hkl}}{\Omega}\right|^2 V\frac{d_{hkl}^2\Delta}{4\pi L\lambda}P \qquad (3).$$

where I_o is intensity of primary beam radiation, λ is electron wavelength, Φ is structural amplitude of diffraction reflection which is calculated from atomic scattering factors in kinematic approximation, Ω is volume of elementary cell, V is irradiated volume of polycrystal preparation. Parameters d_{hkl} and Δ show the interplanar spacing and small region of Debye ring correspondingly, P is multiplicity factor of diffraction reflex amplification, $L\lambda$ is device constant which is defined in the dependence on applied voltage accelerating electrons.

The measurements of diffraction lines on electron diffraction pattern show that process of amorphous film crystallization takes place regularly, i.e. $I_{hkl} \sim V$. The widths and intensities of lines from different regions of kinematic electron diffraction pattern is defined by microphotometer MF-4 (Fig.2).

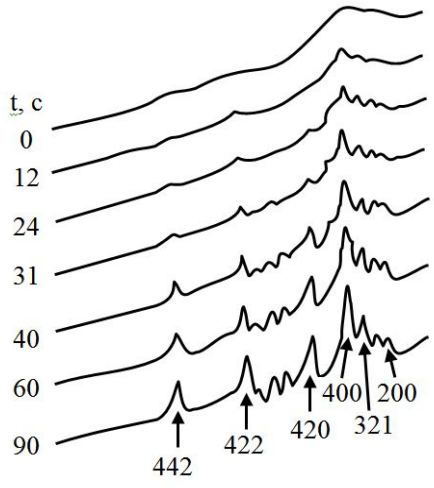

Fig.2. Microphotograms from different regions of kinematic electron diffraction pattern taken at 450K.

The temperature-time dependences of crystallization are formed with taking under consideration the intensities of diffraction lines of increasing crystal phase corresponding to different annealing moments (Fig.3).

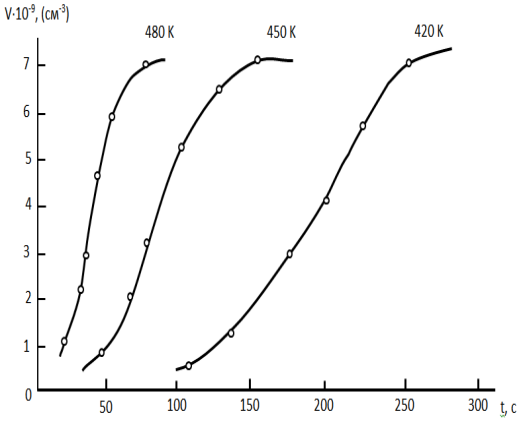

Fig.3. Kinematic curves of crystallization of amorphous $TlIn_{0.93}Sn_{0.07}Se_2$.

The obtained isotherms are compared with analytical expression (4) for kinetic curves of phase transformation:

$$V_t = V_o[1 - \exp(-kt^m)] \qquad (4)$$

where V_t is crystallized volume in the given time moment t; V_o is amorphous phase volume in the process beginning; $k=1/3\pi\omega c^3$ is reaction rate constant; ω is the rate of germ-formation of new phase in unit of non-transformed volume; c is crystal linear rate of growth; m is parameter characterizing the crystal growth dimension which is seemed equal approximately to 3 (m~3) in considered case. This confirms the two-dimensional growth of forming germs. The dependence graph $\ln\ln V_0/V_0\text{-}V_t$ on lnt for 420, 450 and 480K temperatures (Fig.4) which is described by analytic expression (4) is constructed on the base of electric registration on reflex intensities of diffraction pattern (t,I,V_t).

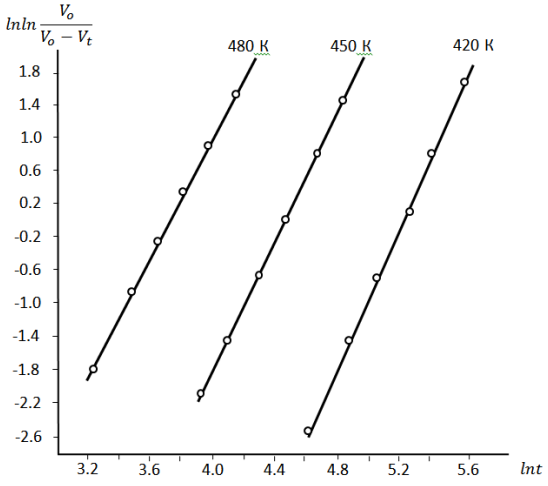

Fig.4. Dependence of $\ln\ln V_0/V_0\text{-}V_t$ on lnt for crystallization of amorphous $TlIn_{0.93}Sn_{0.07}Se_2$.

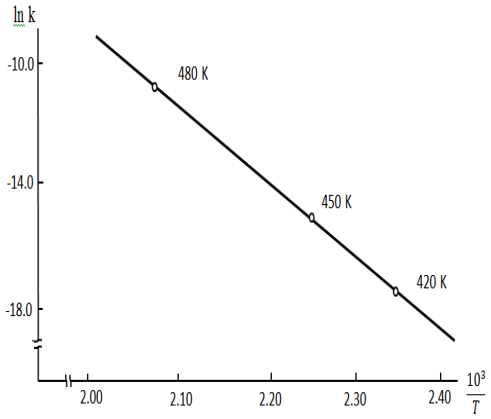

Fig.5. Dependence of lnk on reversal temperature for crystallization of amorphous $TlIn_{0.93}Sn_{0.07}Se_2$.

The value of total activation energy of crystallization process is equal to E_{tot}= 48.85 kcal/mol and it is defined by inclination of lnk dependence on inverse temperature $10^3/T$ (Fig.5). The values of germ-formation activation energy E_g and activation energy of their further growth E_{gr} which are given in table are also defined.

Table

Compounds	m	Activation energy		
		E_{tot}(kcal/mol)	E_{gr} (kcal/mol)	E_g (kcal/mol)
$TlInSe_2$	3	45.74	14.71	16.32
$TlIn_{1-x}Sn_xSe_2$	3	48.85	15.69	17.47

CONCLUSION

The investigation results by electron diffraction methods of crystallization kinetics of $TlIn_{0.93}Sn_{0.07}Se_2$ thin amorphous films are presented in the given paper. It is confirmed that for these compounds the effective crystallization activation energy increases on 6,8%, i.e. crystallization of amorphous films with impurity takes place at more high temperatures than without impurity. The increase of temperature interval of amorphous film crystallization up to 60^0C is observed. It is established that in phase transition process in the investigated temperature interval the two-dimensional crystal growth takes place. The lattice parameters of elementary cells increase correspondingly to syngonies in the given composition (at x=0.07) on 3.5% in crystalline films obtained after phase transition. The change of lattice parameters in the dependence on composition is non-lineal one. The increase of activation energy and lattice parameters at doping of $TlInSe_2$ with Sn impurity at unchangeable space symmetry group with taking under consideration of tin physical properties can be considered as regular one.

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Received:12.11.2020