CRYSTALLIZATION KINETIC PARAMETERS OF $Yb_{1-x}Sm_xAs_4S_7$(x=0,02 at.%) AMORPHOUS FILMS

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Crystallization kinetics of amorphous films of $Yb_{1-x}Sm_xAs_4S_7$(x=0,02 at.%) compounds obtained in both usual conditions and external electric field influence ones is investigated. The kinetic parameters of phase transformations at amorphous film crystallization have been defined.

The interaction of thin amorphous films of As_2S_3–$Yb_{1-x}Sm_x$ (x=0,02 at.%) system has been investigated by us in the work [1] and it is shown that the phase corresponding to chemical formula $Yb_{1-x}Sm_xAs_4S_7$ primarily forms at interaction of thin layers. The formation processes of other phases are limited by dominant formation of this phase. The present paper is dedicated to study of crystallization kinetics and definition of kinetic crystallization parameters of amorphous layers of $Yb_{1-x}Sm_xAs_4S_7$ (x=0,02 at.%) compounds by thickness 30nm obtained by vacuum condensation of molecular beam in both usual conditions and interaction conditions of external electric field on molecular beam.

Thin amorphous layers $Yb_{1-x}Sm_xAs_4S_7$ by thickness 30nm are obtained by the evaporation way of synthesized compound and steam condensation with rate ~30nm/sec in vacuum of 10^{-5}Pa order on NaCl, KCl crystals and amorphous celluloid being at room temperature. The polycrystalline phase $Yb_{1-x}Sm_xAs_4S_7$ relating to rhombic syngony with elementary cell periods a=0,724; b=0,568; c=1,025 nm [2] forms at substrate temperature T_{sub}=523 K.

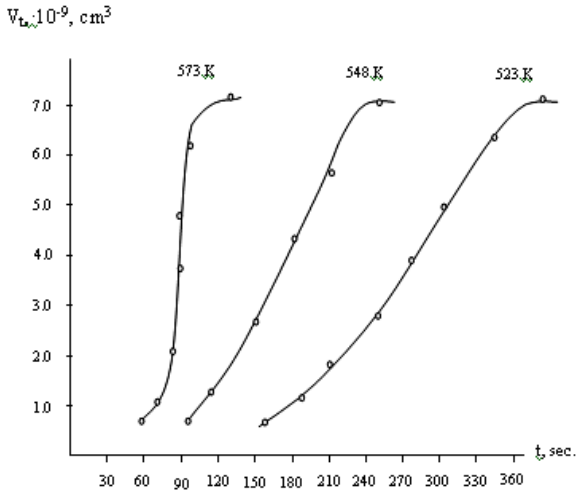

Fig.1. Kinetic crystallization curves of amorphous films $Yb_{1-x}Sm_xAs_4S_7$.

The kinematic method of electron diffraction [3] is used for establishment of kinetic parameters of $Yb_{1-x}Sm_xAs_4S_7$ amorphous film crystallization. The isothermal kinematic electron-diffraction patterns are obtained from amorphous films at T=523 K, T=548 K, T=573 K. At given temperatures it is seen on electron-diffraction patterns how diffusion lines relating to amorphous phase disappear and crystalline phase lines appear. The intensities of diffraction lines of crystalline $Yb_{1-x}Sm_xAs_4S_7$ are defined in the dependence on time of film thermal treatment. The transfer from intensity values to quantity of crystallized substance is carried out by the way of normalization taking into consideration the fact that intensities of electron scattering proportional to volume of scattering substance according to work [4] in kinematic approximation. The crystallization kinetic curves of amorphous $Yb_{1-x}Sm_xAs_4S_7$ are constructed in the investigated temperature interval (fig.1). The dependences $lnln(V_o/(V_o-V_t))$ on $ln\ t$ for temperatures T=523 K, T=548 K, T=573 K have been defined. The experimental points for all temperatures are put on direct lines (fig.2).

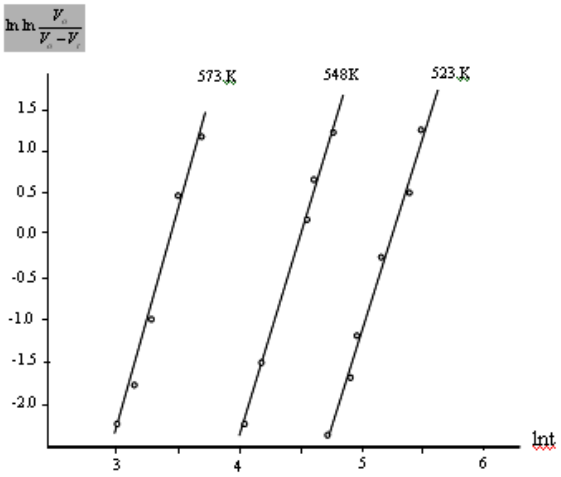

Fig.2. The dependence ln ln($V_o/(V_o - V_t)$) on $ln\ t$ for $Yb_{1-x}Sm_xAs_4S_7$.

The correlation of isotherms with analytic expression of phase transformation kinetic curves $V_t=V_o[1–exp(-kt^m)]$ shows that the better coincidence takes place at m equal to3 (m=2.90; 3,05; 3,10 for T=523, T=548, T=573 K).

The crossovers of lines of $lnln\ \frac{V_o}{V_o - V_t}$ dependence on $ln\ t$ with ordinate axis give $ln\ k$ values for the given temperatures. On the base of these data the plot of $ln\ k$ dependence on reverse temperature $1/T$ has been constructed. The general crystallization activation energy is defined on line inclination of $ln\ k$ dependence on $1/T$ which is linear one. It is equal to 112,4 kcal/mol. The nucleation activation energy $E_з$ calculated on line inclination of $1/\tau_o$ on $ln\ t$ (where τ_o is experimentally observable time of crystallization beginning) is equal to 34,2 kcal/mol. The activation energy of crystal growth E_p defined from ratio $E_p=(E_{общ} - E_з)/2$ is equal to 39,1 kcal/mol.

It is necessary to note that Sm impurities in $Yb_{1-x}Sm_xAs_4S_7$ influence on crystallization process and decrease the activation energy values [5].

The crystallization kinetics of amorphous films of $Yb_{1-x}Sm_xAs_4S_7$ compositions obtained in the conditions of external electric field influence by strength 3000 V·см$^{-1}$ is also investigated in the given paper. It is shown that the electric field significantly influencing on crystallization processes of amorphous layers, increases the rate of germ nucleation and rate of their further growth and ipso facto the crystallization rate increases.

Table

Electric field strength	Growth dimension	E_{gen} (kcal/mol)	E_p (kcal/mol)	E_3 (kcal/mol)
U=0	м=3	112,4	39,1	34,2
U=3000 в·см$^{-1}$	м=3	100,2	35,3	29,6

The value results of crystallization general activation energy, germ nucleation activation energy and crystallization growth of $Yb_{1-x}Sm_xAs_4S_7$ amorphous films obtained in both usual conditions and conditions of electric field influence by strength 3000V·cm^{-1}. As it is seen from the table the activation energy values decrease upon the average 10%.

The electric field influence which leads to acceleration of crystallization process and cause the decrease of activation energy values, can be explained by its interaction with electrically charged point defects or their accumulations in the films. Both potential of ion alkaline-haloid crystals used in our experiments as substrates and ionized atoms of condensated substances themselves are the charge sources.

Nowadays the fact that the electric interaction at condensation plays the significant role in film structure formation by the way of directed influence on all process stages beginning from vapor phase selection and ending by the influence on reorientation of continuous film, can be no doubt.

According to G.I. Distler, the nucleation takes place selectively on point defects of crystal surfaces having the electric charge, i.e. are “electric active” ones [6]. Bethge considers that electric fields with strength 10^5-10^6 V/m [7] can exist in NaCl surface layers.

The micro-crystals (islands) open to thermally activated or electrically stimulated migration [8]. That’s why the situation when micro-crystals shift from nucleation state, moreover the nucleation act of new germ can repeat on the latest ones, is quite real one. The migration increases at application of electric field and ipso facto crystallization process accelerates.

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$Yb_{1-x}Sm_xAs_4S_7$ (x=0,02 ат.%) AMORF NAZİK TƏBƏQƏLƏRİNİN KRİSTALLAŞMASININ KİNETİK PARAMETRLƏRİ

Adi şəraitdə və elektrik sahəsinin təsiri altında alınmış amorf $Yb_{1-x}Sm_xAs_4S_7$ nazik təbəqələrinin kristallaşma kinetikası tədqiq edilmişdir. Kristallaşma zamanı baş verən faza keçidlərinin kinetic parametrləri təyin edilmişdir.

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КИНЕТИЧЕСКИЕ ПАРАМЕТРЫ КРИСТАЛЛИЗАЦИИ АМОРФНЫХ ПЛЕНОК $Yb_{1-x}Sm_xAs_4S_7$(x=0,02 ат.%)

Исследована кинетика кристаллизации аморфных пленок соединений $Yb_{1-x}Sm_xAs_4S_7$ (x=0,02%), полученных как в обычных условиях, так и в условиях воздействия внешнего электрического поля. Определены кинетические параметры фазовых превращений при кристаллизации аморфных пленок.

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