ELECTRON DIFFRACTION INVESTIGATION OF CRYSTALLIZATION KINETICS OF $AgInSe_2$ AMORPHOUS FILMS

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The kinetics of phase transformations taking place in the result of amorphous $AgInSe_2$ film crystallization has been investigated by the method of kinematic electronography. It is established that thin amorphous layer crystallization $AgInSe_2$ obtained by vacuum precipitation on NaCl, KCl single crystals, takes place on regularities established by Avrami-Kolmogorovim and it is expressed by $V_t=V_0[1-exp(-kt^m)]$. The growth regularity at amorphous film crystallization $AgInSe_2$ which is equal to 2 and also the values of activation energies of germ-formation and their further growth which are equal to $E_з=20,2$ *kcal/mol* and $E_p=27,6$ *kcal/mol* have been defined correspondingly.

Spatially homogeneous germ-formation probability at similar rate and further their growth is described by Avrami-Kolmogorov (A-K) [1-2] in the case of amorphous substances. One can obtain the information about phase transformation mechanism in everlasting volume in the supposition about the fact that phase transitions take place with the formation of big amount of new phase germs occasionally distributed in the space and time with their following growth by the studying of temperature-time dependence of amorphous film crystallization. The following kinetic equation

$$V_t = V_0\left[1 - exp\left(-\kappa t^m\right)\right] \qquad (1)$$

is the general one for description of formation kinetics of new phase germs in the given time moment with their further growth as in the case of constant origin rate, so at decreasing one.

The analytical expression (1) allows us to define temperature-time dependence of film crystallization which is the dependence on time of relative part of initial phase, where V_t is part of substance volume endured the transformation to moment t, V_0 is initial volume which is volume of amorphous phase in the beginning of phase transformation process, K is reaction rate constant equal to $0,8\omega_3(\kappa_s c)$ where ω_3 is origin rate of new phase germs in the unit of non-switched volume, k_s is shape form, c is growth linear rate. The m value is different for different possible transformation types and depends on crystal growth size: the conclusions about possible transformation mechanism are done on the base of the value of m-degree index. Note that one should have the detail experimental data about V_t for obtaining of reliable results with the help of A-K theory.

In the given paper the crystallization process of amorphous films $AgInSe_2$ obtained on new-spalled single crystals NaCl, KCl and amorphous celluloid obtained by evaporation of synthesized substance in vacuum ~10^{-4}Pa has been investigated by the method of kinematic electronography. The isothermic kinematic electronograms at 423, 438, 453 and 473K have been obtained for studying of kinetic crystallization of amorphous layers $AgInSe_2$ by the thickness ~25 nm. The strong phase transition in the result of which one can't observe the transformation dynamics takes place higher 473K. The kinematic electronogram on which the amorphous and crystal phases and also the coexistence region of both phases are observed, is given on the fig.1.

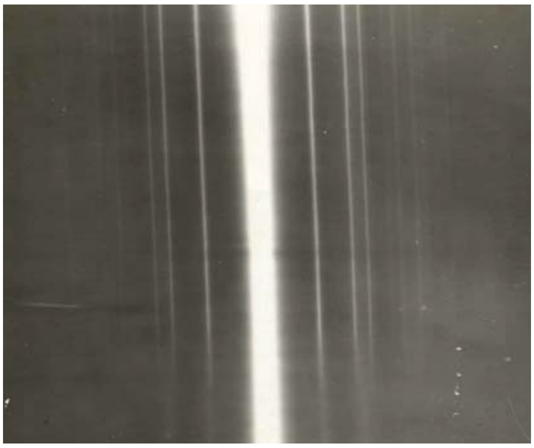

Fig.1. Kinematic electronogram from $AgInSe_2$.

The microphotogram from defined regions of kinematic electronograms corresponding to different time moments of film annealing are obtained for measurement of diffraction line intensity of increasing crystal phase $AgInSe_2$ on microphotometer MPh-4. The transition from intensity values to quantity of crystallized substance is carried out by the way of normalization taking into consideration the fact that electron dispersion intensity in kinematic approximation is proportional to the volume of dispersed substance $I_{hkl} \sim V$ [3]. On kinematic electronogram the intensification with line intensity time on crystal phase at crystallization is caused by increase of polycrystal phase volume radiated by electron beam, i.e. the intensity changes of diffraction lines of one phase is connected with quantity change of this phase in radiated volume as the general substance quantity in it stays constant. As the small region from diffraction part is fixed on kinematic electronogram, then one can said about local intensity of Debye ring corresponding to small region Δ which is expressed by the following formula according to [2]:

$$I_{hkl} = I_0\lambda\left|\frac{\Phi_{hkl}}{\Omega}\right|^2 V\frac{d_{hkl}^2\Delta P}{4\pi L\lambda} \qquad (2)$$

where I_0 is intensity of primary radiation beam; λ is length of electron wave, Φ is structural amplitude of diffraction reflection which is calculated from atom dispersion factor in kinematic approximation, Ω is volume of elementary crystal cell, V is radiated volume, d_{hkl}^2 is interplanar spacing, is small region of Debye ring, P is multiplicity factor of diffraction reflex increase, $L\lambda$ is device constant.

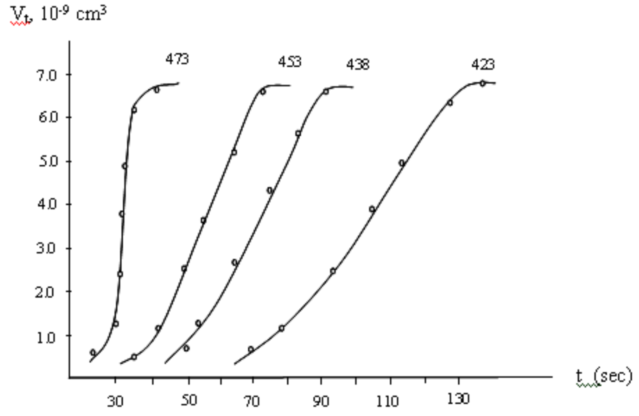

Fig.2. Kinetic curves of crystallization of $AgInSe_2$.

The intensity max value is compared with totally crystallized substance volume and the volume corresponding to intensity unit, has been defined. The kinetic crystallization curves of amorphous $AgInSe_2$ have been constructed in the investigated interval (fig.2).

The value of index *m* in (1) defined from line inclination of $ln\,ln(V_0 / V_0 - V_t)$ on lnt for temperatures mentioned above is close to 3 (*m*=2,72; 2,80; 2,93 and 2,99 for 423, 438, 453 and 473K) correspondingly. This shows that the crystal two-dymensional growth takes place in the case of amorphous crystallization $AgInSe_2$. The general activation energy of crystallization equal to 75,3kcal/mol has been defined on line inclination of *ln k* dependence on reverse temperature. The activation energy of germ formation calculated on line inclination of *l/t* dependence on *ln t* (here τ is incubation time, experimentally observable time of crystallization beginning) is equal to 20,2kcal/mol. The activation energy of crystal growth E_{gr} defined from relation $E_{gr} = (E_{gen} - E_3)/2$, is equal to 26,7kcal/mol.

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$AgInSe_2$ AMORF TƏBƏQƏLƏRİNDƏ KRİSTALLAŞMA KİNETİKASININ ELEKTRONOQRAFİK TƏDQİQİ

Kinematik elektronoqrafiya üsulunun tətbiqi ilə $AgInSe_2$ amorf təbəqələrinin kristallaşması nəticəsində baş verən faza çevrilmələri tədqiq edilmişdir. Müəyyən olunmuşdur ki, NaCl KCl monokristalları üzərində vakuumda çökdürmə ilə alınmış $AgInSe_2$ nazik amorf təbəqələrin kristallaşması Avrami-Kolmoqorov qanunauyğunluqları əsasında baş verərək $V_t=V_0[1-exp(-kt^m)]$ analitik tənliyi ilə təsvir olunur. $AgInSe_2$ amorf təbəqələrin kristallaşması zamanı əmələ gələn kristallitlərin iki ölçülü (*m*=3) olması təyin edilmiş, kristallit rüşeymlərin əmələ gəlməsi və onların sonrakı böyümələri üçün tələb edilən aktivləşmə enerjilərinin (E_r və E_b) qiymətləri müəyyən olunmuşdur: E_r*=20,2 kkal/mol*; E_b*=27,6 kkal/mol*.

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ЭЛЕКТРОНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ КИНЕТИКИ КРИСТАЛЛИЗАЦИИ АМОРФНЫХ ПЛЕНОК $AgInSe_2$

Методом кинематической электронографии исследована кинетика фазовых превращений, происходящих в результате кристаллизации аморфных пленок $AgInSe_2$. Установлено, что кристаллизация тонких аморфных слоев $AgInSe_2$, полученных вакуумным осаждением на монокристаллы NaCl, KCl происходит по закономерностям, установленным Аврами- Колмогоровым, и описывается аналитическим выражением $V_t=V_0[1-exp(-kt^m)]$. Определены мерность роста при кристаллизации аморфных пленок $AgInSe_2$, равная двум, а также значения энергий активаций зародышеобразования и дальнейшего их роста, равные $E_з$*=20,2ккал/моль* и $E_р$*=27,6 ккал/моль* соответственно.

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