THE KINETICS OF PHASE TRANSITIONS IN AMORPHOUS FILMS TlInSe$_2$, OBTAINED UNDER THE CONDITIONS OF THE ACTION OF THE EXTERNAL ELECTRIC FIELD

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The kinetics of crystallization of TlInSe$_2$ amorphous films obtained by thermal evaporation under the conditions of the action of external electric field (E=3000 V·cm^{-1}) is studied by kinematic electron diffraction method.

The summary activation energy of crystallization is equal to 36,04Kkal/mol. Crystallization velocity of films obtained in electric field is higher than one of films obtained under ordinary conditions.

The kinematic electron diffraction method is applied for the investigations of phase transition processes. It can be applied also for the measurements of diffusion velocities in the thin films, basing mainly on the optical measurements.

For every concrete material of any substance class the stationary activation energy values showing the final of phase transitions carrying out with the creation of new phase bud and the further their growth are defined by this method. The results obtained by this method can't be achieved with the enough definiteness by the method of optical reflection and other optical methods, which are potentially not useful for the thin films of the width from the several nm till the some decades of nm, on the investigation results of *X*-ray spectrometry, ellipsometry.
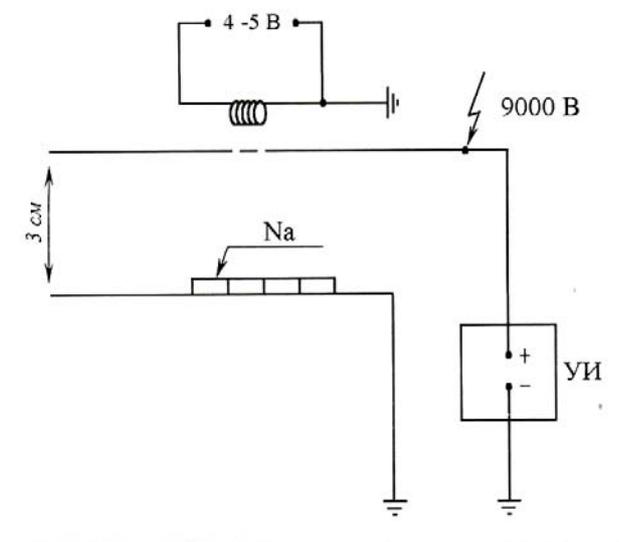

Fig1 The circuit of electric field creation.

The investigation objects (amorphous films TlInSe$_2$) are obtained by the way of condensation of the given compound in the vacuum 10^{-4} Pa. The amorphous films that crystallized at the different temperatures are prepared at the similar conditions. The steam condensation is carried out in the constant electric field (fig.1) of the strength E=3000V·cm^{-1}. The substrates are the small fresh chips of stone salt. The films from these substrates are taken by the dissolution of NaCl in the water and put on the special furnaces, which are especially for the kinematic shooting of the diffraction figures, allowing to register the phase transformations photographically.

In the electron diffraction study the photographic registration of phase transitions is interest not only by its expressivity, but by the possibility to obtain the all picture of electron scattering immediately. From the electron diffraction pattern, it is possible to take the information about the sample microstructure: about superstructural reflections, reflexes from twins and general character of background distribution.
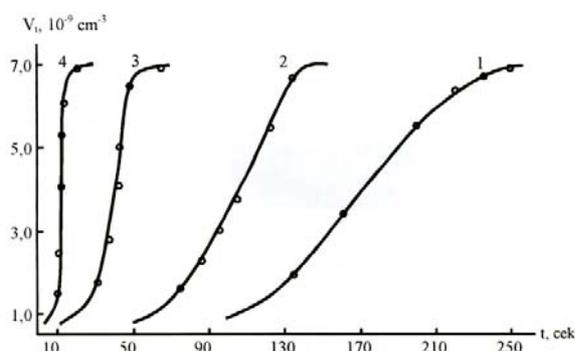

Fig. 2. Kinetic crystallization curves of amorphous TlInSe$_2$. Values T$_{кр}$: 1 - 358 K; 2 - 368 K; 3 - 403 K; 4 - 443 K.

For the definition of kinetic parameters of phase transformations in the amorphous films TlInSe$_2$ of the width 25 nm obtained under the conditions of the action of electric field the isothermal kinematic electron diffraction patterns at the four different temperatures: 398, 408, 423, 443K have been obtained. The three diffusion lines corresponding to $S=4\pi sin\theta/\lambda=0,2061$; 0,3395; 0,5040nm^{-1}; are observed on the kinematic electron diffraction pattern (fig.2), taken at 423K, on which the process of phase transformation is observed. The disappearance of diffusion lines according to amorphous phase is accompanied by the appearance of the lines of crystalline phase, the intensities of which correspond to the different moments of film annealing. The electron diffraction pattern calculation shows that amorphous film TlInSe$_2$ is crystallized in the tetragonal crystal system with the periods of unit cell of crystalline lattice, a=0.8075±0.001, c=0.6847±0.002nm, c/a=0.8479, SGS I4/mcm, the number of formulae units in the cell z=4 [1].

The photomicrograms have been taken with the aim of the measurement of line intensities of crystalline TlInSe$_2$ from the different areas of kinematic electron diffraction patterns obtained in the process of amorphous film crystallization. The intensities of lines of crystalline phase of TlInSe$_2$ are defined by them. The transition from the intensity values to the quantity of crystallized substance is carried out with the

help of Vainshtein formula [2], taking into consideration, that intensity of electron scattering is proportional to the volume of scattering substance.

$$I_{hkl} \;=\; I_o\lambda \;\cdot\; \left|\frac{\Phi_{hkl}}{\Omega}\right|^2 \;\cdot\; \frac{Vd_{hkl}^2\Delta p}{4\pi\lambda l} \;. \qquad (1)$$

Here I_0 is intensity of primary beam, λ is wave length of primary beam, Φ is structure factor, Ω is the volume of unit cell, V is the irradiated volume of polycrystalline substance, d_{hkl} are interplanar distances, Δ is small area of Debye ring, p is repeatability factor, λl is device constant.

The values stay constant during the kinematic film, besides of the volume V. It is followed, that defining the line intensities change on the kinematic electron diffraction patterns, one can possible to find the change of substance quantity in the dependence on the crystallization time. During the transition from the intensity to the volume maximum value of intensity is compared with the irradiated volume $V=S\cdot h$, where S is the cross-section of electronic beam~$2,8\cdot10^{-3}$cm⁻¹, h is the film width~$2,5\cdot10^{-6}$ cm.

Defining by the given comparisons, the volume of intensity unit, the value of volume of crystallized phase in every given time moment on the base of which the plots of dependence of phase volume changing on time are constructed, are found (fig.3).
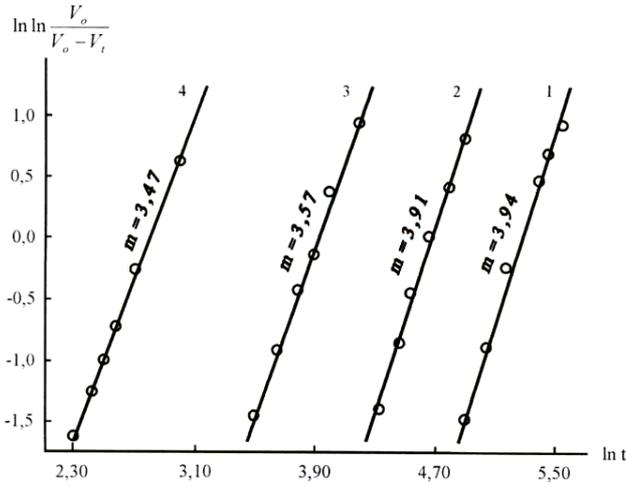

Fig. 3. Dependence $lnln[V_0/(V_0-V_t)]$ on lnt for crystallization of amorphous TlInSe₂. Denotes are as on Fig. 2.

The obtained isotherms are compared with the famous analytic expression of Avraami-Colmogorov for the kinetics of phase transitions carrying out with the creation of the new phase buds with the following their growth.

$$V_t = V_o\left[1 - exp(-kt^m)\right] \qquad (2)\ [3\text{-}4],$$

or

$$ln\,ln\left[\frac{V_o}{V_o - V_t}\right] = ln\,k + m\,ln\,t \quad, \qquad (3)$$

where V_t is crystallized volume in time moment t, V_0 is the initial volume, K is reaction velocity constant, m is constant, characterizing the growth of size of new phase center.

From the formula (3), it is followed, the linear dependence $lnln[V_0/(V_0-V_t)]$ on the lnt. The plot of the dependence $lnln[V_0/(V_0-V_t)]$ on the lnt for temperatures 398, 408, 423, 443K given on the fig.3 has been constructed on the base of experimental data.

The plot, given on the fig.3 shows, that this dependence is described by direct lines, on which all experimental points for given temperatures are put. From these line inclinations the values of "m" exponent on t have been calculated. These values were close to four. It shows, that in the case of amorphous film Tl In Se₂ crystallization obtained in the electric field the three-dimensional growth of small crystals, depending on the law established by Avraami-Colmogorov takes place and is described by the equation (2).

The values of lnk, established for temperatures 398, 408, 423, 443K are equal to -15,80; -12,27; -10,57; -8,43 correspondingly. The plot of the dependence lnk on inverse temperature has been constructed on the base of these data. The linear dependence lnk on $1/T$ shows that velocities of bud creation and linear growth of small crystals need to describe by the expression of the type of Arrenius equation [5]

$$ln\,k = A - \frac{(E_3 + 3E_p)}{RT}, \qquad (4)$$

where A is constant independent on the temperature, R is universal gas constant, T is absolute temperature, E_3 is activation energy of bud creation, E_p is activation energy of small crystals growth.

From the direct line inclination lnk on $1/T$, the general activation energy of crystallization process, which is equal to 36,04 kkal/mol, has been estimated.

The activation energy of bud creation, calculated from the plot dependence $ln(l,\tau)$ on $1/T$ (where τ is experimentally observed time of crystallization beginning) is equal to $E_3=tg\alpha\cdot R=15,3$. Here $tg\alpha$ is inclination angle of direct line from the plot $ln(l/\tau)$ on $1/T$.

The activation energy of small crystals growth E_p defined from the ratio $E_p=(E_{общ}-E_3)/3$, is equal to 10,35 kkal/mol. The values of activation energies of bud creation and their further growth, including the general activation energy of film TlInSe₂ crystallization obtained in the conditions of electric field action are smaller than corresponding values for films obtained outside the field [5].

The only one acceptable explanation of decrease of activation energy values for amorphous films in the electric field can be given in the terms of ordering process. This means, that during the process of molecular beam condensation on the surface of ion crystals NaCl, the ordered under the action of electric field, the additional centers of bud creation of crystalline phase, which can be point, line, two-dimensional defects, having electric charges or their collections, simplifying their further growth, have been created.

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XARİCİ ELEKTRİK SAHƏSİNİN TƏSİRİ ŞƏRAİTİNDƏ ÇÖKDÜRÜLMÜŞ TlInSe₂ AMORF TƏBƏQƏLƏRİNİN KRİSTALLAŞMA KİNETİKASI

Vakuumda elektrik sahəsinin (E=3000 V·sm^{-1}) təsiri şəraitində çökdürülmüş TlInSe₂ amorf təbəqələrinin kristallaşma kinetikası kinematik elektronoqrafiya üsulu ilə tədqiq edilmişdir.

Kristallaşmanın ümumi aktivləşmə enerjisi 36,04 kkal/mol-a bərabərdir. Elektrik sahəsində alınmış təbəqələrin kristallaşma sürəti adi şəraitdə alınanlara nisbətən böyükdür.

Д.И. Исмаилов

КИНЕТИКА ФАЗОВЫХ ПЕРЕХОДОВ В АМОРФНЫХ ПЛЕНКАХ TlInSe₂, ПОЛУЧЕННЫХ В УСЛОВИЯХ ВОЗДЕЙСТВИЯ ВНЕШНЕГО ЭЛЕКТРИЧЕСКОГО ПОЛЯ

Методом кинематической электронографии исследована кинетика кристаллизации пленок TlInSe₂ , полученных термическим напылением в условиях воздействия внешнего электрического поля напряженностью E=3000 В см$^{-1}$.

Общая энергия активации кристаллизации равна 36,04 ккал/моль. Скорость кристаллизации пленок, полученных в электрическом поле, больше, чем для пленок полученных в обычных условиях - вне электрического поля.