

**ELECTRON DIFFRACTION STUDY OF THE TEMPERATURE-TIME  
DEPENDENCES OF CRYSTALLIZATION OF NANOTHICK AMORPHOUS  
CuIn<sub>5</sub>Te<sub>8</sub> FILMS**

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Kinematic electron diffraction was used to study the crystallization processes of amorphous CuIn<sub>5</sub>Te<sub>8</sub> films obtained under normal conditions and under the influence of an external electric field with a strength of 500Vcm<sup>-1</sup>. Isothermal curves of phase transitions are constructed and the kinetic parameters of phase transformations are determined: the dimensions of crystal growth and activation energies are established. It is shown that during the crystallization of amorphous CuIn<sub>5</sub>Te<sub>8</sub> films, the rates of nucleation and their further growth follow the Arrhenius relations.

**Keywords:** kinematic electron diffraction pattern, thin films, crystallization isotherms, activation energy.

**PACS:** 61.66.Fn

## 1. INTRODUCTION

The study of the temperature-time dependences of the kinetics of phase transitions (*PT*) in nano thick semiconductor amorphous carriers, along with the study of the structure, the distribution of impurities in crystalline and amorphous films, the establishment of superstructural phases resulting from deformations of crystal lattices, the formation of phases due to reactions of chemical elements, etc... is an important area of electron diffraction research, for which nanoscale thin semiconductor layers are characteristic objects. In the work [1] by the synthesis of double compounds of pseudobinary sections of the system  $A^I C^{VI} - B_2^{III} C_{3n}^{VI}$  ( $n=0,1,2...$ ) and chemical elements of the Cu-In-Te ternary system, taken in the ratios Cu:In:Te=1:5:8 components, which were subjected to chemical-thermal treatment before being loaded into double quartz ampoules, ternary compounds included in the common chemical group  $A^I C^{VI} - B_{2n+1}^{III} C_{3n+2}^{VI}$ . Phase composition indices of ternary compounds in this formula group of compounds refer to a series of natural numbers  $n=0,1,2...$  X-ray diffraction analysis found that the synthesized bulk single crystals (Cu:In:Te=7,18:35,31:57,51 at.%) are consistent with the composition of the initial samples (Cu:In:Te=7,14:35,72:57 at.%). The crystallographic parameters of the tetragonal lattices of the grown single crystals with the chalcopyrite structure of composition CuIn<sub>5</sub>Te<sub>8</sub> are equal to  $a=6,162$ ;  $c=12,29\text{\AA}$ .

## 2. EXPERIMENTAL METHODS

This work is devoted to the experimental study of the temperature-time dependences of the *PT*, as a result of the crystallization of nanothick amorphous films of the composition CuIn<sub>5</sub>Te<sub>8</sub>, obtained by sublimation of binary compounds Cu<sub>2</sub>Te and In<sub>2</sub>Te<sub>3</sub> in vacuum with a residual pressure of  $\sim 10^{-4}$  Pa, as well as the components of the Cu-In-Te system of the highest purity deposited by evaporation, taken in ratios 1:5:8.

The study of the kinetics of any process, i.e., Establishing a relationship between the proportion of the undergoing change due to *PT* and the transformation time *t* determines the kinetics of any physical and chemical processes. Establishing the kinetic parameters of the *PT* is associated with a certain complexity, since the mechanism of the formation of centers during the crystallization of amorphous substances and their further growth is often unknown, information about which can only be obtained by studying the temperature-time dependences of the *PT*. To establish the dependence between the volume undergoing *PT* and time, it is necessary to find the values of two interrelated parameters: the rate of nucleation ( $v_3$ ) and their further growth ( $v_p$ ). The rate of formation of new phase centers ( $v_3$ ) in the "mother medium" is defined as the number of nuclei that turn into crystallization centers per unit time per unit volume of the metastable phase. The rate of change in the linear dimensions of growing crystalline particles is the linear rate of crystallization. However, by setting the values of  $v_3$  and  $v_p$ , only the problem of the *PT* time is solved and such an essential issue as the filling of the initial volume with emerging and growing nuclei of crystals of the new phase is not addressed, since in this case the statistical nature of the overlap of the growing centers of the new phase is not taken into account and is not taken into account. The rate of change in the linear dimensions of growing crystalline particles is the linear rate of crystallization. However, by setting the values of  $v_3$  and  $v_p$ , only the problem of the *PT* time is solved and such an essential issue as the filling of the initial volume with emerging and growing nuclei of crystals of the new phase is not addressed, since in this case the statistical nature of the overlap of the growing centers of the new phase is not taken into account and is not taken into account.

$$V_t = V_0 [1 - \exp(-1/3 v_3 v_p^3 t^4)] \quad (1)$$

where,  $Vt$  is the volume of the substance undergoing transformation by the moment  $t$ ,  $V_0$  is the initial volume. Equation (1), however, without taking into account the dimensionality of growth, gives only a general statistically probabilistic solution of the problem of the transformation time and does not reveal the physical features of the kinetics of a particular process, assuming that the total volume of the initial phase is infinitely large. The time of the *FP* half-cycle according to (1) is equal to  $t_{0,5} = \sqrt{0,65/v_3 v_p}$ , and the complete isothermal transformation  $V_t = V_0$  occurs at infinity  $t_{tot} = \infty$ .

The rate of invariant isothermal phase transitions in time is described by the expression

$$\left(\frac{dV}{dt}\right) = (V_0 - V_t) v_3 q_t \quad (2)$$

here,  $q_t$ -crystallized by time  $t$  volume in the "metastable mother medium", the rate of increase, which is proportional to the active surface of the growing center  $S$  (1) and the linear rate of its growth  $v_p$

$$\frac{dq_t}{dt} = S_1 v_p \quad (3)$$

The active surface of the growing crystal is expressed as a function of the volume of the growing center of the forming phase

$$S_t = k_s q^v \quad (4)$$

where,  $k_s$ -is the crystal shape coefficient,  $v$  is the exponent characterizing the growth dimensions of the growing center. At values of  $v$  equal to  $2/3$  and  $1/2$ , three-dimensional and two-dimensional formations of a new phase are formed in the process of crystallization, respectively, and with a growth dimension equal to zero  $v=0$ , the volume growth is limited by the process of nucleation itself by finite volumes that do not grow further. Taking into account the dimensionality of the growth of crystals, in order to estimate the crystallized part of the volume of the initial phase by time  $t$ , using (3) and (4) in [3], the following formula was obtained:

$$q_t = [(1-v) A_t + \delta_s^{1-v} J^{1/(1-v)}] \quad (5)$$

here,  $A_t$  and  $\delta_s$  are the product of the form factor and the linear growth rate ( $k_s v_p$ ) and the value of the growing center of the formed phase, respectively. Taking into account (5) in (2) and solving the resulting equation for  $V_t$ , we obtain the general analytical equation presented in [3] as

$$V_t = V_0 [1 - \exp(-kt^m)] \quad (6)$$

which describes the kinetics of the phase transition that proceeds with the appearance of nuclei of a new phase, taking into account the statistical nature of the overlap of growing centers. In (6),  $k$  is the reaction rate constant equal to  $1/3\pi v_3 v_p^3$ , the value of  $m$  depends on the growth dimension and is different for possible types of *FP*. Conclusions about the possible mechanism of the *FP* are made on the basis of the value of the exponent  $m = (2-v)/(1-v)$ .  $v = c_1 \exp(-U_3/kT)$ , where,  $c_1$  is a temperature-independent quantity,  $U_3$  is the nucleation activation energy. Relationship (6) characterizes the

kinetic curve of the isothermal process, which determines the dependence of the volume of the new phase  $V$  on the duration of heat treatment of thin films. It was shown in [4-5] that bypassing the cumbersome quantitative analysis of the transformation processes, the regularities and kinetic parameters of the phase transition can be established by formula (6) by molecular-kinetic consideration of the crystallization of amorphous substances. For continuous time monitoring of the course of the transformation process, the methods given in [6-7] are known, with the help of which, during the heating of the sample, changes in the intensities of diffraction reflections are recorded, in which the angular positions change during the phase transition. The shifts of the diffraction peaks are measured by a slit-aperture counter. In this case, errors in determining changes in the intensities of diffraction peaks can reach ~15%.

The kinematic electron diffraction method developed in [8] makes it possible to obtain continuous electron diffraction images in terms of accuracy and sharpness of the diffraction field that are not inferior to discrete electron diffraction patterns, which are recorded on photographic plates. The essence of the method of kinematic electron diffraction as a physical method is to fix the diffraction pattern on a uniformly moving photographic plate, uniform movement, which is achieved with a reduced electric motor. During the crystallization of the studied amorphous films, due to their heat treatment, a diffraction pattern from a polycrystal is established with a slit located along the horizontal radius of the diffraction concentric rings, a narrow strip is established, which turns the diffraction pattern into parallel lines symmetrical with respect to the electron beam. Kinematic surveys were carried out by us at a speed of  $1/3$ ,  $1/2$ ,  $1/6$  and  $1/10 \text{ mm/sec}$ . Heat treatment of  $\text{CuIn}_5\text{Te}_8$  films  $250 \text{ \AA}$  thick was carried out using a tantalum tape with several holes  $0.1-0.5 \text{ mm}$  in diameter. The films under study were heated directly in the column of an *EMR-102* electron diffraction recorder. The calibration of these special furnaces, consisting of tantalum tapes with dimensions of  $25 \times 1,5 \times 0,07 = 0.1 \text{ mm}$ , was carried out using a copper constant or chromel-alumel thermocouple, as well as according to the melting points of In, Sn, Pb. Experiments on obtaining amorphous  $\text{CuIn}_5\text{Te}_8$  films suitable for research were similar to the experiments carried out in [9]. In [10], a curve of the radial distribution of atoms was plotted for amorphous  $\text{CuIn}_5\text{Te}_8$  films and the structure of the short-range atomic order in them was determined.

### 3. RESULTS AND DISCUSSION

In order to obtain and study the kinetics of crystallization of amorphous films of composition  $\text{CuIn}_5\text{Te}_8$ , simultaneous thermal evaporation of binary compounds  $\text{Cu}_2\text{Te}$  and  $\text{In}_2\text{Te}_3$  was carried out in a vacuum of  $\sim 10^{-4} \text{ Pa}$  under normal conditions and under the influence of an external electric field with a strength of  $500 \text{ Vcm}^{-1}$  from tungsten spiral-shaped conically wound spirals. Thin  $\text{CuIn}_5\text{Te}_8$  films with a calculated thickness of  $\sim 250 \text{ \AA}$  were obtained by us by sublimation

of the synthesized binary compounds mentioned above on NaCl substrates preliminarily cooled to 203K. With heating of amorphous  $\text{CuIn}_5\text{Te}_8$  films with values  $S=4\pi s \sin\theta/\lambda=1,66; 3,20$  and  $4,91\text{\AA}^{-1}$ , corresponding to diffuse lines on the kinematic electron diffraction patterns (fig.1), at relatively low temperatures, they pass into a crystalline state.

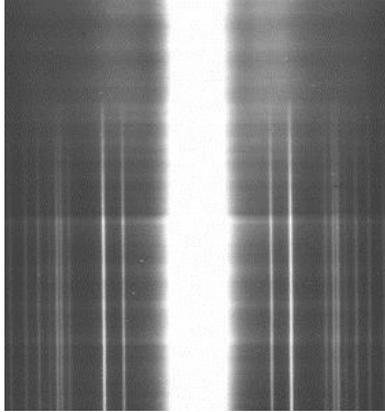


Fig.1. Kinematic electron diffraction pattern of amorphous  $\text{CuIn}_5\text{Te}_8$  undergoing a phase transition at 403K.

The intensities of diffraction lines with indices (210), (301) and (420) were determined, which had the best resolution and, therefore, were most convenient for intensity measurements. From the values of the intensities of diffraction reflections of crystalline  $\text{CuIn}_5\text{Te}_8$  to the corresponding values of the volume  $V_c$ , we passed according to the procedure given in [9]. As can be seen from the crystallization isotherms of amorphous films plotted for temperatures of 350, 373

and 403K (fig.2), the slope of the curves sharply increases with increasing temperature, which indicates a rapid increase in the crystallization rate with an increase in the annealing temperature of the films.

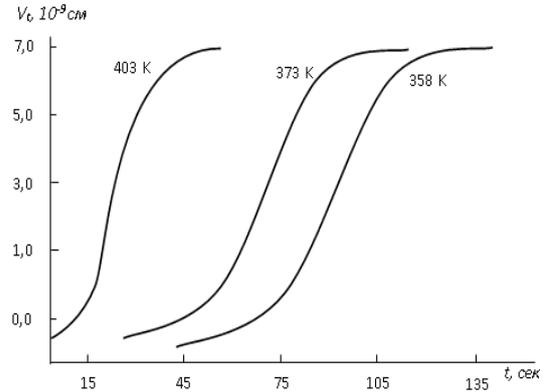


Fig.2. Kinetic curves of crystallization of amorphous  $\text{CuIn}_5\text{Te}_8$ .

To compare the experimental isotherms with the analytical expression of the crystallization kinetics, the dependences  $\ln \ln V_0/(V_0 - V_t)$  on  $\ln t$  were plotted. Almost parallel lines are obtained for all temperatures, which indicate that the experimental isotherms can be described by expression (6). From the slope of the straight lines to the abscissa axis, the value of the exponent  $m$  in expression (6) is found to be equal to  $\sim 4$ . This value of  $m$  indicates that in the case of crystallization of amorphous  $\text{CuIn}_5\text{Te}_8$  films with a thickness of  $\sim 250\text{\AA}$ , as well as in the case of  $\text{CuIn}_5\text{S}_8$  [9], three-dimensional growth of crystals takes place.

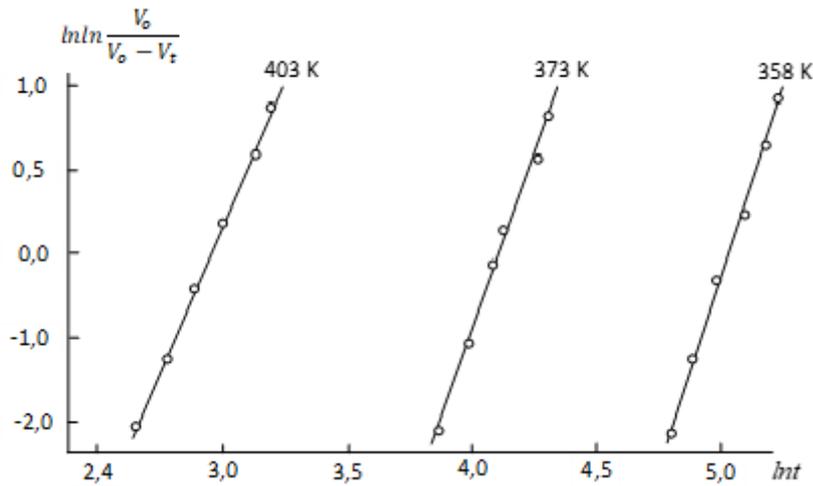


Fig.3. Dependence of  $\ln \ln V_0/(V_0 - V_t)$  on  $\ln t$  for crystallization amorphous  $\text{CuIn}_5\text{Te}_8$ .

The value of  $\ln K$  determined using the plot of  $\ln \ln V_0/(V_0 - V_t)$  versus  $\ln t$  is as follows: at 358K  $\ln K=-33.7$ ; at 373K  $\ln K=-23.2$ ; and at 403K  $\ln K=12.9$ . The graph of  $\ln K$  dependence on the reciprocal temperature (fig.3), built on the basis of the above data, shows that the experimental points lie on one straight line.

The linear dependence of  $\ln K$  on  $1/T$  is explained by the fact that in the temperature range under study, the rate of nucleation  $v_3$  and the rate of crystal growth

$v_p$  can be described by an Arrhenius type expression: Representing  $v_3$  and  $v_p$  in an Arrhenius type equation and taking the logarithm of  $K$ , we obtain:

$$\ln K = c - \frac{U_3 + 3U_p}{RT} \quad (7)$$

here,  $c$ - is some temperature-independent constant,  $U_3$  and  $U_p$  - are the activation energies of nucleation and growth of crystals, respectively,  $R$ - is the universal gas

constant. The value of the sum  $U_3+3U_p$ , established by the slope of the straight line shown in fig.4 to the abscissa axis, is  $32,8\text{kcal/mol}$ . The activation energy of nucleation  $U_3$ , calculated from the slope of the direct dependence of  $1/\tau$  on  $\ln t$  (where  $\tau$  is the incubation time,

i.e. the experimentally observed crystallization onset time) is  $12,6\text{kcal/mol}$ .  $U_p$  determined from the ratio  $U_p=(U_{gen}-U_3)/3$  was equal to  $6,7\text{kcal/mol}$ .

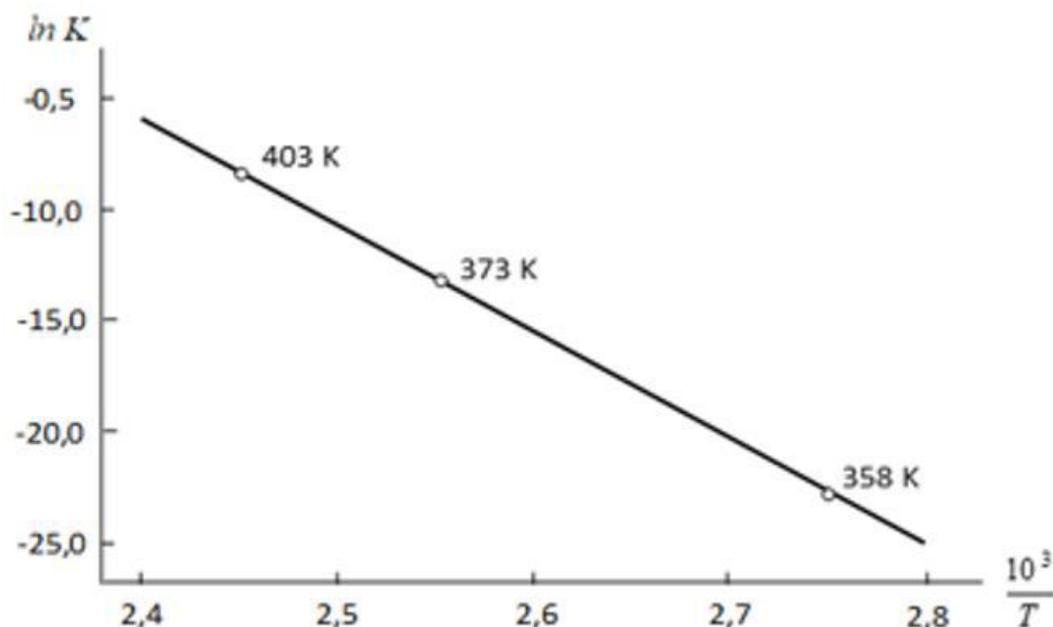


Fig.4. Temperature dependence of  $\ln K$  for crystallization amorphous  $\text{CuIn}_5\text{Te}_8$ .

Since electric fields (constant and variable) have a significant effect on the crystallization processes, experimentally confirmed in [10–12], we also studied the crystallization kinetics of amorphous  $\text{CuIn}_5\text{Te}_8$  films condensed under the influence of an external electric field with a strength of  $500\text{V}\cdot\text{cm}^{-1}$ . A constant electric field was created between two parallel copper plates. On the surface of the negatively charged bottom plate, there were substrates-fresh NaCl cleavages. The upper plate had two holes  $5\text{mm}$  in diameter through which the molecular beams passed and reached the surface of the substrates. The substrate temperature was  $203\text{K}$ . The deposition rate was  $20\text{\AA}/\text{sec}$ . The study of the crystallization kinetics of amorphous  $\text{CuIn}_5\text{Te}_8$  films obtained under the action of a field was carried out similarly to that for films obtained under ordinary conditions. Isothermal kinematic electron diffraction patterns were obtained at temperatures of  $358$ ,  $373$  and  $403\text{K}$ . From the plot of  $\ln \ln V_0/(V_0-V_t)$  versus  $\ln t$ , built

on the basis of the  $\text{CuIn}_5\text{Te}_8$  crystallization kinetic curves for the above temperatures, for which the intensities of diffraction lines with the indices indicated above for crystallized films obtained under normal conditions, the dimensionality of the growth of crystals  $m=4$  was determined. The total activation energy of the crystallization process is:  $U_{gen}=U_3+3U_p=55,8\text{kcal/mol}$ . The values of the activation energies of nucleation ( $U_3$ ) and growth ( $U_p$ ), established similarly to the case of the absence of a field, are  $33,5$  and  $7,4\text{kcal/mol}$ , respectively. From the experimental data obtained as a result of the performed it is clear that in both cases there is a three-dimensional growth of crystals. The crystallization activation energies for  $\text{CuIn}_5\text{Te}_8$  films obtained under the action of an electric field are slightly higher than the corresponding values for films sublimated outside the field. For comparison, the found values of the kinetic parameters of crystallization are given in table 1.

Table 1.

Values of activation energies of crystallization of amorphous  $\text{CuIn}_5\text{Te}_8$  films obtained under the influence of an electric field and outside it

Electric field voltage	$m$	$U_{gen}$ kcal/mol	$U_3$ kcal/mol	$U_p$ kcal/mol
$E=500\text{V}\cdot\text{cm}^{-1}$	4	55,8	33,5	7,4
$E=0$	4	32,8	12,6	6,7

Thus, it has been established that during the condensation of films of the  $\text{Cu}_2\text{Te-In}_2\text{Te}_3$  system under the influence of an electric field, the resulting amorphous films of the composition  $\text{CuIn}_5\text{Te}_8$  are formed in a more stable state. The degree of deformation of chains of molecules decreases and, as a

result, the degree of rupture of chains of molecules into short fragments decreases, which in turn leads to a decrease in their mobility during subsequent heat treatment, resulting in an increase in the activation energies of crystallization of  $\text{CuIn}_5\text{Te}_8$ .

**CONCLUSION**

Crystallization kinetics of amorphous films of composition  $\text{CuIn}_5\text{Te}_8$  obtained by vacuum preparation of the synthesized binary compounds  $\text{Cu}_2\text{Te}$  and  $\text{In}_2\text{Te}_3$ , as well as by evaporation of the components of the Cu-In-Te system, taken in ratios of 1:5:8, sublimated from separate sources, obey the laws established by Avrami-Kolmogorov. In amorphous films formed under the conditions of deposition of molecular beams in an electric field, the crystallization activation energies are overestimated compared to the

corresponding values for thin layers obtained outside the field. Under the conditions of deposition of molecular beams in an electric field, it is possible, just as in  $\text{CuIn}_5\text{S}_8$  films [9], that the bonds that hold the structure together shorten, i.e., the distances in the nearest environment of atoms in  $\text{CuIn}_5\text{Te}_8$  films change. Regardless of the method and conditions for the formation of  $\text{CuIn}_5\text{Te}_8$  films obtained under ordinary conditions and reconstructed under the influence of an external electric field, three-dimensional growth of crystals occurs.

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**AMORF  $\text{CuIn}_5\text{Te}_8$  NAZİK TƏBƏQƏLƏRİNİN KRİSTALLAŞMASININ TEMPERATUR-ZAMAN ASILLIQLARİNİN ELEKTRON DİFRAKSİYASİNİN TƏDQIQI**

Normal şəraitdə və gücü  $500\text{V}\cdot\text{sm}^{-1}$  olan xarici elektrik sahəsinin təsiri altında alınan amorf  $\text{CuIn}_5\text{Te}_8$  nazik təbəqələrinin kristallaşma proseslərini öyrənmək üçün kinematik elektron difraksiyasından istifadə edilmişdir. Faza keçidlərinin izotermik ayrılırları qurulmuş və faza çevrilmələrinin kinetik parametrləri təyin olunmuşdur: kristalın böyüməsi və aktivləşmə enerjilərinin ölçüləri müəyyən edilmişdir. Amorf  $\text{CuIn}_5\text{Te}_8$  nazik təbəqələrin kristallaşması zamanı rüşeyməmələgəlmə sürətləri və onların sonrakı artımı Arrhenius münasibətlərinə uyğun göstərilmişdir

**Г.Е. Дашдамирова**

**ЭЛЕКТРОНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ ТЕМПЕРАТУРНО-ВРЕМЕННЫХ ЗАВИСИМОСТЕЙ КРИСТАЛЛИЗАЦИИ НАНОТОЛЩИННЫХ АМОΡФНЫХ ПЛЕНОК  $\text{CuIn}_5\text{Te}_8$**

Методом кинематической электрографии исследованы процессы кристаллизации аморфных пленок  $\text{CuIn}_5\text{Te}_8$ , полученные в обычных условиях и в условиях воздействия внешнего электрического поля напряженностью  $500\text{В}\cdot\text{см}^{-1}$ . Построены изотермические кривые фазовых переходов и определены кинетические параметры фазовых превращений: установлены мерности роста кристаллов и значения активационных энергий. Показано, что при кристаллизации аморфных пленок  $\text{CuIn}_5\text{Te}_8$ , скорости зародышеобразования и дальнейшего их роста следуют соотношениям Аррениуса.