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Electron Diffraction Study of the Temperature — Time Dependences of Crystallization of Nano thick amorphous CuIn_5Te_8 Films Sublimated Under Normal Conditions and under the Action of an External Electric Field

© G.E. Dashdamirova

Institute of Physics, National Academy of Sciences of Azerbaijan,
AZ1143 Baku, Azerbaijan

E-mail: Uli200909@rambler.ru

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Kinematic electron diffraction was used to study the crystallization processes of amorphous CuIn_5Te_8 films obtained under normal conditions and under the influence of an external electric field with a strength of $500 \text{ V} \cdot \text{cm}^{-1}$. Isothermal curves of phase transitions are examined and the kinetic parameters of phase transformations are determined: the dimensions of crystal growth and of activation energies are established. It is shown that during the crystallization of amorphous CuIn_5Te_8 films, the rates of nucleation and their further growth follow the Arrhenius relations.

Keywords: electronographic structural analysis, thin films, crystallization isotherms, activation energy.

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1. Introduction

In the study [1], electron microscopic studies have established that CuIn_5Te_8 has a somewhat disordered thiogallate structure. The domain structure, due to the different arrangement of cations inside a common face-centered cubic tellurium sublattice, is consistent with the symmetry of the thiogallate structure. In the work [2], based on the analysis of RAMAN scattering data, a comparative study of the vibrational modes of crystal lattices of compounds of the Cu–In–Te system, including a triple compound of the composition CuIn_5Te_8 , was carried out. It was established that the highest phonon frequencies observed at 237 and 270 cm^{-1} , are associated with a combination of modes E and B_2 . According to the data of [3], the energy of the band gap of the CuIn_5Te_8 compound crystallizing into the chalcopyrite structure varies from 1.10 to 1.02 eV in the temperature range 10–300 K. It was established that the change of E_g as a function of temperature is due to the contribution of optical phonons with an energy of 17 meV.

The study of temperature-time dependences of the kinetics of phase transitions (PT) in nanotollen 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 direction of electronographic research. Nanoscale thin semiconductor layers are characteristic objects for these studies. In the study [4] synthesis of double compounds of pseudobinary sections of the system $A^I C^{VI} - B_2^{III} C_{3n}^{VI}$

($n = 0, 1, 2, \dots$) and chemical elements of the triple system Cu–In–Te, taken in the ratios Cu:In:Te = 1:5:8 components that were subjected to chemical and thermal treatment before loading into double quartz ampoules, triple compounds included in the general chemical group $A^I C^{VI} - B_{2n+1}^{III} C_{3n+2}^{VI}$ were synthesized. The indices of the phase compositions of ternary compounds in this formula refer to a series of numbers $n = 0, 1, 2, \dots$. X-ray diffraction analysis revealed that the synthesized bulk monocrystals (Cu:In:Te = 7.18:35.31:57.51 at%) are consistent with the composition of the original attachments (Cu:In:Te = 7.14:35.72:57 at%). The crystallographic parameters of tetragonal lattices of grown monocrystals with chalcopyrite structure of the composition CuIn_5Te_8 are equal to $a = 6.162$ and $c = 12.29 \text{ \AA}$.

In the studies [5,6] for various connections of Cu(Ag) systems–In–Te of type 2:4:7 and 1:5:8 with the chalcopyrite structure, the conditions for obtaining nanocrystals are established and the values of their optical forbidden zones are determined.

2. Experimental methods

The present work is devoted to the experimental study of the temperature-time dependences of PT as a result of crystallization of nanotollen amorphous films of the composition CuIn_5Te_8 obtained by sublimation of double compounds Cu_2Te and In_2Te_3 in vacuum with a residual pressure of $\sim 10^{-4} \text{ Pa}$, as well as components of the Cu–In–Te system applied by evaporation of the highest purity, taken in the ratios 1:5:8. In order to obtain and

study the crystallization kinetics of amorphous films of the composition CuIn_5Te_8 , simultaneous thermal evaporation of double compounds Cu_2Te and In_2Te_3 was performed in vacuum $\sim 10^{-4}$ Pa under normal conditions and under the influence of an external electric field with a strength of $500 \text{ V} \cdot \text{cm}^{-1}$ of tungsten spiral-shaped conically wound spirals. Thin films CuIn_5Te_8 , the estimated thickness of which was $\sim 250 \text{ \AA}$, were obtained by sublimation of the above synthesized double compounds on pre-cooled to 203 K NaCl substrates.

The study of the kinetics of any process, i.e., the establishment of the ratio between the fraction undergoing changes due to PT and the conversion time t determines the kinetics of any physical and chemical processes. Since electric fields, constant and variable, have a significant effect on the crystallization processes, we also investigated the kinetics of crystallization of amorphous films CuIn_5Te_8 , condensed under the influence of an external electric field with a voltage of $500 \text{ V} \cdot \text{cm}^{-1}$. A constant electric field was created between two parallel copper plates. The substrates were located on the surface of the negatively charged lower plate — fresh NaCl cleaved facets. In the upper plate there were two holes with diameters of 5 mm, through which the molecular beams passed and reached the surface of the substrates. The substrates temperature was 203 K. The deposition rate was 20 \AA/s . The determination of 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 relationship between the volume undergoing PT and the transformation time, it is necessary to find the values of two interrelated parameters: the rate of germination (v_n) and their further growth (v_{gr}). A general analytical equation containing a solution and describing the kinetic processes of PT is given in the works [7,8]:

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

This expression describes the kinetics of PT occurring with the emergence of the embryos of a new phase, taking into account the statistical nature of the overlap of growing centers. In the formula (1) k is a reaction rate constant equal to $\frac{1}{3} \pi v_3 v_{gr}^3$, the value m depends on the dimension of growth and it is different for possible types of PT.

In the studies [9,10] it is shown that the regularities and kinetic parameters of the PT can be established, bypassing the cumbersome quantitative analysis of the transformation processes, by molecular kinetic consideration of the crystallization of amorphous substances according to the formula (1). For continuous time observation of the course of the transformation process, the methods given in the studies [11,12] are known, with the help of which, during the heating of the sample, changes in the intensities of diffraction reflexes are recorded, in which angular positions change during the PT process. The displacements of the

diffraction peaks are measured by a counter with a gap aperture. Errors in determining changes in the intensities of diffraction peaks can reach $\sim 15\%$.

By the method developed in the study [13], it is possible to obtain continuous electronographic images that are not inferior in accuracy and sharpness of the diffraction field to discrete electronograms, fixed on photographic plates. The essence of the kinematic electronography method as a physical method is to fix the diffraction pattern on a uniformly moving photographic plate, the uniform movement of which is achieved by a reduced electric motor. The diffraction pattern from a polycrystal is obtained using a slit located along the horizontal radius of the diffraction concentric rings. In this case, a narrow band is formed, which turns the diffraction pattern into parallel lines symmetrical with respect to the electron beam. We carried out kinematic surveys at a speed 1/3, 1/2, 1/6 and 1/10 mm/s. Heat treatment of CuIn_5Te_8 films with a thickness of 250 \AA was performed using tantalum tape with several holes with a diameter 0.1–0.5 mm. The studied films were heated directly in the column of the electronograph of the brand EMR-102. The calibration of these special stoves, consisting of tantalum ribbons with a size of $25 \times 1.5 \times 0.07\text{--}0.1 \text{ mm}$, was performed using a copper-constant or chromel-alumel thermocouple, as well as by melting points In, Sn, Pb. Experiments on obtaining amorphous films of the composition CuIn_5Te_8 suitable for research were similar to the experiments conducted in [14,15].

3. Results and discussion

With heating, amorphous films CuIn_5Te_8 with values $S = 4\pi \sin \theta / \lambda = 1.66, 3.20$ and 4.91 \AA^{-1} corresponding to diffuse lines on kinematic electronograms (Fig. 1), at relatively low temperatures they pass into a crystalline state.

The intensities of diffraction lines with indices (210), (301) and (420) were determined, which had the best resolutions, and therefore were the most convenient for measuring intensities. From the values of the intensities of diffraction reflections of the crystalline CuIn_5Te_8 to the corresponding values of the volume V_t were transferred according to the method given in the work [16]. As can be seen from the crystallization isotherms of amorphous films constructed for temperatures 350, 373 and 403 K (Fig. 2), with increasing temperature, the slope of the curves increases sharply, which indicates a rapid increase in the crystallization rate with an increase in the annealing temperature of the films.

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 built (Fig. 3). For all temperatures, almost parallel lines are obtained, which indicate that experimental isotherms can be described by the expression (1). From the slope of the straight lines to the abscissa axis, the value of the indicator m

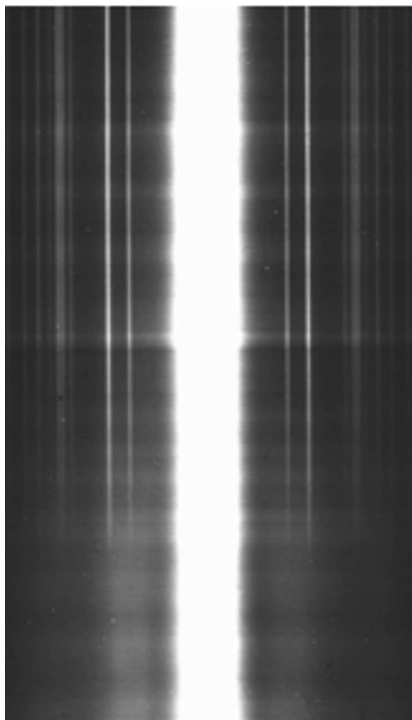


Figure 1. Kinematic electronogram from amorphous CuIn₅Te₈ undergoing PT at 403 K.

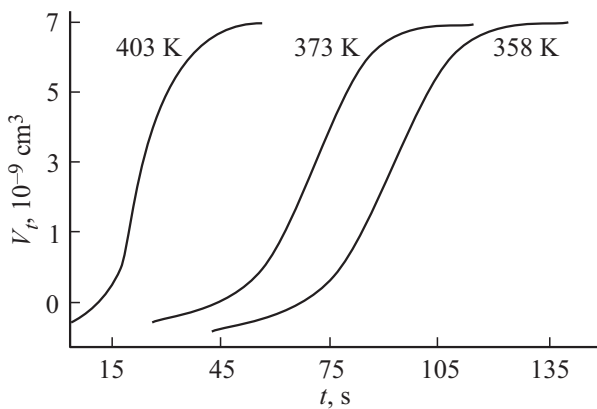


Figure 2. Kinetic crystallization curves of amorphous CuIn₅S₈.

in the expression (1) is set that equals ~ 4 . This value m indicates that in the case of crystallization of amorphous films CuIn₅Te₈ with a thickness of ~ 250 Å the same as in the case of CuIn₅S₈ [14], there is a three-dimensional growth of crystals. The values $\ln k$, set using the dependence graph $\ln \ln V_0/(V_0 - V_t)$ from $\ln t$, are as follows: at 358 K $\ln k = -33.7$, at 373 K $\ln k = -23.2$ and at 403 K $\ln k = -12.9$. From the graph of the dependence of $\ln k$ on the inverse temperature (Fig. 4), constructed on the basis of the above data, it can be seen that the experimental points lie on one straight line.

The linear dependence $\ln k$ on $1/T$ is explained by the fact that in the temperature range under study, the rate of

nucleation of v_n and the rate of crystal growth v_{gr} can be described by an Arrhenius type expression. Introducing v_n and v_{gr} into an Arrhenius type equation and logarithm k , we get

$$\ln k = c - \frac{U_n + 3U_{gr}}{RT}, \quad (2)$$

here c — some constant independent of temperature, U_n and U_{gr} — activation energies of nucleation and crystal growth, respectively, R — universal gas constant. The value of the sum $U_n + 3U_{gr}$, set by the slope of the straight line shown in Fig. 4 to the abscissa axis, is 32.8 kcal/mol. The activation energy of nucleation U_n , calculated by the slope of the direct dependence $1/\tau$ on $\ln t$ (where τ — incubation time, i.e. experimentally observed time of crystallization onset), is equal to 12.6 kcal/mol. U_{gr} , determined from the ratio $U_{gr} = (U_{tot} - U_n)/3$, turned out to be 6.7 kcal/mol.

The study of the kinetics of crystallization of amorphous CuIn₅Te₈ films obtained under the influence of a field was carried out similarly to the study of films obtained under normal conditions. Isothermal kinematic electronograms were obtained at temperatures 358, 373 and 403 K. From the graph of the dependence $\ln \ln V_0/(V_0 - V_t)$ on $\ln t$, constructed on the basis of kinetic crystallization curves CuIn₅Te₈ for the above temperatures, for

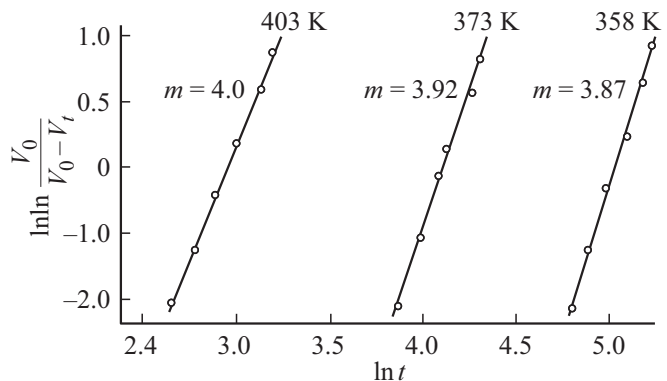


Figure 3. The dependence $\ln \ln V_0/(V_0 - V_t)$ on $\ln t$ for crystallization of amorphous CuIn₅Te₈.

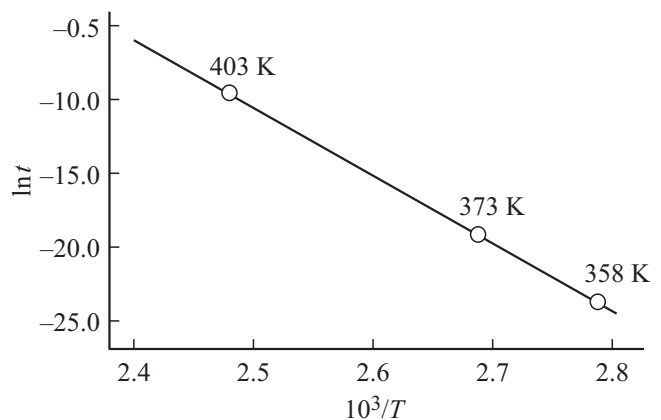


Figure 4. The dependence $\ln k$ on the inverse temperature for crystallization of amorphous CuIn₅Te₈.

Values of activation energies of crystallization of amorphous films CuIn_5Te_8 obtained under the influence of an electric field and outside it

The electric field strength	m	U_{tot} , kcal/mol	U_n , kcal/mol	U_{gr} , 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

this purpose, the intensities of diffraction lines with the indices indicated above were determined for crystallized films obtained under normal conditions, the dimensionality of crystal growth $m = 4$ was determined. The total activation energy of the crystallization process is equal to: $U_{tot} = U_n + 3U_{gr} = 55.8 \text{ kcal/mol}$. The values of the activation energies of nucleation (U_n) and growth (U_{gr}), established similarly to the case of the absence of a field, are 33.5 and 7.4 kcal/mol, respectively. From the experimental data obtained as a result of the performed electronographic studies, it can be seen that in both cases there is a three-dimensional growth of crystals. The values of the crystallization activation energies for CuIn_5Te_8 films obtained under the influence of an electric field are slightly higher than the corresponding values for films sublimated outside the field. For comparison, the values of the kinetic parameters of crystallization found are given in the table.

Thus, it is established that during condensation of films of the $\text{Cu}_2\text{Te}-\text{In}_2\text{Te}_3$ system, amorphous films of the composition CuIn_5Te_8 are formed under the influence of an electric field are formed in a more stable state. The degree of deformation of the chains of molecules decreases and, as a consequence, the degree of breaking of the chains of molecules into short fragments decreases, which in turn leads to a decrease in their mobility during subsequent heat treatment, as a result of which the values of the activation energies of crystallization CuIn_5Te_8 increase.

4. Conclusion

The kinetics of amorphous films' crystallization of the composition CuIn_5Te_8 , obtained by vacuum preparation of synthesized double compounds Cu_2Te and In_2Te_3 , and also by evaporation of the components of the Cu–In–Te system, taken in the ratios 1 : 5 : 8, sublimated from separate sources, obeys the laws established by Avrami–Kolmogorov. For amorphous films formed under conditions of deposition of molecular beams in an electric field, the values of the activation energies of crystallization are overestimated in comparison with the corresponding values for thin layers obtained outside the field. Under conditions of deposition of molecular beams in an electric field, as well as in the films CuIn_5Se_8 [17], the bonds binding the structure are shortened — the distances in the immediate environment of atoms in the films CuIn_5Te_8 change. Regardless of the method and conditions for the formation of CuIn_5Te_8 films

obtained under normal conditions and reconstructed under the influence of an external electric field, three-dimensional crystal growth occurs.

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Conflict of interest

The author declares that he has no conflict of interest.

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