

CRYSTALLIZATION KINETICS OF AMORPHOUS NANOTHICKNESS CuGa_5Se_8 A.Ch. MAMEDOVA¹, N.K. KERIMOVA², I.T. MAMMADOVA¹¹*Institute of Physics of Azerbaijan National Academy of Sciences, AZ-1143,
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The processes of phase formation and phase transitions in CuGa_5Se_8 thin layers allowing the carrying out of the continuous object shooting at treatment different conditions are investigated by kinematic electronography method. It is shown, that amorphous films form at evaporation of synthesized compound and thermal spraying of binary compounds Cu_2Se and Ga_2Se_3 in ratio 1:5. There have been established kinetic parameters of CuGa_5Se_8 compositions amorphous films crystallization. The crystal growth regularity, activation energy values of germ – formation and their further growth are obtained.

Keywords: crystallizations kinetics, amorphous film, nano-thickness.

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1. INTRODUCTION

The interest in defective-ordered compounds $\text{CuGa}_5(\text{In}_5)\text{Se}_8$ related to the system $A^1 - B^3 - C^6[A - \text{Cu}, B - (\text{In}, \text{Ga}), C - (\text{S}, \text{Se}, \text{Te})]$ is caused by the width of their band gaps. For CuGa_5Se_8 , the band gap (E_G) is 1.85 eV [3].

To study the processes of phase formation and phase transformations in nanothick films $\text{Cu}(\text{In}, \text{Ga})_5\text{Se}_8$, recognized in [4,5] as promising materials for creating high-efficiency solar cells of a new generation, the high-energy diffraction method was used.

The aim of this work is to determine the conditions of the synthesis of CuGa_5Se_8 formed during the vacuum condensation of double compositions Cu_2Se , Ga_2Se_3 , and kinetic parameters of the crystallization of amorphous CuGa_5Se_8 films.

The main method for determination of crystal structure and phase compositions of thin layers is the electron beam diffraction on nanodimensional films. The essence of kinematic electronography method based on rapid electron diffraction on objects, the dimensions of which are commensurable ones with wavelength of incident radiation, is the fact that diffraction picture is fixed on moving photographic plate which is mechanically drawn. The stationary values of activation energies showing on phase transition end when whole material of different compositions taking part in process transits from the amorphous state into crystal one or from the one crystal modification into another one, are obtained by kinematic electronography for thin films of each compound. The coherently scattered electrons having the big sensitivity to relatively scattered substance allow us to fix the reaction beginning and follow its further motion. This method can't be considered as alternative one to X – ray spectrometry and other optic methods not applying to nano – thickness films. The kinematic electronography is the unique independent

method for quantitative investigations of phase transformation kinetics taking place in nano - thickness amorphous and crystalline films: texture, polycrystalline, monocrystalline films. The data obtained by this method can't be found with enough definiteness by other above-mentioned methods which aren't potentially suitable for films by thickness by several decades nanometers. The result interpretation obtained by kinematic electronography presents the big interest for semiconductor material science. They can be based on optical measurements up to present time and give the direct comparison possibility of obtained result for thin films with data for massive samples.

2. EXPERIMENT TECHNIQUE

The very narrow strip is cut from total diffraction patterns by kinematic method with the help of shutters being in electron diffractograph EMR-102. using these shutters one can make the gap of any width. As diffraction maximum width on photo – plate increases with gap increase then the diffraction ring curvature strongly reveals with gap increase. However, the diffraction lines from polycrystalline sample keep its width and sharpness within limits of gap width change. The gap width at photo – plate drawing is selected by shutter establishment and in dependence on primary beam intensity one can be established in limits 0,1; 0,3; 0,5 mm. The instrument constant $2L\lambda$ was 52,73 mm Å at an accelerating voltage of 75 kV. It should switch off the forepump and close the fore valve for neutralization of vibrations from vacuum forepump at electron diffraction pattern kinematic shooting.

The study complexity of kinetics amorphous film crystallization processes and appearance of new crystalline modifications in case of phase transformations is in the fact that mechanism crystallization center formation and their further growth is often unknown. The data on crystal growth

mechanism and dependence of phase transformation rate on temperature one can obtain by studying of time – temperature dependences of amorphous film crystallization and thin crystal layers recrystallization with establishment of phase transition kinetic parameters.

The thin – film materials suitable for investigations by diffraction method of high – energy electrons are obtained by both evaporation of synthesized compound CuGa_5Se_8 and thermal spraying of binary compounds of Cu_2Se and Ga_2Se_3 in ratio 1:5. At simultaneous and layer – by – layer precipitation of Cu_2Se and Ga_2Se_3 the evaporation sources which are tungsten baskets of conic profile lag behind each other on distance 150 mm at height 70 mm relatively to freshly cleaved NaCl and grids covered by celluloid serving as substrates. The vapor condensation is carried out on substrates being at room temperature in vacuum, the residual gas pressure in which is $\sim 10^{-4}$ Pa. The precipitation rate is $\sim 0,2$ nm/sec. For prevention of re – evaporation and thin – film sample oxidation in case of their thermal treatment at high temperatures, the thin films are covered by celluloid thin layer so that they are involved in singular capsule. It should be noted that at temperatures 423 K and higher the celluloid protective film destroys. For removal of such processes, the probabilities of oxidation in air and decomposition in the process of following thermal treatments at increased temperatures or at their long storage, the investigated samples are capsulated by thin layers of amorphous carbon [1-2]. Taking into consideration the carbon layer thickness the total thickness of investigated objects doesn't exceed ~ 50 nm. The structural characteristics of CuGa_5Se_8 thin layers obtained on NaCl and KCl surfaces being at different temperatures and film phase composition formed by simultaneous and consistent evaporation of Cu_2Se and Ga_2Se_3 are studied on electron diffractograph EMR-102.

3. RESULTS AND THEIR DISCUSSION

The layer-by-layer precipitation of Cu_2Se and Ga_2Se_3 on substrates at room temperature leads to phase distribution on condensation plane corresponding to calculated component composition at both simultaneous evaporation and independent on evaporation order.

On the base of scheme of phase according to experimental data obtained as the result of analysis of electron diffraction pattern taken from points situated from each other on distance 4 mm, it is established that forming films are amorphous ones in substrate region where by calculation the triple compound of CuGa_5Se_8 composition should form. The diffuse lines of electron diffraction pattern from amorphous films contain values $S = 4\pi \sin \theta / \lambda = 27,42; 35,87; 55,08 \text{ nm}^{-1}$. The amorphous films forming in sufficiently wide region of condensation plane at temperature 443 K crystallize with structural characteristics $a=0,5483; c= 1,094 \text{ nm}$ according with data for hexagonal compound given in [3]

With the to study of CuGa_5Se_8 amorphous film crystallization kinetics the isothermal kinematic electron diffraction patterns showing diffraction patterns showing the crystallization process at 413 K, 428 K, 443 K are obtained.

The kinematic electron diffraction pattern, on which the crystallization process of amorphous CuGa_5Se_8 at temperature 373 K is registered, is given in fig.1.

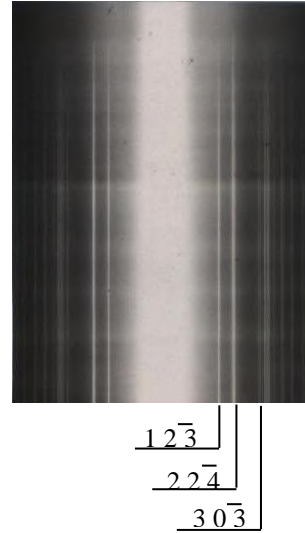


Fig 1. Kinematic electron diffraction pattern form CuGa_5Se_8 thin films.

The polycrystalline hexagonal CuGa_5Se_8 forms in the crystallization process. The diffuse lines of the amorphous phase of the CuGa_5Se_8 film which become “weaker” as result of annealing disappear completely with time, and the intensities of diffraction lines of the hexagonal crystal phase increase.

The lines with $(1\bar{2}30)$, $(2\bar{2}40)$ and $(30\bar{3}0)$ indexes not overlapping with amorphous phase lines and neighboring crystal phase lines that could make mistakes in intensity measurements, are chosen for both photometric definition and intensity electrometric measurement of CuGa_5Se_8 hexagonal diffraction lines in dependence on annealing time. The electron diffraction patterns from the polycrystalline CuGa_5Se_8 sample were indexed and the formed phases were identified by comparison of the experimentally observed interplanar distances d_{hkl} with the calculated ones.

The intensity maximal value is compared with one of fully crystallized volume of investigated object for transition of intensity values to quantity of crystallized CuGa_5Se_8 . The volume fitting on intensity unit is defined by the way finally allows us to find the values of substance crystallized part volume in dependence on annealing time.

We use the following expression:

$$I_{hkl} = I_o \lambda^2 \left| \frac{\Phi_{hkl}}{\Omega} \right|^2 V \frac{d_{hkl} \Delta P}{4\pi L \lambda} \quad (1) [6]$$

where I_o is primary beam intensity, λ is electron beam wave length, Φ is structural factor, Ω is elementary cell volume, V is radiated volume of polycrystalline substance, d_{hkl} is interplanar spacing, Δ is Debye ring small sector, P is multiplicity factor, $L\lambda$ is device constant.

Crystallization isotherms of amorphous films shown in Fig. 2 were constructed by normalizing and passing from the intensity values to the volume of the crystallized substance.

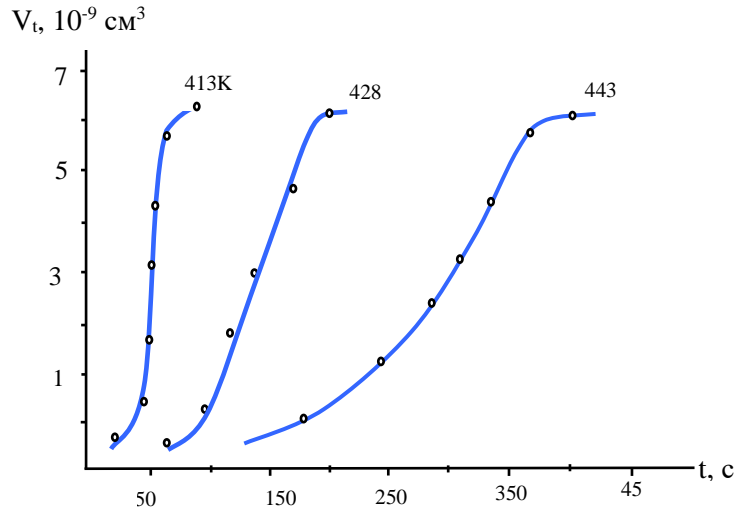


Fig. 2. The kinetic crystallization curves of amorphous CuGa₅Se₈

The comparison of isotherm data with following analytical expression

$$V_t = V_o [1 - \exp(-kt^m)] \quad (2)$$

Established by Avrami – Kolmogorov for phase transmutation kinetics shows that the best coincidence takes place at $m \approx 4$. The value $m=4$ shows that in case of crystallization of amorphous CuGa₅Se₈ the three-dimensional crystal growth takes place. $\ln K$ values for 413, 428, 443 K are equal to -17,7; -15,3 and -12,2 correspondingly. $\ln K$ dependence on reversal temperature for CuGa₅Se₈ is linear one.

According to arrhenius equation:

$$\ln K = A - \frac{1}{RT} (E_{gf} + 3E_g) \quad (3)$$

where E_{gf} and E_g are activation energies of germ-formation and growth correspondingly. The sum value $E_{gf} + 3E_g$ defined by straight line inclination of $\ln K$ dependence on $1/T$, is equal to 125 kcal/mol. The activation energy of germ-formation (E_{gf}), established

from dependence $1/\tau_o$ on $1/T$, is equal to 27 kcal/mol. The value of growth activation energy, obtained by equality $E_{tot.} = E_{gf} + 3E_g$, is equal to 32,6 kcal/mol. Thus, it is established that at crystallization of amorphous CuGa₅Se₈ the values of activation energy necessary for crystallization center formation, i.e. germ-formation and their further growth have approximately identical values: 27 kcal/mol and 32,6 kcal/mol, that is very seldom.

CONCLUSION

The phase transformation kinetics in CuGa₅Se₈ amorphous films takes place on regularities established by Avrami – Kolmogorov and is described by analytical expression $V_t = V_o [1 - \exp(-kt^m)]$. At crystallization of CuGa₅Se₈ amorphous films, the three – dimensional crystal growth takes place. The activation energies of germ-formation and growth have approximately identical values: 27 kcal/mol and 32,6 kcal/mol.

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