KINEMATIC ELECTRON DIFFRACTION STUDY OF CRYSTALLIZATION KINETICS OF AMORPHOUS $Yb_{1-x}Sm_xAs_4Te_7$ NANOTHICK FILMS

E. Sh. HAJIYEV
Institute of Physics, Academy of Sciences of Azerbaijan,
33 H. Javid, Baku Az – 1143, Azerbaijan

The crystallization kinetics of ternary $Yb_{1-x}Sm_xAs_4Te_7$ amorphous thin films has been investigated by kinematic electron diffraction method. It is shown that crystallization takes place in accordance with Avrami – Kolmogorov law. The kinetics parameters and the growth dimensionality of the crystallization have been determined.

The systems on base of chalcogenide glasses containing the rare – earth elements have been widely studied last years. In these systems, it is established that formation of ternary compounds which can be applied in devices controlled by external magnetic field. Amorphous alloys containing rare – earth elements represent a new class of amorphous materials [1].The main interest in these materials is the environment of $As_2Te_3 – Yb_{1-x}Sm_x$(x=0.2 at. %) system is one of these classes of above-mentioned materials. According to state diagram, the $Yb_{1-x}Sm_x$ As_4Te_7, $Yb_{1-x}Sm_x$ As_2Te_4 and $Yb_{3(1-x)}Sm_x$ As_4Te_9 ternary compounds are formed in this system. Thin films of $Yb_{1-x}Sm_x$ As_4Te_7 with thickness ~ 30 nm obtained by vacuum evaporation and deposition on substrates of fresh cleavage surfaces of NaCl , KCl crystals and amorphous celluloid at room temperature were amorphous. Amorphous phase is formed on NaCl up to T_s=523K. Using electron diffraction method we have investigated the structure of obtained films. The electron diffraction pattern shows seven diffuse diffraction ring corresponding $S=4\pi\sin\theta/\lambda$=20.3; 33.0; 51.7; 71.4; 96.0; 119.0; 152.0 nm^{-1}. Amorphous films crystallization at T=523K results in the formation of $Yb_{1-x}Sm_x$ As_4Te_7 polycrystalline with parameters of the rhombic lattice rhombic unit cell with a=1,214; b=1,470; c=0,410 nm. This is agreement the data of ref: 4

The general form describing the kinetics of growth is written as [5,6]

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

where V_t is volume of substance transforming to t time, V_o is initiation volume of substance, k is reaction rate constant. "m" quantity is different for variety transformation types and is depend on growth measure. To obtain reliable results using this theory, it is need to have exact experimental data for V_t. Studying of crystallization processes depending on temperature and time gives information about mechanism of growth and crystal growth rate on depended temperature.

To determine the kinetic parameters of crystallization of $Yb_{1-x}Sm_x$ As_4Te_7 amorphous films we have used kinematic electron diffraction method from amorphous films with thickness ~30nm, at T=523K, T=548K, T=573K temperatures [7]. It is quite clear, that much more temperature, than fast occurs the crystallization process.

Electron diffraction pattern taken from annealing samples shows how diffuse rings relating to amorphous phase are disappearance and the lines of the polycrystalline phase of $Yb_{1-x}Sm_xAs_4Te_7$ are occur. There is the area where crystal and amorphous phases exist together.

Intensities of lines of the $Yb_{1-x}Sm_x$ As_4Te_7 polycrystalline phase were measured by micro photometric method. The intensities of diffraction lines with h, k, l index were determined depending on annealing time. To get quantity of crystallized matter we use standardization method taking account of intensity of scattering of electrons is proportional to the volume of scattering matter [8].

the rare – earth atom because it determines the electric, optic and magnetic properties of these materials. The structure and crystallization of some ternary compounds of system containing rare-earth elements have been investigated in the film state before [2-3]. Therefore, the purpose of the present work is study crystallization of $Yb_{1-x}Sm_x$ As_4Te_7 amorphous nanothick films.

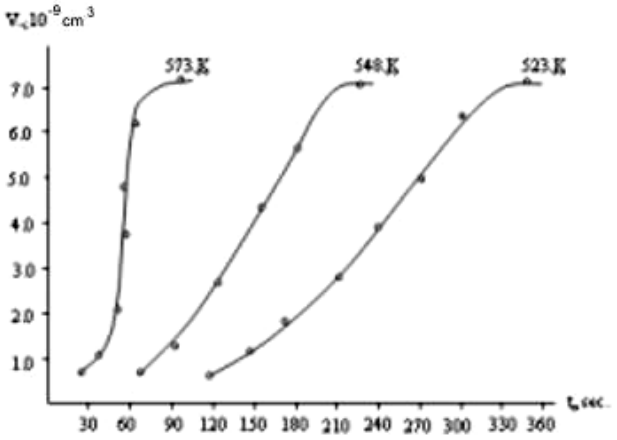

Fig 1. The kinetic curves of crystallization of $Yb_{1-x}Sm_xAs_4Te_7$ amorphous films.

In investigation interval of temperature the kinetic curves of crystallization of $Yb_{1-x}Sm_x$ As_4Te_7 amorphous films have been calculated i.e. the curves of the crystallized volume as a function of the time for variety temperatures. (fig. 1).

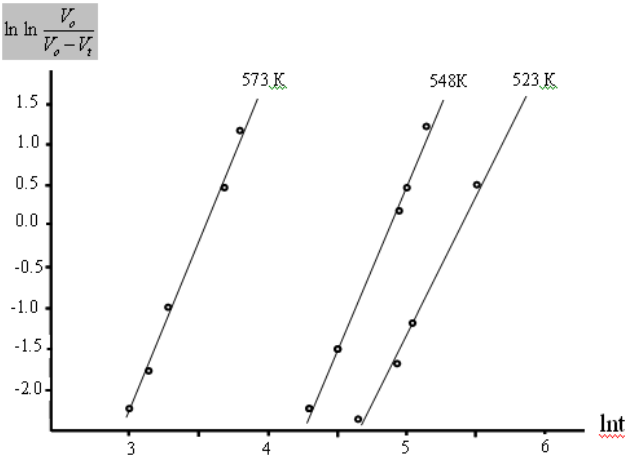

Fig.2. The $lnln(V_o/(V_o-V_t))$ dependence on lnt for $Yb_{1-x}Sm_xAs_4Te_7$.

The $lnln(V_0/(V_0 - V_t))$ dependences on lnt were calculated at T=523K, T=548K, T=573K temperatures. The lines drawing through the experimental points are straight lines for all temperatures (fig.2).

The value of "m" in (1) form determined from slope is equal to about 4 (m=3,80 at 573 K; m=3,95 at 548 K; m=3,93 at 523 K). That is witness for the three-dimensionality growth of crystals at investigation temperatures.

$ln\ k$ dependence on $1/T$ is linear . The nucleation rate and crystal growth rate are described by Arrenius form

$$\upsilon_n = C\, e^{-\frac{E_3}{RT}}$$
$$\upsilon_g = C\, e^{-\frac{E_p}{RT}} \qquad (2)$$

where υ_n is the formation rate of the nucleation centre and determined as number of nucleus creating in unit time in unit volume of metastable phase; υ_g is crystal growth linear rate and determined as the change rate of linear sizes of growthing crystal of the new phase.

Summary nucleation activation energy - E_s is determined from slope of the $ln\ k$ curve as function $1/T$ and equal to 79,6 kcal/mol. The nucleation activation energy is calculated from slope of the $1/\tau_o$ curve as a function lnt (where τ_o is experimental beginning time of crystallization) and equal to 26,2 kcal/mol. E_g is crystal growth activation energy is determined by $E_g = (E_s - E_n)/3$ and equal to 17,8 kcal/mol.

In this work we also investigated the crystallization of $Yb_{1-x}Sm_x\ As_4Te_7$ amorphous films obtained in condition of electric field action (U=3000 V/cm).It is shown that the influence of electric field on crystallization process leads to an increasing of nucleation (υ_n) and growth (υ_g) rate, that is , decreasing of activation energies about 10-12% [Table 1].

Table 1

Amorphous compound	Electric fields (U)	m	activation energy		
			E_s kcal/mol	E_n kcal/mol	E_g kcal/mol
$Yb_{1-x}Sm_xAs_4Te_7$	$U = 0$	3	79,6	26,2	17,8
	U =3000 V·cm $^{-1}$	3	70,8	23,1	15,9

[1] *I.V. Zolotukhin.* Fizicheskie svoystva amorfnykh metallicheskih materialov, Metallurgiya, Moscow (1986) 176.

[2] *E.Sh. Hajiyev.* Kinematic electron diffraction study of crystallization kinetics of amorphous $YbAs_4Te_7$ nanothick films. Izv.AN Az. ser.fiz.-tekh. i mat. nauk XXVII, №2,s.105-107,2007.

[3] *E.Sh. Hajiyev.* Electron diffraction study of short-range order parameters in new semiconductor amorphous films of $Yb_{1-x}Sm_xAs_4Te_7$ compound. Izv. AN Az. ser.fiz.-tekh. i mat. nauk. XXVII, №5, s. 84-86, 2007.

[4] *P.G. Rustamov, T.M. Ilyasov, A.I. Mamedov*. Zh. Neorg.Khim. 30 (1985) 769.

[5] *A. N. Kolmogorov.* Izv. AN SSSR. Ser. Matem. 1937. №3. s.355.

[6] *M. Avrami.* J. Chem. Phys. 1940. v.8. №2. p.212.

[7] *R. B. Shafizade, F. I. Aliev, D.I. Ismailov.* Doklady AN Az. SSR 1988, t. 64, №6, s. 21.

[8] *B.K Vaynshteyn.* Strukturnaya elektronoqrafiya (Electron diffraction study of structure), Izd.vo AN SSSR, M. 1956.

E.Ş. Hacıyev

KINEMATIK ELEKTRONOQRAFIYA METODU ILƏ NANOQALINLIQLI AMORF $Yb_{1-x}Sm_xAs_4Te_7$ TƏBƏQƏLƏRIN KRISTALLAŞMA KINETIKASININ TƏDQIQI

Kinematik elektronoqrafiya metodu ilə $Yb_{1-x}Sm_xAs_4Te_7$ üçqat birləşməsinin nanoqalınlıqlı amorf təbəqələrinin kristallaşma kinetikası tədqiq edilmişdir. Göstərilmişdir ki, kristallaşma prosesi Avrami – Kolmoqorov qanunauyğunluğu ilə baş verir. Kristallaşmanın kinetik parametrləri və kristallik rüşeymlərin böyümə ölçüsü müəyyən edilmişdir.

Е.Ш. Гаджиев

ИССЛЕДОВАНИЕ КИНЕТИКИ КРИСТАЛЛИЗАЦИИ АМОРФНЫХ НАНОТОЛЩИННЫХ ПЛЕНОК $Yb_{1-x}Sm_xAs_4Te_7$ МЕТОДОМ КИНЕМАТИЧЕСКОЙ ЭЛЕКТРОНОГРАФИИ

Методом кинематической электронографии исследована кинетика кристаллизации тройных аморфных нанотолщинных пленок $Yb_{1-x}Sm_xAs_4Te_7$. Показано, что кристаллизация происходит по закономерностям, установленным Аврами – Колмогоровым. Определены значения кинетических параметров и мерность роста.

Received:16.01.08