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AMORPHOUS, VITREOUS, POROUS, ORGANIC, AND MICROCRYSTALLINE SEMICONDUCTORS; SEMICONDUCTOR COMPOSITES

Structure and Kinetics of Crystallization of Thin Amorphous Films of $Yb_{1-x}Sm_xAs_4S_7$

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Abstract—The curve of the electron's scattering intensity depending on the scattering angle has been obtained for amorphous films of $Yb_{1-x}Sm_xAs_4S_7$ ($x = 0.02$ at %). The curve of the radial distribution of atoms has been built, and radii of coordination shells and partial coordination numbers have been determined. Kinetic parameters of phase transformations that occur upon the crystallization of amorphous films $Yb_{1-x}Sm_xAs_4S_7$ ($x = 0.02$ at %) obtained both under normal conditions and under the effect of an external electric field have been established.

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1. INTRODUCTION

In modern science and technology of semiconductor devices, amorphous semiconductors in the film state are widely employed together with crystalline materials. The parameters of devices created on the basis of thin films depend on the conditions of the formation of thin layers with different substructures, kinetic parameters of phase transformations, and structures of short-range order.

In this work, we studied the structure of amorphous $Yb_{1-x}Sm_xAs_4S_7$ films and the kinetics of phase transformations during their crystallization.

2. EXPERIMENTAL

The thin amorphous $Yb_{1-x}Sm_xAs_4S_7$ layers with a thickness of 30 nm were obtained by evaporating preliminarily synthesized substances and condensation of the vapors at a rate of ~5.0 nm/s in vacuum at a residual pressure of $\sim 10^{-5}$ Pa on crystals of NaCl and KCl, and on amorphous celluloid substrates held at room temperature. At a substrate temperature $T_s = 523$ K, there is formed a polycrystalline $Yb_{1-x}Sm_xAs_4S_7$ phase, which has an orthorhombic structure with lattice parameters $a = 0.724$, $b = 0.568$, and $c = 1.025$ nm [1]. The crystallization of the amorphous films showed the identity of the composition of the amorphous and crystalline films. The structure of short-range order in the $Yb_{1-x}Sm_xAs_4S_7$ films was studied by the method of diffraction of fast electrons (accelerating voltage $U = 75$ kV) with the application of a rotating sector, which made it possible to reveal maxima of diffraction reflection in the far-angle region (Fig. 1). By microphotometering the electron's diffraction patterns, a curve of the intensity of electron scattering was constructed, for which the maximum value of the intensity $s = 4\pi\sin\theta/\lambda$ (where θ is the scattering angle, and λ is the electron wavelength), was found to be equal to $s_{\max} = 100\ \text{nm}^{-1}$ (Fig. 2). In the curve of the intensity of electron scattering, five maxima are observed, depending on the scattering angle: $s = 21.0$, 45.0, 64.0, 83.0, and $96.0\ \text{nm}^{-1}$.

3. RESULTS AND DISCUSSION

For determining the structures of the amorphous films, we used the method of the radial distribution of atoms. Based on the known formula [2]

$$4\pi r^2\sum_i\sum_j c_i k_i k_j \rho_{ij}(r) = 4\pi r^2\rho_0\left(\sum_i c_i k_i\right)^2 + \frac{2r}{\pi}\alpha\int_0^s s[a(s)-1]\sin sr\,ds, \qquad (1)$$

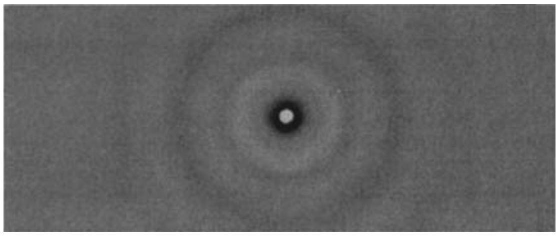

Fig. 1. Electron diffraction pattern of an amorphous $Yb_{1-x}Sm_xAs_4S_7$ film.

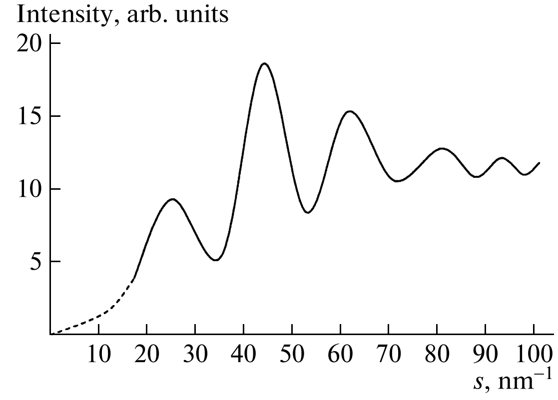

Fig. 2. Intensity of electron scattering for $Yb_{1-x}Sm_xAs_4S_7$.

we constructed curves of the radial distribution of atoms (CRDA) for amorphous compounds. Here, $\rho_{ij}(r)$ is the partial radial-distribution function of the atomic density of atoms of the jth type around atoms of the ith type; r is the distance, α is the normalizing factor, and $a(s)$ is the structure factor. The coefficients c_i in (1) correspond to the relative contents of the atoms of elements entering into the chemical formula of the compounds investigated. The relative scattering powers of the atoms of each chemical element k_i were determined from the formula

$$k_i = \frac{k(s)}{\sqrt{\sum_{i=1}^{3} c_i f_i^2(s)}}, \qquad (2)$$

where $f_i(s)$ is the atomic scattering factor of the ith element. The average atomic density ρ_0 of the amorphous films investigated was calculated according to the formula

$$\rho_0 = \frac{\rho N_A}{\sum_i c_i A_i}, \qquad (3)$$

where ρ is the density of the crystalline substance in g/cm^3, A_i are the atomic masses of the elements entering into the chemical formula, and $N_A = 6 \times 10^{23}$ mol^{-1} is the Avogadro number. The normalizing factor α for the passage from the relative to absolute units of intensity determined from the average atomic density proved to be equal to 0.0534 for $Yb_{1-x}Sm_xAs_4S_7$. The average atomic density ρ calculated according to (3) is equal to 0.425 nm^{-3}. For the scattering powers of ytterbium, arsenic, and sulfur, we obtained $k_{Yb} = 2.000$, $k_{As} = 1.098$, and $k_S = 0.625$. On the basis of the experimental intensity, we calculated, using Eq. (1), and plotted curves of the radial distribution of atoms (Fig. 3). From the CRDAs, we determined the radii of the first and second coordination shells, equal to 0.232 and 0.360 nm, respectively. The decrease in the radii of the coordination shells in $Yb_{1-x}Sm_xAs_4S_7$, in comparison with the amorphous $YbAs_4S_7$ is connected, apparently, with the influence of the impurities of Sm [3]. The first coordination maximum in the CRDA of the amorphous $Yb_{1-x}Sm_xAs_4S_7$ corresponds to the distance As–S; in this case, the atoms of arsenic and sulfur are connected by a covalent bond, which follows from the fact that the sum of the covalent radii of arsenic and sulfur ($r_{As} + r_S = 0.121 + 0.117 = 0.238$ nm) is close to the radius of the first coordination shell ($r_1 = 0.232$ nm). The Yb^{2+} ions in the structure of the amorphous $Yb_{1-x}Sm_xAs_4S_7$ are located on the second coordination shell of the arsenic atoms and are the nearest neighbors of sulfur atoms. This follows from the sum of radii of the first coordination shell and Yb^{2+} ion ($r_1 + r_{Yb} = 0.232 + 0.107 = 0.339$ nm) close to the radius of the second coordination shell ($r_2 = 0.360$ nm). From the area under the maxima of the first and second coordination in the CRDA of amorphous $Yb_{1-x}Sm_xAs_4S_7$, we determined the partial coordination numbers for the shells of the first and second coordination of arsenic atoms in amorphous $Yb_{1-x}Sm_xAs_4S_7$: $n_{13} = 3$, $n_{23} = 3$, $n_{32} = 2$, $n_{31} = 4$, and $n_{11} = n_{22} = n_{12} = n_{21} = n_{33} = 0$ (where 1 stands for Yb, 2 for As, and 3 for S). According to our data, $n_{13} = 3$, i.e., near the Yb^{2+} ion, there are located three atoms of sulfur. The coordination number for sulfur was found to be six: $n_{32} + n_{31} = 6$ (two atoms of As and four Yb^{2+} ions); for As atoms, the coordination number is equal to three ($n_{23} = 3$). The coordination number six obtained for sulfur indicates that upon the transition from crystalline to amorphous $Yb_{1-x}Sm_xAs_4S_7$ the short-range order is partially retained. The structures of the short-range order of these compounds in the amorphous and crystalline states are close. The differ-

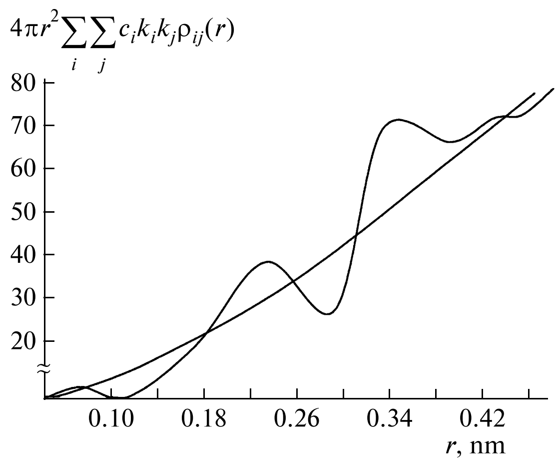

Fig. 3. Curve of the radial distribution of atoms for $Yb_{1-x}Sm_xAs_4S_7$.

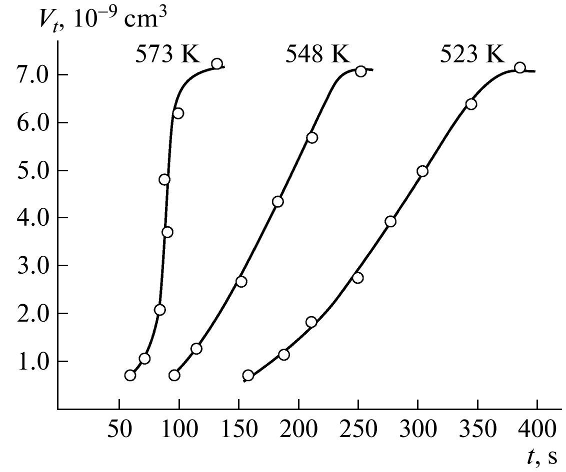

Fig. 4. Kinetic curves of crystallization of amorphous $Yb_{1-x}Sm_xAs_4S_7$ films.

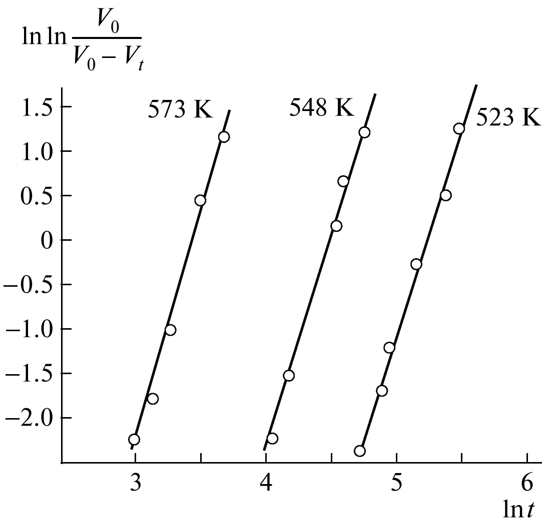

Fig. 5. The $\ln\ln[V_0/(V_0 - V_t)]$ dependence on $\ln t$ for $Yb_{1-x}Sm_xAs_4S_7$.

ence consists in a spread of bond lengths between like and unlike atoms.

Then, we give the results concerning the study of the kinetics of crystallization and the determination of the kinetic parameters of crystallization of the amorphous layers of the $Yb_{1-x}Sm_xAs_4S_7$ ($x = 0.02$ at %) compound 30 nm thick obtained by vacuum condensation from a molecular beam both under normal conditions and under the effect of an external electric field onto the molecular vapor.

For establishing the kinetic parameters of crystallization of the amorphous films $Yb_{1-x}Sm_xAs_4S_7$, we used the kinematic method of electron diffraction [4]. The isothermal kinematic electron's diffraction patterns were obtained from the amorphous films at temperatures $T = 523$, 548, and 573 K. The intensities of the diffraction lines of the crystalline $Yb_{1-x}Sm_xAs_4S_7$ films were determined depending on the time of the heat treatment of the films. The transition from the values of intensity to the quantity of crystallized substance was accomplished by normalization taking into account the fact that in the kinematic approximation, in accordance with [5], the intensities of electron scattering were proportional to the volume of the scattering material V_t. In the range of temperatures investigated (Fig. 4), we plotted kinetic curves of crystallization of the amorphous $Yb_{1-x}Sm_xAs_4S_7$ and determined the dependences $\ln\ln[V_0/(V_0 - V_t)]$ on $\ln t$ (where V_t is the volume of substance that underwent transformation by the time moment t, and V_0 is the initial volume) for temperatures $T = 523$, 548, and 573 K. For all the temperatures the experimental points fit a straight line (Fig. 5).

The comparison of the isotherms with the analytical expression of the kinetic curves of phase transformations $V_t = V_0[1 - \exp(-kt^m)]$ (k is the reaction rate's constant) showed that a better agreement occurs at the following values of the exponent: $m = 2.90$, 3.05, and 3.10 for $T = 523$, 548, and 573 K, respectively.

The intersections of the straight lines of the $\ln\ln[V_0/(V_0 - V_t)]$ dependences on $\ln t$ with the ordinate axis give values of $\ln k$ for the temperatures indicated. On the basis of these data, we constructed the dependence of $\ln k$ on the reciprocal temperature $1/T$. From the slope of the linear dependence of $\ln k$ on $1/T$, the total energy of activation of crystallization was found to be $E_{\text{tot}} = 112.4$ kcal/mol. The energy of activation for the crystallization-center's nucleation E_n calculated from the slope of the straight line $1/\tau_0$-vs-$\ln t$ (where τ_0 is the experimentally observed time of the onset of crystallization) proved to be 34.2 kcal/mol. The energy of activation for growth of crystallites E_p determined from the relation $E_p = (E_{\text{tot}} - E_n)/2$, is equal to 39.1 kcal/mol. Thus, the precision experimental studies with the application of a method of the kinematic electron's diffraction established that the values of the energies of activation for the crystallization of amorphous films $YbAs_4S_7$ doped with samarium are somewhat smaller in comparison with those for the films free of impurities [6].

In this work, we also investigated the kinetics of crystallization of the amorphous films $Yb_{1-x}Sm_xAs_4S_7$ obtained under the effect of an external electric field of strength 3000 V cm^{-1}.

The table gives the values of the total energy of activation for crystallization, nucleation, and growth of crystallites in the amorphous $Yb_{1-x}Sm_xAs_4S_7$ films obtained under normal conditions, and under the effect of an electric field of 3000 V cm^{-1}. As can be seen from the table, the values of the activation energy in the field decrease on the average by 10%.

At present, there is no doubt that the electrical interaction during condensation plays a significant

Table

Strength of electric field, V cm^{-1}	m	E_{tot}, kcal/mol	E_g, kcal/mol	E_n, kcal/mol
0	3	112.4	39.1	34.2
3000	3	100.2	35.3	29.6

role in the formation of the structure of films by the direct action on all stages of the process, beginning from the selection of the vapor phase and ending with the influence on the formation of the film structure. Nucleation, according to [7], occurs selectively at point surface defects which possess an electric charge, i.e., are electrically active. The authors of [8] believe that in surface layers of NaCl there can exist electric fields with the strength of up to 10^5–10^6 V/m. The microcrystals (islands) are subject to thermally activated or electrically stimulated migration. Therefore, a situation can be quite real where the microcrystals are displaced from the positions where they had been nucleated, and at the thus-freed positions, new nuclei can form. The migration increases in the presence of an electric field, and the process of crystallization is thus accelerated.

The influence of an electric field, which leads to an acceleration of the process of crystallization and causes a decrease in activation energies, can be explained by the field interaction with the electrically charged point defects or with their pileups in the films. As the sources of charges in our case, there can serve a potential of the ionic alkali-halide crystals used as substrates or ionized atoms of the condensed substances themselves.

4. CONCLUSIONS

Radii of coordination shells and partial coordination numbers of atoms in the amorphous films of $Yb_{1-x}Sm_xAs_4S_7$ have been determined. Upon an analysis of the structure of short-range order in the amorphous $Yb_{1-x}Sm_xAs_4S_7$ films, differences in the interatomic spacings have been revealed, namely, the radii of coordination shells decrease in them in comparison with the interatomic distances in $YbAs_4S_7$.

It has been shown that the electric field exerts a substantial influence on the processes of crystallization of the amorphous layers, namely, it increases the rate of formation of crystallization nuclei, the rate of their further growth, and thus increases the crystallization rate.

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