The influence of doping by samarium on the structure and surface morphology of the $As_{33.3}Se_{33.3}S_{33.4}$, $As_{33.3}Se_{33.3}Te_{33.4}$ chalcogenide glass semiconductor films

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The surface morphology of $As_{33.3}Se_{33.3}S_{33.4}$, $As_{33.3}Se_{33.3}Te_{33.4}$ films have been investigated by AFM method and also influence on them of doping by samarium. It was determined the values of the surface roughness parameters and its change by doping. The results are explained within void-cluster model and intrinsic charged defects based on the structural features of the materials studied and the distribution of atoms in the amorphous matrix.

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1. Introduction

Chalcogenide glassy semiconductors (CGS) are promising materials for applications in electronics and optoelectronics [1-4], which requires the establishment of ways to manage their electronic properties. It is known that in CGS materials has correlation between physical properties and structural features which depend on the sample preparation process, the chemical composition and the presence of impurities. This allows for modify the structure of CGS material and thus impact on the electronic and optoelectronic properties.

In addition, CGS materials due to such properties as the capacity infrared communication of information and exercise a number of photo-induced phenomena (photodarkening, fotocrystalization, photopolymerization, etc.), leading to a non-linear change of optical constants, are already used in the diffraction gratings, planar waveguides, holography, optical storage devices, etc. [5-8]. Recent years films based on chalcogenide glasses, as promising materials with high photosensitivity, low power consumption for use in chemical and gas sensors have been intensively studied [9-11]. In connection with this require the production of films with a smooth, homogeneous surface, uniform thickness and minimum residual stress, which is dedicated to the presented work. Besides, such studies help to obtain information about changes in the local structure at change of chemical composition and alloying.

2. Experimental

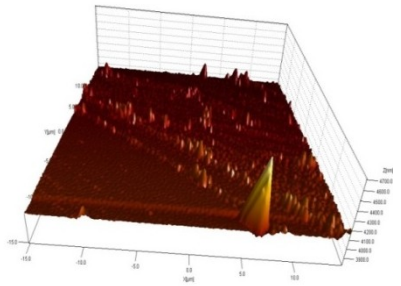
2.1. Sample preparation

Synthesis of CGS materials $As_{33.3}Se_{33.3}S_{33.4}$, $As_{33.3}Se_{33.3}Te_{33.4}$ with Sm impurity is conducted in the following sequence: specially pure elementary substances in equal atomic percentages are filled into the quartz ampoules and after evacuating the air down to 10^{-4} mm Hg they are heated up to T = 900-950°C for 3 hours and kept for about 12 hours at this temperature. To maintain sample homogeneity the synthesis has been carried out in rotating furnace but cooling has been carried out in furnace OFF. Sm impurities are introduced in synthesis process. The films of 4 μm in thickness have been obtained by thermal evaporation with the rate 0.4-0.5 μm /min on the glass substrate in vacuum under the pressure 10^{-4} mm Hg. Surfaces of samples with size 2x2 mm were cleaned with pure nitrogen and were performed on an AFM sample holder. Study of the surface of the films made by means of an atomic force microscope (AFM) Bruker Nano GmbH.

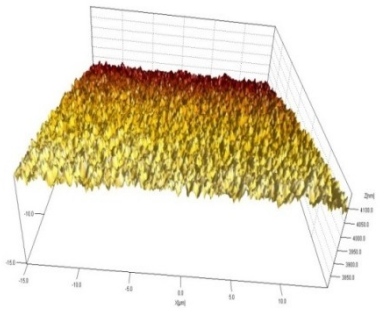
To obtain information about the surface were used optical lenses, by which that surface area has been increased to 10 and 50 times. Similar observations have helped to choose more clean and smooth areas of the sample and scan it cantilever.

3. Results and discussion

In figures are presented the three-dimensional -3D (Fig. 1) and two-dimensional - 2D (Fig. 2) AFM images of the surface of materials CGS $As_{33.3}Se_{33.3}S_{33.4}$(a) and $As_{33.3}Se_{33.3}Te_{33.4}$(b) doped with samarium.



a)



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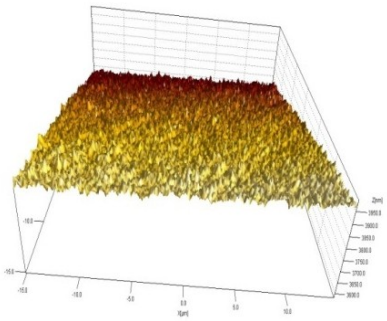

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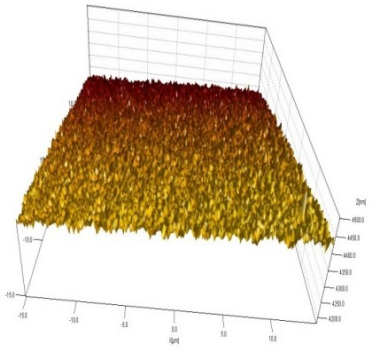

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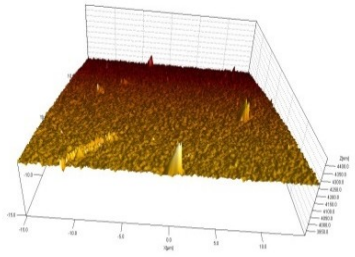
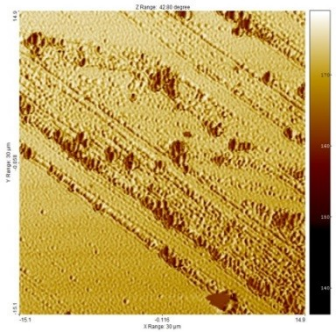
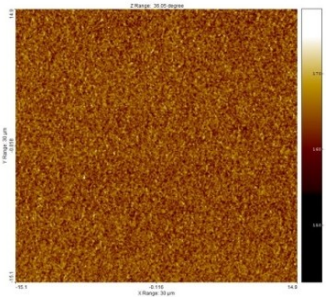


e)

Fig. 1. 3D AFM images of the surface of films; a) $As_{33.3}Se_{33.3}S_{33.4}$ b) $As_{33.3}Se_{33.3}S_{33.4}$: $Sm_{1\%}$, c) $As_{33.3}Se_{33.3}S_{33.4}$:$Sm_{5\%}$ d) $As_{33.3}Se_{33.3}Te_{33.4}$, e) $As_{33.3}Se_{33.3}Te_{33.4}$: $Sm_{1\%}$



a)



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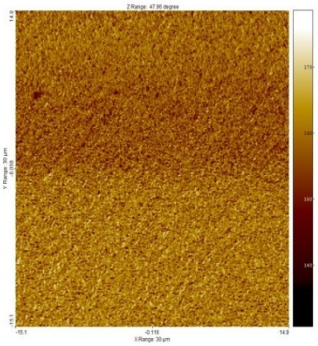

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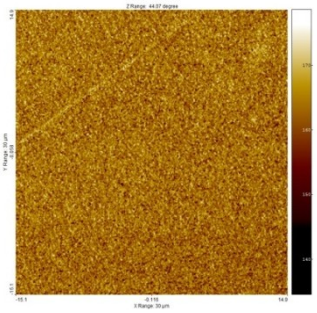

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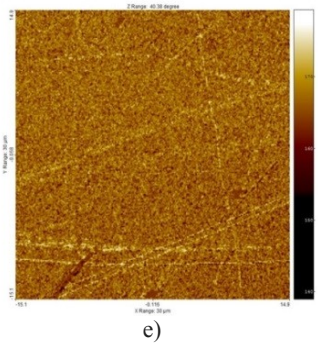

e)

Fig. 2. 2D AFM images of the surface of the films a) $As_{33.3}Se_{33.3}S_{33.4}$ b) $As_{33.3}Se_{33.3}S_{33.4}$: $Sm_{1\%}$ c) $As_{33.3}Se_{33.3}S_{33.4}$:$Sm_{5\%}$ d) $As_{33.3}Se_{33.3}Te_{33.4}$, e) $As_{33.3}Se_{33.3}Te_{33.4}$: $Sm_{1\%}$

As shown in figure the AFM - image are undergoing significant changes depending on the chemical composition and alloying. The parameters characterizing the morphological characteristics of the surface were calculated the application of V6.0.2.0 software SPIP, whose results are presented in Tables 1 and 2.

Table 1

Parameters	**$As_{33.3}Se_{33.3}S_{33.4}$**	**$As_{33.3}Se_{33.3}S_{33.4}$:$Sm_1$ at%**	**$As_{33,3}Se_{33,3}S_{33,4}$:$Sm_5$ at%**
Ra, nm	15,2347	12,5865	11,817
Rq, nm	28,2347	15,7176	14,7631
Rsk	5,5097	-0,170901	0,0615677
Rku	69,7618	2,95354	2,91872
Rt, nm	700,829	132,266	119,557
Rp, nm	572,522	67,0142	59,6547
Rv, nm	128,306	65,2519	59,9019
Rds, 1/ m^2	4,36444	4,36889	6,17556
Rsc, 1/ m	0,000927979	0,00148507	0,00189437

Table 2

Parameters	$As_{33.3}Se_{33.3}Te_{33.4}$	$As_{33.3}Se_{33.3}Te_{33.4}$:$Sm_5$ at%
Ra, nm	8,39452	10,8638
Rq, nm	10,6039	13,8308
Rsk	- 0,223837	0,36039
Rku	3,28829	8,72042
Rt, nm	128,018	241,807
Rp, nm	76,4066	161,312
Rv, nm	51,6114	80,4292
Rds, 1/ m^2	5,61444	6,43444
Rsc, 1/ m	0,00132715	0,00129762

Where Ra - arithmetic mean roughness, i.e. the arithmetic mean of the absolute value of the vertical deviation from the mean line through the profile, Rq-mean square roughness, is the square root of the arithmetic mean square deviation from the vertical reference line, Rsk- asymmetry coefficient surface describing the asymmetry of the distribution histogram of heights, Rku - the excess of surface describes "peakedness" of the surface topography. R_{sk} = 0 and R_{ku}=3 indicate the symmetry of (Gaussian) distribution of heights, wherein there are equal numbers of local maxima and minima from a certain height above and below the centerline. The high negative Rsk-value and low value excess (R_{ku} <3) indicate a large number of local maxima above the midline compared with a Gaussian distribution. For positive values of R_{sk} and high excess (R_{ku}>3) is characterized by a large number of local minima below the midline compared with Gaussian distribution. The R_t - maximum roughness indicates the distance between the highest peak and the lowest minimum R_p - maximum peak height to the midline, R_v - maximum depth of the minimum to the midline, R_{ds}, R_{sc} - density of peaks per unit area and per unit length of the profile [12].

As shown in table the values of the amplitude of the roughness parameters (Ra, Rz, Rt, Rp, Rv) in $As_{33.3}Se_{33.3}Te_{33.4}$ is less than that $As_{33.3}Se_{33.3}S_{33.4}$. Alloying is not alone influences the values of these parameters: the values of parameters decrease for $As_{33.3}Se_{33.3}S_{33.4}$, but increase for $As_{33.3}Se_{33.3}Te_{33.4}$. The asymmetry coefficient is negative for $As_{33.3}Se_{33.3}Te_{33.4}$, indicating that a large number of local maxima above the middle line. As a result of alloying specified parameter becomes positive, indicating that the increase the relative amount of peaks below the midline. The asymmetry coefficient is negative for films $As_{33.3}Se_{33.3}Te_{33.4}$ and $As_{33.3}Se_{33.3}S_{33.4}$ alloyed by samarium (1 at %), i.e. they have a large number of local maxima above the mean line, which is considerably in their histograms (Fig. 3).

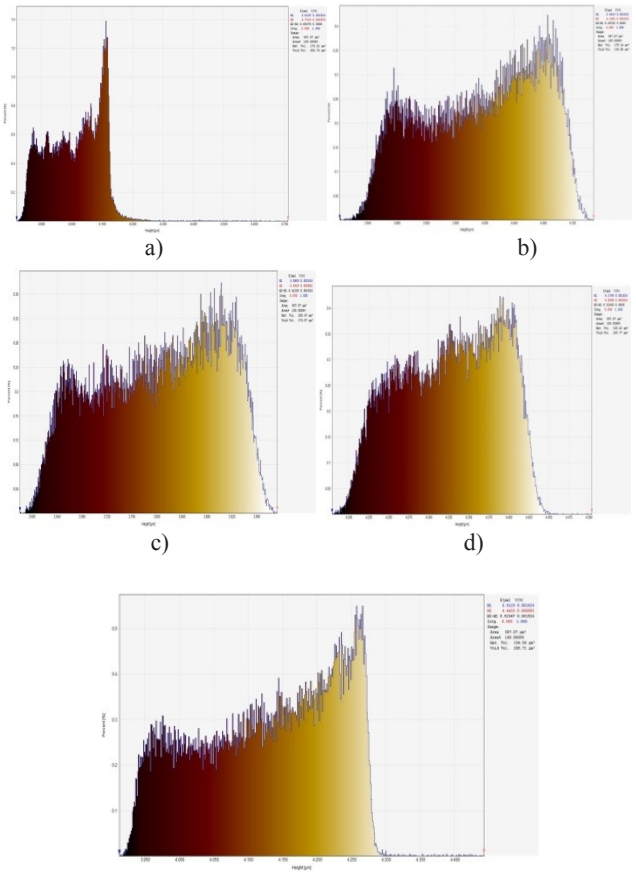

Fig. 3. Histograms of the height distribution of the films a) $As_{33.3}Se_{33.3}S_{33.4}$ b) $As_{33.3}Se_{33.3}S_{33.4}$: $Sm_{1\%}$ c) $As_{33.3}Se_{33.3}S_{33.4}$:$Sm_{5\%}$ d) $As_{33.3}Se_{33.3}Te_{33.4}$, e) $As_{33.3}Se_{33.3}Te_{33.4}$: $Sm_{1\%}$

The Values of parameters characterizing the distribution along the surface of roughness (R_{ds}) and the profile (R_{sc}) in $As_{33.3}Se_{33.3}S_{33.4}$ is less than in the $As_{33.3}Se_{33.3}Te_{33.4}$, wherein alloying both parameters increases.

According to [13-17] the morphological features of films depend on such factors as process conditions, the thickness of the impact of powerful radiation, heat treatment, material and surface morphology of the substrate, the nature of the film material etc. In our case changes only the nature of the material, due to changes in the chemical composition and alloying of Sm. Therefore, changes in the morphological characteristics of the surface of the films would be appropriate to associate with the modification of the local structure. For glassy materials with tetrahedral structural units in [18-19, 21] has been proposed void-cluster model, i.e. it is believed that these atomic group forming clusters are separated by voids or areas with a reduced atomic density. According to [20] is acceptable to the majority of CGS the void- cluster model. Because of the mutual repulsion between electrons on chalcogen atoms solitary pairs or pnyctides they have a low packing density of atoms and the presence of voids is a characteristic feature of their structure.

X-ray diffraction analysis by us [22] estimated the size of the empty spaces and has shown that they $As_{33.3}Se_{33.3}S_{33.4}$ almost twice more than in $As_{33.3}Se_{33.3}Te_{33.4}$ and are about 6 and 3,5Å, respectively. Furthermore please be aware that the size of the macromolecules of the first composition is more than the second [23], which should be reflected in the surface morphology. As shown in table the values of surface roughness of the first composition significantly is higher than the second. Such a difference in sizes of macromolecules (or structural elements) also leads to the fact that the density of the peaks on both the surface and along the profile in the second case is more than in the first.

Influence of a doping of samarium on the surface morphology can be interpreted in view of their activity and distribution feature. In the composition of $As_{33.3}Se_{33.3}S_{33.4}$ Sm atoms in small amounts mostly fill empty spaces and due to the chemical activity of cross linked chain molecules and broken bonds by reducing the roughness. At higher concentrations Sm ions distributed throughout an amorphous matrix and increase the degree of roughness. It is known [24] that the addition of tellurium into amorphous selenium occurs break of selenium chain macromolecules, thereby increasing the concentration of dangling bonds, and charged defect centers (D^+, D^-) [25]. At alloying of $As_{33.3}Se_{33.3}Te_{33.4}$ positive Sm ions accumulates around D^- - centers operate and screens their electric field and at the same time increase the degree of heterogeneity of the material, the amplitude characteristics of surface roughness (Ra, Rq, Rt, Rp, Rv) and density peaks (Rds, Rsc).

4. Conclusions

The surface morphology of $As_{33.3}Se_{33.3}S_{33.4}$, $As_{33.3}Se_{33.3}Te_{33.4}$ films has been investigated by AFM method and also the changes happening in them at an alloying samarium. It is shown that the amplitude roughness (R_a and the average arithmetic mean square - R_q roughness, the maximum roughness -R_t, the maximum height of the peak-R_p minimum and maximum depth - R_v) of the first composition is substantially greater than the second, and the density peaks (peak density of surface - R_{ds} and profile -Rsc) in the first case is smaller than the second. As a result alloying the amplitude parameters of the first composition are reduced, but the second increase and the density peaks increase in both cases. The obtained results are explained within of void - cluster model and intrinsic charged defects based on differences in the size of macromolecules investigated CGS materials as well as the peculiarities of the distribution of samarium atoms in the amorphous matrix and their chemical activity.

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