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AMORPHOUS ARSENIC CHALCOGENIDE FILMS MODIFIED USING RARE-EARTH COMPLEXES

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The optical and electrical properties of thin arsenic chalcogenide As-X (X=S, Se) films modified by rare-earth complexes with organic mixed-ligands have been studied. There were two types of complexes used: europium dipivaloylmethanate $Eu(thd)_3$ and lanthanide diethyldithiocarbamates $Ln(ddtc)_3$ (Ln=Pr, Eu). It was shown that the use of rare-earth mixed-complexes with neighbor volatility to chalcogenide volatility permits the deposition of amorphous films by thermal evaporation. The decrease in absorption coefficient at the Urbach's edge after introduction of the complexes containing oxygen in arsenic selenide has been revealed. The type of organic ligands incorporated in amorphous matrix determinates the shape of current-voltage characteristic. Such complexes decrease considerable the activation energy for electrical conduction as well. The observed results have been discussed on the basis of different levels of structural modification in non-crystalline materials.

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1. Introduction

Chalcogenide glassy semiconductors (ChGSs) exhibit a number of interesting optical properties with various potential applications as recently reviewed in, for example, [1]. As frequently pointed out by various researchers, ChGSs are promising materials for telecommunication applications and integrated optics because they are transparent over a wide range of wavelengths in the infrared region, possess high refractive index, low phonon energy and can be easily fabricate. Rare-earth-doped ChGSs are employed in designing optical fibers of IR range spectrum for various telecommunication devices. The basic properties of such glasses are widely discussed [2÷4]. Most of researchers use wide-band multicomponent glasses for that purpose, e.g. the systems like Ga-La-S, Ge-Ga-Se, Ge-As-S, As-Se-S, As-S. The most frequently used dopants for ChGSs are rare-earth sulphides [5], chlorides and oxides [6]. Rare-earth metals are used less frequently [2].

The glasses can be prepared in quartz ampoules heated up to 1000 ^{0}C in rotating furnaces with subsequent quenching. It is difficult to obtain amorphous thin film structures from such source glasses by means of thermal vacuum evaporation because of infusibility of the material and difference between saturated vapor pressures of ChGS's components. Amorphous films with satisfactory optical characteristics could be produced using method of laser ablation [7, 8], but this technique isn't widely practiced. Therefore search of alternative methods of producing thin film structures based on rare-earth ions doped chalcogenide glasses thought to be of great interest.

In the present paper, the method of preparation of arsenic chalcogenide As-X (X=Se, S) thin films modified by rare-earth complexes with organic ligands and its electrical and optical properties are reported. The key feature of this approach is the co-evaporation of inorganic material (ChGSs)

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and a volatile complex from separate sources. It is essential to notice that employment of organic components in the synthesis of hybrid amorphous materials possessing new properties is a contemporary approach which attract researcher's attention [9,10]. This method is preferably used for synthesis of oxide fusible glasses like P_2O_5 or nanocomposites based on SiO_2 [11].An application of this technique to chalcogenide systems is practically unknown. In [12] we described in details criteria of rare-earth complexes selection as modifying component. It is necessary to mention at this point that main factors are volatility and thermal stability of the complexes under chalcogenide evaporation conditions. Two types of the mixed-ligand compounds were picked up: lantanide dipivaloylmethanates with o-phenanthroline – $Ln(thd)_3(Phen)$ [13] and lantanide diethyldithiocarbamates with o-phenanthroline – $Ln(ddtc)_3(Phen)$[14]. The key distinction between these compounds is the elements surrounding rare-earth ion. In the case of dipivaloylmethanates central sphere was formed by oxygen and nitrogen atoms, in other compound oxygen is replaced by sulfur atoms.

In this paper, preparation, identification and specific properties of amorphous films As-X (X=Se, S) modified by rare-earth complexes are reported and discussed.

2. Experimental

Glasses with the composition As_2Se_3 and As_2S_3 were synthesized by melting appropriate amounts of As, Se or S in evacuated, fused silica ampoules at 750 ^oC in rotating furnace. The ampoules were subsequently subjected to furnace-cooling. Examination of the glasses under an IR-microscope revealed no opaque (crystalline) inclusions. The content of gas-forming impurities was on the order of 1 ppm by weight, as inferred from IR spectroscopy results. The $Ln(ddtc)_3(Phen)$ (Ln = Pr, Sm, Eu) and $Eu(thd)_3(Phen)$ complexes were synthesized by well-known methods [15] and identified by elemental analysis and IR spectroscopy. It is necessary to notice that dipivaloylmethanate $Eu(thd)_3$ and diethyldithiocarbamates $Ln(ddtc)_3$ are more volatile than ChGSs, but conversion of these compounds into mixed-ligand complexes with 1,10-phenantroline (Phen), raises the vaporization temperature of the complex, which then vaporizes only after detachment of the (Phen) ligand [15]. This enables coevaporation of ChGSs and complexes.

Thermal deposition was carried out using a purpose-designed apparatus [12]. The process conditions were optimized in experiment so as to ensure the best possible uniformity of the film, required thickness and composition reproducibility controlled by the ratio ChGSs-complex compounds in the film. The current-voltage characteristics measurement was conducted for "sandwich" type structure of the sample with aluminum electrodes. In each technological cycle samples were manufactured both for electrical and optical investigations. The samples for optical measurements did not have aluminum electrodes on the surface. Film thickness was measured by means of interferometric microscope and varied in the range of 0,2-5,4 μm.

The chemical and phase compositions of the films were determined by X-ray fluorescence analysis (Spectroscan scanning spectrometer) and X-ray diffraction (DRON-3 powder diffractometer and Nonius focusing camera). Film surfaces were analyzed using a Tesla BS 300 scanning electron microscope (resolving power of 100 nm/cm), Soever Pro-NT-MDT atomic force microscope (resolving power of 10 nm/cm) and JEOL JSM-840A scanning electron microscope equipped with a PGT elemental analysis. The IR spectra of films deposited on KBr substrates were recorder on a Perkin-Elmer FTIR 1600 spectrometer between 400 and 4000 sm^{-1}. All combined results allowed to determinate phase and elemental composition of the prepared films as well as to make speculations about possible mechanism of incorporating rare-earth complex in amorphous matrix [12].

3. Results

Fig. 1 shows optical absorption edge spectra of amorphous films As-Se (Fig. 1a) and As-S (Fig. 1b) containing different rare-earth complexes. These dependences have following peculiarities:

- Amorphous arsenic sulphide films modified by $Ln(ddtc)_3$ or $Eu(thd)_3$ have an increased absorption coefficient which corresponds to the darkening of the material.
- Amorphous arsenic selenide films after modified by $Eu(ddtc)_3$ or $Eu(thd)_3$ have a decreased absorption coefficient which corresponds to the bleaching of the material.
- Elemental analysis indicates that films produced by the method described above are enriched with arsenic up to 5% with respect to bulk source glass As_2X_3. It indicates that evaporation is an

incongruence process during the film deposition. As a result, the dependence $\alpha = f(h\nu)$ of the unmodified films differs from the published data [16].

The darkening effect, and especially photodarkening effect, has been studied extensively in As-chalcogenide glasses for the past three decades, bleaching has been observed much seldom. Therefore current-voltage characteristics measured for arsenic selenide films have revealed the bleaching. Fig. 2 shows current-voltage characteristics of As-Se films modified by Ln(thd)$_3$ measured at room temperature; corresponding characteristics for As-Se films with Ln(ddtc)$_3$ complexes are shown on Fig. 3. As can be seen, the type of organic ligands incorporated in amorphous matrix has fundamental importance and determines the shape of characteristics.

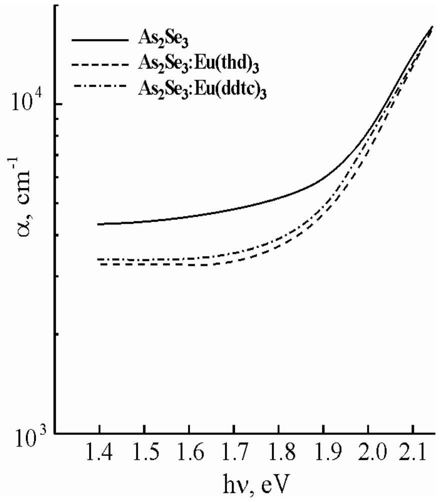

Fig. 1a. The absorption spectra of arsenic selenide films modified by Eu(ddtc)$_3$ and Eu(thd)$_3$.

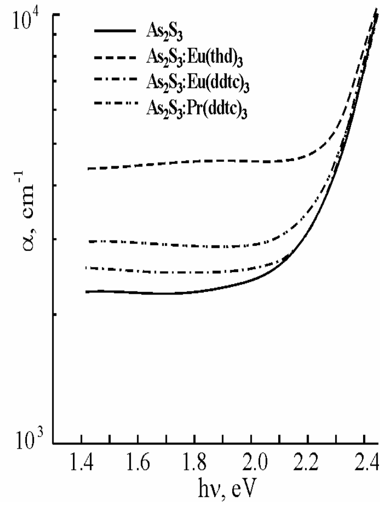

Fig. 1b. The absorption spectra of arsenic sulfide films modified by Ln(ddtc)$_3$ (Ln = Pr, Eu) and Eu(thd)$_3$.

In the case of oxygen-free complex Ln(ddtc)$_3$ a shift of the crossover of the liner and nonlinear regions in the current-voltage characteristics is observed in comparison with non-modified As-Se film. As can be seen, the crossover point is shifting to higher electrical fields. In the linear region curves are close enough to each other.

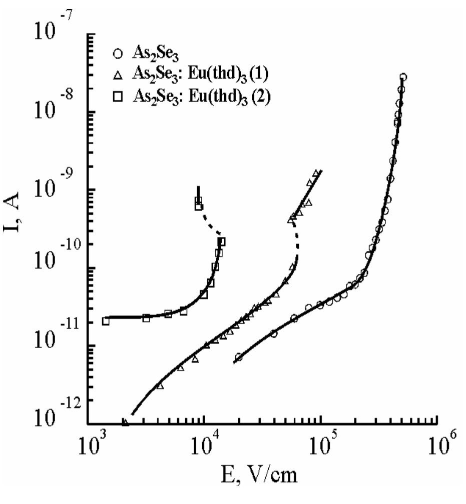

Fig. 2. Current-voltage characteristics of arsenic selenide films modified by Eu(thd)$_3$. The concentration of Eu in the sample (1) is 0.7 at.% and in the sample (2) is 1.4 at.%.

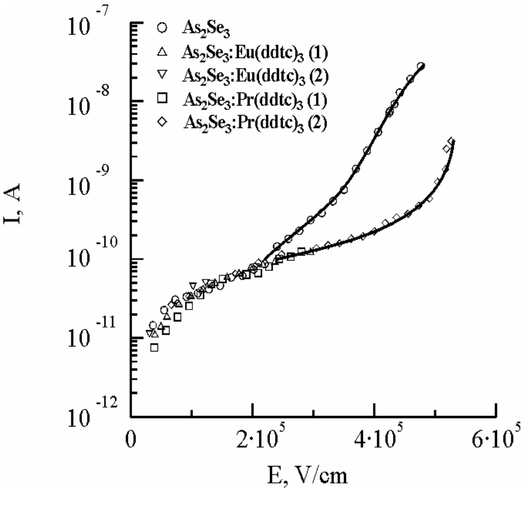

Fig. 3. Current-voltage characteristics of arsenic selenide films modified by Ln(ddtc)$_3$.(Ln=Eu, Pr). The concentration of Ln in the sample (1) is 0.7 at.% and in the sample (2) is 1.4 at.%.

If oxygen containing material Eu(thd)$_3$ was used for modification, the current-voltage characteristic principally is shifted up to the region with negative differential resistance. In the material containing Eu(thd)$_3$ the conductivity of the films significantly increased. Temperature dependences of the conductivity of these films were measured in the range 200÷300 K. The most interesting result of this experiment is the decrease of activation energy with an increase of rare-earth concentration.

4. Discussion

For qualitative explanation of the obtained results, the concept of different levels of structural modification in ChGSs developed by A. Popov [17] was employed. According to the concept, the structures of arsenic sulphide As-S and arsenic selenide As-Se shall be placed on the other sides of the border determining the rigidity of the structural network. The structure of arsenic sulphide must exhibit certain flexibility and flexible bonds are to be present. During the modification by complexes it allows the transformation on the level of structural units going without destruction of the network continuity. As shown in [17], this occurs on the level of medium-range order. The pre-condition of such structural adjustment is a sufficient concentration of bridging bonds, e.g. homo-bonds like As-As or chalcogen-chalcogen. In these materials “macroheterogeneities” are absent.

As for less flexible and more rigid matrix of arsenic selenide, its structural transformations are less probable. Incorporation of sufficiently complicated and relatively massive complex compounds like Ln(ddtc)$_3$ in such matrix can interrupt network continuity and lead to formation of well-ordered regions. During the formation of borders between that kind of regions (micro-heterogeneities) is possible as well as growth of the latter and organization of film morphology. In that case modification is applicable not only at the medium-range level, but also at the morphology level. In [8] it was demonstrated that bleaching may be connected with oxidation of the initial components in the process of the film preparation In our case, bleaching could be related to incorporation of “light” elements into the film, first of all oxygen, and formation of new chemical bonds in macroheterogeneities.

Presence of oxygen in the complex compound appears to be principal for electrical properties, as it follows from Fig. 2 and 3. Negative resistance region is typical for ChGSs revealing switching effect. Switching effect is often supposed to be due to local changing of amorphous film morphology, leading to formation of heterogeneities which are able to create conducting channels [18, p.455÷487]. An experiment on electrical breakdown was carried out, results of which are the following: in modified films of arsenic selenide switching effect occurred at higher electrical fields than in unmodified ones (respectively 1.2×10^6 V/cm vs. 6×10^5 V/cm).

5. Conclusions

The investigation of electrical properties of arsenic selenide and arsenic sulfide films modified by rare-earth complexes reveals the influence of ligand type on the feature of current-voltage characteristics. The most significant changes are typical for the films containing the complexes with oxygen Eu(thd)$_3$.This phenomena may be connected with the formation of macroheterogeneities in arsenic selenide films during modification.

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References

[1] A. Zakery, S. R. Elliott, J. Non-Cryst. Solids **330**, 1 (2003).
[2] S. G. Bishop, D. A. Turnbull, B. G. Aitken, J. Non-Cryst. Solids **266&269**, 867 (2000).
[3] H. Tamorin, M. T. de Araujo, E. A. Gouveia, A. S. Gouveia-Neto et. al. J. Luminescence **78,** 271 (1998).
[4] H. Harada, K. Tanaka, J. Non-Cryst. Solids **246**, 189 (1999).
[5] A. M. Lozac'h, S. Barnier, M. Guitard et. al. In: Infrarouge chim. solids, Paris, 1974, p.127.
[6] K. Wei, D. P. Machewirth, J. Wenzel, E. Snitzer, G. H. Sigel, J. Non-Cryst. Solids **182**, 257 (1995).
[7] S. G. Devinder, R. W. Eason, C. Zaldo, H. N. Rutt, N. A. Vainos, J. Non-Cryst. Solids **191**, 321 (1995).
[8] E. N. Borisov, V. B. Smirnov, A. Tverjanovich, Yu. S. Tveryanovich, J. Non-Cryst. Solids **326&327**, 316 (2003).
[9] M. Takahashi, H. Niida, Y. Tokuda, T. Yoko, J. Non-Cryst. Solids **326&327**, 524 (2003).
[10] El. C. Zampronio, D. N. Greggio, H. P. Oliveira, J. Non-Cryst. Solids **332,** 249 (2003).
[11] E. L. Alexandrova, E. I. Terukov, M. E. Kompan, N. N. Himich, Proc. 4-th Intern. Conf. Amorph. Microcryst. Semic., St. Petersburg, Russia, 2004, p. 194.
[12] S. A. Kozyukhin, N. A. Markova, A. R. Fairushin, N. P. Kuz'mina, E. N. Voronkov. Inorganic Materials **40**(8), 908 (2004).
[13] N. G. Dzubenko, L. I. Martynenko, in: Problems of chemistry and application of β-diketonats of metals (in Russ.). M.: Nauka. 1982, p. 19.
[14] N. P. Kuz'mina, R. A. Ivanov, A. B. Il'yukhin, S. E. Paramonov, Coordination chemistry (in Russ.) **25**(8), 635 (2000).
[15] R. A. Ivanov, I. E. Korsakov, A. A. Formanovsky, S. E. Paramonov, N. P. Kuz'mina, Coordination chemistry (in Russ.) **28**(9), 713 (2002).
[16] N. F. Mott, E. A. Davis, Electron Processes in Non-Crystalline Materials, Clarendon Press, Oxford (1979).
[17] A. Popov, in: Semiconductors and Semimetals, **78**, Amsterdam, Ed. R. Fairman and B. Ushkov, 2004, p. 51.
[18] A. Madan, M. P. Shaw, The Physics and Applications of Amorphous Semiconductors, Academic Press (1988) (in Russ.).