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$(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ THIN FILMS FOR GAS SENSING APPLICATIONS

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În lucrare sunt prezentate rezultatele elaborării tehnologiei de obținere şi cercetare a proprietăților electrofizice ale straturilor subțiri $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$, destinate în calitate de elemente gazosensibile ale detectoarelor. Straturile subțiri au fost depuse prin metoda evaporării termice în vid (P=10^{-5} Torr) pe suporturi dielectrice. Grosimea straturilor depuse varia între 0,5 şi 2 μm. Cercetarea influenței componenței materialului sursă şi a unui sir de parametri tehnologici ai depunerii asupra rezistivității, concentrației capcanelor şi a benzii interzise în straturile obținute a demonstrat că în dependență de mărimea *x* rezistivitatea se schimbă de la 10^{10} până la 10^{14} Ohm·cm, concentrația capcanelor în regiunea (2,1-7,9)x10^{16} см$^{-3}$ şi a benzii interzise ΔE_g – de la 1,75 până la 2,35 eV corespunzător.

Pentru cercetarea sensibilității gazoase față de gazele CO şi NO_2 prin metoda depunerii consecutive în vid au fost obținute structurile săndvici de Al/As-S-Se/SnO_2. Structurile obținute au demonstrat o sensibilitate mai pronunțată la NO_2, decât la monooxidul de carbon.

Introduction

For the timely detection of different toxic and inflammable gases in atmosphere there are widely used in our days the relatively simple solid state sensors on the basis of SnO_2 and some other oxides, operating on the principle of their conductivity changing in the presence of atmospheric pollutants [1-4]. Nevertheless, the attempts to widen the material basis of gas sensors and principles of their functioning are continued [5-8]. As a part of such general process, some investigations directed on the creation of innovative air quality monitoring systems to substitute the standard analytical tools with a new generation of portable detectors had been undertaken recently [9-12]. In these research works it was proposed to use amorphous semiconductors on the basis of chalcogenide glasses as gas sensitive material. Band gap width in chalcogenide glass semiconductor (ChGS) is varied in the range 1-3 eV and electronic properties are controlled by the species of chalcogen (S, Se, Te) atoms and can be modified through the disarray of the film matrix structure.

Given semiconducting materials due to their disordered structure possess a huge amount of broken bonds both in the bulk and on the surface of films. The last ones can serve as centers for gaseous species adsorption that represent interest from the point of view of novel gas sensors creation. In particular, D. Tsiuleanu with coworkers had been used chalcogenide semiconductor system As-S-Te for gas sensitive element creation [9-11]. As further development of this direction the As-S-Se solid solution based thin films were tested as sensors of CO and H_2 gases at room temperature [12]. However, the mechanism of gas sensing and influence of technologic factors on gas sensing performance of developed structures remains unclear. Characterizing these materials we should mention that their atomic bonding structure is more rigid than in polymeric materials and, simultaneously, more flexible than in oxide glasses. As result, the ChGS can be prepared in bulk, fiber, thin film and multilayer structures. It opens technologic possibilities for development of new class of gas sensors on rigid and flexible substrates (platforms). But we should emphasize that given class of semiconducting materials for a long time was used for optical information recording and so their formation technology was adapted for the needs of information registration. The last one supposes the obtaining of extremely high resistive (10^{14}-10^{16} Ohm·cm) photosensitive thin layers. In the case of gas sensors we need for thin films with specific resistance on the level 10^8 Ohm·cm.

So, the purpose of presented work was to develop deposition technology for As-S-Se solid solution thin film obtaining with decreased, most corresponding to the gas sensor creation requirements resistance.

EXPERIMENTAL

Technologic features of ChGS films preparation

ChGS thin films were obtained by means of thermal evaporation under vacuum 10^{-5} Torr. For evaporation there was used the finished powder of the binary As_2S_3 and As_2Se_3 compounds and ternary solid solutions on

their basis with composition described as $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$, where x=0.3; 0.5; 0.7. Variation of the composition had aim to optimize electrophysical parameters of thin ChGS films.

Evaporation process was performed from Gunter type evaporator consisted of molybdenum boat and graphite insert for providing of the uniform powder heating up. Thin films of ChGS had been deposited at the substrate temperatures 20, 40, 60 and 80°C. Film's deposition rate had been varied from 1 to 5 nm/s.

Electrophysical Characterization

Thicknesses of deposited films had been measured by means of interference microscope MII-4 and were in the interval 0.5-2 μm.

For electrophysical and photoelectrical characterization of ChGS thin films there were developed structures Al/ChGS/SnO_2 shown in Figure 1. Top electrode was formed by semitransparent Al layer but the bottom one was also transparent layer of low-resistive SnO_2. Specific resistances ρ of deposited ChGS films were determined from the linear regions of I-V curves measured in dark and light regimes as well as in the presence of CO and NO_2 gases.

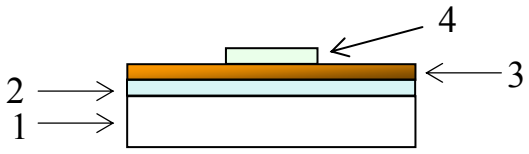

Fig.1. Structure of ChGS based gas sensitive element: 1 – dielectric substrate; 2 – bottom SnO_2 electrode; 3 – ChGS thin film; 4 – thin film Al top electrode.

For photoelectrical and optical measurements the ChGS samples were prepared on the transparent substrates (glass or polyethylentereftalat (lavsan)). Diffraction monochromator MDR-23 (LOMO, Russia) was used for photoelectrical and optical spectra study.

Obtained measurement results are summarized in Table 1.

Gas sensitive characteristics measurement

There were used the laboratory produced gas-air mixtures in our experiments for determination of gas sensitivity of $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ thin films toward CO and NO_2 gases. Used concentration of both gases has amounted 0.1 vol. % in dry air. For gas sensitive characteristics of obtained ChGS thin films investigation current-voltage characteristics were measured in measurement cycles air⇒ air+gas mixture ⇒ air again. Applied voltage was changed with a step of 0.5 V between –6 V and +6 V. All measurements were carried out at room temperature.

Results and discussion

Compounds of As_2S_3 and As_2Se_3 possess capability to form a continuous series of solid solutions that allows to varying material parameters in wide diapason in accordance with concrete practical task. In this connection, aiming the purpose to optimize characteristics of obtained multilayered structures for gas sensing application, we have studied the dependence of the basic electro-physical properties of ChGS thin films on the chemical composition of solid solutions $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ system and evaporation conditions. It was established that at the thickness of 1-2 μm the deposited layers have specific resistance ρ in the range 10^{11}-10^{14} Ohm·cm on dependence on chemical composition (Table).

Table

Electrophysical characteristics of thin films of As-S-Se system

Parameters	Composition $(As_2S_3)_x(As_2Se_3)_{1-x}$				
	x=0	x=0.3	x=0.5	x=0.7	x=1.0
Resistivity ρ (Ohm·cm)	2.0×10^{11}	9.1×10^{12}	1.1×10^{13}	2.0×10^{14}	1.2×10^{14}
Concentration of trap states n_t (cm^{-3})	2.1×10^{16}	3.4×10^{16}	4.3×10^{16}	6.2×10^{16}	7.9×10^{16}
Optical ΔE_g, (eV)	1.75	1.93	2.05	2.17	2.35

I-V characteristics study has shown that with decreasing of As_2Se_3 concentration in solid solution leads to the growth of film resistance (current decrease) (Fig.2). Simultaneously, I-V curves are shifted to the higher voltage field although the shape of curves is, in general, kept. At that, every region of I-V curve can be described by expression

$$I = A \cdot U^n \quad (1)$$

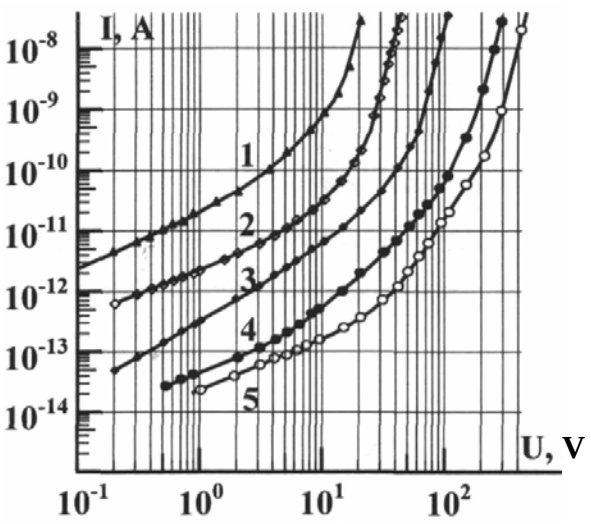

Fig.2. I-V curves of $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ thin films for different *X*: 1–0; 2–0.3; 3–0.5; 4–0.7; 5–1.0. Deposition rate *w*=6 nm/s.

At the low electrical fields the Ohmic current dependence on voltage (n≈1) is observed. Further curve trend is described by the expression (1) with n≈2.2-3.5 that is evidence of the currents restricted by the bulk charge passing through the ChGS films at the exponential trap distribution in the last ones. Following Lambert and Mark [13] the concentration of the traps in the films as function of composition was calculated (Table 1).

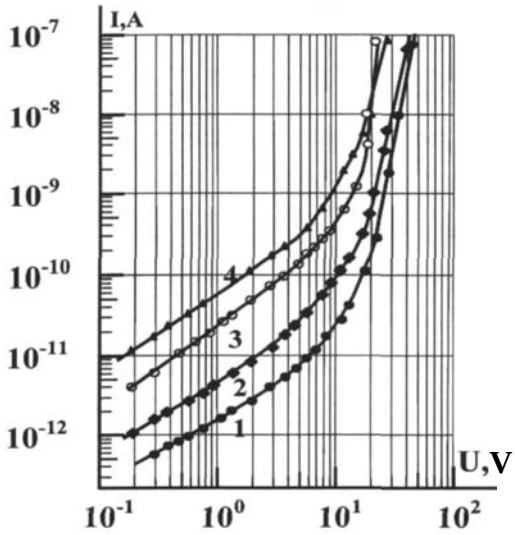

Fig.3. I-V curves of $(As_2S_3)_{0.3}$-$(As_2Se_3)_{0.7}$ thin films for different deposition rates *w* (nm/s): 1–4.3; 2–5.6; 3–9.0; 4–1.4.

Figure 3 shows the behavior of I-V curves on dependence on deposition rate. One can see that curves 1 and 4 are very close to each other although deposition rates (1.4 and 9.0 nm/s correspondingly) difference between them amounts 6-7 times deposition. At the same time we observe that for intermediate deposition rates the Ohmic region of I-V curves lays lower that in the case smallest and highest deposition rates. We connect this phenomenon with distinction in the density of ChGS films obtained at different deposition rates. In the case of intermediate rates films are formed more continuous, with less amount of micro and nano pores, which possess a large quantity of additional surface states, trapping charge carriers. As result, electrical current, passing through such thin film, is decreasing.

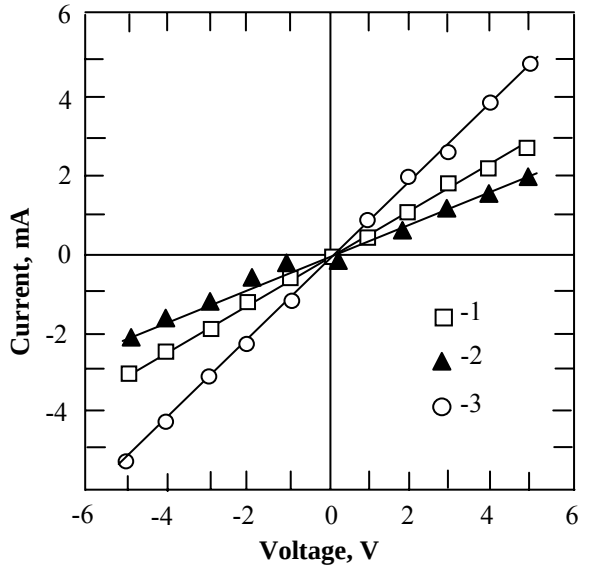

Fig.4. I-V characteristics of $(As_2S_3)_{0.5}$ $(As_2Se_3)_{0.5}$ thin films: 1 – in air; 2 – (1 vol. % CO in air); 3 – (1 vol. % NO_2 in air).

One can see also from Figure 3 that only at the voltages in the range 20-30 Volts current increases up to ~10^{-8}-10^{-7} A, i.e. required for gas sensorics values of resistance are achieved.

Photoelectrical and optical study has allowed us to estimating the value of optical bandgap width on dependence on film's composition. One can see that obtained ΔE_g values for As_2S_3 and As_2Se_3 are in good correspondence with literature [14].

The gas sensitive properties of the As–S–Se based chalcogenide layers were studied through conductance measurement method. Figure 4 shows the typical current-voltage characteristics (only Ohmic interval of voltages) of thin films studied in air and in the presence of carbon oxide and nitrogen dioxide molecules presence in atmosphere at the concentrations 1000 ppm. First of all, we

will mention that the linear character of dependences is not changed at the leaking-in of the gas impurities containing air. Another point is connected with *p*-type conductivity of practically all ChGS materials, i.e. we can expect that gas response of these materials to the gases of different origin (reducing or oxidizing) should manifest itself in response sign [7]. In particular, introducing of reducing gas CO leads to decrease of the current value at the growth of voltage and, oppositely, the presence of NO_2, manifests itself in the current increase.

The value of gas sensitivity ***S*** was estimated in our experiments as the ratio of $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ thin film conductivity ***G*** measured in pure air and in the presence of gaseous impurities (CO or NO_2) in atmosphere correspondingly Eq. (2)). Results of gas sensitivity estimating calculations for $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ thin films of different composition toward CO and NO_2 gases are presented in Figure 5.

$$S = \frac{G_{gas}}{G_{air}} \qquad (2)$$

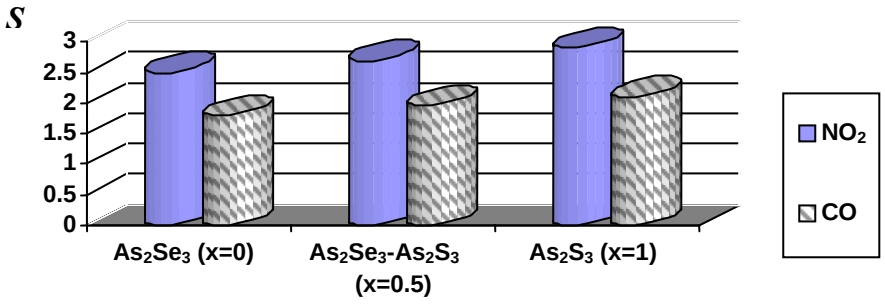

Fig.5. Gas sensitivity of $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ thin films (for different *x*) to the test gases with concentration 0.1 vol. % in air.

Conclusions

Performed research has shown that a new class of thin film gas sensors can be produced on the base of $(As_2S_3)_x$-$(As_2Se_3)_{1-x}$ ternary solid solutions. ChGS thin films obtained by thermal evaporation method in our experiments have demonstrated sufficient for gas detection sensitivity toward toxic (CO) and NO_2 gases correspondingly. One of the advantages of developed ChGS based gas sensors in comparison with metal oxide based solid state sensors consists of their capability to "feel" gas impurities at room temperature. In this case the manufacturing and operational costs decrease because you don't need for any additional heating element in the integrated sensor structure.

Nevertheless the origin of room temperature gas sensitivity of ChGS materials remains unclear. In this connection, further stage of investigation will be dedicated to the theoretical consideration of gas phase-semiconductor surface interaction and modeling of ChGS based gas sensor as well as experimental study of gas sensitivity.

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