Chemical Deposition of Photosensitive Media for Recording of the Optical Information

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Abstract. **Thin layers of amorphous chalcogenides semiconductors of mixed composition $As_2(S_xSe_{1-x})_3$ for x in the interval 0 - 1 were obtained from chemical solutions of compounds arsenic selenide (As_2Se_3) and arsenic sulfide (As_2S_3). Research of the composition and optical properties of thin layers in the spectrum range of 0.3 - 3 µm of different compositions of the obtained layers had identified the compound of mixed composition $As_2(S_xSe_{1-x})_3$. Ultraviolet irradiation of the samples leads to shift of their absorption edges to the infrared region.**

Key words: **photosensitive media, recording of the optical information.**

I. INTRODUCTION

Amorphous chalcogenide semiconductors of mixed composition are promising for application in various fields of optics, especially nonlinear, as media for recording of optical and holographic information, the planar or fiber guides for transfer and processing of optical information, various optical sensor controls, in microlithography, etc. They allow obtaining more extensive properties comparing with binary semiconductors (e.g., the photosensibility of the intermediate components of the binary, etc.). Usually, the maximum sensibility of the holographic recording of information in $As_2(S_xSe_{1-x})_3$ is attained at various lengths of waves in dependence of x. Therefore, it is necessary to determine x for given wavelengths to have such photosensitive material. In the traditional scheme for the deposition of the layers of the mixed semiconductor it is necessary to obtain the unique composition in bulk form using synthesis in vacuum at high temperatures, and then deposit them by the method of thermal evaporation in vacuum. To perform this procedure we need sophisticate equipment and a long time.

It is known the method of chemical deposition from solutions of thin layers of amorphous calcogenides compounds, for example, As_2S_3, As_2S_2, As_2Se_3, As_2Te_3 or *GeSe* [1,2]. The essence of the method is dissolving amorphous inorganic chalcogenides compounds in organic amine solvents (e.g., etilendiamine), with deposition of the solution to the glass substrates using spin-coating, and drying them subsequently.

We develop in the recent work the technology of photosensitive media of thin films $As_2(S_xSe_{1-x})_3$ of mixed composition that excludes the necessity of synthesis of bulk of amorphous chalcogenide semiconductor, application of vacuum techniques, heats and other labour-consuming operations. Thin layers are obtained from solutions of chemical compounds separate binary As_2Se_3 and As_2S_3 with combine of their, deposition and subsequent drying. The resulting medium has optical characteristic and photosensibility that permit to position it for optical registration of information.

II. EXPERIMENTAL

The mixed compound $As_2(S_xSe_{1-x})_3$ was obtained on the base of dissolution of amorphous binary compounds As_2Se_3 and As_2S_3 each taken separately in organic solvents diethylamine or monoethanolamine [3]. Then solutions were taken in the necessary proportion for obtaining ratio x of the given compound $As_2(S_xSe_{1-x})_3$ and then were thoroughly mixed for 1 hour to obtain homogeneity. The obtained mixture of solution are deposited on flexible substrates in the 80%-transparent (polyethylenethereftalate) films as thick as 63 µm, or on substrates of optical silica glass by well-known methods: by filing drops, "meniscus", spin-coating method, etc..

In the spin-coating method it is possible to receive more perfectly layers on round glass substrates controlling the rotation speed (approx. 1000 rpm), the heating temperature (20 ºC - 100ºC), and the inert environment (argon, nitrogen, or vacuum) during the time of the layer deposition up to the necessary thickness. Thickness of layers after drying in the dark chamber at T = 40°C during 24 hours were dependent on the rotation speed of a disk and of the viscosity of the solution varying within the limits of 0.1 - 3.0 µm. The homogeneous and transparent layers with periodical reflection of the layer were obtained by drying.

The molecular composion of the mixed compound $As_2(S_xSe_{1-x})_3$ layers were measured by a TESCAN microscope and also indirectly by comparison with a threshold of absorption of the layers obtained in thermally vacuum deposited method from the bulk $As_2(S_xSe_{1-x})_3$ of the same composition.

Optical properties of photosensible layers were investigated by spectral methods. The transmission spectra at the room temperature before and after UV treatment were measured. The optical transmission spectra have been measured using the spectrophotometers SPECORD UV VIS (spectrum in the range 0.3 ÷ 0.8 µm) and SPECORD 61 NIR (spectrum in the range 0.8 ÷ 3.2 µm). The optical absorption of thin films $As_2(S_xSe_{1-x})_3$ was investigated for different value of x and different doses of ultraviolet irradiation. Treating the sample with ultraviolet radiation of mercury lamp with intensity of 5 mWt was performed for 0.5 hours.

III. RESULTS AND DISCUSSION

As a result of experimental research we identified that the molecular composition of $As_2(S_xSe_{1-x})_3$ layers received by both methods of production are the same. This was confirmed additionally by measurements of the absorption spectra.

Spectra of optical transparency (*T(hν)*) of the thin layers of the mixed compound $As_2(S_xSe_{1-x})_3$ (Fig.1 - Fig.5 and Table) have absorption threshold that corresponds the known from the literature absorption threshold of amorphous chalcogenide semiconductor compounds, obtained by the thermal evaporation in vacuum apart from material synthesis [3]. With increasing concentration of the compound As_2S_3 mixed material has displacement threshold field for ultraviolet absorption. Optical absorption ($\alpha=1/d*ln(T/T_0)$) was investigated to evaluate the parameters of the obtained layers.

The dependence of optical absorption from energy in coordinates $\alpha(h\nu)^{1/2}$ - $h\nu$ for all researched mixed compounds $As_2(S_xSe_{1-x})_3$ gives the value of the energy of forbidden band of amorphous material by extrapolation $\alpha^{1/2} \rightarrow 0$ (Table). In the higher range of energy, decreasing the absorption of *α(hν)* in comparison with such thermally deposited films in vacuum was observed.

We see from Fig.2 - Fig.5 the influence of irradiation with ultraviolet light in a layer of transparent material (which characterize photosensibility of recording for the compound $As_2(S_xSe_{1-x})_3$) over the transparency spectra (curves 2 versus curves 1). The *UV* irradiation of samples has revealed as follows. At the initial moment some enlightenment (shift of absorbance to *UV* part of spectrum) takes place, but later during irradiation, it is replaced by more significant photodarkening (that has the inverse shift of absorbance). The small enlightenment of the sample can probably be explained by luminescence of mixed material. In the energy range less than Eg, the darkening (increasing of absorption) always takes place. For the constant wavelength, the increasing concentration of As_2S_3 in $As_2(S_xSe_{1-x})_3$ leads to the increasing of darkening. In the Table, characteristic dates from experimentally obtained absorbance of $As_2(S_xSe_{1-x})_3$ are shown both as grown layers and layers after irradiation with ultraviolet light with equal dose. The maximum photosensitivity ($\Delta\alpha/\alpha_o$) is attained on $x = 0.43$, where αo is the absorbance of as-deposition layers and α is the absorbance after *UV* irradiation one. This is also confirmed in [3].

In Table are presented the obtained experimental measurements of the spectral photosensitivity of absorbance.. Advantage is observed (increase) of the photosensibility at the recording (the ratio $\Delta\alpha/\alpha_o$ where α_o - absorption layers before irradiation and $\Delta\alpha = \alpha-\alpha_o$, where α - is the absorption of the layer on the same wavelength of light and after UV radiation) for the material with mixed composition of amorphous chalcogenide semiconductor $As_2(S_xSe_{1-x})_3$.

TABLE. THE CHARACTERISTICS OF THE $As_2(S_xSe_{1-x})_3$ THIN LAYERS

Name of the substance $As_2(S_xSe_{1-x})_3$, *x*	Forbidden energy band of the compound, E_g, *eV*	Optimal photosensibility, $\Delta\alpha/\alpha_o$*100%, %
0	1.75	11
0,33	1.96	15
0,43	2.02	30
0,50	2.11	45
0,56	2.16	29
1,0	2.45	9

IV. CONCLUSION

We developed and characterized the method of deposition of thin layers of chalcogenide photosensible semiconductor of mixed amorphous $As_2(S_xSe_{1-x})_3$ from chemical solution. The photosensitive material has obtained at normal atmospheric pressure and at the room temperature upon various substrates. Optical properties of the layers are similar to those for the layers deposited by the thermal deposition in vacuum.

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REFERENCES

[1]. G.C. Chern and I. Lauks. Spin-coating amorphous chalcogenide films. J. Appl. Phys. **53**(10), October, 6979-6982, (1982)Literatura

[2]. Mitzi, David B., Copel, Matthew W. Hydrazine-free solution deposition of chalcogenide films. United States Patent Application 20050009225 Kind Code A1 January 13, 2005

[3]. S.A. Buzurniuc, V.I. Verlan. 3-rd International conference on materials science and condensed matter physics, Report MSCMP, p. 141, 2006, Chişinău.

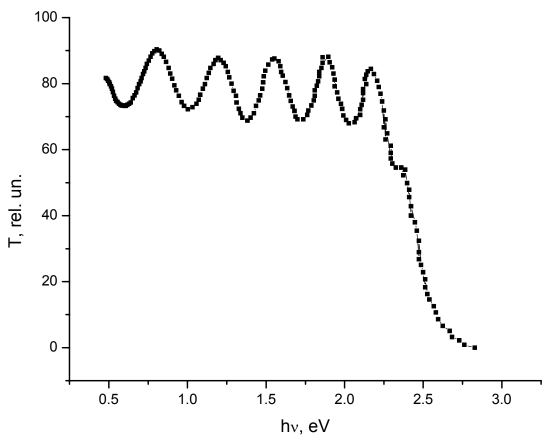

Fig.1. The transmission spectrum of the thin film $As_2(S_xSe_{1-x})_3$, x = 0.65.

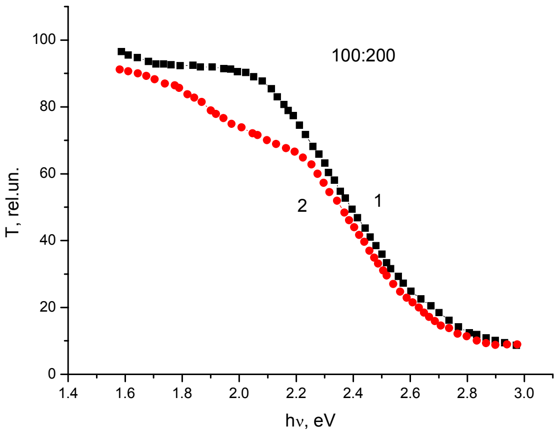

Fig.2. The transmission spectrum of the thin film $As_2(S_xSe_{1-x})_3$, x = 0.33. 1 -.as-grown, 2 – after UV irradiation.

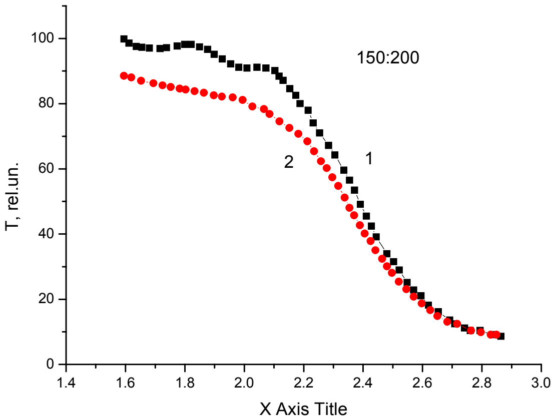

Fig.3. The transmission spectrum of the thin film $As_2(S_xSe_{1-x})_3$, x = 0.43. 1 -.as-grown, 2 – after UV irradiation.

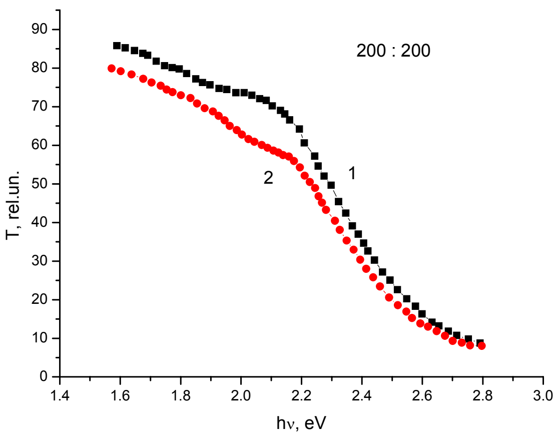

Fig.4. The transmission spectrum of the thin film $As_2(S_xSe_{1-x})_3$, x = 0.50. 1 -.as-grown, 2 – after UV irradiation.

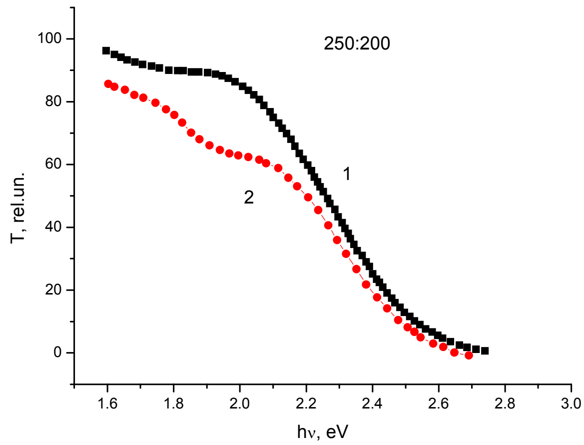

Fig.5. The transmission spectrum of the thin film $As_2(S_xSe_{1-x})_3$, x = 0.56. 1 -.as-grown, 2 – after UV irradiation.