Direct one-stage plasma-chemical synthesis of chalcogenide films doped with ytterbium

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Abstract. In this paper we described the plasma-enhanced chemical vapor deposition (PECVD) approach for preparation of the arsenic sulfide thin films modified by ytterbium. Radio frequency (40.68 MHz) plasma discharge at low pressure (0.1 Torr) was used for the initiation of chemical interactions between precursors. Arsenic monosulfide (As\textsubscript{4}S\textsubscript{4}) and high-pure S and Yb were employed as the starting materials. The composition of the films was controlled by regulating the temperature of the ytterbium source supplied with external heater. The Yb concentration in the Yb:As\textsubscript{x}S\textsubscript{y} films was from 1 to 7 at%. The chalcogenide materials were also studied by Scanning Electron Microscopy (SEM), Optical spectroscopy in the range of 250-1000 nm, and Raman spectroscopy.

1. Introduction
Chalcogenide semiconducting materials doped with rare-earth elements are widely implemented in IR optics, nanoelectronics and optoelectronics. In particular, on their basis it seems possible to assemble sensitive planar detectors of mid-IR range, including frequencies of vibrational transitions of a large number of chemical compounds, which is well-known as a “fingerprint region” [1, 2].

Chalcogenide thin films seem to be the most appropriate for utilization as the working matrix in such devices due to their wide (up to 20 μm) transparency window [3]. In conjunction with low-phonon energies (cut-off phonon energies) it gives the possibility to exploit the radiative transitions of low energy of certain rare earth ions [4, 5]. It was established that the addition of rare-earth elements to chalcogenide glasses results in modification of their electrical-physical, structural properties and window of transparency [6].

Moreover, the factors restricting of doping become a very limited solubility of the rare-earth elements in the chalcogenide materials, a partial generation of active luminescent centers and magnification of the inclination of the materials to crystallization [7, 8].

Chalcogenide derivatives of rare-earth elements attract much attention due to their unique luminescent properties [9]. Heterolanthanide chalcogenide clusters are synthesized by the reactions of lanthanides iodides and sulfur [10, 11]. Besides, the reductive ability of divalent lanthanides’ derivatives was investigated in [10, 12]. In the paper [13] we have recently announced that the...
formation of the arsenic sulfide thin films of different macrocompositions can be provided by conversion of arsenic monosulfide As$_2$S$_3$ in a low-temperature non-equilibrium RF plasma discharge at a low pressure. In this case the arsenic monosulfide serves as the source of both arsenic and sulfur. The chemical composition of the resulting chalcogenide thin films is the function of the energy supplied to the plasma [14]. The claimed approach has no fundamental limitations in the stoichiometry of the deposited structures. Furthermore, due to the deposition process is non-equilibrium one in terms of thermodynamics it makes possible to obtain amorphous materials [15-17] just through the precise control of the relaxation parameters for excited species forming the final solid phase.

It is necessary to mention that the properties of optical and semiconducting materials based on chalcogenide glasses strongly depend on the content of carbon-containing impurities. The behavior of carbon heteroinclusions during plasma-chemical synthesis was studied in [18, 19].

Based on the facts given above, there is a reason to think that the preliminarily created technological approach will allow us overcoming certain barriers of the traditional methods of preparation of the chalcogenide materials doped with rare-earth elements.

The goal of this work is to obtain the arsenic sulfide amorphous thin films doped with ytterbium of the wide range of compositions in low-temperature non-equilibrium plasma, when As$_2$S$_3$, elemental sulfur and ytterbium are the initial substances and also to determine the features of the morphology and transparency of the obtained samples.

2. Experimental part
A number of the Yb:As$_2$S$_3$ chalcogenide thin films of various stoichiometry was prepared utilizing a PECVD setup, the operating principles of that have been given in detail in [13]. As$_2$S$_3$ of high purity, elemental S and Yb were the initial substances. The ampoules with arsenic monosulfide and sulfur were constantly remained at temperatures of 345 and 132 °C, respectively during the experiments.

The ytterbium reservoir temperature was changed in the range from 610 to 710 °C. Ar of high-purity served as the plasma feed gas as the carrier gas to deliver mixture of arsenic monosulfide and sulfur vapors into the plasma discharge zone. The total gas flow rate through the plasma-chemical chamber was constantly ml/min at the total pressure in the system equal to 0.1 Torr.

The inductively coupled plasma discharge was ignited by means of the external radio frequency (40.68 MHz) inductor. As the material of the substrate the epi-polished sapphire (1-102) was used. The substrate temperature during the process of deposition was constantly kept at 0 °C.

The PECVD process has been studied in the range from 182 to 1150 nm by the Optical emission spectrometer of the high-resolution Ava-Spec-Mini 4196 CL (UV-VIS-NIR) (1210 lines/mm with the resolution 0.11 nm). The spectra of transmission and reflection have been investigated by the two-beam spectrophotometer Agilent1 Carry 5000 (Agilent Technologies Inc., USA) in the wavelength range from 210 to 3010 nm with a step of 2 nm.

3. Results and discussion
The PECVD process compared to the traditional methods of synthesis may be controlled in-situ by Optical emission spectroscopy (OES). OES spectra allow us to determine the appearance of the intermediate excited particles in plasma discharge and their concentrations in dependence on the concrete conditions of the experiments. By analysing of the OES images we may deeply understand the whole process of plasma deposition as a sequence of plasma chemical reactions.

The capacity of the Optical Emission Spectroscopy in terms of study of peculiarities of the PCVD growth of chalcogenide thin films for optimization of the parameters of the process has been reported in the paper [20].

The optical emission spectra of As$_2$S$_3$ in Ar inductively-coupled RF plasma are reported in paper [13]. The OES images of elemental Yb at the permanent ampule temperature of 752 °C and different values of the plasma energy are depicted in Figure 1.
Together with the Ar bands of optical emission, atomic spectral lines are found at 327.8, 345.3, 368.9, 399.0, 492.9 and 556.0 nm and are referred to Yt atoms at different degrees of ionization (ytterbium (I), ytterbium (II), ytterbium (III)).

At the minimal plasma energy of 30W (plot 1) the OE spectrum is saturated mainly by ytterbium (I) emission bands located near 345.9 nm (4f^46s^2 - 4f^35d6s) due to migration of electron from level 4f to level 5d and near 399.0 nm (4f^46s^2 - 4f^34d3f) because of migration of electron from level 4f to level 6s. The pick at 556.7 nm (4f^36s^2 - 4f^36s6p) is addressed to moving of electron from level 6s to 6p sublevel.

The enlargement of the plasma energy results in the rise in the concentration of ytterbium (II) atomic fraction in the discharge zone (plot 2), while the reduction in the depth of the ytterbium (I) bands is noted in the OE spectrum.

Additionally, the rise in the magnitude of the ytterbium (II) picks near 329.0 and 368.9 nm, induced by the 4f^16s - 4f^16p jump, is found. Moreover, at the peak of the energy input into the plasma discharge (plot 3). The band of low intensity near 303.0 nm arises due to appearance of the ytterbium (III) atomic states.

At the permanent energy of plasma discharge equal to 50 W and various rare earth element ampoule temperatures – 610, 660 and 710 °C a few chalcogenide thin films with the stoichiometries As_{60}S_{60}Yb, As_{57}Yb_{3} and As_{55}S_{55}Yb_{7} were deposited.

It may be supposed that Yb substitutes sulfur in the gross stoichiometry of As_{60}S_{60} due to the appearance of ytterbium sulfides – YbS (ytterbium monosulfide) and Yb_{2}S_{3} - pursuant to the chemical equations (1) and (2):

\[ 2Yb + 3S \rightarrow Yb_2S_3, \]
\[ Yb + S \rightarrow YbS, \]

The surface morphology was studied by scanning electronic microscopy. As it is seen in Figure 2, addition of ytterbium sufficiently modifies the surface structure of the arsenic sulfide thin films. When the addition of Yb to macrocomposition of As_{60}S_{60} was only one at%, the surface structure stays true to type for the arsenic sulfide thin films manufactured by the plasma-chemical approach [13].

When the concentration of ytterbium reaches four at% the sharp growth in size of the structural units, building the surface lattice, is registrated as well as the decline of the surface homogeneity and augmentation of its roughness. And, last, when the ytterbium content becomes equal to seven at%,
the ulterior consolidation of the surface structural fragments takes place at the same time with growth of the surface rugosity.

Thereby, the magnification of the ytterbium content brings the expansion of structural fragments and the height of the arsenic sulfide thin film surface heterogeneity.

**Figure 2.** SEM images of the film surfaces of the As$_{40}$S$_{59}$Yb$_1$, As$_{39}$S$_{57}$Yb$_4$ and As$_{38}$S$_{55}$Yb$_7$ samples.

The spectra Vis-Near IR transparency of the arsenic sulfide thin films in the range 500-2500 nanometers with various ytterbium concentration are represented in Figure 3.

It is apparent that the augmentation of the ytterbium concentration in the chalcogenide thin films macrocomposition brings the shift of the absorption edge to the long-wave area. The optical width of the chalcogenide films band gap is a significant feature for the application of the chalcogenide materials in nanoelectronic devices and is estimated by the formula given below [21]:

$$\alpha h\nu = C(h\nu - E_g)^2,$$

where $\alpha$ is the absorption coefficient; $h\nu$ is the energy of photon; and $C$ – is a constant. The value of the width of the optical band gap was calculated by the “Tauc relation”. With the enlargement of the ytterbium concentration in macrocomposition of the thin films the value of the optical width of the band gap diminishes from 2.55 to 2.01 eV.

**Figure 3.** Transmission spectra of the As$_{40}$S$_{60}$ (1), As$_{40}$S$_{59}$Yb$_1$ (2), As$_{39}$S$_{57}$Yb$_4$ (3), and As$_{38}$S$_{55}$Yb$_7$ (4) thin films.

The structure of the obtained samples was studied by the Raman spectroscopy. The data are presented in Figure 4. Spectrum 1 of As$_{40}$S$_{60}$ with zero concentration of Yb is shown for simile. By tradition, the picks in the range of (131-172 cm$^{-1}$) with high near 151 cm$^{-1}$ and at 476 cm$^{-1}$ are addressed to the vibrations of sulfur atoms in S8 rings; the vibration lines of the chain sulfur allotropic
modification are at 496 cm$^{-1}$ [22]. The lines in the range of (171-202 cm$^{-1}$) may be referred to the oscillation of arsenic–arsenic homeopolar bindings in the arsenic monosulfide (As$_4$S$_4$) “realgar structures” [23, 24]. In the range of (201-272 cm$^{-1}$) there are a pair of obvious maxima, at 221 and 235 cm$^{-1}$, that as well are referred to arsenic–arsenic bond oscillations in the As$_4$S$_4$ “realgar” and in the S$_2$As–AsS$_2$ “bridges”, respectively. The broad band of near 345 cm$^{-1}$ may be tied with the oscillations of As-S$_{3/2}$ – the basic structural-forming units [25, 26].

When 1.0 at.% of ytterbium is added to the arsenic sulfide As$_{40}$S$_{60}$ sample the reduction of the lines magnitude near 151 and 496 cm$^{-1}$ and growth of the novel picks at 211 and 274 cm$^{-1}$ takes place that may be addressed to formation of the ytterbium sulfide (Yb$_2$S$_3$) crystals [27, 28]. The further supplementation of ytterbium up to 4.0 at% results in a dramatical decline in the magnitude of the picks at 151, 476, and 495 cm$^{-1}$ with the synchronous growth in the maxima altitude at 186, 211, 235, and 274 cm$^{-1}$. The expand and rise of the intensity of the line near 221 cm$^{-1}$ is most likely tied with the increase in intensity of the peak at 226 cm$^{-1}$, that the researchers in [29] as well referred to the ytterbium sulfide (Yb$_2$S$_3$) framework.

Whether the ytterbium concentration achieves 7.0 at.%, the bands at 475 and 496 cm$^{-1}$ become barely noticeable. Nevertheless, the growth of the As concentration over the stoichiometry arsenic/sulfur-40/60 results in the growth of the altitude of the band addressing to the oscillation of the arsenic-arsenic homeopolar bindings in the As$_{40}$S$_{60}$ monosulfide pararealgar fragments and in the “S$_2$As–AsS$_2$ bridges” and arising of the maximum at 364 cm$^{-1}$. In this way, the assumption may be formulated that the supplementation of the Yb into the arsenic sulfide 40/60 thin film causes the the generation of the ytterbium sulfide (Yb$_2$S$_3$) crystal fragments because of the replacement of As in the AsS$_{3/2}$ structural units.

As it is seen in Figure 5, all the prepared arsenic sulfide thin films pose photoluminescence at ambient conditions in the range from 931 to 1020 nm. This phenomenon refers to the emission transitions of ytterbium ions (Yb$^{3+}$) from the energized level $^2$F$_{5/2}$ to the ground level $^2$F$_{7/2}$. It was established that the amplitude and location of these conversions rely on the closest surroundings and the material array [30].

With the augmentation of the Yb concentration in the arsenic sulfide thin films, a slight reduction of the whole luminescence depth is found. This phenomenon is likely tied with its quenching because of the process of self-absorption. In this respect, the most presumable emission jump becomes the junction from the lower suborbital $^2$F$_{7/2}$ to the lower suborbital $^2$F$_{5/2}$, that produces photoluminescence in the region of 977 nm.

Figure 4. Raman spectra of the As$_{40}$S$_{60}$ (1), As$_{40}$S$_{60}$Yb$_1$ (2), As$_{30}$S$_{57}$Yb$_1$ (3), and As$_{30}$S$_{55}$Yb$_1$ (4) thin films.
4. Conclusion
The novel plasma-chemical technique has been implemented for the immediate one-step preparation of amorphous chalcogenide thin films of the binary arsenic sulfide system modified with ions of the REE - Yb. The concentration of ytterbium in the grown thin films was in the range of 1.0-7.0 at. %.

Based on the Raman data it was supposed that the supplementation of the Yb into As$_{60}$S$_{60}$ material results in the generation of the ytterbium sulfide Yb$_2$S$_3$ crystal phase because of the replacement of As in the AsS$_{3/2}$ structural units.

Judging by the data of the IR transparency, the value of the optical width of the band gap diminishes from 2.55 to 2.01 eV with the growth of the Yb content. All the plasma prepared chalcogenide thin films pose photoluminescence at ambient conditions in the range of 931-1020 nm, this ties with the emission jumps of Yb$^{3+}$ from the excited level $^2F_{5/2}$ to the ground level $^2F_{7/2}$. With the increase of the ytterbium content in the films, a noticeable decrease of the total luminescence intensity is observed; this is apparently connected with its quenching due to the phenomenon of self-absorption.

5. References
[1] Wu Y, Meneghetti M, Troles J and Adam J-L 2018 Appl. Sci. 8 1637
[2] Shen M, Furniss D, Farries M, Jayasuriya D, Tang Z, Sojka L, Sujecki S, Benson T M and Seddon A B 2019 Scientific Reports 9 11426
[3] Calvez L 2017 Comptes Rendus Physique 18 314
[4] Yang Z, Luo L and Chen W 2006 J. Appl. Phys. 99 076107
[5] Koughia C, Craig C, Hewak D W and Kasap S 2019 Opt. Mater. 87 157
[6] Gubanova A, Kryskov Ts, Paitik O, Lahio R, Lahderanta E and Stronski A 2009 Mold. J. Phys. Sci. 8 178
[7] Ohishi Y, Mori A, Kanamori T, Fujiura K and Sudo S 1994 Appl. Phys. Lett. 65 13
[8] Seddon A B, Tang Z, Furniss D, Sujecki S and Benson T M 2010 Opt. Express 18 26704
[9] Balashova T V, Baranov E V, Fukin G K, Ilchev V A, Grishini D, Yablonskiy A N, Andreev B A and Bochkarev M N 2019 Russ. J. Coord. Chem. 45 712
[10] Fagin A A, Kuznetsova O V, Rumyantcev R V, Fukin G K, Marugin A V and Bochkarev M N 2019 J. Clust. Sci. 30 1277
[11] Fagin A A, Kuznetsova O V, Balashova T V, Cherkasov A V, Fukin GK and Bochkarev M N 2018 Inorganica Chim. Acta 469 227
[12] Bochkarev M N, Logunov A A and Burin M E 2007 Russ Chem Bull 56 1953
[13] Mochalov L, Logunov A, Kornev R, Zelentsov S, Vorotyntsev A, Vorotyntsev V and Mashin A
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