

## LUMINESCENCE OF ARSENIC SULPHIDE DOTS DOPED WITH EUROPIUM, PREPARED BY THERMAL EVAPORATION AND PULSED LASER DEPOSITION METHODS

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Networks of dots made of As<sub>2</sub>S<sub>3</sub> chalcogenide has been obtained by Vacuum Evaporation and Pulsed Laser Deposition from bulk glassy As<sub>2</sub>S<sub>3</sub> by the adapted method of SCEV (screen evaporation method). A very thin layer of Eu<sub>2</sub>O<sub>3</sub> was deposited from a different target in the final deposition process. After a heat treatment at 180 °C for 90 minutes in nitrogen atmosphere a structural transformation of the amorphous As<sub>2</sub>S<sub>3</sub> to realgar (AsS) occurred in the PLD deposited dots and the network of dots develops a luminescence effect.

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### 1. Introduction

There is an increased interest in special glasses, in particular chalcogenide glasses, with the aim to use them as matrix material for doping with rare earth ions [1]. Investigations have shown that chalcogenide glasses appear to be very suitable materials for this purpose. A main characteristic of these glasses is the high transparency in the IR spectral range. The transparency of matrix with no absorption transitions in IR region is of special importance since this is exactly the region in which rare-earth ions exhibit emission transitions [2, 3]. The interest is primarily related to the transitions within the 4f orbital of the rare-earth ion, which appear in the near or middle range of IR spectrum [4]. Chalcogenide glasses doped with erbium (Er<sup>3+</sup>) and europium (Eu<sup>3+</sup>) are used in optical fibers, as passive fibers, in the power transmission systems, but also as active fibers in laser YAG: Er ( $\lambda = 2.97 \mu\text{m}$ ). The breakthrough made in the area of these wavelengths is of great importance in optoelectronics and it is thought the chalcogenide glasses doped with rare-earths will take the leading role of optical amplifiers similar to the one that transistor had in the era of electronics. Some glasses in the system As-S-Ge with Er<sup>3+</sup> have been synthesized [5]. The up-conversion luminescence properties of Erbium doped GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>. KCl has been recently observed by J. Zhang, H. Tao and X. Zhao [6]. No information exists about of development of systems that transforms the excitation radiation in the UV range into luminescent radiation in red range to be used in optoelectronic devices.

In the paper by Kozyukhin et al [7] it is demonstrated that the use of rare-earth complexes to modify the chalcogenides is a promising approach which makes it possible to raise the rare-earth concentration in amorphous matrices. The fact that arsenic sulphide films with Eu exhibit room temperature luminescence suggests that complexes are incorporate into the glass without destruction of the glass network. The introduction of different rare-earth complexes allows the

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optical characteristics of amorphous films to be varied, which probably is associated with changing in the degree of disordering.

In this paper we report the preparation of dots made of  $\text{As}_2\text{S}_3$  glass that become luminescent by adding a thin film of  $\text{Eu}_2\text{O}_3$  followed by a thermal annealing at a moderate temperature. Two methods have been used in preparation: the Evaporation method (EV) and Pulsed Laser Deposition method (PLD). The dots were obtained in the frame of screen evaporation (SCEV) procedure [8].

## **2. Experimental**

### **2.1 Preparation of chalcogenide dots**

The network of amorphous chalcogenides dots have been deposited both by vacuum evaporation (EV) and pulsed laser deposition (PLD) methods using a version of the method SCEV already developed by us [8]. As substrate for the network deposition were used ordinary glass plates of size  $25 \times 25 \text{ mm}^2$  cleaned in potassium di-chromate solution in water and washed finally in double distilled water. The deposition was carried out from two different targets  $\text{As}_2\text{S}_3$  and  $\text{Eu}_2\text{O}_3$ . Firstly a thick deposition of  $\text{As}_2\text{S}_3$  through a metallic network of meshes of 150 micrometers was carried out. Thereafter, in the same process a very thin film of  $\text{Eu}_2\text{O}_3$  (several nanometers) has been deposited. Finally the metallic network was taken off the substrate. We in fact obtained a sandwich of one thick dot of  $\text{As}_2\text{S}_3$  with a layer of  $\text{Eu}_2\text{O}_3$  formed on every dot.

The luminescence was stimulated by thermal annealing in nitrogen atmosphere at  $180 \text{ }^\circ\text{C}$  for 90 minutes.

### **2.2 Characterization of the networks of dots.**

The chalcogenide films prepared by both EV and PLD were characterized by X-ray diffraction, scanning electron microscopy (SEM) and optical spectroscopy.

#### **2.2.1. X-ray diffraction analysis**

The X-ray diffraction patterns of the dots obtained by EV are shown in Fig. 1. The X-ray diffraction patterns of the same dots prepared by PLD are shown in Fig. 2.

In the “as deposited” states the dots prepared by both methods are amorphous. The dots deposited by EV exhibits crystalline  $\text{As}_2\text{O}_3$  on the surface. After annealing of dots prepared by EV a decrease of peaks intensity of  $\text{As}_2\text{O}_3$  is observed (Fig. 1).

In the dots prepared by PLD arsenic oxide is not observed in samples and after annealing a transformation of the  $\text{As}_2\text{S}_3$  towards  $\text{AsS}$  occurs (Fig. 2) as a consequence of a significant loss of sulphur. In the same time the surrounding of Europium is reorganized in the material. No traces of  $\text{As}_2\text{O}_3$  crystallites were observed.

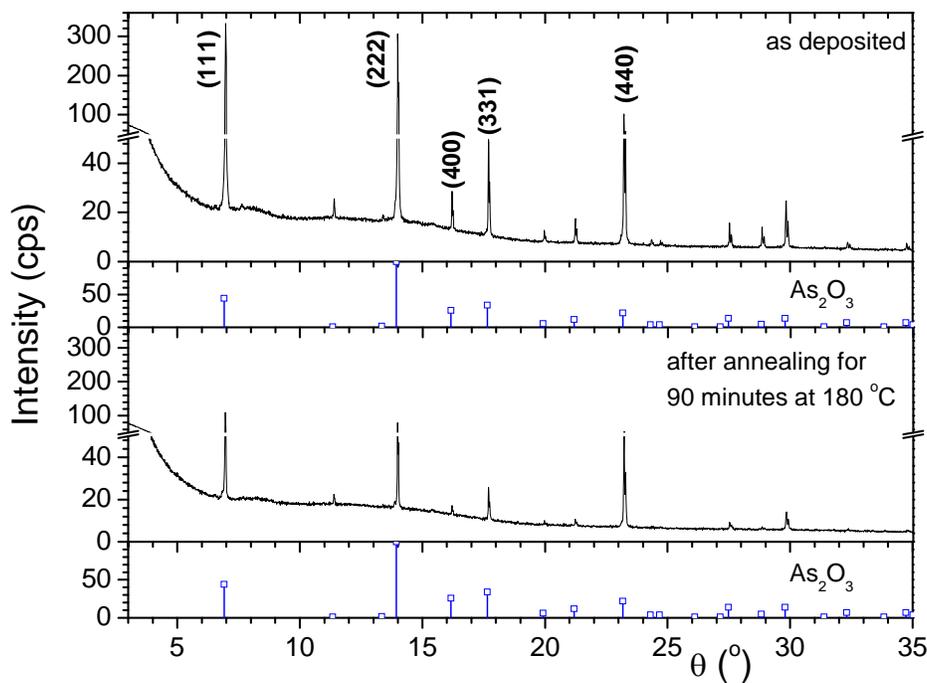


Fig. 1. The X-ray diffraction patterns of the network of dots prepared by EV (before and after thermal annealing at 180 °C at 90 minutes). There is a polycrystalline phase of  $As_2O_3$  face-centered cubic (according to ASTM file No. 36-1490).

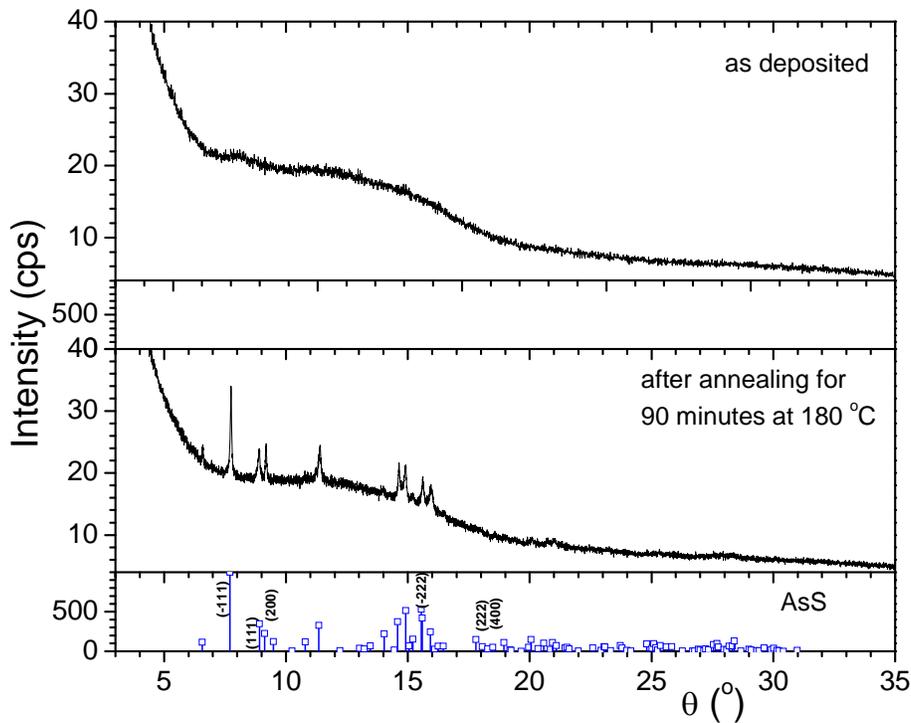


Fig. 2. The X-ray diffraction patterns of the network of dots prepared by PLD (before and after thermal annealing at 180 °C at 90 minutes). There is a polycrystalline phase of AsS monoclinic (according to ASTM file No. 89-1371).

### 2.2.2 Morphology of the chalcogenide dots

The structure and morphology of the network of dots was investigated by scanning electronic microscopy. A SEM Type Zeiss Evo 50 XVP was used in the measurements. Because the dots are not conducting we have deposited on the samples a very thin layer of copper. Figures 3 and 4 show the results.

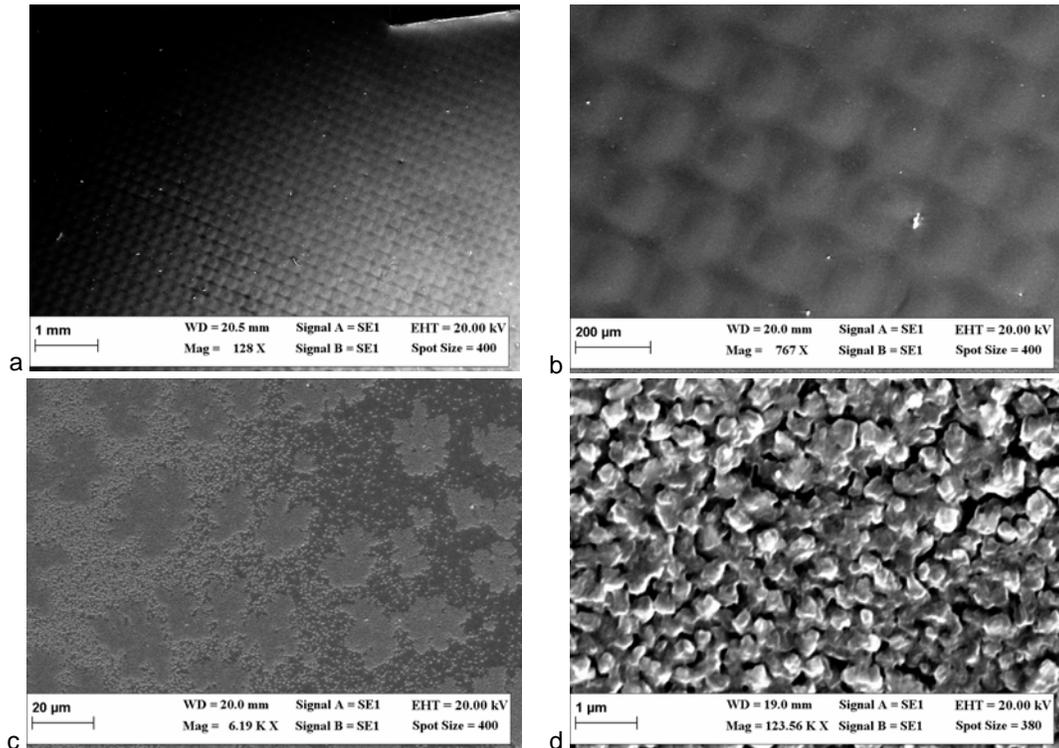


Fig. 3. a, b, c, d. SEM pictures of a SCEV network deposited by vacuum evaporation method.

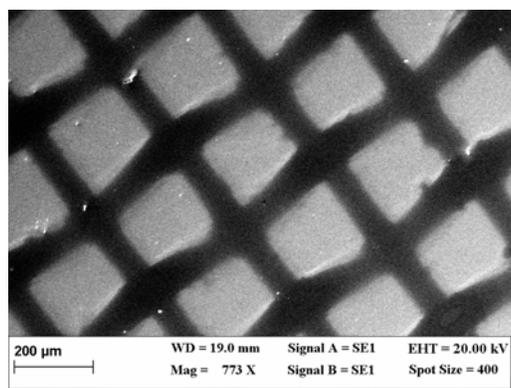


Fig. 4. SEM pictures of a SCEV network deposited by pulsed laser deposition method.

In Figure 3 the dots obtained are a little bit extended under the metallic network and the morphology of every dot is not exactly well defined. Irregular dots with dendrite character are visible. The presence of small dots is also visible on the images (Fig. 3 c-d). By PLD it is possible to get a network of dots with well-defined borders (Fig. 4). The size of the dots is roughly 150 micrometers corresponding to the mesh of the metallic network.

### 2.2.3. Luminescence of the dots

The excitation of the luminescence was performed at the wavelength of 395 nm. The luminescence of the initial and heat treated sample deposited by EV is shown in Figure 5a. Fluorescence spectrum clearly shows the high intensity fluorescent emission of  $\text{Eu}^{3+}$  ions.

The luminescence of the initial and heat treated sample deposited by PLD is shown in Figure 5b. After annealing in inert atmosphere the element obtained reacts to light radiation  $\lambda = 395$  nm emitting orange light ( $\lambda = 590$  nm).

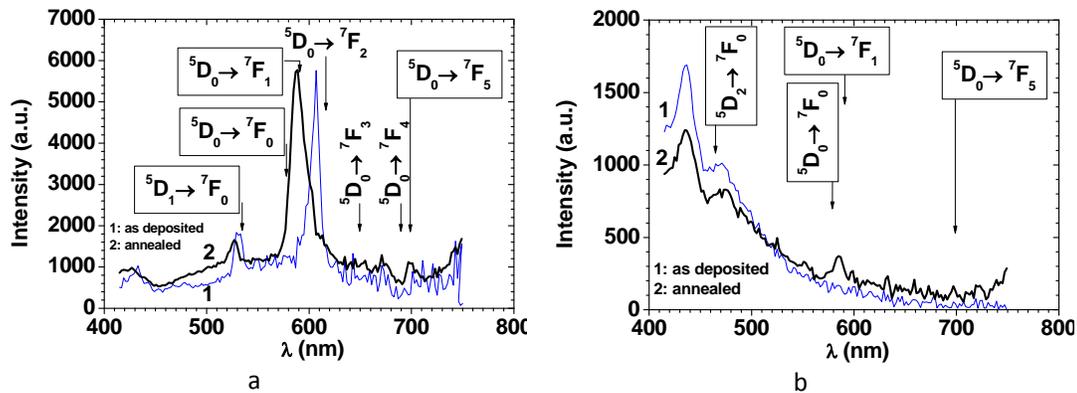


Fig. 5. The luminescence of the  $\text{Eu}_2\text{O}_3 / \text{As}_2\text{S}_3$  before and after heat treatment. Excitation is at 395 nm wavelength.  
a. prepared by EV, b. prepared by PLD

Figures 6 a and 6 b show the position and shape of the absorption edge before and after annealing of the network of  $\text{As}_2\text{S}_3$  dots for the sample obtained by evaporation and for the sample deposited by PLD. While the absorption edge does not change significantly for evaporated samples, in the PLD films the absorption edge exhibits a not linear shape in as deposited films and shifts toward lower wavelengths.

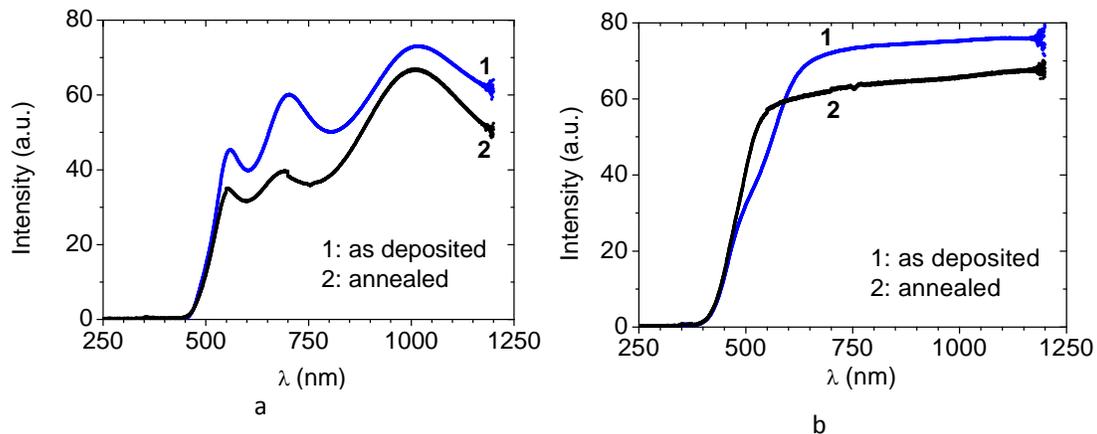


Fig. 6. The position and the shape of the absorption edge of the dot network before and after heat treatment of evaporated:  
a. prepared by EV, b. prepared by PLD

### 3. Discussion

In the initial sample deposited by evaporation method by using the SCEV method one gets dots of not very well defined shape. This is due to a larger scattering of the atom beam. In the PLD deposited network of dots the dots exhibit a well-defined margin due to a low angular scattering of the impinging atoms.

In the initial sample, during PLD deposition, most of Europium oxide diffused in  $\text{As}_2\text{S}_3$ . Due to the unfavorable surrounding of Europium and due to the matrix of amorphous arsenic sulphide the luminescence is not present. Because  $\text{As}_2\text{S}_3$ , whose absorption edge covers the excitation domain and the main luminescence line, the effect of luminescence of Eu cannot be evidenced.

The position of the absorption edge in  $\text{As}_2\text{S}_3$  is situated at  $\lambda_{\text{edge}}(\text{EV initial}) = 513.7 \pm 0.5$  nm ( $2.414 \pm 0.002$  eV) (Figures 6 a). After the annealing the absorption edge is shifted a little bit towards smaller wavelengths ( $\lambda_{\text{edge}}(\text{EV annealed}) = 510.5 \pm 0.5$  nm).

### 4. Conclusions

Strong luminescence was obtained in Eu doped arsenic sulphide dots deposited by vacuum evaporation method.

Luminescence was obtained in Eu doped arsenic sulphide dots deposited by PLD and annealing at 180 °C for 90 minutes. The appearance of luminescence is due to the modification of the arsenic sulphide matrix in realgar crystalline form of the material by some loss of sulphur and changing of the Eu configuration.

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