CHARACTERIZATION OF As_2S_3 THIN SURFACE FILMS USING SEM AND AFM METHODS

A. MOLDOVAN[1], M. ENĂCHESCU[1], A. A. POPESCU[2], M. MIHĂILESCU[3], C. NEGUȚU[3], L. BASCHIR[2], G. C. VASILE[3], D. SAVASTRU[2], M. S. IOVU[4], V. I. VERLAN[4], O. T. BORDIAN[4], I. M. VASILE[5], N.N. PUŞCAŞ[3]

In this paper we report several experimental results concerning the characterization of As_2S_3 thin films using scanning electron microscopy (SEM), and atomic force microscopy (AFM). The chalcogenide films were obtained by vacuum thermal deposition.

The SEM and AFM analysis of the surfaces emphasized that in the above mentioned thin films, the nanometric structure of the surface is uniform and continuous, without cracks and has a roughness of about 10 nm. From the SEM analysis in fracture of the sample fabricated by the deposition of the As_2S_3 thin films on glass, we determined their thickness of about 150-160 nm. We highlighted its good adherence to the substrate and the absence of the holes between film and substrate.

The investigation of the silver thin (50 nm) films obtained by pulsed laser deposition show the column and island surface topography that may induce light scattering and produce broadening of plasmonic dip. Further development should be done in order to increase surface quality.

Keywords: As_2S_3 thin films, SEM, AFM, amorphous chalcogenide materials.

1. Introduction

Nanostructures (for instance multilayer structure chalcogenide films) with sub 15 nm dimensions have attracted significant interest due to their unique chemical and physical properties and potential applications in: enhancement of

[1] Center for Surface Science and NanoTechnology, University POLITEHNICA of Bucharest, Splaiul Independentei, 313, 060042, Bucharest, Romania.
[2] National Institute R&D of Optoelectronics, INOE 2000, 409 Atomistilor str., PO BOX MG. 5, 77125 Magurele, Ilfov, Romania
[3] University POLITEHNICA of Bucharest, Physics Department, Splaiul Independentei, 313, 060042, Bucharest, Romania
[4] Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academiei str. Chisinau, MD-2028, R. of Moldova
[5] University POLITEHNICA of Bucharest, Materials Technology and Welding Department, Splaiul Independentei, 313, 060042, Bucharest, Romania
Corresponding authors: M. Enăchescu marius.enachescu@upb.ro, A. A. Popescu apopescu@inoe.ro

Raman scattering, catalysis, sensing, nanofabrication for the next generation of electronic devices, photoluminescence, bio-light emission devices, and solar cells.

Due to their many convenient optical properties the amorphous chalcogenide films are of great interest for photonics [1] and for integrated optics [2]. The optical properties of thin films are not always the same as those of corresponding bulk glasses, thus many techniques have been proposed to prepare thin films of chalcogenide glasses. Pulsed laser deposition [3], RF sputtering of $70Ga_2S_3{:}30La_2S_3$ [4] or $Ge_{33}As_{12}Se_{55}$ and $Ge_{28}Sb_{12}Se_{60}$ [5] films are well established deposition methods that maintain the stoichiometry of multi-element amorphous chalcogenide compounds [6]. However, a columnar structure may be observed. The average column size up to 20 nm [5] was estimated in such cases by providing AFM images. Surface roughness at the nanoscale and below plays a crucial role in determining the functional performance of many devices [7]. Understanding and characterizing nanoscale and even sub-angstrom roughness is becoming increasingly important in our ability to continue exploring and building devices at ever smaller length scales.

AFM is essential for studying surface roughness (Ra, or average deviation) at the nanoscale, having resolution far exceeding that of other stylus and optical based methods [8]. Thermal vacuum evaporation remain one of the basic deposition methods for materials which do not exhibit decomposition and whose evaporation temperature isn't too high. Low loss planar waveguides were obtained with amorphous As_2S_3 thin films prepared by RF sputtering [9]. As_2S_3 may be deposited by thermal evaporation and is one of the promising materials for plasmonic applications [10, 11].

The article has the following structure: In Section 2 we present the sample fabrication and results concerning the characterization of the As_2S_3 thin films surface using scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods. In section 3 we present our conclusions concerning the obtained results.

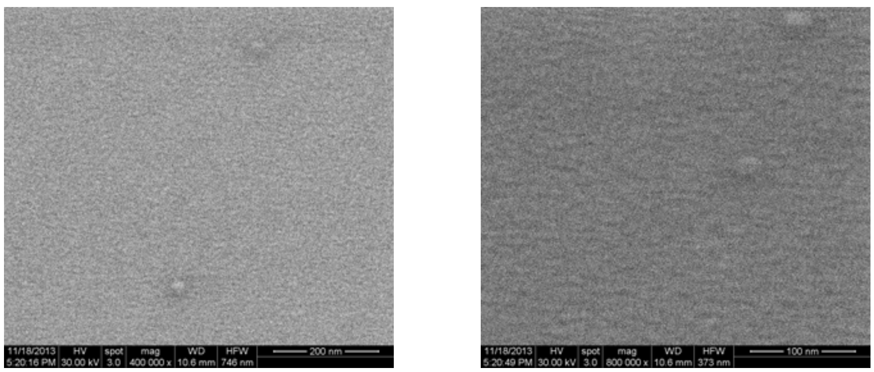
2. Studies of the As_2S_3 thin surface films using SEM and AFM methods

The As_2S_3, bulk chalcogenide glasses were synthesized using high purity elements As and S. Thin As_2S_3 films were obtained by vacuum thermal evaporation of granular materials on microscope slide glasses. In order to determine the characteristics of the As_2S_3 surface films at nanometric scale we used the SEM and AFM methods. We used a FEI Quanta Ispect F scanning electron microscope. The AFM system is based on a home-built mechanical setup interfaced with controllers SPM1000 and PLLPro2 from RHK Technology.

We investigated three types of samples:

1) As_2S_3 thin film deposited on Au layer (sample S1).
2) surface of the chipset Au layer (situated below the As_2S_3 thin film) (sample S2), and
3) As_2S_3 deposited on glass substrate (sample S3).
For the samples S1 and S2 the substrates are optical glasses.

Several characteristics of the As_2S_3thin film and Au layer were analysed:
1) the roughness of the surfaces,
2) the As_2S_3 thin film continuity,
3) the adherence of the As_2S_3 thin film deposited on the glass substrate,
4) the thickness of the deposited As_2S_3 thin film, and
5) the chemical local composition.



a) b)

Figs. 1. SEM images of the sample S1 of the As_2S_3 thin film surface deposited on Au layer with a) magnification of 400000x and b) detail of the same sample with a magnification of 800000x.

We analysed the As_2S_3 thin film surfaces and also the cross sections obtained by fracture. Fig. 1 present a SEM image of the sample S1 of the surface of As_2S_3 thin film deposited on Au with a magnification 400000x, and a detail of the same sample with a magnification 800000x for 30000kV acceleration voltage. One can observe that the nanometric structure of the surface is uniform and continuous.

In the same sample, a scratch procedure was performed in order to measure the thickness of the As_2S_3 thin film in the zones in which fragments of As_2S thin film are perpendicular on the image plane (Fig. 2). One can remark that the thickness is about 160 nm.

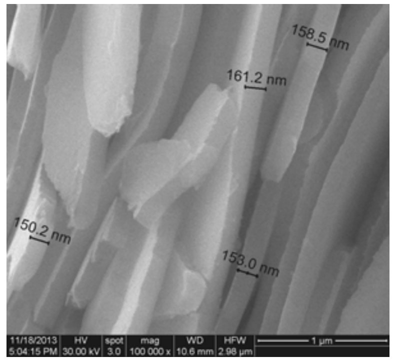
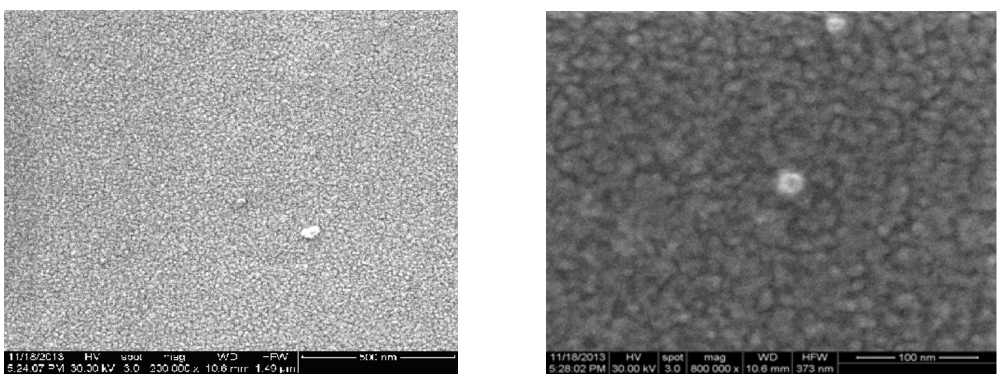


Fig. 2. The thickness of the As_2S thin film from the S1 sample, in the fracture zone in which its fragments are perpendicular on the image plane.

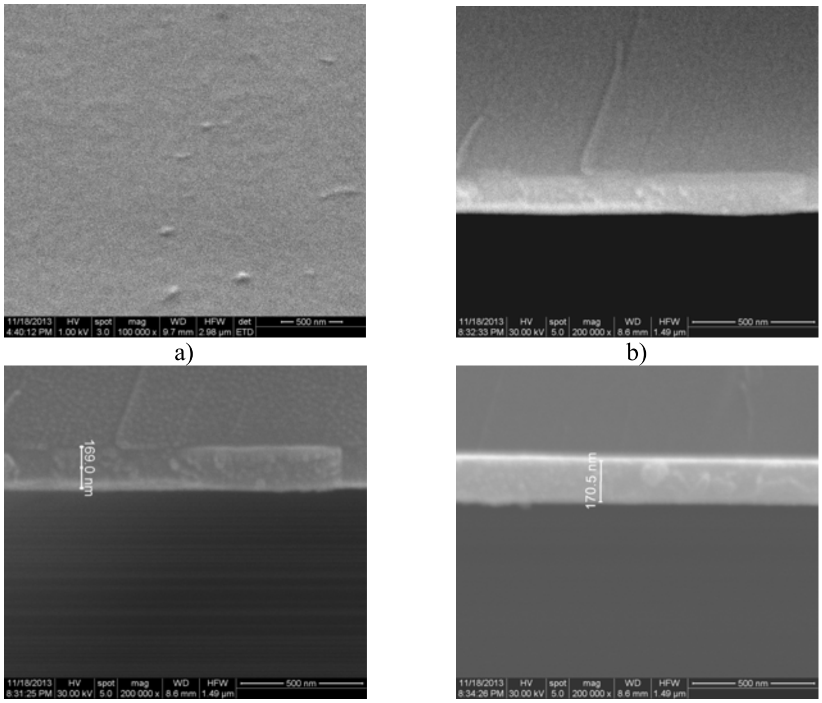
In Fig. 3a) an image of the sample S2 of the Au thin film surface with a magnification of 400000x, while in Fig. 3b) a detail of the same sample with a magnification of 800000x are presented. One can observe the homogeneous nanostructured thin film with a nanograins characteristic structure with a 10-15 nm grain size.



a) b)

Fig. 3. SEM images of the sample S2, the Au layer surface with a magnification 400000x and b) detail of the same sample with a magnification 800000x.

The dimension of the grains is much less than the wavelength of the probing light in plasmonic resonance experiments, emphasizing a good quality of the film which does not produce scattering of the light.



a) b) c) d)

Fig. 4. SEM images of the As_2S_3 thin film surface deposited on glass. a) top view, b-d) cross section views.

In Figs. 4 are presented the SEM images of the As_2S_3 nanostructured thin film surface deposited on glass having high homogeneity and continuity (magnification 100000x). In Fig. 4a) the SEM image of the sample S3 is enlarged.

One can observe a good adherence of the A_2S_3 thin film on the glass surface (there are no holes between glass substrate and A_2S_3 thin film). Also, one can observe the uniformity of the thin film thickness in several zones. All the SEM images are secondary electrons images.

Energy dispersive X-ray microanalysis (EDAX) was performed in order to obtain the chemical local composition of the samples. The spectrum presented in Fig. 5 shows the presence in the thin film of the As, S on Au substrate. Due to the small thickness of the thin film (smaller than 1 μm) one remarked the presence of the elements which compose the glass substrate in S1 sample (Fig. 5).

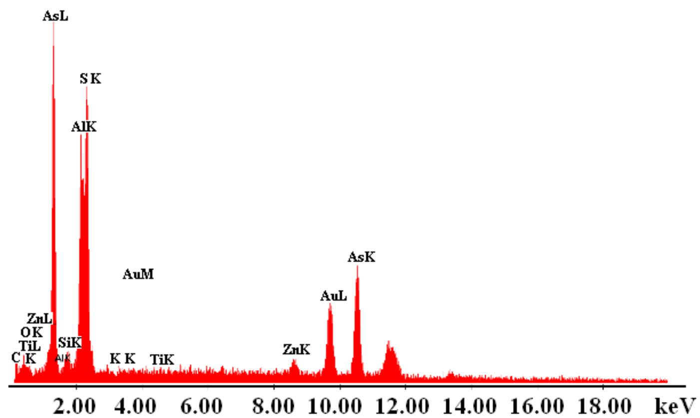


Fig. 5. The energy dispersive X-ray spectra of the As_2S_3 thin film on the Au layer chipset using glass substrate.

The AFM analysis confirms the several nanometers roughness of the As_2S_3 thin films. In Fig. 6a) the 2D image of the samples S3 and respectively, Fig. 6b) for the sample S1 are presented. One can observe a structure having nanograin shape due to the Au layer situated below the As_2S_3 thin film.

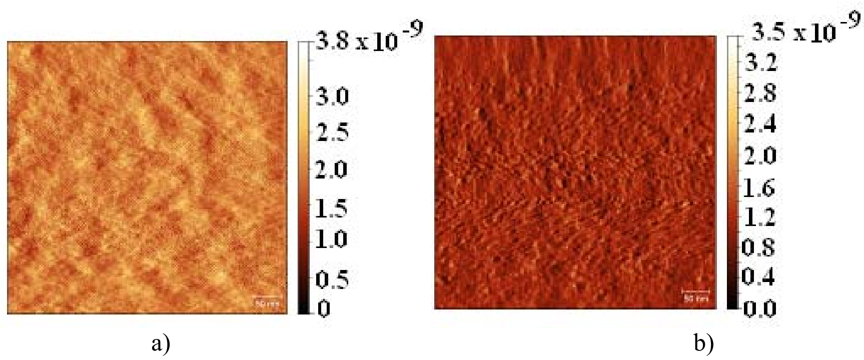
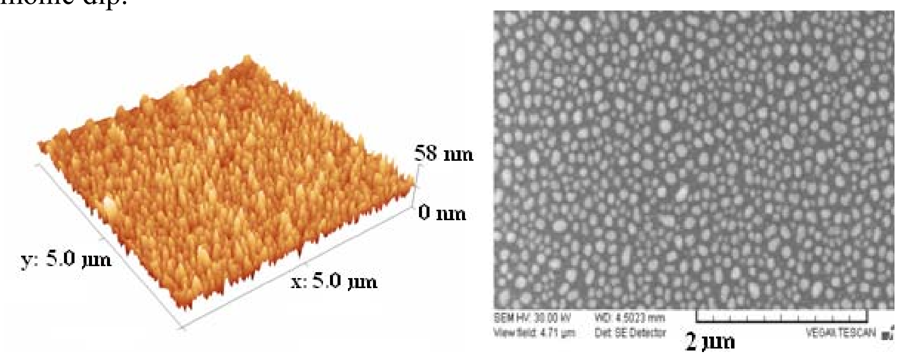


Fig. 6. AFM images for a) topography of As_2S_3 thin films surface deposited in vacuum on homogeneous glass and b) Au layer from the chipset.

From the 2D images analysis of the surfaces (SEM and AFM) we concluded that the above mentioned thin films have very high homogeneity and continuity, without fissures and a roughness about 10 nm. Also, taking into account the SEM analysis in perpendicular fracture (cross section) of the sample fabricated by the deposition of the As_2S_3 thin films on glass, we determined their thickness of about 160 nm, and observe a very good adherence of the thin film on the glass substrate and the absence of the holes between them.

The silver thin films were obtained in laboratory in order to make own plasmonic chipsets. The chipsets consist of gold or silver film on planar glass substrate. The calculated optimal thickness is of 45-50 nm. The pulsed laser deposition method was used in order to obtain the films from a silver target. The target with the diameters of 2” was melted from 99,9% purity silver material. The films continuity was investigated by SEM and AFM methods. The images are shown in Fig.7. As was established, the surface topography consists of columns and islands which lead to the unwanted light scattering and broadening of the plasmonic dip.



a) b)

Fig. 7. AFM (a) and SEM (b) images of silver thin films obtained by pulsed laser deposition. Columns with a height of 30 nm and islands with the dimensions of 200 nm may be observed.

An effective method for depositing smooth silver (Ag) films was demonstrated [12] using a thin seed layer of evaporated germanium (Ge). The deposited Ag films exhibit smaller root-mean-square surface roughness, narrower peak-to-valley surface height distribution, smaller grain-size distribution. Silver films deposited with ~1−2 nm Ge nucleation layers show more than an order of magnitude improvement in the surface roughness. The Ag thin films technology demonstrated in this paper is very promising for large-scale applications as optical metamaterials, plasmonic devices, and other areas of nanophotonics. Another prospective method [13] uses copper (Cu) seed thin layer. The inclusion of the Cu seed layer leads to the deposition of films with extremely low surface roughness (<0.5 nm). Optical measurements together with X-ray diffraction and electrical resistivity measurements confirmed that the Ag film undergoes a layer-by-layer growth mode resulting in a smaller grain size.

3. Conclusions

We reported several experimental results concerning the characterization of As_2S_3 thin films surface using SEM and AFM methods.

Using the 2D images analysis of the surfaces obtained by SEM and AFM techniques we concluded that the above mentioned thin films are homogeneous and continuous, without cracks and with a roughness of about 10 nm. Also, from the SEM analysis in fracture of the sample fabricated by the deposition of the As_2S_3 thin films on glass we determined their thickness of about 160 nm. The images highlighted a very good adherence of the thin film on the substrate and the absence of the holes between them.

Acknowledgements.
This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI – UEFISCDI, project number PN-II-PT-PCCA-2011-25/2012.

REFERENCES

[1] *Benjamin J. Eggleton, Barry Luther-Davies & Kathleen Richardson*, Chalcogenide photonics, Nature Photonics **5**, p. 141–148, (2011).

[2] *A. Popescu,* Components for integrated optics based on amorphous chalcogenide materials, Romanian Reports in Physics, **51**,(3-4), p.327-330, (1999).

[3] *Aurelian Popescu, Dan Savastru, Roxana Savastru, Sorin Miclos, Gabriel Socol and Ion N. Mihailescu*, High contrast 2D etched holes array obtained by direct laser writing on chalcogenide As2S3 films, Phys.Status Solidi A, **209**,(11), p. 2173-2178, (2012).

[4] *A. A. Popescu, D. Savastru, S. Miclos, V. Braic, M. Popescu, A. Manea*, A. Kiss, Properties of rare earth Ga-La-S glasses obtained by RF inductor heating, Digest Journal of Nanomaterials and Biostructures, **Vol. 6**, (2), p. 341 - 348, (2011),

[5] *V. Balan, C. Vigreux, A. Pradel*, Chalcogenide thin films deposited by radio-frequency sputtering, Journal of Optoelectronics and Advanced Materials **6,**(3), p. 875 – 882, (2004).

[6] *R. Tintu, K Sulakshna, K Saurav, V P N Nampoori, P Radhakrishnan and Sheenu Thomas*, $Ge_{28}Se_{60}Sb_{12}$ /PVA Composite Films For Photonic Applications, Journal of Non-Oxide Glasses., **2**, p. 167- 174, (2010).

[7] *Bhushan, B*., Modern Tribology Handbook, **Vol. 1** - Principles of Tribology, (2001)

[8] *R. Kuroda, T. Suwa, A. Teramoto, R. Hasebe, S. Sugawa and T. Ohmi*, IEEE T-ED **56**, p. 291-298, (2009).

[9] *W. C. Tan, M. E. Solmaz, J. Gardner, R. Atkins and C. Madsen*, Optical characterization of a-As2S3 thin films prepared by magnetron sputtering, J. Appl. Phys. **107**, 033524, (2010),

[10] *Georgiana C.Vasile, Roxana Savastru, A.A. Popescu, M. Stafe, D. Savastru, Simona Dontu, L. Baschir, V. Sava, B. Chiricuta, M. Mihailescu, C. Negutu And N.N. Puscas*, Modelling the 2d plasmonic structures with active chalcogenide glass layer, Romanian Reports in Physics, **65**,(3), p. 1012–1018, (2013).

[11] *Georgiana C. Vasile, Aurelian A. Popescu , Mihai Stafe, S.A. Koziukhin, Dan Savastru, Simona Donțu, L. Baschir, V. Sava, B. Chiricuță, Mona Mihăilescu, Constantin Neguțu, Niculae N. Puşcaş*, Plasmonic waveguides features correlated with surface plasmon resonance performe with a low refractive index prism, U.P.B. Sci. Bull., Series A, **75**,(4), p.311-325, (2013).

[12] *Nobuhiko P. Kobayashi, M. Saif Islam, Wei Wu, Pratik Chaturvedi, Nicholas X. Fang, Shih Yuan Wang and R. Stanley Williams,* Ultrasmooth Silver Thin Films Deposited with a Germanium Nucleation Layer, Nano Lett., **9**,(1), p 178–182, (2009).

[13] *Nadia Formica, Dhriti S. Ghosh, Albert Carrilero, Tong Lai Chen, Robert E. Simpson, and Valerio Pruneri*, Ultrastable and Atomically Smooth Ultrathin Silver Films Grown on a Copper Seed Layer, ACS Appl. Mater. Interfaces, **5**,(8), p 3048–3053, (2013).