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I.P. Studenyak[1], Yu.Yu. Neimet[1], Y.Y. Rati[1], O.Ye. Petrachenkov[1], A.M. Solomon[2],
S. Kökényesi[3], L. Daróci[3], R. Bogdán[3]

Deposition and Structure $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ Thin Films

[1]Department of Applied Physics, Faculty of Physics, Uzhhorod National University, 3 Narodna Sq., 88000 Uzhhorod, Ukraine, tel. +380(3122)32012, e-mail: studenyak@dr.com
[2]Institute of Electron Physics, 21 Universitetska St., 88017 Uzhhorod, Ukraine, tel. +380(312)643524, fax +380(312)643650, e-mail: iep@iep.org.ua
[3]Department of Experimental Physics, Faculty of Science and Technology, University of Debrecen, 18/a Bem Sq., 4026 Debrecen, Hungary, tel. +36(52)316012, e-mail: kiki@science.unideb.hu

Thin $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ chalcogenide films were deposited upon a quartz substrate by rapid thermal evaporation. Structural studies of the as-deposited and annealed films were performed using scanning electron and atomic force microscopies. Surfaces of all the films were found to be covered with Ag-rich crystalline cone-shaped micrometer sized whiskers. Thermal annealing of the films at 50°C and 100°C for 1 h in vacuum is shown to cause a mechanical deformation of part of the whiskers and their detachment from the base film surface. Pronounced crystalline silver and α-Ag_2S peaks were observed in the XRD patterns of the as-deposited and annealed thin films, respectively. Optical transmission spectra of the fresh and annealed films investigated at room temperature show a considerable increase of transmittance for the last ones.

Keywords: thin film, SEM, AFM, whiskers.

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Introduction

A wide variety of conductive, semiconductor, and insulating thin films can be prepared by physical vapour deposition (PVD) techniques including direct vacuum evaporation, sputtering, and ion plating. They are used as active or passive components in various devices for microelectronics, optics, micromechanics, and other advanced technologies [1]. PVD thin films should be tightly adherent to the substrate surface to ensure performance and reliability of devices. Usually, PVD thin films prepared under appropriate conditions are firmly bonded to thick substrates. As a result, any change in length along the film plane, which is not matched, will generate a stress in the film. Excessive stresses in thin films may cause defect formation and delamination at the film–substrate interface, mechanical damage in the film (film fracture), adhesion failures, and defect formation in the substrate. Elimination and release of stress can also cause formation of hillocks, whiskers, holes, and other defects which affect physical properties of the films [1].

Whisker structures, discovered rather long ago [2], can be formed on the basis of an amorphous or crystalline material. A monocrystalline whisker is a filament of material that is structured as a single, defect-free crystal. Well-known techniques for obtaining whiskers are vapour-liquid-solid (VLS) method [2], plasma-assisted growth [3], thermal evaporation [4], metal-catalyzed molecular beam epitaxy [5], electrospinning [6], etc. Although the number of reports describing the growth of novel quasi-one-dimensional structures has increased rapidly over the last decade, fundamental understanding of their formation is still limited. One of the main applications of such whiskers is sensing based on changes in the proximity of the active material, which leads to changes in its electrical or optical properties. In most cases interaction between adsorbed species is responsible for these effects [7]. In the recent years biosensors, gas detectors, and devices for various energy storage and conversion applications using whiskers are being developed.

In the present paper, we report on the formation of crystalline Ag-containing whiskers from an Ag-As-S chalcogenide composite material using simple thermal evaporation technique on a cold substrate. Ag-doped Ag–As–S chalcogenide glasses and films have found many current and potential applications, such as solid electrolytes for batteries, electrochemical sensors, photoresists, optical waveguides, diffraction elements, Fresnel lenses, optical recording materials, surface patterns for different applications, formed by a laser beam, and other optical and optoelectronic elements [8]. Recently we have demonstrated high values of electrical (mostly ionic) conductivity in superionic Ag_3AsS_3-As_2S_3 glasses and composites [9, 10]. This, in combination with a strong photosensitivity, attracts a great interest towards

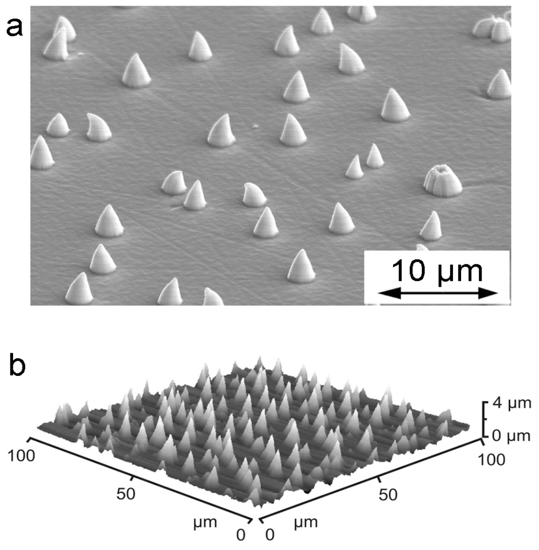

Fig. 1. Tilted SEM (a) and AFM (b) images of as-deposited composite $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film.

fabrication and studies of Ag_3AsS_3–As_2S_3 thin films.

I. Experimental

Synthesis of $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ composite material which consists of crystalline Ag_3AsS_3 and glassy As_2S_3 [10] was carried out at a temperature of 700°C for 24 h with subsequent melt homogenization for 72 h. Thin $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ films were prepared by rapid thermal evaporation from the corresponding composite material at near 1350ºC in vacuum (3×10^{-3} Pa) using a VU-2M setup. The composite material was initially placed in a perforated tantalum evaporator for preventing the material falling out onto a glass substrate kept at room temperature. The film thickness was measured using an Ambios Stylus Profiler XP-1 profilometer. X-ray studies were performed using a DRON-3 diffractometer (conventional $q - 2q$ scanning technique, Bragg angle $2q$ ranging from 10 to 60°, Cu K_α Ni filtered radiation). Structural properties of the thin films under investigation were studied using scanning electron microscopy (SEM: Hitachi S-4300) and atomic force microscopy (AFM: Nanoscope Dimension 3100). Energy-dispersive X-ray spectroscopy (EDX) was used to ensure the film chemical composition. Annealing was performed for 1 h at 50ºC and 100ºC in vacuum. Optical transmission spectra $T(l)$ of the thin films were studied at room temperature using a MDR-3 grating monochromator.

II. Results and discussion

Analyzed by SEM and AFM, a characteristic surface view of $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films is given in Fig. 1. Microscopy studies revealed the presence of cone-shaped whiskers on the top of a fresh evaporated film surface. The average height of the whiskers is found to be 2,5 µm which is well seen from the AFM image in

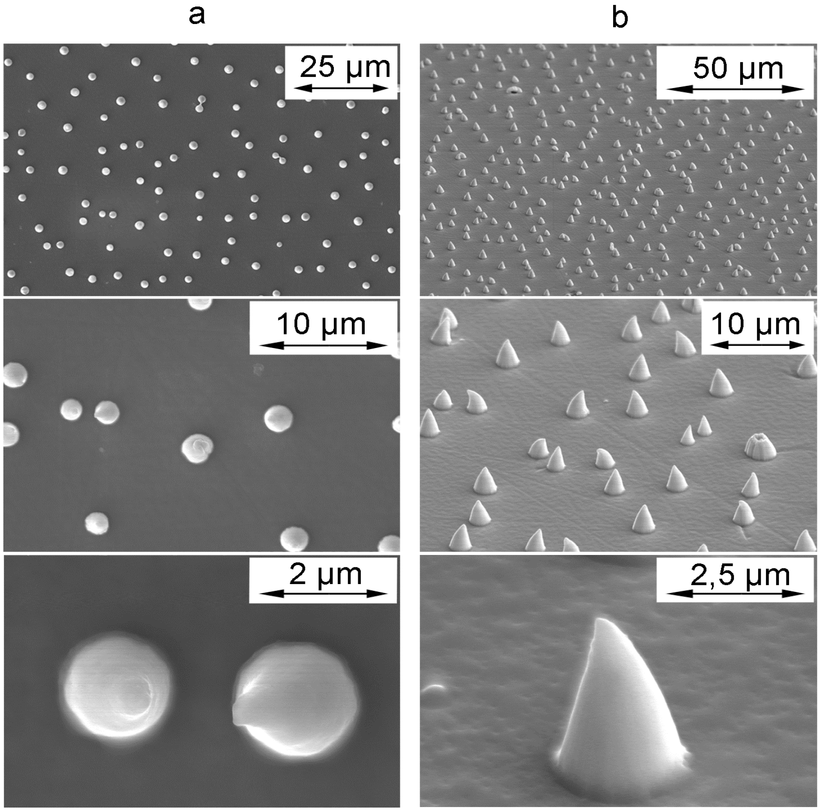

Fig. 2. Scaled SEM images of as-deposited composite $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films: top (a) and tilted (b) view of the surface.

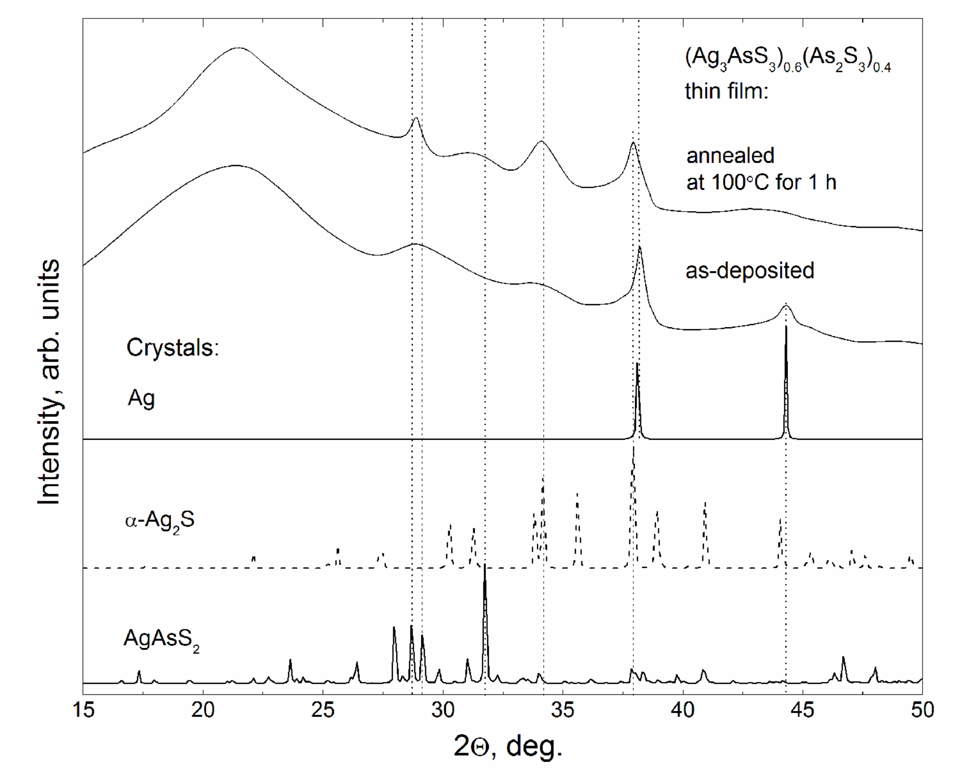

Fig. 3. X-ray diffraction patterns of as-deposited and 100ºC 1 h annealed composite $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films.

Fig. 1, b, and is also confirmed by the profilometer. As estimated by the profilometer, the thickness of the base film layer is about 0.5 μm. Meanwhile, the average base diameter of the cones is about 2 μm. This value is in a good agreement with the detailed SEM study of the film under investigation. The average aspect ratio (height over diameter) of the whiskers was estimated from the Fig. 1 and found to be 1.2. This fact obviously prejudices the cone-like structures obtained at the $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film surface to be called whickers in a strict way of its definition, as far as generally whiskers have the aspect ratio of the order of hundreds. Nevertheless, we call the obtained cones as whiskers in order to point out the similarity between them, as well as to simplify the description of the thin film properties. The images of the fresh as-deposited film obtained by SEM at different scales are shown in Fig. 2. Top (Fig. 2, a) and tilted (Fig. 2, b) views of the film surface give a better understanding of the $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film surface formed from the composite material at the above evaporation conditions. Top view image (Fig. 2, a) helped to estimate the average density of the cones at the surface of the film which equals approximately 14000 per mm^2 (0.014 per μm^2).

Recently we reported on the nanocrystalline layer which appeared on the bulk $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ composite surface after it had been heated to 450 K [9]. Simultaneously, this material was found to be phase separated, or, more exactly, having smithite ($AgAsS_2$) crystalline inclusions in the amorphous As_2S_3 matrix [10]. Hence, it is obvious that quick high temperature evaporation of the $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ composite results in the phase segregation.

Figure 3 shows X-ray diffraction patterns of the fresh and annealed $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films. The presence of local maxima at the patterns shows that both studied thin films very likely have crystalline inclusions in their structures. Comparing the crystalline patterns of silver, high-temperature α-Ag_2S, and smithite ($AgAsS_2$) crystals with the obtained XRD patterns of thin films under investigation gives us the possibility to find out the nature of those inclusions.

From the Fig. 3 one can see broad amorphous maxima in the 15-27º 2θ-region in both investigated samples. The presence of crystalline peaks was revealed in both thin film patterns. The X-ray diffraction experiment for the as-deposited thin film enable us to treat a pronounced peak at 2θ≈38.2º, and a small maximum at 2θ≈44.2º as Ag crystalline peaks. Figure 3 also reveals signatures of smithite (in the vicinity of 2θ≈29º) and α-Ag_2S (2θ≈34º) crystals in the X-ray diffraction pattern of the fresh $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film. Opposite to the as-deposited $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$

Table 1

The elemental content (in at.%) of as-deposited $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films and corresponding initial bulk composite. The composition in atomic percentage is given for the whiskers formed on the fresh thin film surface as well

Elements, at. %	Initial bulk composite	As-deposited thin film	The obtained whiskers
Ag	29	29	62,8
As	22,6	32	18
S	48,4	39	19,2

thin film, the diffraction pattern of the annealed at 100°C for 1 h thin film exhibits a clearly pronounced narrow peak of high-temperature α-Ag_2S crystalline phase ($2\theta \approx 37.9^{\circ}$) which is very close to that of pure silver, and a broader maxima at $2\theta \approx 34^{\circ}$. Somewhat less pronounced smithite ($AgAsS_2$) maxima in the vicinity of $2\theta \approx 29^{\circ}$ and $2\theta \approx 31.5^{\circ}$ enable us to consider the annealed film or even the fresh one to have the smithite crystalline inclusions in its structure, as it was proved for the bulk $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ composite in [10].

EDX combined with SEM technique enabled us to ensure that the films formed are As-enriched and have a deficiency of sulphur percentage in comparison with the initial bulk composite, as follows in the Table 1. Simultaneously, local EDX analysis estimated an excess of silver in the atomic composition of the whiskers. The presence of small amounts of arsenic and sulphur in the whiskers shown by the EDX can be explained by the fact that the minimum estimation area covers not only the whisker itself, but some part of the base film as well. An excess of silver in the EDX results on whiskers and the corresponding peaks in XRD pattern of the fresh $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film enable us to ascribe the whiskers, obtained in the present work, to silver crystals or crystalline Ag-rich structures.

Figure 4 presents SEM images of $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films thermally annealed in vacuum at 50°C and 100°C for 1 h. The thermal annealing process can be seen to result in the cone destruction and detachment from the base film surface which is enhanced at the annealing temperature increase (Fig. 4). On the other hand, the film surface and the whiskers of the film annealed at 50°C for 1 h are covered with new formations, whereas for the film annealed at 100°C for 1 h only the whiskers and areas in their vicinity are changed while the base surface remains flat. The detachment of the cones is most likely caused by the presence of additional thermal strain due to the film temperature increase related to the annealing process. The second reason is an arising of new outgoing formations which changes the surface of the film, an intrinsic energy distribution in thin film volume, and, probably, reorients local bonds between constituent molecules and atoms in the material. For the $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film annealed at 100°C one can observe formations (Fig. 4) which, as follows from the XRD data (Fig. 3), can be ascribed to α-Ag_2S crystals. Moreover, as we can see from small scale pictures in Fig. 4, the whiskers are embedded with their basements into the base film which can be the additional reason for the presence of arsenic and sulfur in the EDX compositional spectra of the whiskers (Table 1).

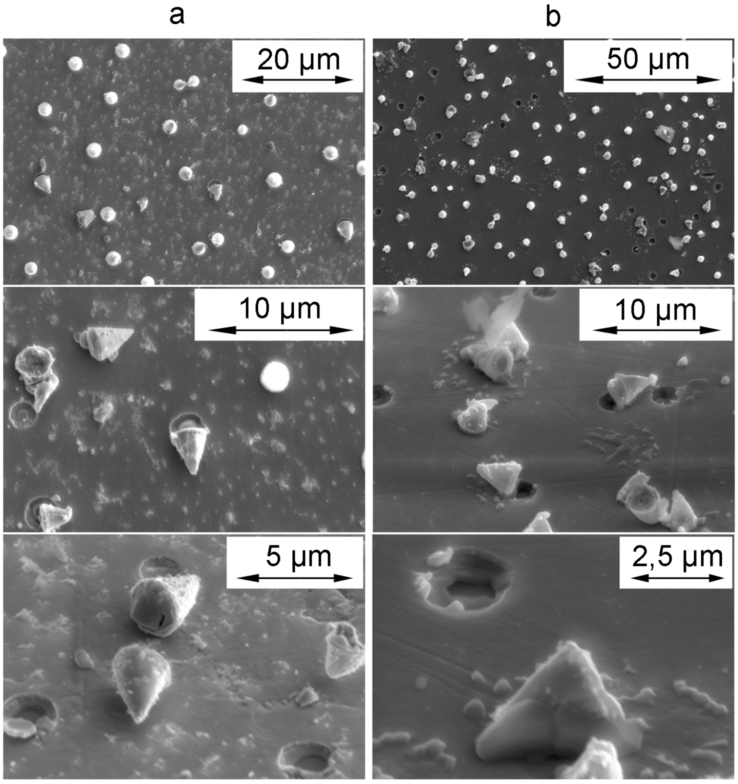

Fig. 4. Scaled SEM images of annealed composite $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films: 50°C 1 h (a) and 100°C 1 h (b) annealing in vacuum.

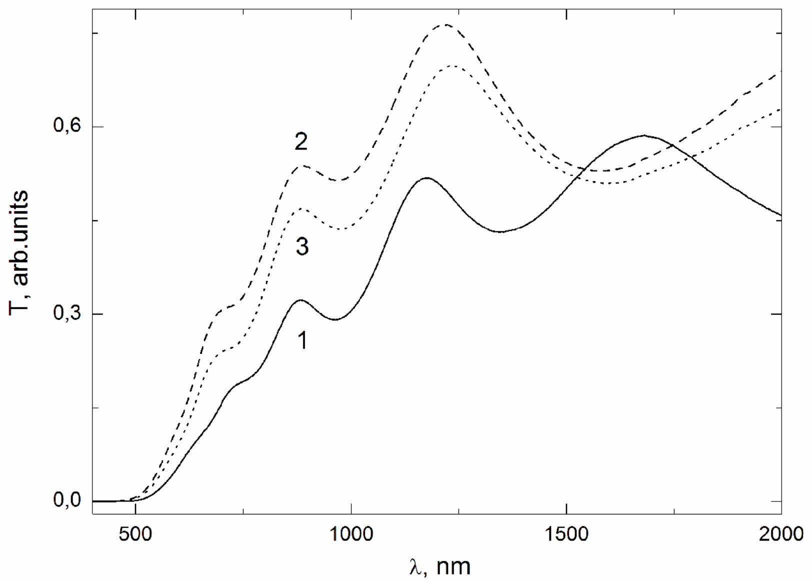

Fig. 5. Optical transmittance of as-deposited (1) and annealed during 1 h at 50°C (2) and 100°C (3) composite $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin films.

Fig. 5 shows the optical transmittance of the as-deposited $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ thin film as well as those annealed at both 50°C and 100°C. One can observe a considerable increase of transmittance by almost 30 % in the annealed films spectra. This fact is characteristic for a structural ordering, which occurs in the film structure as a consequence of thermal annealing. One should note that annealing at 50ºC for 1 h causes the transmission onset (measured for the transmission coefficient $T = 0.1$) to shift towards shorter wavelengths by 60 nm. On the other hand, annealing at the increased to 100ºC temperature involves an opposite reaction, i.e. causes the transmission onset to slightly shift towards longer wavelengths by 20 nm (at $T = 0.1$). The spectra of the annealed films at the onset of transmission are seen to be less smeared or, in the other words, the slopes of the plots are seen to be sharper. Although a reduction of smearing is observed for the annealed at 100ºC film, this film remains still more ordered comparing to the as-deposited fresh one. The increase of the optical transmittance can be caused by the detachment of the whiskers as well, which either involves the decrease of the average thin film thickness or creates holes in places where initially the cones were located.

Conclusions

$(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ chalcogenide thin films were prepared by rapid thermal evaporation in vacuum. Subsequently, the films were annealed at 50 °C and 100 °C for 1 h in vacuum. SEM and AFM imaging of the as-deposited and annealed films revealed numerous cone-shaped micrometer-sized whiskers on their surfaces. The presence of crystalline peaks was revealed in the XRD patterns of both fresh and annealed thin films. The EDX analysis showed an excess of silver in the obtained whiskers, which, together with the pronounced peak of Ag in the XRD pattern, enabled us to ascribe the last one to the whiskers. Annealing at 50°C and 100 °C was shown to result in a mechanical deformation of part of the whiskers and their detachment from the base film surface. Another result of annealing is probable appearance of crystalline α-Ag_2S on the surface of the whiskers and the base film. The optical transmission spectra of the annealed films have shown an increase of transmission for both annealed samples, whereas the largest change of transmittance almost by 30 % was observed after annealing at 50 ºC.

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Studenyak I. P. - doctor, prof., head of Applied Physics department of Physical Faculty;
Neimet Y.Y. - PhD student;
Rati Y.Y. _ MA student;
Petrachenkov O.Y. - senior researcher;
Solomon A.M. – researcher;
Kökényesi S. - doctor, prof;
Daróci Lajos - doctor, prof;
Bogdán Rolánd – researcher.

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І.П. Студеняк[1], Ю.Ю. Неймет[1], Й.Й. Раті[1], О.Є. Петраченков[1], А.М. Соломон[2],
Ш. Кокенєші[3], Л. Дороуці[3], Р. Богдан[3]

Отримання та структура тонких плівок $(Ag_3AsS_3)_{0,6}(As_2S_3)_{0,4}$

[1]Кафедра прикладної фізики, Фізичний факультет, Ужгородський національний університет,
пл. Народна, 3, 88000 Ужгород, Україна, e-mail: f-physics@uzhnu.edu.ua
[2]Інститут електронної фізики, вул. Університетська, 21, 88017 Ужгород, Україна, e-mail: iep@iep.org.ua
[3]Кафедра експериментальної фізики, Факультет науки і технології, Дебреценський університет,
пл. Бем, 18/а, 4026 Дебрецен, Угорщина, e-mail: kiki@science.unideb.hu

Тонкі плівки $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ були нанесені на кварцову підкладку методом термічного напилення. Структурні дослідження напилених та відпалених плівок проводилися за допомогою методики дифракції рентгенівських променів, скануючої електронної та атомно-силової мікроскопії. На поверхні аморфних плівок $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ виявлено збагачені сріблом мікрокристалічні конусоподібні утворення, т.з. віскери. Внаслідок відпалу спостерігається деяка механічна деформація та відривання частини віскерів від поверхні плівки. Крім того, у результаті відпалу віскери покриваються речовиною зі структурою α-Ag_2S. Досліджено при кімнатній температурі та проаналізовано спектри оптичного пропускання напилених та відпалених плівок.