

## Surface-enhanced Raman scattering of $\text{As}_2\text{S}_3$ and Se thin films formed on Au nanostructures

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**Abstract.** The effect of plasmonic nanostructures (NSs) on the Raman spectra and underlying structural changes in thin chalcogenide films is investigated. Several tens of nanometers thick  $\text{As}_2\text{S}_3$  and Se films were deposited by thermal sputtering on glass and surface-enhanced Raman spectroscopy (SERS) substrates based on gold nanostructures for comparison. The films on glass were practically not detectable by the Raman spectroscopy. Using gold NSs as the substrates enabled reliable registration of the Raman spectra of both the  $\text{As}_2\text{S}_3$  and Se films. The registered Raman spectra contained all the features usually present in the films with the thicknesses  $\sim 1 \mu\text{m}$  or more. Based on our analysis of the spectra obtained at different excitation wavelengths, we may conclude that the SERS chemical mechanism makes the main contribution to the enhancement of the Raman signal from chalcogenide films. Adjustment of the parameters of SERS substrates to tune their plasmon band position in resonance with the excitation laser radiation enables increasing the plasmonic enhancement contribution. Besides the effect of enhancement, localized plasmon resonance in the gold NSs causes local heating of the chalcogenide film around them leading to local structural transformations, which can be controlled using the Raman spectra.

**Keywords:** Raman scattering, SERS, thin films, arsenic sulphide, selenium, gold nanostructures.

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### 1. Introduction

Surface-Enhanced Raman Spectroscopy (SERS) is widely used as an effective, non-destructive method of rapid diagnosis of various materials based on their vibrational spectra [1]. Unlike ordinary Raman spectroscopy, SERS allows one to register the spectra of molecules present in small quantities in solutions or deposited on nanostructured noble metal films. A significant increase in the Raman scattering intensity in the case of SERS may be explained by two mechanisms, namely, electromagnetic and chemical enhancement of both the absorption of the excitation laser light and the Raman scattering signal itself.

Historically, the focus of the SERS studies was on organic substances, which resulted in many applications. For example, several SERS-based methods were proposed to determine the level of sugar in the blood:

non-invasively [2], in a drop of blood [3], and *in vivo* by a sensor placed on a contact lens and monitoring the chemical composition of tears [4]. Furthermore, SERS is used in forensics to identify biological substances and drugs [5], for detecting the type and concentration of pesticides and harmful additives in food products [6], to diagnose diseases in medicine [7], for detecting and quantifying toxic compounds in the environment [8], in the identification of pigments in artworks [9], and other areas of science and everyday life.

On the other hand, the number of reports on SERS diagnostics of inorganic materials is currently very small due to several reasons. Firstly, the deposition of a continuous (*e.g.* semiconductor) film on a SERS substrate can affect certain characteristics of the film itself and change the plasmon resonance in the SERS substrate, deteriorating its efficiency. Secondly, as the intensity of the electric field created by metal nanostructures

decreases exponentially, the SERS enhancement related to it is noticeable only within a few atomic or molecular layers closest to the metal surface. Therefore, during SERS diagnostics of semiconductor films even of a small thickness, which is at least 10 nm or more, the Raman signal from most of the film volume will not be enhanced. Finally, increase in the amplitude of individual molecules vibrations due to the increase in the intensity of the local electric field is a very likely situation, while increase in the amplitude of atomic lattice vibrations (phonons) is presumably much less efficient.

The rare SERS studies of inorganic semiconductors reported so far mostly evaded the listed above challenges. In particular, monolayers of semiconductor quantum dots (QDs) of different materials such as CdSe, CdS, ZnO, GaN, and CuS, formed by the Langmuir–Blodgett method were studied [10–12]. Another approach was used in the works [13, 14] to enhance the Raman signal from amorphous carbon and silicon films, namely, the formation of gold nanostructures in their bulk. However, local heating of the films in the regions adjacent to NPs due to significant absorption of the excitation laser radiation by the isolated plasmonic nanoparticles was observed in the latter case. As a consequence, structural changes may be induced in the films due to local thermal annealing. Several articles were also published, in which the enhancement of Raman scattering of vibrational modes of fairly thick semiconductor films by SERS substrates was investigated [15, 16]. In one of them, the formation of Schottky-type metal-semiconductor heterostructures is considered to explain the enhancement of the signal from the semiconductor film [15]. The latter mechanism enables the enhancement of the Raman signals from semiconductor films with band gaps significantly greater than the energy of the excitation laser radiation. In this case, the enhancement of the Raman signal is explained by the significant contribution of the chemical mechanism of enhancement.

At the same time, practically no works contain application of SERS to glass-like films. The nature of atomic vibrations in such materials is, in a certain sense, intermediate between the cases of crystalline semiconductors and molecules. That is why their vibrational spectra are formed by the vibrations of small groups of atoms, but not by the collective oscillations of large numbers of lattice atoms as in crystalline semiconductors. As embedding plasmonic nanoparticles (NPs) is used to enhance the optical response of semiconductors and dielectric functional films in a fairly wide range of applications – photovoltaics, photoluminescence (PL), nonlinear optics – study of the interaction mechanisms in such type of hybrid materials is important from the application point of view.

Therefore, one of the key ideas of this article is the realization of the enhancement of Raman scattering spectra of chalcogenide films through their direct contact with plasmonic nanostructures. The latter was achieved by the thermal evaporation of chalcogenide material on

nanostructured gold layers formed by vacuum thermal evaporation. Glassy  $\text{As}_2\text{S}_3$  and Se were chosen as the film materials.  $\text{As}_2\text{S}_3$  was selected because it is a fairly important semiconductor used for photosensitive devices has a fairly wide range of optical transmission from 0.7 to 10  $\mu\text{m}$ , and has a high nonlinear refractive index. Today,  $\text{As}_2\text{S}_3$  films are widely used for integrated optical microcircuits and biochemical sensors. On the other hand, to understand the role and delimitation of photoinduced processes in the semiconductor material itself as well as the resonance effects related to plasmon excitation, it was important to study another chalcogenide (glass-like) film, the band gap of which would be significantly different from that of  $\text{As}_2\text{S}_3$  (2.35 eV). Therefore, a Se chalcogenide film with the band gap of 1.94 eV was chosen for comparative studies.

As it is well known, the effectiveness of the enhancement of the spectra of semiconductor materials depends on the characteristics of the SERS substrates. The substrates should be laterally uniform, have stable characteristics in certain temperature range, and preferably tuned into resonance with the excitation laser radiation to achieve a significant enhancement of the Raman signal [17–19]. All these requirements were taken into account for fabricating the SERS substrates in the present work.

## 2. Methodology of the experiment

Formation of plasmonic Au nanostructured arrays was carried out by the method of rapid radiation heating of thin (4...35 nm) gold films in an air atmosphere, which enables a wide range of heating rates (up to 20...25 K/s) in the temperature range of 473...773 K. Note that the design of the deposition equipment allows continuous monitoring during the heat treatment of the dynamics of the change in the transmission spectrum of a gold film in the range of 400...1000 nm using an Ocean Optics fiber spectrophotometer. Use of the latter during the heat treatment of Au films made it possible to control the change in the surface plasmon resonance (SPR) spectrum during the formation of nanostructures (NPs) and to stop annealing when the required SPR characteristics were reached.

The surface morphology of the Au nanostructured arrays was studied by scanning electron microscopy (SEM) using a JSM 6064-LV (JEOL) microscope. The sample surfaces were scanned by an electron beam at an accelerating voltage of 15 kV and a current of 0.1 nA with a spatial resolution of 10 nm in the secondary electron mode.

Using the method of rapid radiation heating of samples, the Au nanostructured arrays were formed having the average size of the nanostructures ( $d_{NSs}$ ) from 25 to 50 nm. The position of the SPR band maxima ( $\lambda_{SPR}$ ) was in the range from 530 to 575 nm. Moreover, the halfwidths of the plasmon absorption bands varied slightly, since the latter depends on the size distribution of gold NSs.

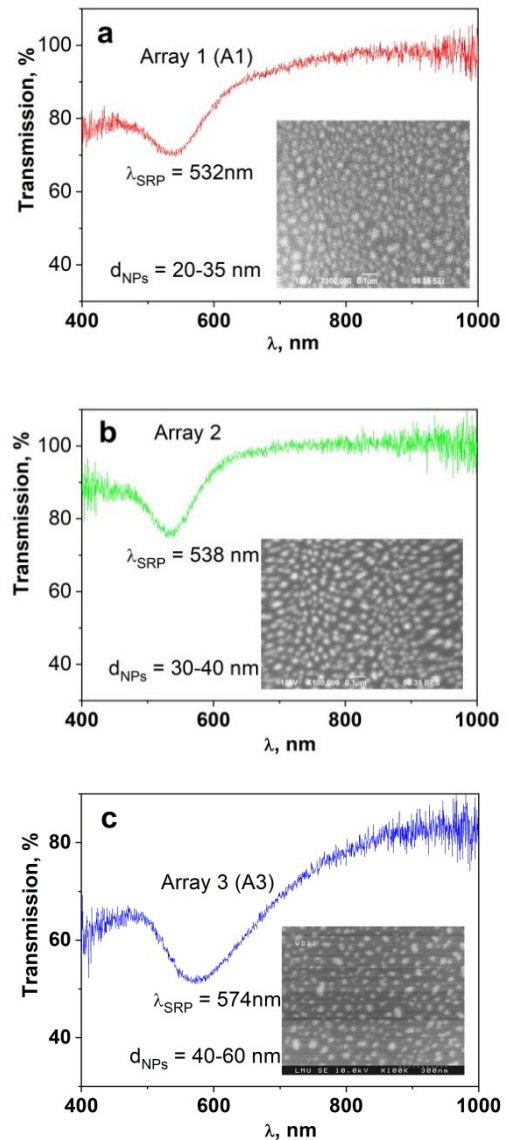
As<sub>2</sub>S<sub>3</sub> and Se thin films with the thicknesses of 30, 50, and 60 nm and composite structures ‘Au NSs/As<sub>2</sub>S<sub>3</sub> film’ and ‘Au NSs/Se film’ were obtained by thermal evaporation of vitreous arsenic sulphide and selenium onto respective substrates from quasi-closed effusion cells. The deposition rate of the As<sub>2</sub>S<sub>3</sub> and Se films was 1–5 nm/s. The arrays with different average NS sizes determined from the plasmon absorption spectra and SEM images (see Fig. 1) were labelled A1, A2, and A3.

The Raman spectra of the freshly prepared and annealed As<sub>2</sub>S<sub>3</sub> and Se films and composite structures ‘Au NSs/As<sub>2</sub>S<sub>3</sub> film’ and ‘Au NSs/Se film’ were studied at room temperature. Raman spectra were excited by the radiation of solid-state lasers with  $\lambda_{exc} = 532$  and 671 nm and acquired using a single-stage spectrometer MDR-23 (LOMO) equipped with a cooled CCD detector (AndoriDus420,UK). The laser power density on the samples was less than  $10^3$  W/cm<sup>2</sup> to preclude any unintentional thermal or photo-induced modification of the samples during the spectrum acquisition. A spectral resolution of 3 cm<sup>-1</sup> was determined from the width of the Si phonon peak of a single-crystalline Si substrate. The Si phonon peak position of 520.5 cm<sup>-1</sup> was used as a reference for determining the position of the Raman peaks of the samples. An additional (*ex-situ*) annealing of the As<sub>2</sub>S<sub>3</sub> and ‘Au NSs/As<sub>2</sub>S<sub>3</sub> film’ samples, needed for understanding the Raman results, was carried out at a temperature of 450 K for 1 hour in a vacuum.

### 3. Results and discussion

As As<sub>2</sub>S<sub>3</sub> and Se films are photo- and thermo-sensitive, they can change their local structure under the influence of laser radiation [21–24]. Therefore, their Raman diagnostics are to be performed very carefully. Indeed, when the photon energy corresponding to  $\lambda_{exc}$  exceeds the bond energy between certain atoms in the film, or when the film is heated by this radiation to a critical temperature, some bonds may get broken causing other bonds to form, resulting in rearrangement of the structural units of a chalcogenide film and significantly affecting the film properties.

In order to realize enhancement of the Raman signal from the chalcogenide films *via* an electromagnetic mechanism, the SPR peak of the SERS substrate should be tuned into resonance with the excitation laser radiation ( $\lambda_{exc}$ ). However, efficient absorption of radiation by the gold NSs may also lead to their significant heating. If the resulting temperature increase in the adjacent volume of the chalcogenide films does not exceed the critical level, at which the local structure begins to change, such SERS substrates may be used. In another case, when the chosen  $\lambda_{exc}$  does not excite plasmons in the gold NSs, the effect of SERS substrates on the Raman signal enhancement can only be due to the chemical mechanism. The latter, as a rule, is due to the charge transfer between the Fermi level of the gold nanostructures and the electronic levels of the studied molecules or, as in our case, inorganic semiconductor films.



**Fig. 1.** Transmission spectra of gold NSs A1, A2, and A3 and SEM images of their surfaces (insets).

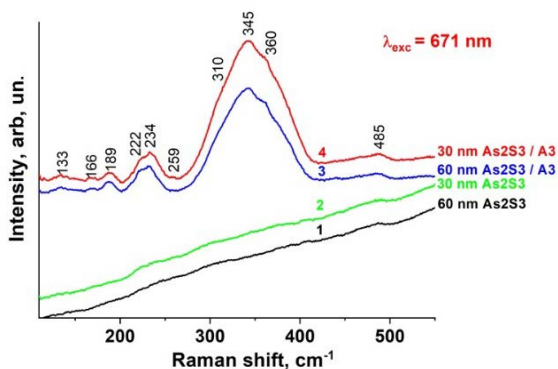
Analysis of the plasmon absorption spectra of the different arrays of gold NSs shows that the arrays A1 and A2 are configured to excite LSPR in them by  $\lambda_{exc} = 532$  nm, while for A3 excitation of plasmons is possible at  $\lambda_{exc} = 532$  nm and  $\lambda_{exc} = 671$  nm because both wavelengths fall into the plasmon absorption band.

It should be noted that it is also necessary to take into account the effect of increasing the absorption of the excitation laser radiation due to the ordinary Raman resonance, at which the energy of the excitation radiation coincides with or is close to the band gap of the material under study. As mentioned above, the band gap of As<sub>2</sub>S<sub>3</sub> is 2.35 eV. Therefore, laser radiation with a wavelength of 532 nm (2.33 eV) will be resonant for it, and its use will lead to an increase in the intensity of Raman spectra. On the other hand, significant absorption of the resonant excitation can lead to more significant heating of the film,

resulting in its structural transformation. No resonance enhancement in the Se film is expected at  $\lambda_{exc} = 532$  nm (2.33 eV) because the band gap of this material is 1.94 eV. At the same time, excitation of Raman spectra by the radiation with  $\lambda_{exc} = 671$  nm (1.85 eV) is not resonant for both  $As_2S_3$  and Se films. Hence, use of this wavelength does not lead to excitation of plasmons in the gold NS arrays A1 and A2, but only in the SERS substrate A3. The materials chosen for investigation and the excitation conditions selected in this way are aimed at understanding the role of photoinduced processes in the semiconductor material itself and the role of resonance effects in plasmon excitation as well as at distinguishing the contribution of these factors to the formation of Raman spectra of the studied systems.

Fig. 2 shows the Raman spectra excited by laser radiation with the wavelength of 671 nm of the freshly prepared  $As_2S_3$  films with the thicknesses of 30 and 60 nm (curves 1 and 2) deposited on the glass substrates and the same films deposited on the gold NSs A3 (curves 3 and 4). It can be seen from this figure that the Raman signal from the  $As_2S_3$  films deposited on the glass substrates is practically absent. That is, no Raman spectra from the  $As_2S_3$  films, even 60 nm thick, on a glass substrate can be registered under non-resonant conditions. At the same time, Raman signals from the  $As_2S_3$  films with the same-order thicknesses (30, 50, and 60 nm) but deposited on the gold NSs A3 (Fig. 2, curves 3 and 4) and A1 and A2 (Fig. 3, curves 2, 3) are reliably detected.

It can be seen from Fig. 2 that the intensities of the Raman bands of the arsenic sulphide films of both thicknesses (30 and 60 nm), which were deposited on the A3 arrays, are practically the same. This indicates that in both cases, only the regions of the  $As_2S_3$  film in the vicinity of the gold NSs contribute to the Raman scattering. It is rather difficult to estimate the signal enhancement factor in this case, since the signal from the  $As_2S_3$  film is not registered without the SERS substrate except for the band at  $485\text{ cm}^{-1}$  from the linear sulfur chains. However, the intensity of the latter band is



**Fig. 2.** Raman spectra of the  $As_2S_3$  films with the thicknesses of 30 and 60 nm deposited on the glass substrates (1, 2) and on the gold NSs (A3) (3, 4), the SEM image of which is shown in Fig. 1.

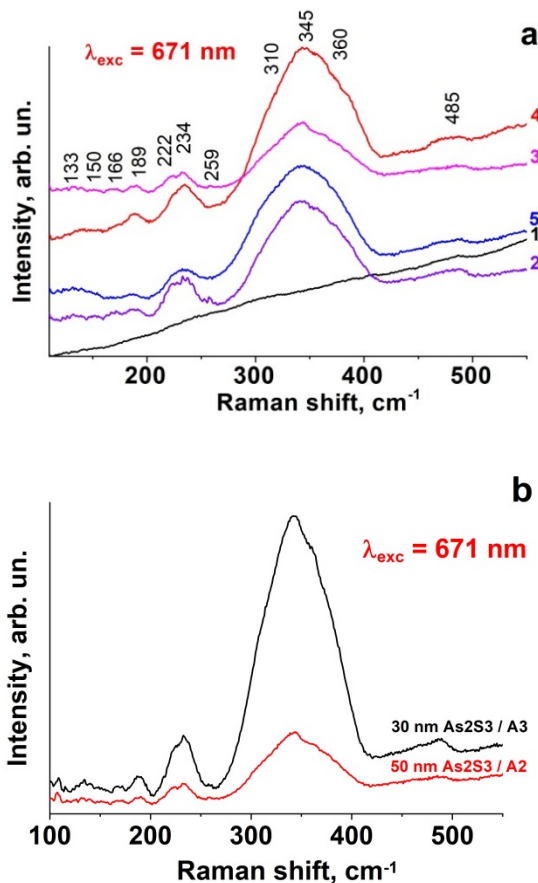
practically not increased by the SERS substrate, presumably because the enhancement in our system is not sufficient to increase the magnitude of vibrations of large groups of atoms. At the same time, the Raman signal of other bands of the  $As_2S_3$  film on the SERS substrates is quite intense and allows registering even the low-intensity vibrational modes.

The SERS spectra of the  $As_2S_3$  films are characterized by an intense and broad band with a maximum at  $345\text{ cm}^{-1}$ , which is a characteristic of the symmetric vibrational stretching modes of As–S, and several less intense bands at 133, 166, 189, 234, 259, and  $485\text{ cm}^{-1}$ . Also the features in the form of a small shoulder at 222, 310, and  $360\text{ cm}^{-1}$  are observed. As to the bulk  $As_2S_3$  glass and the “thick” ( $\sim 1\text{ }\mu\text{m}$ )  $As_2S_3$  film [26], the characteristic band at  $345\text{ cm}^{-1}$  in the spectrum of the composite structure ‘Au NPs/ $As_2S_3$  film’ is due to the vibrations of arsenic and sulphur atoms in the trigonal pyramids  $AsS_3$ . The shoulder at  $\sim 310\text{ cm}^{-1}$  is associated with the deformation vibrations of S–As–S bonds of the  $AsS_3$  pyramids. Quite intense bands with the frequencies of 189 and  $234\text{ cm}^{-1}$  and less pronounced features at 133, 222, and  $362\text{ cm}^{-1}$  indicate the presence of a significant number of molecular fragments ( $As_4S_4$ ) with homopolar bonds in the structural network of the arsenic sulphide films. All available features of the SERS spectra of the  $As_2S_3$  glasses are explained within the framework of the glass network model containing two types of  $As_4S_4$  clusters [25–27]. In the monomeric form, two As–As bonds are connected by four bridging sulphur atoms in such a way that a closed cage-like structural unit is formed. At the same time, the valence condition is satisfied for all atoms. In the second type of clusters, the cage is opened and two more sulphur atoms are added to it. Such clusters make it possible to form a spatially branched structural frame of glass and largely determine the nature of the vibrational spectra. Analysis of the obtained results allows us to conclude about the nanoheterogeneous structure of the freshly prepared  $As_2S_3$  films. Their structural network is a mixture of pyramidal structural elements  $AsS_3$  and partially polymerized disordered molecules  $As_4S_4$ ,  $As_4S_3$ , and fragments of rings and chains of sulphur atoms.

Fig. 3a shows the Raman spectra of the freshly deposited 50 nm  $As_2S_3$  films on a glass substrate (curve 1) and the gold NSs A1 and A2 (curves 2 and 3, respectively), as well as of the same arrays after additional annealing (curves 4, 5). Since plasmons in the gold nanostructures of the A1 and A2 arrays are not excited when Raman spectra are excited by laser radiation with  $\lambda_{exc} = 671$  nm, the significant increase in the intensity of the Raman scattering from the  $As_2S_3$  film deposited on these arrays, compared to the film on a glass substrate, may be explained by the chemical enhancement mechanism. The intensities of the Raman bands of the freshly deposited and annealed films on the arrays A1 and A2 are comparable, which may indicate the same effect of these SERS substrates on signal enhancement. At the same time, comparison of the

Raman spectra of the  $\text{As}_2\text{S}_3$  films deposited on the A2 and A3 gold nanostructure arrays, recorded under the same conditions, shows that the intensity of the characteristic band with a frequency of  $345\text{ cm}^{-1}$  in the case of the A3 array is 4 times greater. That is, additional enhancement of the Raman signal due to the electromagnetic mechanism may play an important role in the case of the SERS substrate A3.

Annealing of glasses and amorphous films can lead to significant changes in their atomic structure, a decrease in the number of defects, *etc.* [26, 28]. In our case, some features disappear in the spectra upon annealing the films, especially the bands related to the presence of molecular fragments with homopolar As–As bonds in their structural network, making the spectra more similar to the spectrum of bulk glassy arsenic sulphide [25, 26]. This is also confirmed by the absence of the bands at  $133$ ,  $222$ , and  $259\text{ cm}^{-1}$  in the spectra of the annealed films and the less pronounced bands at  $189$  and  $234\text{ cm}^{-1}$ . This fact allows us to conclude that increased mobility of atoms during annealing the films



**Fig. 3.** (a) Raman spectra of the  $\text{As}_2\text{S}_3$  films with the thickness of  $50\text{ nm}$  deposited on a glass substrate (1); the gold NSs A1 and A2 (2, 3), respectively; the gold NSs A1 and A2 with thermal annealing of the composite at the temperature of  $450\text{ K}$  (4, 5). (b) Comparison of the intensities of the Raman spectra of the  $\text{As}_2\text{S}_3$  films deposited on the gold NSs A2 and A3, recorded under the same conditions.

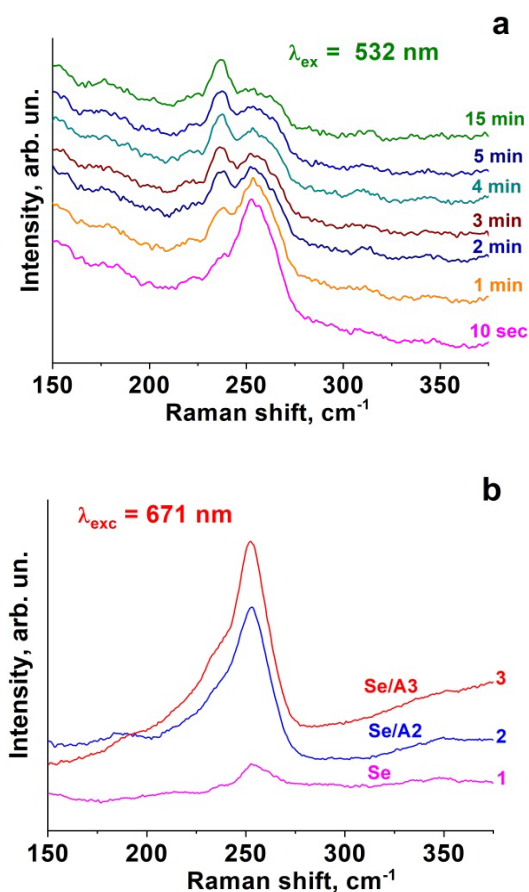
makes homopolar chemical bonds get broken and transformed into the corresponding molecular fragments of  $\text{As}_4\text{S}_4$ ,  $\text{As}_4\text{S}_3$ , and  $\text{S}_n$ , which, in turn, causes their polymerization into a structural network of pyramidal elements  $\text{AsS}_3$ . In the Raman spectra, this process is manifested by a significant decrease in the intensities (or even disappearance) of the bands related to homopolar bonds and a change in the angles of the As–S–As bonds.

In its turn, the latter manifests itself by a significant change in the frequencies of deformation vibrations. This can be explained by the presence of a weak band at  $148\text{ cm}^{-1}$  in the Raman spectrum of the annealed Au NSs/ $\text{As}_2\text{S}_3$  film. Noteworthy is that for the initial (not annealed)  $\text{As}_2\text{S}_3$  film on the gold NSs A3, the band related to the As–S–As vibrations was detected at  $168\text{ cm}^{-1}$  (Fig. 2, curves 3 and 4). Based on the obtained results, it may be concluded that the concentration of molecular fragments with homopolar bonds in the annealed  $\text{As}_2\text{S}_3$  films is significantly lower than in the initial ones, but remains significant.

Fig. 4a shows the Raman spectra of the Se films deposited on the gold nanostructures A1 for various exposures by the excitation radiation with  $\lambda_{\text{exc}} = 532\text{ nm}$ . As can be seen from this figure, when the irradiation time increases, the spectrum changes significantly due to a partial transition of the illuminated volume of the film from the glass to the crystalline phase. This is due to the resonant excitation of plasmons in the gold NSs and related to it annealing of the adjacent film volume. At the same time, use of  $\lambda_{\text{exc}} = 671\text{ nm}$  for excitation of Raman spectra practically does not change the spectra during prolonged exposure (the spectrum is not shown).

Fig. 4b (curves 2 and 3) shows the Raman spectra of the Se films with the thickness of  $50\text{ nm}$  deposited on the gold NSs A2 and A3 measured under excitation by radiation with  $\lambda_{\text{exc}} = 671\text{ nm}$ . It is worth noting that the spectra of the Se films of other thicknesses deposited on the arrays of Au NSs could be registered as well. All of them contain an intense band at  $253\text{ cm}^{-1}$  and weak features at  $235$ ,  $185$ ... $188$ , and  $135\text{ cm}^{-1}$ . A similar Raman spectrum for amorphous Se was obtained in [29], but the micron-thick Se films were used in the latter work.

Note that for trigonal Se, the dominant band in the Raman spectrum is at  $237\text{ cm}^{-1}$ , while for  $\alpha$ -monoclinic and glassy Se at  $250\text{ cm}^{-1}$  [29–31]. Moreover, the spectra of  $\alpha$ -monoclinic Se show bands at  $111$ ... $115$  and  $187$ ... $189\text{ cm}^{-1}$ , and the spectra of trigonal and glassy Se show bands at  $143$  and  $140\text{ cm}^{-1}$ , respectively [29–31]. Therefore, the bands at the frequencies of  $253$  and  $107\text{ cm}^{-1}$  observed in our spectra in Fig. 4 may be attributed to vibrations in  $\text{Se}_8$  fragments, and the others to vibrations of atoms in the chain groups of  $\text{Se}_n$ . This means that similar to glasses and “thick” amorphous selenium films, the “disordered chain” model [32] is suitable for interpreting the structure of nanoscale Se films. According to this model, this structure is characterized by irregular sequences of *cis* and *trans* configurations, that is, one molecule can contain both  $\text{Se}_8$  ring elements and  $\text{Se}_n$  helical chain elements.



**Fig. 4.** (a) Raman spectra of the Se films deposited on the gold NSs A1 measured at  $\lambda_{exc} = 532$  nm and different exposure times; (b) Raman spectra of the Se films deposited on glass substrate (1); gold NSs A2 and A3 (2, 3), respectively, measured at  $\lambda_{exc} = 671$  nm.

It follows from our research that SERS amplification can be effectively applied for Raman diagnostics of vitreous  $As_2S_3$  and Se films with the thicknesses of only a few tens of nanometers. For this purpose, the investigated thin glass-like film is to be deposited on preliminarily formed arrays of gold nanostructures of the required shape and size exhibiting plasmon resonance at the wavelength used for excitation of the Raman spectra. Note that during Raman studies of such films, it is important to prevent their structural changes, which may be caused by photo and/or thermal effects. In particular, excitation of plasmon resonance in Au NSs by intense laser radiation can lead to significant heating of the probed film near the Au NSs. At the same time, as we have shown in our work, Raman spectra can be obtained from nanometer films only due to the chemical mechanism of SERS amplification without involvement of the plasmonic mechanism. This case allows us to analyze the peculiarities of the manifestation of this mechanism in the Raman spectra by considering the relative contribution of different vibrational modes.

#### 4. Conclusions

$As_2S_3$  and Se chalcogenide films with the thicknesses of several tens of nanometers on glass and SERS substrates based on gold nanostructures were obtained using the thermal sputtering method. The  $As_2S_3$  films deposited on glass are practically not detectable by ordinary Raman spectroscopy. The spectrum of the selenium films exhibits the bands of very low intensities. At the same time, use of gold NSs as the substrates enables reliable registration of Raman spectra of both  $As_2S_3$  and Se films with all the features usually manifested in the films with the thicknesses of 1  $\mu\text{m}$  or more.

Moreover, an enhancement of the Raman signal is observed even in the case when the plasmon resonance is not in resonance with the excitation wavelength  $\lambda = 671$  nm. It is concluded therefore that the main contribution to the enhancement of the Raman signal from chalcogenide films is provided by the chemical mechanism, presumably due to the involvement of the Fermi level of the gold NSs in the resonant Raman scattering in the chalcogenide. Additional adjustment of the parameters of SERS substrates to tune their plasmon in resonance with the excitation laser radiation allows one to increase the enhancement factor. It is shown that  $As_2S_3$  and Se chalcogenide films are quite sensitive to photo- and thermal excitation leading to rearrangement of the local structure, which can in turn affect the other film properties.

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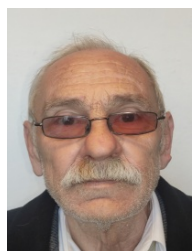
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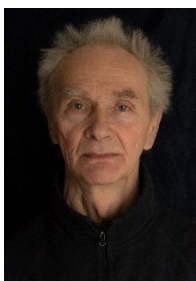


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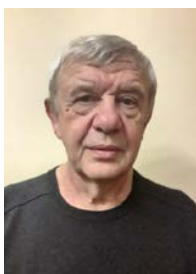
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**Поверхнево-підсилене раманівське розсіювання  $As_2S_3$  та Se тонких плівок, сформованих на Au наноструктурах**

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**Анотація.** Досліджено вплив плазмонних наноструктур (НС) на спектри раманівського розсіювання світла та структурні зміни в тонких халькогенідних плівках. Плівки  $As_2S_3$  і Se товщиною кілька десятків нанометрів були осаджені методом термічного напилення на SERS-підкладки, сформовані на основі золотих наноструктур, та, для порівняння, на скляні підкладки. Плівки на склі практично не реєструються за допомогою раманівської спектроскопії, водночас використання в ролі SERS підкладок золотих НС дозволяє надійно реєструвати спектри плівок  $As_2S_3$  і Se з наявними в них усіма особливостями, які зазвичай проявляються тільки при дослідженні плівок товщиною  $\sim 1$  мкм або більше. На підставі нашого аналізу спектрів, отриманих з використанням випромінювання з різними довжинами хвиль, зроблено висновок, що основний внесок у підсилення раманівського сигналу від халькогенідних плівок дає хімічний механізм SERS. Варіювання параметрів SERS підкладок для налаштування положення плазмонної смуги в резонанс зі збуджуючим випромінюванням дозволяє збільшити внесок плазмонного підсилення. Окрім ефекту підсилення, локалізований плазмонний резонанс у золотих НЧ викликає локальне нагрівання халькогенідної плівки навколо НЧ, що може приводити до локальних структурних перетворень, які можна контролювати за допомогою раманівських спектрів.

**Ключові слова:** раманівське розсіювання, SERS, тонкі плівки, сульфід арсену, селен, золоті наноструктури.