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SHAPE EFFECT OF LATERALLY ORDERED NANOSTRUCTURES ON THE EFFICIENCY OF SURFACE-ENHANCED RAMAN SCATTERING

Bigratings of two types, with laterally arranged domes or holes, are formed on relief-forming chalcogenide layers $As_{10}Ge_{30}S_{60}$ using the interference photolithography method. Coating such bigratings with aluminum (80 nm), silver (70 nm), and gold (10 nm) layers makes it possible to obtain surface-enhanced Raman scattering (SERS) substrates of two types. Changes in the surface morphology of SERS substrates during the process of their formation are studied using the atomic force microscopy. It is shown that the periods of SERS substrates of both types are about 1200 nm, and the holes' depth and the domes' height are about 350 nm. The subsequent deposition of metal layers on the formed reliefs had little effect on the holes' diameters and the domes' dimensions. The measurements of the spectral-angular dependences of the polarized light reflection from the formed SERS substrates in a wavelength interval of 0.4–1.1 μm and at incidence angles of 10–70° demonstrated the excitation of both local plasmon resonances (in the structures with domes) and plasmon-polariton surface waves (in the structures of both types) in those substrates. It is shown that the formed structures with laterally ordered domes and holes are effective SERS substrates. It is found that the structures with domes used to excite the Raman spectra of the laser radiation with wavelengths of 457, 532, and 671 nm are an order of magnitude more effective when enhancing the Raman signal from the standard R6G analyte. It occurs, because, when the exciting laser radiation is normally incident on the structures with domes, localized plasmons are effectively excited in spectral intervals with maxima at 488 and 676 nm, whereas such features were not observed in the absorption spectra of the structures with holes.

Keywords: SERS, Raman spectroscopy, bigratings, localized plasmon resonance, surface plasmon resonance, atomic force microscopy (AFM), interference photolithography.

1. Introduction

Surface-Enhanced Raman Scattering (SERS) spectroscopy is an effective analytical method that has been intensively developed during the last two decades [1–6] and finds more and more applications for the diagnosis of substances in chemistry [7], in medicine [8], biology [9], ecology and criminology [10], art [11], and other domains. The giant amplification of the Raman signal (up to 10^{14} times [12]) can be achieved using two mechanisms: 1) excita-

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tion of surface plasmon resonances in metal (usually gold or silver) nanostructures formed (e.g., deposited) on the surface of SERS substrates [13]; and 2) the mechanism of chemical amplification [14], where electrons tunnel from metal nanostructures into analyte molecules, thereby changing the electronic structure of the molecule-metal nanoparticle system and, accordingly, the polarization of molecules.

To realize effective amplification of the Raman signal from analytes, both local surface plasmon resonances (LSPRs) [13], which are excited in metal nanoparticles or rough metal film irregularities, and surface plasmon polaritons (SPPs) [15] are used. The latter are excited at the surface of metal films using prisms in the Kretschmann and Otto configuration [16] or periodic one-dimensional or binary structures (gratings) with a metal film deposited on their surface. It is worth noting that the Kretschmann and Otto techniques [16] are used more often, because the application of prisms makes the implementation of resonance excitation conditions easier and, finally, cheaper as compared with gratings. On the other hand, by varying the grating parameters, namely, its period a and the relief modulation depth h/a , where h is the ridge height, it is possible to choose the conditions under which the LSPR and the SPP resonance will be realized simultaneously or to achieve the required surface plasmon excitation angle.

Another important point concerning providing conditions for effective amplification of various analytes is the creation of a large number of the so-called “hot spots” on SERS substrates. The research of SERS mechanisms [17] showed that, in many cases, the main contribution to the amplification of the Raman signal from analytes is given just by hot spots. Thus, it can be asserted that the efficiency of SERS spectroscopy depends mainly on the morphology of the partially or completely metalized SERS substrate surface onto which the analyzed substances are deposited. Moreover, for the application of SERS to be effective, it is necessary to develop substrates that would be characterized by chemical stability, a high amplification factor, lateral homogeneity, and relative ease of manufacture.

Nowadays, many various types of SERS substrates are known. The most widespread of them are based on laterally ordered [18] or disordered [19,20] arrays of silver or gold nanoparticles deposited onto dielectric wafers. However, their fabrication, as a rule, requires

a high-tech equipment and is rather expensive. SERS substrates in the form of plates with a surface relief can be cheaper; they can be replicated by stamping and afterward covered with a metal layer. The simplest technology for the manufacture of such plates with a required surface relief is interference lithography. In our previous studies, it was shown that this technology with the application of high-resolving chalcogenide photoresist is promising for the formation of one- and two-dimensional submicronic periodic structures on the surface of semiconductors and insulators [21]. Wafers with the surface relief of two types can be used as SERS substrates: in the form of laterally ordered arrays of either cavities (holes) or bumps (domes); see Fig. 1. Depending on the morphologic parameters of such structures (the spatial period and the modulation depth), LSPRs and/or SPPs can be excited in them.

In this work, a comparative study is performed concerning the SERS parameters of the substrates of those two types, as well as their efficiency of Raman signal amplification on the standard R6G analyte.

2. Experimental Part

Laterally ordered relief structures for SERS substrates were formed by means of the interference photolithography method and applying a two-layer chalcogenide photoresist [22]. An adhesive Cr layer 30 nm in thickness, a relief-forming layer of $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ 700 nm in thickness, and a photosensitive layer of $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ 100 nm in thickness were successively deposited onto polished glass plates using the thermal evaporation in a vacuum of 2×10^{-3} Pa. The thickness of the layers was monitored with the help of a quartz thickness gauge KIT-1 during the film deposition, and with the help of an MII-4 microinterferometer after the deposition.

The interference structures on the $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ film were registered using the interference patterns obtained from the radiation of a helium-cadmium laser ($\lambda = 441.6$ nm). When registering two-dimensional matrices of holes or domes, a double scanning of specimens was carried out. Before the second scanning, the specimen was rotated by 90° around the normal to its surface. After the scanning process, the selective liquid etching of the $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ layer was carried out in order to form a lithographic mask with holes (their size depended on the etching time) that reached the surface of the $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ layer. At this stage, the se-

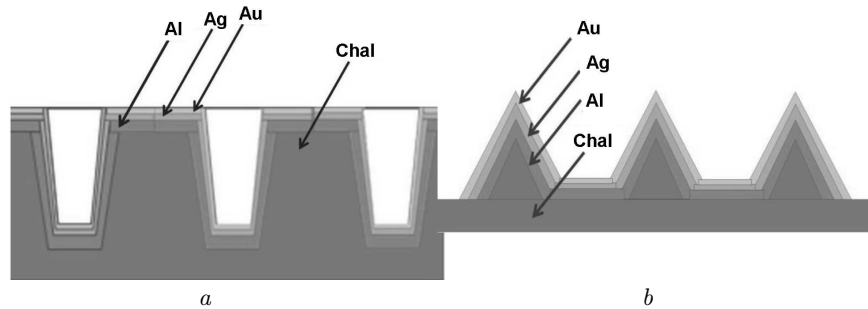


Fig. 1. Schematic images of formed reliefs on SERS substrates of two types: with holes (a) and with domes (b). Designations: Chal is a relief-forming $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ layer 700 nm in thickness, Al is an aluminum layer 80 nm in thickness, Ag is a silver layer 70 nm in thickness, and Au is a gold layer 10 nm in thickness

lective etchant of photoresist $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ was used, which did not dissolve the relief-forming $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ layer.

The next stage included the relief formation by etching through the holes in the lithographic mask, but in a solvent for $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ that did not dissolve the photoresist. The shape of the elements in the obtained periodic structures (holes or domes) was mainly determined by the etching time at this stage of the technological process. Etching of the photoresist and the relief-forming layer was monitored *in situ* by registering the non-photoactive long-wave radiation diffracted from the relief structure. After removing the remnants of the $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ photoresist, washing and drying the specimens, formed periodic $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ -based structures were obtained.

The obtained periodic structures were covered with an Al layer 80 nm in thickness, which was then covered with an opaque 70-nm Ag layer and a 10-nm Au layer (the indicated metal layers were deposited using the method of thermal deposition in vacuum); see Fig. 1. The aluminum layer was deposited in order to prevent the diffusion of silver into the relief-forming chalcogenide layer and its subsequent interaction with the latter. Deposition of the thin gold layer prevented the oxidation of silver during the measurements. The manufacturing technique of such structures was described in more details in our work [23].

To determine the profile shape and the size of the relief elements in the obtained periodic structure, a Dimension 3000 Scanning Probe atomic force microscope (Digital Instruments Inc., Tonawanda, NY, USA) was used. The spatial frequency of periodic relief structures was determined with an accuracy of

± 1 line/mm on an optical stand based on a G5M goniometer.

The optical properties of manufactured structures were studied by measuring the spectral-angular dependences of the polarized light reflection in a wavelength interval of 0.4–1.1 μm and for incidence angles within an interval of 10–70°. The automated installation for performing such measurements consisted of an illuminator, a mechanical light modulator, a monochromator with a Glahn prism at its output, and a rotary stage for specimens. The intensity of the light specularly reflected from a specimen was measured by means of a silicon photodetector, whose output signal, after the amplification and demodulation, was fed to the input of an analog-to-digital converter. Such spectrometric measurements made at several angles of light incidence allow the dispersion dependences of excited optical modes to be plotted and their nature to be identified.

The specular reflection spectra of the specimens at the normal light incidence were studied on a StellarNet Silver Nova 25 BWI6 spectrometer. Raman spectra were excited by the radiation emitted from solid-state lasers with wavelengths of 457, 532, and 671 nm and registered on a single-stage spectrometer MDR-23 (LOMO) equipped with a cooled CCD detector (Andor iDus 420, UK). In order to prevent heat-induced modifications of the specimens during their research, the power density of laser radiation at the specimens was lower than 10^3 W/cm^2 . The spectral resolution of the spectrometer was determined using the width of the phonon band from a monocrystalline silicon substrate, and it amounted to 3 cm^{-1} . The frequency position of the phonon band from Si (521.0 cm^{-1}) was applied as a ref-

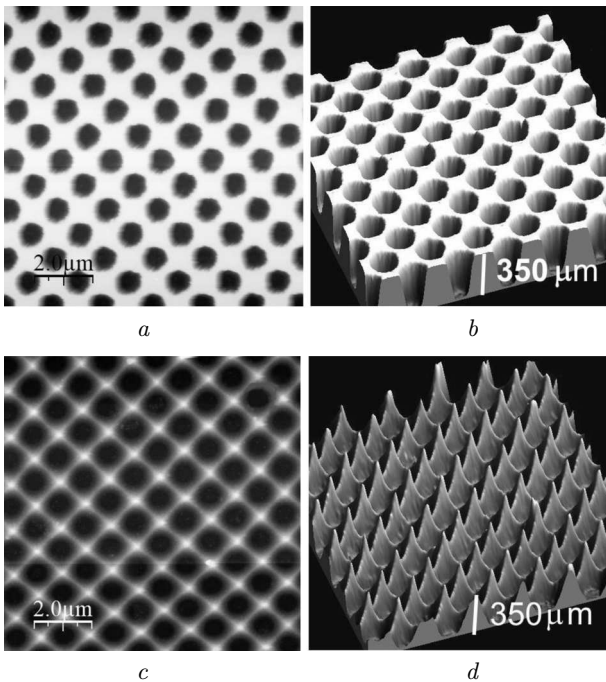


Fig. 2. AFM images of researched SERS substrates: specimen with holes (top view) (a), specimen with holes (side view) (b), specimen with domes (top view) (c), and specimen with domes (side view) (d)

erence while determining the frequency positions of other Raman bands.

3. Results and Their Discussion

Figure 2 demonstrates an AFM image of two SERS substrates with the surface relief in the form of laterally ordered arrays of holes (panels a and b) and domes (panels c and d). Both SERS substrates have the same spatial arrangement period of elements in mutually perpendicular directions, which is equal to 1200 ± 1 nm (the spatial frequency $\nu = 833$ nm⁻¹). The difference is that the etching time of the relief-forming As₁₀Ge₃₀S₆₀ layer for the specimen whose surface morphology is shown in Figs. 2, a and 2, b was 8 min, and that for the specimen with domes (Figs. 2, c and 2, d) was 15 min, which led to the formation of reliefs with different shapes. For the illustrated SERS substrates (Figs. 2, a and 2, b), the relief depth $h \approx 350$ nm, and the ratio between the relief depth and the structure period d (the relief modulation depth) equals $h/a \approx 0.33$.

As was shown by AFM studies, the deposition of metal layers [aluminum (80 nm), silver (70 nm), and

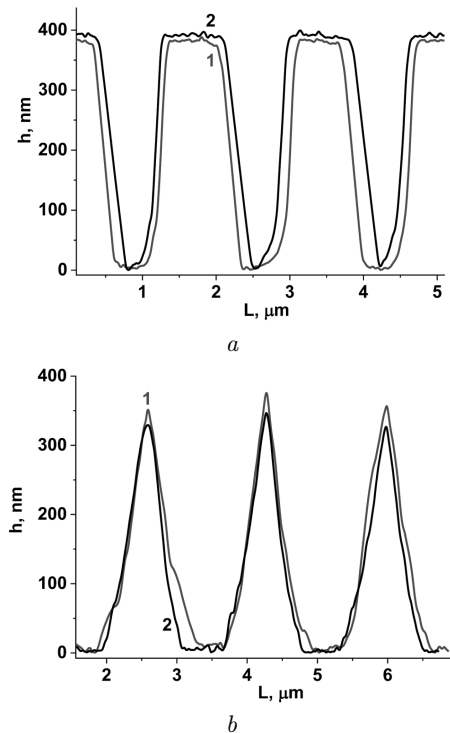


Fig. 3. Reliefs of formed structures before (curves 1) and after (curves 2) the sputtering deposition of metal layers: with holes (a) and with domes (b)

gold (10 nm)] decreased the width of the holes by 10–15%, with the relief depth remaining almost unchanged (Fig. 3, a). As for the domes, their height increased by 10–15%, whereas the lateral dimensions increased by only 5% (Fig. 3, b).

As mentioned above, the Al film 80 nm in thickness prevented the silver atoms from penetrating into the chalcogenide layer and reacting with it. The next layer (70-nm, silver) covering the aluminum one played a major role in the excitation of plasmon resonances – in particular, LSPRs – in the holes and the domes' tops, as well as SPPs at the surface of the periodically profiled silver film. The top layer (10-nm, gold) played a dual role. On the one hand, it was a protective layer that did not allow silver to be oxidized; on the other hand, it slightly shifted the plasmon absorption band toward the long-wavelength region. It is important to note that both LSPR and SPP excitation are possible in such metalized periodic structures.

With regard for the sufficient total thickness of the metal layers on the surface of examined structures

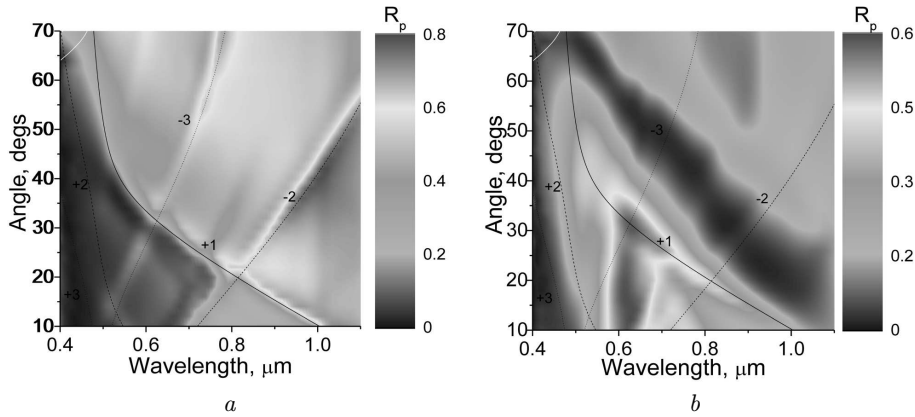


Fig. 4. Spectral-angular dependences of the light reflection by a periodic binary structure of holes (*a*) and domes (*b*) with a period of 1200 nm, with superimposed dispersion dependences of surface plasmon-polariton modes at the air/silver interface calculated for $m = +1, -2, +2$, and -3

(~ 160 nm), plasmon resonances can be excited only at the metal layer-air interface, if the specimen is illuminated from the metal side. The condition for the SPP excitation is the conservation of the quasi-momentum with making allowance for the components of the wave vectors of incident radiation ($k_0 = 2\pi/\lambda$, where λ is the incident radiation wavelength) and plasmon-polaritons (k_{SPP}) that are parallel to the surface of the periodic structure, as well as the reciprocal structure vector ($G = 2\pi/a$, where a is the spatial period of the structure). The researched structures (see Fig. 2) were matrices symmetric with respect to the rotation by 90° and consisting of mutually perpendicular rows of holes (or domes). If the incidence plane of p -polarized excitation radiation is oriented perpendicularly (in parallel) to those substrate rows, the SPP excitation condition can be written in the scalar form as follows [24]:

$$\text{Re } k_{\text{SPP}} = nk_0 \sin \theta \pm mG, \quad (1)$$

where $\text{Re } k_{\text{SPP}}$ is the real part of k_{SPP} , θ is the light incidence angle, m is an integer number ($m \neq 0$) denoting the SPP diffraction order, and n is the refractive index of the environment.

For an approximate estimate of the SPP wave vector value, the expression obtained for the flat interface between semiinfinite media is often used [24]. In this approximation, formula (1) makes it possible to determine the incidence angle at which the SPPs are excited at a given incident radiation wavelength, i.e., to plot the $\theta(\lambda)$ dispersion dependences for SPPs excited

at the metal/air interface. In the calculations, the optical constants of silver were taken from work [25].

The excitation of SPPs in relief periodic structures (gratings or bigratings) with a small relief modulation depth ($h/a < 0.2$) manifests itself as a minimum in the angular or spectral dependence of specular reflection [26]. For structures with larger h/a -values (as for our both examined specimens), this minimum “degrades”, and the plasmon resonance can manifest itself in the form of a sharp variation of the reflection value or its maximum.

Figure 4 demonstrates the measurement results obtained for the spectral-angular dependences of the specular reflection R_p of p -polarized radiation from the studied SERS substrates in the form of matrices of holes (panel *a*) and domes (panel *b*). The plane of radiation incidence at those measurements was oriented perpendicularly (in parallel) to the rows formed in the SERS substrates. From Fig. 4, *a*, one can see that the SPP excitation of orders $+1, -2$, and $+2$ was observed for the specimen with holes. Some deviations of the calculated curves from the experimental results are associated with the application of the “shallow relief” approximation in the calculations and with the neglect of the influence of the thin Au layer (10 nm) that covered the Ag one (70 nm).

The matrix of domes (Fig. 4, *b*) demonstrated only the SPP excitation of the order $+1$ in the restricted spectral-angular interval ($0.6 \mu\text{m} \leq \lambda \leq 1 \mu\text{m}$, $10^\circ \leq \theta \leq 37^\circ$). In addition, in the same angular interval, one can observe an intensive reflection

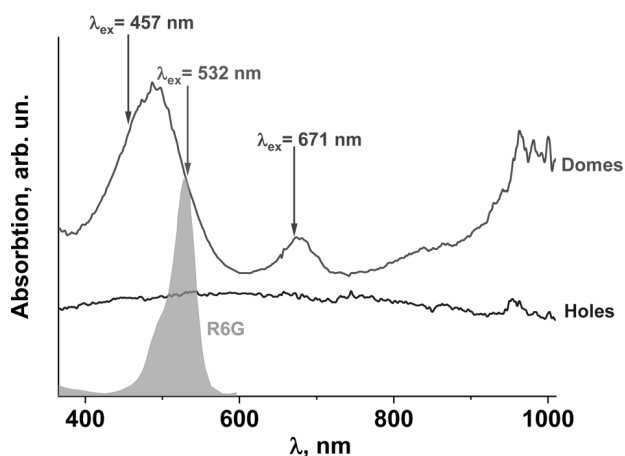


Fig. 5. Absorption spectra of bigratings with domes and holes, and the absorption spectrum of the analyte (rhodamine 6G). The arrows mark the wavelengths of laser radiation used to excite the Raman spectra

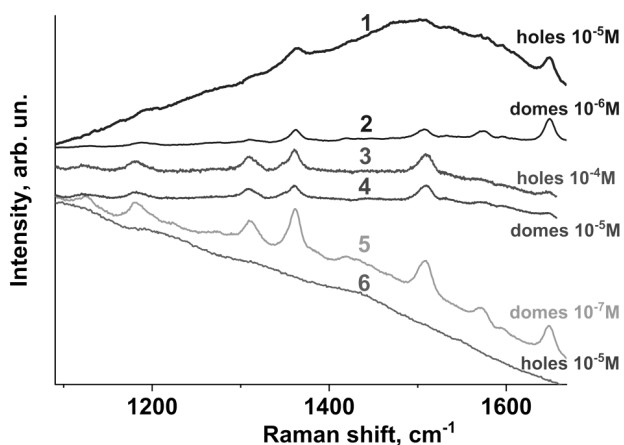


Fig. 6. Raman spectra of the standard R6G analyte with various concentrations deposited onto the SERS substrates with domes and holes. Excitation was performed by laser radiation with various wavelengths: 457 (1 and 2), 671 (3 and 4), and 532 nm (5 and 6)

band in the spectral interval $0.57 \mu\text{m} \leq \lambda \leq 0.7 \mu\text{m}$, whose spectral position practically did not change when the incidence angle was varied. This feature is typical of the LSPR excitation in metalized periodic structures [27]. Hence, it can be asserted that the studied specimens showed the excitation of both local plasmon resonances (in the matrix of domes) and plasmon-polariton surface waves (in both specimens). It is known [26] that the dependence of the SPP excitation efficiency on the quantity h/a has a maximum, i.e., there is an optimal h/a -value at which

the energy transfer from the incident electromagnetic wave to the surface plasmon-polariton mode is maximum. For silver, this value equals 0.042 [28], which is significantly lower than the modulation depth of the studied specimens. Therefore, the efficiency of the SPP excitation in the researched periodic structures was low.

As mentioned above, the spectral-angular dependences of R_p , which are shown in Fig. 4, were obtained within the interval of light incidence angles from 10° to 70° . But, the Raman spectra of those SERS substrates were studied at the normal incidence of excitation radiation. Therefore, the reflection spectra of the researched specimens were measured at $\theta = 0^\circ$ as well. In Fig. 5, the absorption spectra of bigratings with domes and holes, as well as the absorption spectrum of rhodamine 6G, are shown. The arrows point the spectral regions to which the exciting laser radiation belongs. Namely, the laser radiation with wavelengths of 457 and 532 nm had frequencies within the band of the localized plasmon resonance at the SERS substrate with domes, and the frequency of radiation with $\lambda = 671$ nm belongs to another, less intensive absorption band. Therefore, we expected that if the Raman spectra from the R6G analyte are excited by means of radiation with the indicated wavelengths, the Raman signals would be amplified. At the same time, the SERS substrate with holes was characterized by an absorption spectrum without local maxima.

Figure 6 demonstrates the Raman spectra registered at minimum concentrations of the standard R6G analyte deposited onto the SERS substrates with domes and holes, and excited by means of laser radiation with various wavelengths. As the research showed, the minimum concentration of the R6G analyte (10^{-7} M) was registered on the SERS substrate with domes if the spectrum was excited by means of radiation with $\lambda = 532$ nm. At the same time, under the same conditions, no Raman spectrum at all was registered from the SERS substrate with holes at an R6G concentration of 10^{-5} M (Fig. 6, curve 6). On the one hand, this is a result of the absence of a local plasmon absorption band (Fig. 5) that would stimulate a considerable plasmon amplification of the Raman signal for these gratings; on the other hand, this is a manifestation of intensive photoluminescence (PL) of rhodamine 6G. Photoluminescence from R6G also manifested itself on the SERS substrate with

domes. However, a more substantial amplification of Raman modes in this case allowed us to register Raman bands against the background of intensive PL (Fig. 6, curve 5).

When Raman spectra were excited by means of the radiation with $\lambda = 457$ nm, signals from R6G with concentrations of 10^{-6} M and 10^{-5} M were registered on the SERS substrates with domes and holes, respectively. This means that, for a reliable registration of Raman spectra on SERS substrates with holes, the R6G analyte with a concentration by an order of magnitude higher must be deposited. In this case, the Raman spectrum can be distinguished well against the intensive PL background, although not all Raman bands clearly manifest themselves (Fig. 6, curve 1).

At the same time, it should be noted that, in the case of the SERS substrate with domes, if the spectra were excited by radiation with $\lambda = 457$ nm, the R6G analyte was registered, only if it was deposited with a concentration of 10^{-6} M, i.e., an order of magnitude higher as compared to the case where the spectra were excited by radiation with $\lambda = 532$ nm. This fact is well understood, because at $\lambda = 532$ nm, besides the plasmon amplification, there is also the amplification owing to the classical resonance Raman scattering.

When the Raman spectra from the R6G analyte were excited using radiation with $\lambda = 671$ nm, the signal amplification for both domes and holes was weaker in comparison with those described above. In this case, reliably registered were signals from R6G on the SERS substrates with domes and holes with concentrations of 10^{-5} M and 10^{-4} M, respectively. The amplification reduction of the signal from R6G by an order of magnitude when using radiation with $\lambda = 671$ nm can have two origins. First, under non-resonance conditions, if the power densities of the exciting laser radiation are identical, the intensity of the Raman signal is proportional to the fourth power of the laser radiation frequency, whence it follows that the shorter the wavelength, the higher the intensity of the Raman bands. Second, as one can see from Fig. 5, in the case of domes, the intensity of the plasmon absorption band at 671 nm is substantially lower than the intensities of the corresponding bands at 457 and 532 nm, so the plasmon amplification of Raman signals will be substantially lower.

It is also worth noting that the morphology of the formed SERS substrates of both types does not favor the formation of hot spots. The latter can consid-

erably enhance the amplification factor for Raman signals from analytes. To some extent, the tops of the domes can mimic them, but their surface density is very low. Therefore, in the future, it is necessary to develop substrates with the nanostructured upper metal layer.

4. Conclusions

In this work, the possibility of the formation of SERS substrates with laterally ordered domes or holes using the interference photolithography method has been demonstrated. The surface morphology of the SERS substrates was determined with the help of the AFM method. In particular, it is shown that the grating periods in both cases are equal to 1200 nm, and the depth of the holes and the height of the domes are equal to about 350 nm. The subsequent deposition of aluminum (80 nm), silver (70 nm), and gold (10 nm) layers practically did not change the depth of the holes and the height of the domes, but it led to a reduction in the holes' diameters by 10–15% and a slight ($\sim 5\%$) increase in the domes' sizes.

By studying the optical properties of the manufactured structures via measuring the spectral-angular dependences of the polarized light reflection in a wavelength interval of 0.4–1.1 μm and an incidence angle interval of 10–70°, it is shown that the excitation of both local plasmon resonances (the structures with domes) and plasmon-polariton surface waves (in the structures of both types) can be observed on the formed SERS substrates.

It is demonstrated that the formed structures with laterally ordered domes and holes are effective SERS substrates, and the structures with domes enhance the Raman signal from the standard analyte R6G more efficiently (by an order of magnitude higher). This discrepancy follows from the fact that if the exciting laser radiation is normally incident on the SERS substrate, the surface of which is an ensemble of domes, localized plasmons are effectively excited in spectral intervals with maxima at 488 and 676 nm, whereas such features do not manifest themselves in the absorption spectrum of the SERS substrate with holes.

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**ВПЛИВ ФОРМИ
ЛАТЕРАЛЬНО-ВПОРЯДКОВАНИХ
НАНОСТРУКТУР НА ЕФЕКТИВНІСТЬ
ПОВЕРХНЕВО-ПІДСИЛЕНОГО
РАМАНІВСЬКОГО РОЗСІЮВАННЯ**

Методом інтерференційної фотолітографії на рельєфоутворюючих халькогенідних шарах As₁₀Ge₃₀S₆₀ сформовано два типи біграток з латерально-впорядкованими куполами та лунками. Покриття таких біграток шарами алюмінію (80 нм), срібла (70 нм) та золота (10 нм) дозволило отримати два типи SERS підкладінок. Методом атомної силової мікроскопії досліджено зміни морфології поверхонь SERS підкладінок в процесі їх формування. Показано, що періоди обох типів SERS підкладінок становлять ~1200 нм, глибини лунок і висоти куполів дорівнюють ~350 нм. Насту-

пне осадження на сформовані рельєфи шарів металів незначно впливає на діаметри лунок та розміри куполів. Вимірювання спектрально-кутових залежностей відбиття поляризованого світла від сформованих SERS підкладінок в діапазоні довжин хвиль 0,4–1,1 мкм та кутів падіння 10–70° продемонструвало, що на цих підкладінках спостерігається збудження як локальних плазмонних резонансів (на структурах з куполами), так і плазмон-поляритонних поверхневих хвиль (на обох типах структур). Продемонстровано, що сформовані структури з латерально-впорядкованими куполами та лунками є ефективними SERS підкладінками. Встановлено, що структури з куполами на порядок ефективніше підсилюють раманівський сигнал від стандартного аналізу R6G при використанні для збудження раманівських спектрів лазерного випромінювання з довжинами хвиль 457, 532 та 671 нм. Цей факт зумовлений тим, що при нормальному падінні збуджуючого лазерного випромінювання на структурах з куполами ефективно збуджуються локалізовані плаزمони в спектральних областях з максимумами 488 та 676 нм, а для структур з лунками, згідно з їхніми спектрами поглинання, такі особливості не спостерігаються.

Ключові слова: SERS, раманівська спектроскопія, бігратки, локалізований плазмонний резонанс, поверхневий плазмонний резонанс, атомна силова мікроскопія (АСМ), інтерференційна фотолітографія.