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The effect of surface plasmon-polaritons on the photostimulated diffusion in light-sensitive Ag–$As_4Ge_{30}S_{66}$ structures

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Abstract. The effect of surface plasmon-polaritons (SPPs) excited at the interface between the profiled surface of the silver layer (in the form of a diffraction grating) and the $As_4Ge_{30}S_{66}$ layer on the photostimulated diffusion of silver into chalcogenide has been studied. The gratings with the period a = 519 nm and modulation depth $h/a \approx 0.037$ (where h is the grating depth) were formed on chalcogenide photoresist films by using interferential lithography and covered with the 80-nm-thick aluminum layer, 85-nm-thick silver layer, and thin $As_4Ge_{30}S_{66}$ layer. Photostimulated changes in this structure were studied measuring the angular dependences of specular reflection (R_p) of p-polarized light with the wavelength 632.8 nm. It was found that as a result of exposure, "degradation" (broadening, increase in reflection at the minimum) of the minimum in the angular dependence of R_p (which is associated with the SPP resonance) occurs faster, when the samples are irradiated at the angle corresponding to SPP excitation. This observation indicates acceleration of the photostimulated diffusion process in this structure under the plasmon field action.

Keywords: surface plasmon-polariton, photostimulated diffusion, chalcogenide glass, Ag, $As_4Ge_{30}S_{66}$.

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1. Introduction

Surface plasmon-polariton (SPP), or surface plasma wave, is an electromagnetic wave that propagates along the interface between a metal and a dielectric material. SPPs are characterized by localization of the electromagnetic field near the interface, where the electromagnetic field strength is much higher than that of the exciting radiation.

The first plasmonic structures on which excitation of SPPs was observed (the so-called "Wood's anomalies" [1], which were later explained by Fano [2]) were diffraction gratings. In two recent decades, fundamental research and development of devices based on SPP has attracted more and more attention [3]. Enhancement of the electromagnetic field near the metal film or nanostructure due to plasmon excitation is widely used in biosensors and chemical sensors [4, 5], surface-enhanced Raman scattering [6], data storage [7, 8], solar cells [9], and subwavelength optics [10]. It was found that the plasmon field of gold nanoparticles affects the light-induced transformations in chalcogenide glass (ChG) films. It accelerates photodarkening, photobleaching, optical recording, mass transfer efficiency, and surface nanostructuring [10–12].

Acceleration of silver photostimulated diffusion into ChG films was also observed under the action of the SPP field, which was excited at the interface between the profiled surface of the silver layer (in the form of a diffraction grating) and the chalcogenide layer upon exposure of the thin-layer Ag–ChG structure [13, 14]. The phenomenon of photostimulated diffusion in Ag–ChG structures has been studied for several decades [15–18]. On its basis, high-resolution optical recording media and technologies for their practical application as an inorganic resist [19], media for holography and interferential lithography [20] for information recording [21] *etc*. have been developed. As a result of studying the mechanism of photostimulated diffusion [15, 16], it was found that the first and decisive stage of this phenomenon is the absorption of photoactive light in the region of the Ag-ChG interface, and the intensity of the Ag photodiffusion process depends on the light intensity at this interface. The intensity of the electromagnetic field in the interface region can be increased by exciting of SPP, which accelerates the photostimulated processes.

In the previous works [13, 14], we investigated photostimulated diffusion under conditions of SPP excitation in the most studied Ag–$As_{40}S_{60}$ structure, which is commonly used as the model one. However, photosensitive structures, in which films of germanium chalcogenides or ternary compounds based on germanium chalcogenides with a low arsenic content have been used, are of wider practical interest. These structures are mechanically and thermally more stable and surpass arsenic compounds in compliance with environmental requirements. Therefore, in this work, we investigated the effect of SPP excitation on the photostimulated diffusion of silver for Ag–ChG structures with thin (5…13 nm) $As_4Ge_{30}S_{66}$ layers.

2. Experimental

To prepare the object for studying, an adhesion layer of Cr with a thickness of 30 nm was thermally deposited on polished glass plates in vacuum, then a layer of chalcogenide photoresist $As_{40}S_{30}Se_{30}$ with the thickness close to 300 nm. After exposure to some interferential pattern formed by two coherent beams of radiation from a helium-cadmium laser (wavelength 441.6 nm) and selective etching in a solution based on amines, a periodic relief structure with a given spatial period and optimal depth of the grating relief was formed on the surface of the photoresist layer. The manufacturing technique for such gratings is described in detail in our previous works (see, for example, [22]).

On the obtained profiled substrate, also by thermal evaporation in vacuum, layer of Al 80-nm-thick, Ag layer 85-nm-thick, and a thin layer (5 to 13 nm) of the $As_4Ge_{30}S_{66}$ were deposited successively. Thermal evaporation of the chalcogenide was carried out using a labyrinth-type molybdenum evaporator, which made it possible to reproduce the ChG stoichiometry in the deposited film with sufficient accuracy (about 1 at.%). The Al layer prevented diffusion of silver into the bottom layer of the chalcogenide photoresist.

During deposition, the film thickness was controlled using the graduated quartz crystal microbalance, and after deposition it was measured using an MII-4 microinterferometer and an LEF-3M-1 ellipsometer. A Dimension 3000 Scanning Probe Microscope of atomic forces (Digital Instruments Inc., Tonawanda, NY, USA) was used to determine the grating groove profile and the depth of the grating relief.

Fig. 1 schematically shows the sample cross-section by the plane perpendicular to the grooves of the grating (*i.e.*, in the plane of incidence of both exposing and probing light beams).

To observe the photostimulated diffusion of silver in the Ag–$As_4Ge_{30}S_{66}$ structures, the samples were exposed from its $As_4Ge_{30}S_{66}$ side by *p*-polarized radiation of a He-Ne laser (λ = 632.8 nm). SPP was registered in the exposed structures by measuring the dependences of specular reflection (R_p) of *p*-polarized radiation of the same He-Ne laser on the angle of incidence θ, which was defined as the angle between the normal to the substrate plane and the laser beam. Both exposure and registration of SPP were carried out using a stand mounted on the base of a G5M goniometer and a FS-5 Fedorov's table.

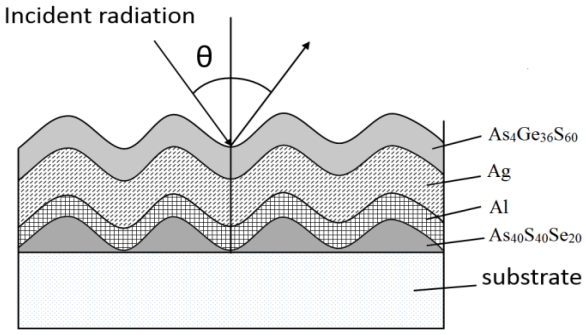

Fig. 1. Cross-section of the multilayer $As_{40}S_{40}Se_{20}$–Al–Ag–$As_4Ge_{30}S_{66}$ grating with the correlated relief.

This enabled to change the angle of incidence θ between 0° and 90° with the 0.01° accuracy. The sample was oriented so that the grating grooves were perpendicular to the plane of incidence of light (azimuthal angle φ = 0°, setting accuracy 0.1°). The power density of the light incident on the sample was $I_p^0\cos\theta$, upon exposure, I_p^0 was 32 mW/cm^2, and, while registering SPP, it was 0.3 mW/cm^2 to reduce the effect of the probe light on the studied photosensitive structure.

3. Results and discussion

To excite SPP at the interface between the silver grating and dielectric medium, it is necessary to match the projection of the light's wave vector ($k_0 = 2\pi/\lambda$, λ is the wavelength of the incident radiation) upon the surface of the sample, with the wave vector of SPP (k_{SPP}), and the grating vector ($G = 2\pi/a$, a is the grating period). When the plane of incidence of the exciting radiation is oriented along the perpendicular to grating grooves, this matching condition can be written in the scalar form [23]:

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

where $\mathrm{Re}(k_{SPP})$ is the real part of the complex wave vector of SPP, $n = \sqrt{\varepsilon}$ – refractive index of the environment with a dielectric constant ε, $m \neq 0$ is an integer that denotes the diffraction order (we used the value m = 1 only). In our case, the depth of the grating groove (h) for the samples, on which the photostimulated diffusion was studied, was significantly smaller than its period. Thus, for an approximate estimate of the SPP wave vector, one can use the expression obtained for a plane interface of semi-infinite media [3].

The equation (1) relates the resonance angle of incidence θ_r, at which SPP can be excited for the selected wavelength and given dielectric constants of the metal and medium, with the grating period. For the measurement convenience, it was necessary to limit ourselves to small values of θ_r (within the range 10…30°). In our case, the measurements were carried out in air, and to provide the specified interval θ_r, silver gratings with a period within the range 740 to 1180 nm, or 414 to 526 nm are required. When performing these calculations, the value ε for Ag was taken from [24] ($\varepsilon_{Ag} = -18.28 + i\cdot 0.481$), and for air $\varepsilon = n = 1$.

Taking these results into account, a series of Ag grating samples was prepared, in which the grating period was 519 nm and the groove depth varied from 5 to 80 nm. The resonant angle of incidence of the laser beam onto this Ag grating for the above values ε and ε_{Ag}, according to Eq. (1), is θ_r = 11.04°. Fig. 2 shows the angular dependences of the specular reflection of *p*-polarized light with the wavelength 632.8 nm from these samples with various groove depths: *h* = 5 nm (1), 11 (2), 19 (3), 37 (4), 51 (5), 77 (6). For the sample with the smallest relief depth (curve *1*), a narrow minimum of R_p is observed at the angle of incidence 10.8°, which is close to the calculated θ_r value.

The observed minimum of R_p (Wood's anomaly) is caused by SPP excitation at the silver layer's upper boundary, and this minimum deepens (Fig. 2, curves *1*–*3*) with increasing the grating modulation depth (*h*/*a*) and reaches the smallest reflection at the minimum (about 0.01) for *h*/*a* ≈ 0.037 (*h* = 19 nm). In this range of groove depths, the position of the minimum of R_p (the value of θ_r) shifts slightly in the direction of the smaller θ with increasing *h*. With a further increase in the depth of the grating relief (Fig. 2, curves *4*–*6*), a decrease in the resonance depth, an increase in its half-width and a more significant shift of θ_r toward smaller angles of incidence are observed. A decrease in the resonance depth indicates a decrease in the efficiency of SPP excitation, and at values *h*/*a* > 0.17 (not shown) the minimum of R_p is not observed at all.

At θ = 12.7°, another anomaly is observed in the angular dependence of R_p (Fig. 2) – a sharp decline in reflection associated with the appearance of the first diffraction order and redistribution of the reflected radiation energy from the zero (specular) order (Rayleigh anomaly). This redistribution of energy is determined by the diffraction efficiency of the grating, which, in its turn, increases with increasing depth of relief in the studied interval of *h*/*a*. Therefore, the Rayleigh anomaly also increases with increasing *h*/*a* for all the samples under

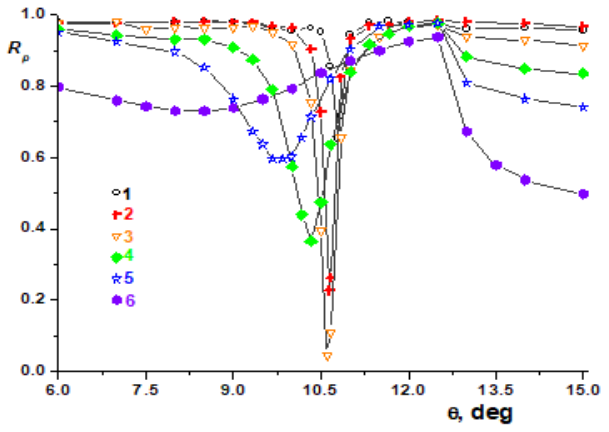

Fig. 2. Dependence of the specular reflection of *p*-polarized light from a He-Ne laser (R_p) on the angle of incidence (θ) for silver-coated gratings with the period 519 nm and modulation depths: *h*/*a* = 0.009 (*1*), 0.021 (*2*), 0.037 (*3*), 0.072 (*4*), 0.098 (*5*), 0.148 (*6*).

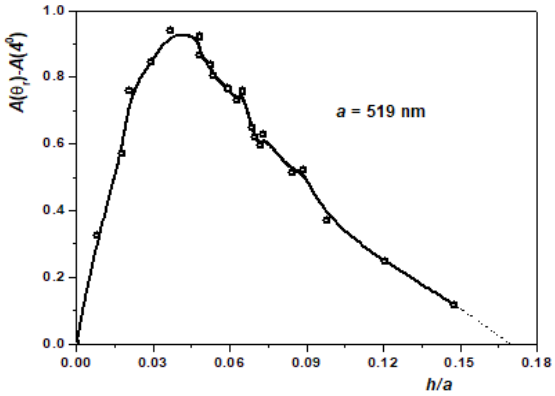

Fig. 3. Dependence of plasmon absorption $\Delta A = A(\theta_r) - A(4°)$ of *p*-polarized light from a He-Ne laser at the angle of incidence θ_r on the modulation depth of a silver-coated grating with the period 519 nm.

study, although its angular position determined by the equation of the diffraction grating does not change. Note that for gratings with a period greater than the excitation wavelength (λ < *d*), the Rayleigh anomaly is observed at smaller angles than Wood's one.

So, there is an optimal grating modulation depth for a given excitation wavelength and coating material, which provides the maximum transfer of the incident electromagnetic wave energy to the surface plasmon-polariton mode. The efficiency of this process can be characterized by the fraction of the absorbed energy inherent to the incident beam $A = 1 - R - T$ in plasmon resonance, where *R* and *T* are the reflection and transmission coefficients, respectively. In our case, the silver layer is opaque, so there is no transmission and $A = 1 - R_p$. We will measure the absorbed energy from absorption at the angle of incidence close to the normal one (at θ = 4°), then the maximum contribution of plasmon absorption (at the angle of incidence θ_r) will be determined as $\Delta A = A(\theta_r) - A(4°)$.

Fig. 3 shows the dependence of Δ*A* on the modulation depth of the studied gratings. The experimental curve is asymmetric about a rather wide maximum, the position of which, as indicated above, corresponds to the *h*/*a* value close to 0.037. Shown in Fig. 3 dependence allows one to determine the range of grating depths in which effective SPP excitation is observed (for Δ*A* ≥ 0.8, this range is *h*/*a* = 0.025…0.055). The point of intersection of the dependence of Δ*A* on *h*/*a* with the abscissa axis, shown by the dashed line, corresponds to such modulation depth of the gratings (*h*/*a* = 0.17) at which the resonant minimum of R_p already disappears.

For further studies of plasmon-stimulated photodoping, gratings with the maximum efficiency of SPP excitation, that is, with a modulation depth close to 0.037, were chosen. Thin $As_4Ge_{30}S_{66}$ layers were deposited on these gratings by thermal evaporation in vacuum. As a result of deposition of the ChG layers, the position of the SPP minimum on the angular dependence of R_p shifts towards smaller angles (Fig. 4).

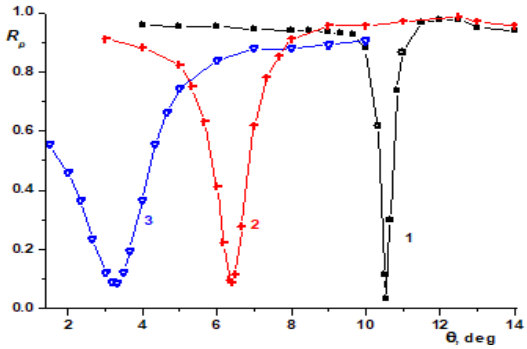

Fig. 4. Dependence of the specular reflection of *p*-polarized light from a He-Ne laser (R_p) on the angle of incidence (θ) for silver-coated grating with the period 519 nm and modulation depth h/a = 0.037 (*1*), and the same grating with the deposited $As_4Ge_{30}S_{66}$ film with the thickness d_f = 10 nm (*2*) and 13 nm (*3*).

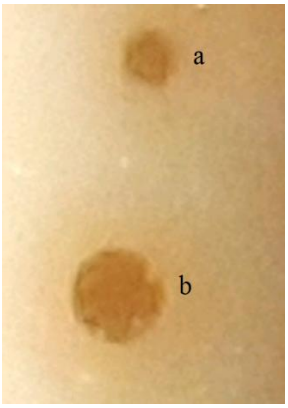

Fig. 5. Photo of the exposed spots of the "Ag grating – 10-nm-thick $As_4Ge_{30}S_{66}$ layer" structure. Exposure angle: (a) $\theta_{exp} = 0°$, (b) $\theta_{exp} = 6.4°$. Exposure time 45 min.

As known from previous studies [25], the angular shift of the plasmon minimum of R_p due to the deposition of the dielectric film on the silver grating is determined mainly by the optical thickness of the layer (that is, by the product of its refractive index n_f by the thickness d_f). Both $n_f d_f$ and the presence of absorption in the dielectric cause the broadening of the minimum. At the same time, the reflection intensity at the minimum of R_p (the resonance depth) depends only on the absorption in the deposited layer. These dependences are also manifested in our samples (Fig. 4, curves *1–3*) – the angular shift of the resonance increases with an increase in the thickness of the ChG layer. At the same time, the broadening of the minimum and a decrease in the resonance depth for $As_4Ge_{30}S_{66}$ layers are much smaller than those observed for $As_{40}S_{60}$ layers of the same thickness [14]. This indicates a lower absorption of light with the wavelength 632.8 nm in $As_4Ge_{30}S_{66}$ layers, which is consistent with the previous measurements [26, 27]. Photostimulated doping of the ChG with silver in these structures leads to a further shift of the R_p minimum in the direction of smaller angles; therefore, the range of thicknesses of $As_4Ge_{30}S_{66}$ layers in our further measurements was 5…10 nm.

The resulting structures, the cross-section of which is schematically shown in Fig. 1, were exposed to a non-attenuated He-Ne laser beam from the side of the chalcogenide layer. To register the effect of SPP excitation on photostimulated changes in the sample, two identical sample regions were irradiated under the same conditions, but at different angles of incidence of the *p*-polarized laser radiation. The control area was exposed with a beam incident perpendicular to the sample surface, and the other area was exposed at the angle corresponding to the minimum of R_p. As a result of exposure, photostimulated diffusion of Ag occurs in both exposed areas of the sample, which leads to a change in the optical properties of the ChG layer.

Fig. 5 shows a photograph of the exposed regions of the studied sample for two directions of irradiation – without (a) and with (b) SPP excitation. The irradiation time is the same for both points, the exposure value per unit area is slightly less for case (b) due to the oblique incidence of the beam. It can be seen that more efficiently photostimulated changes in the optical properties of the Ag–$As_4Ge_{30}S_{66}$ photosensitive structure occur upon exposure with SPP excitation at the silver–ChG interface.

To quantitatively describe these changes, the angular dependences of the specular reflection R_p of the exposed samples were measured, which were carried out using the radiation of the same laser, attenuated by two orders of magnitude. Figs 6 and 7 show, as an example, the results of these measurements for the samples with chalcogenide layer thicknesses equal to 7 and 10 nm, respectively. Figs 6a, 7a correspond to the samples exposed to the laser beam oriented along the perpendicular to the sample surface ($\theta_{exp} = 0°$); *i.e.*, SPP was not excited during exposure. Figs 6b and 7b present the results for the same samples, but exposed at the angle corresponding to SPP excitation ($\theta_{exp} = 7.3°$ for the 7-nm-thick ChG layer and 6.4° for the 10-nm-thick ChG layer). As a result of exposure at the initial stage, there is a decrease in the depth of the minimum R_p (*i.e.*, an increase in reflection at the minimum (R_p^{min})), its expansion, as well as a slight shift of the minimum R_p to smaller angles of incidence. With increasing exposure time, these changes also increase. Comparing the results in Figs 6a, 7a and 6b, 7b, it can be noted that "degradation" of the R_p minimum as a consequence of exposure (namely, an increase in the reflection at the minimum and its expansion) occurs noticeably faster under irradiation with SPP excitation.

The kinetics of the increase in specular reflection at its plasmon minimum (ΔR_p^{min}) and the change in the half-width of this minimum ($\Delta\theta_{1/2}$) during photodoping for these two samples are shown in Figs 8 and 9: curves *1* corresponds to exposure perpendicular to the sample surface, curves *2* – irradiation at the angle corresponding to SPP excitation. A more significant increase in $\theta_{1/2}$ and R_p^{min} is observed upon exposure with SPP excitation, especially in the initial period of irradiation. The maximum ratio of the values of the increase in R_p^{min} for curves *1* and *2* ($\Delta R_p^{min}(1)/\Delta R_p^{min}(2)$) is observed during the first two irradiation intervals and is equal to 6 (Fig. 8a) and 15 (Fig. 9a). With further irradiation, as SPP "degrades",

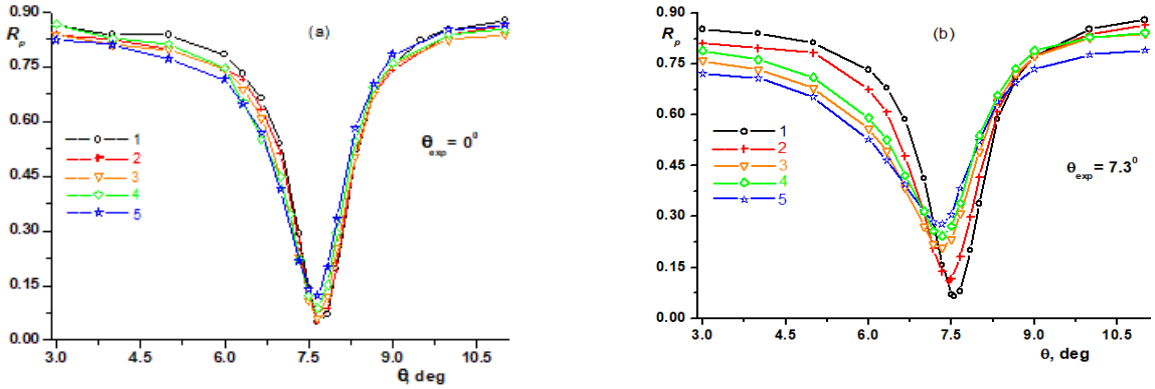

Fig. 6. Angular dependences of specular reflection (R_p) for the 'Ag grating – 7-nm-thick chalcogenide layer' structure exposed at θ_{exp} = 0° (a) and θ_{exp} = 7.3° (b). Exposure time (min): 0 (*1*), 5 (*2*), 15 (*3*), 25 (*4*), 35 (*5*).

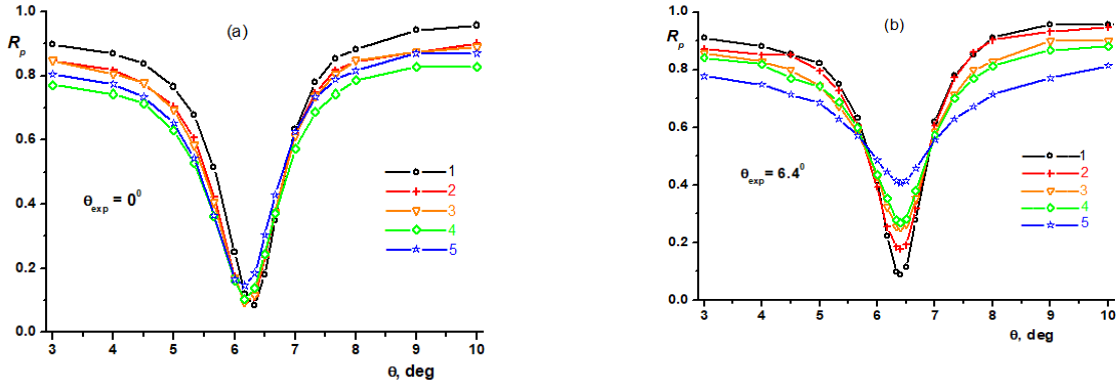

Fig. 7. Angular dependences of specular reflection (R_p) for the 'Ag grating – 10-nm-thick chalcogenide layer' structure exposed at θ_{exp} = 0° (a) and θ_{exp} = 6.4° (b). Exposure time (min): 0 (*1*), 5 (*2*), 15 (*3*), 25 (*4*), 45 (*5*).

the intensity of the plasmon field weakens; in addition, a thin layer of chalcogenide is saturated with silver and the process of photostimulated diffusion slows down.

This is more noticeable in the structure with a thinner chalcogenide (Fig. 8a), where curves *1* and *2* are almost parallel during the third and fourth irradiation intervals, and after the fourth irradiation interval $\Delta R_p^{min}(1)/\Delta R_p^{min}(2) = 2.7$. For irradiation at $\theta_{exp} = 0°$, the increase in R_p^{min} is at the stage of acceleration in the entire exposure range for both structures. For the sample with the thicker $As_4Ge_{30}S_{66}$ layer (Fig. 9a), after the fourth irradiation interval, $\Delta R_p^{min}(1)/\Delta R_p^{min}(2) = 5$, and to achieve a noticeable saturation of the chalcogenide with silver, a longer exposure is required.

Similar results are also observed and for the kinetics of the photostimulated change in the half-width of the reflection minimum $\Delta\theta_{1/2}$ (Figs. 8b and 9b). For both samples, the increase in $\Delta\theta_{1/2}$ is 4-5 times greater when exposed with simultaneous SPP excitation.

Let us consider the possible causes of these changes in the SPP characteristics for the samples under study. As known [15–19], photostimulated diffusion of Ag into ChG layers causes significant changes in their optical constants, in particular, the absorption coefficient, refractive index of the ChG layer (n_f) and the roughness of the Ag–ChG interface increase with increasing exposure time. According to previous theoretical and experimental studies, these changes should be accompanied [25] by a shift and broadening of the R_p minimum, as well as a decrease in its depth, which is observed in our experiment. A significantly larger change in these values (especially at the initial stage of irradiation) upon exposure at the angle corresponding to the resonance angle of SPP excitation indicates acceleration of the process of photostimulated diffusion in the "Ag grating–$As_4Ge_{30}S_{66}$ layer" structures under the action of the SPP field.

Similar results were obtained by us on the structures "Ag grating–$As_{40}S_{60}$ layer" [13, 14]. However, in these structures, the main manifestation of photostimulated diffusion was a significant shift in the position of the R_p minimum, rather than a decrease in its depth, which is observed for the Ag–$As_4Ge_{30}S_{66}$ structures. Apparently, this is caused by peculiarities of photodoping and binding of silver atoms in the matrix of the corresponding chalcogenide. In the case of $As_{40}S_{60}$, photodoping leads to a greater increase in the refractive index at the probe wavelength, and in the case of $As_4Ge_{30}S_{66}$ – to a predominant increase in the absorption coefficient in this spectral region. Note that the interband absorption edge of $As_4Ge_{30}S_{66}$ is located in the shorter-wave part of the spectrum than the interband absorption edge of $As_{40}S_{60}$, farther from the wavelength of the probe radiation. Upon photodoping with silver to saturation, the refractive index of $As_{40}S_{60}$ changes from 2.38 to 3.0, and of $As_4Ge_{30}S_{66}$,

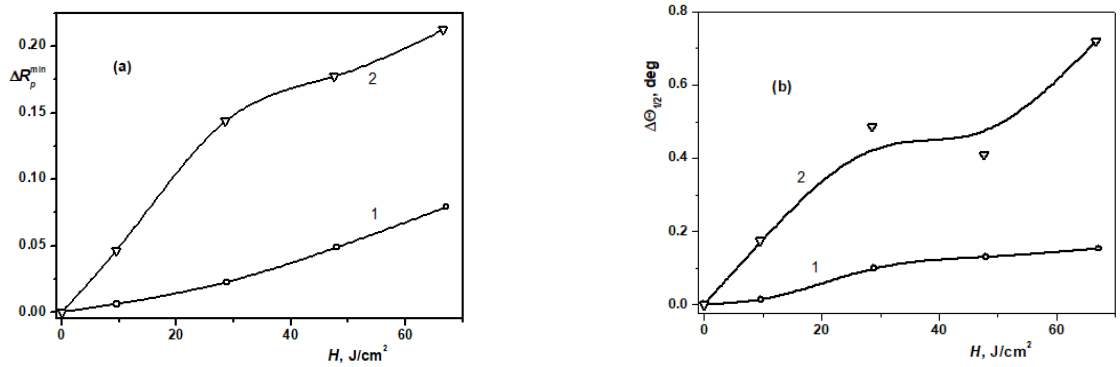

Fig. 8. The reflection change in the $R_p(\theta)$ dependence minimum (ΔR_p^{min}) (a) and the change of angular halfwidth of the $R_p(\theta)$ dependence ($\Delta\theta_{1/2}$) (b) with exposure, H, for the 'Ag grating – 7-nm-thick $As_4Ge_{30}S_{66}$ layer' structure. Irradiation at $\theta_{exp} = 0°$ (*1*) and $\theta_{exp} = 7.3°$ (*2*).

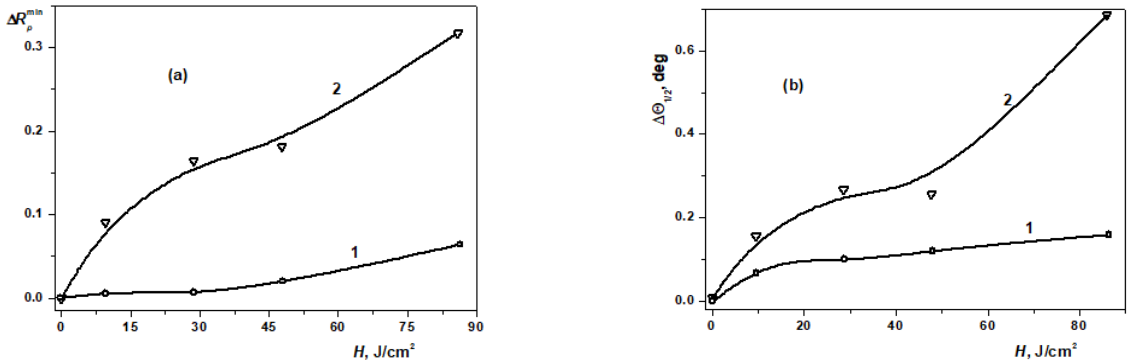

Fig. 9. The same as in Fig. 8 but for the 'Ag grating – 10-nm-thick $As_4Ge_{30}S_{66}$ layer' structure. Irradiation at $\theta_{exp} = 0°$ (*1*) and $\theta_{exp} = 6.4°$ (*2*).

from 2.3 to 2.7. A more significant increase in n_f (and hence $n_f d_f$) should lead to a more noticeable shift in the position of the plasmon minimum on the angular dependence of R_p for Ag–$As_{40}S_{60}$ structures. At the same time, in the Ag–$As_4Ge_{30}S_{66}$ structures, an increase in the absorption coefficient and the roughness of the Ag–ChG interface during photodoping is more pronounced [28]. These changes should be accompanied [25] by broadening of the R_p minimum, as well as a decrease in its depth, which was observed in our experiment (Figs 6 and 7).

As it was mentioned in the introduction, the detailed mechanism of stimulation of Ag diffusion in chalcogenide films by light was studied in detail in [15, 16]. It was found that the first stage of this phenomenon is generation of electron-hole pairs which takes place in the ChG layer near the interface with Ag. The intensity of this process depends on the intensity of light near the Ag–ChG contact. Therefore, the reason for acceleration of photostimulated diffusion in the structures under study appears to be accelerated generation of electron-hole pairs, which takes place in the $As_4Ge_{30}S_{66}$ layer near the interface with Ag, where the strength of the electromagnetic field is increased due to SPP exitation.

Another possible mechanism for generation of carriers that stimulate photoenhanced diffusion upon excitation of plasmon-polaritons may be plasmon assisted internal photoemission. A similar mechanism was considered in some early works on photodoping [29], where the internal photoemission of electrons from the metal was assumed as the initial stage of photostimulated diffusion followed by the movement of silver ions in the field of the created double charged layer. Therefore, further experimental and theoretical studies are required in order to determine the contribution of these two possible mechanisms of photostimulated diffusion acceleration in the Ag–ChG structures upon SPP excitation.

4. Conclusions

We have shown 6- to 15-fold acceleration of the initial stage of photostimulated diffusion of silver in the structure 'Ag grating – thin $As_4Ge_{30}S_{66}$ layer' under action of the SPP field. Thus, excitation of surface plasmon-polaritons at the Ag–$As_4Ge_{30}S_{66}$ interface during irradiation increases the photosensitivity of this structure. Two possible mechanisms have been proposed to explain acceleration of photostimulated diffusion of metal inside the structure under study due to SPP excitation: acceleration of generation of electron-hole pairs in the ChG layer under action of a plasmon field and/or plasmon-stimulated internal photoemission of electrons from the metal to the ChG layer with the subsequent drift of silver ions into chalcogenide under action of the field related to a double charged layer.

References

1. Wood R.W. On a remarkable case of uneven distribution of light in a diffraction grating spectrum. *Phil. Mag*. 1902. **4**, No 21. P. 396–402. https://doi.org/10.1080/14786440209462857.
2. Fano U. The theory of anomalous diffraction gratings and of quasi-stationary waves on metallic surfaces (Sommerfeld's waves). *J. Opt. Soc. Am*. 1941. **31**, No 3. P. 213–222. https://doi.org/10.1364/JOSA.31.000213.
3. Zhang J., Zhang L. and Xu W. Surface plasmon polaritons: physics and applications. *J. Phys. D: Appl. Phys*. 2012. **45**. P. 113001. https://doi.org/10.1088/0022-3727/45/11/113001.
4. Toma K., Vala M., Adam P. *et al.* Compact surface plasmon-enhanced fluorescence biochip. *Opt. Exp*. 2013. **21**, No 8. P. 10121–10132. https://doi.org/10.1364/OE.21.010121.
5. Valsecchi C. and Brolo A.G. Periodic metallic nanostructures as plasmonic chemical sensors. *Langmuir*. 2013. **29**, No 19. P. 5638–5649. https://doi.org/10.1021/la400085r.
6. Ding S.Y., Yi J., Li J.F. *et al.* Nanostructure-based plasmon-enhanced Raman spectroscopy for surface analysis of materials. *Nat. Rev. Mater*. 2016. **1**. P. 16021. https://doi.org/10.1038/natrevmats.2016.21.
7. Zijlstra P., Chon J.W.M. and Gu M. Five-dimensional optical recording mediated by surface plasmons in gold nanorods. *Nature*. 2009. **459**. P. 410–413. https://doi.org/10.1038/nature08053.
8. Atwater H.A. and Polman A. Plasmonics for improved photovoltaic devices. *Nat. Mater*. 2010. **9**. P. 205–213. https://doi.org/10.1142/9789814317665_0001.
9. Kristensen A., Yang J., Bozhevolnyi S. *et al.* Plasmonic colour generation. *Nat. Rev. Mater.* 2017. **2**. P. 16088. https://doi.org/10.1038/natrevmats.2016.88.
10. Trunov M.L., Lytvyn P.M., Nagy P.M. *et al.* Light-induced mass transport in amorphous chalcogenides: Toward surface plasmon-assisted nanolithography and near-field nanoimaging. *phys. status solidi b*. 2014. **251**, No 7. P.1354–1362. https://doi.org/10.1002/pssb.201350296.
11. Csarnovics I., Veres M., Nemec P. *et al.* Surface plasmon enhanced light-induced changes in Ge–Se amorphous chalcogenide – gold nanostructures. *J. Non-Cryst. Solids X*. 2020. **6**. P. 100045. https://doi.org/10.1016/j.nocx.2020.100045.
12. Stafe M., Popescu A.A., Savastru D. *et al.* Optical hysteresis in SPR structures with amorphous As_2S_3 film under low-power laser irradiation. *J. Phys. D.: Appl. Phys*. 2018. **51**. P. 125106. https://doi.org/10.1088/1361-6463/aaa9cf.
13. Indutnyi I.Z., Mynko V.I., Sopinskyy N.V. and Lytvyn P.M. Plasmon-stimulated photodoping in the thin-layer As_2S_3–Ag structure. *Opt. Spectrosc*. 2019. **127**. P. 938–942. https://doi.org/10.1134/S0030400X19110109.
14. Indutnyi I., Mynko V., Sopinskyy M. and Lytvyn P. Impact of surface plasmon polaritons on silver photodiffusion into As_2S_3 film. *Plasmonics*. 2021. **16**, No 1. P. 181–188. https://doi.org/10.1007/s11468-020-01275-8.
15. Kolobov A.V. and Elliott S.R. Photodoping of amorphous chalcogenides by metals. *Adv. Phys*. 1991. **40**. P. 625–684. https://doi.org/10.1080/00018739100101532.
16. Indutnyi I.Z., Dan'ko V.A., Kudryavtsev A.A. *et al*. Photodoping in As_2S_3–Ag structures *J. Non-Cryst. Solids*. 1995. **185**, No 1–2. P. 176–182. https://doi.org/10.1016/0022-3093(94)00660-1.
17. Sakaguchi Y., Hanashima T., Aoki H. *et al*. Kinetics of silver photodiffusion into amorphous $Ge_{20}S_{80}$ films: case of pre-reaction. *phys. status solidi a.* 2018. **215**, No 12. P. 1800049. https://doi.org/10.1002/pssa.201800049.
18. Khan P., Xu Y., Leon W. *et al*. Kinetics of photo-dissolution within Ag/As_2S_3 heterostructure. *J. Non-Cryst. Solids*. 2018. **500**. P. 468–474. https://doi.org/10.1016/j.jnoncrysol.2018.09.001.
19. Stronski A.V. Production of metallic patterns with the help of high resolution inorganic resists. In: Harman G., Mach P. (Eds). *Microelectronic Interconnections and Assembly NATO ASI Series, 3: High Technology*, **54**. Springer, Dordrecht, 1998. P. 263–293. https://doi.org/10.1007/978-94-011-5135-1_31.
20. Indutnyi I.Z., Stronski A.V., Kostioukevich S.A. *et al*. Holographic optical element fabrication using chalcogenide layers. *Opt. Eng*. 1995. **34**, No 4. P. 1030–1039. https://doi.org/10.1117/12.197144.
21. Kozicki M.N. and Barnaby H.J. Conductive bridging random access memory – materials, devices and applications. *Semicond. Sci. Technol.* 2016. **31**. P. 113001. https://doi.org/10.1088/0268-1242/31/11/113001.
22. Dan'ko V., Dmitruk M., Indutnyi I. *et al*. Fabrication of periodic plasmonic structures using interference lithography and chalcogenide photoresist. *Nanoscale Res. Lett.* 2015. **10**. Pap. 497. https://doi.org/10.1186/s11671-015-1203-x.
23. Hibbins A.P., Sambles J.R., Lawrence C.R. Azimuth-angle-dependent reflectivity data from metallic gratings. *J. Mod. Opt.* 1998. **45**, No 5. P. 1019–1028. https://doi.org/10.1080/09500349808230894.
24. Johnson P.B. and Christy R.W. Optical constants of the noble metals. *Phys. Rev. B.* 1972. **6**. P. 4370–4379. https://doi.org/10.1103/PhysRevB.6.4370.
25. Raether H. *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*. Springer, 1988.
26. Onari S., Inokuma T., Kataura H. and Arai T. Absorption edge of the amorphous $(GeS_2)_x(As_2S_3)_{1-x}$ system under hydrostatic pressure. *Phys. Rev. B.* 1987. **35**, No 9. P. 4373–4379. https://doi.org/10.1103/PhysRevB.35.4373.
27. Abdel-Wahab F., Ashraf I.M. and Ahmed F.B. Optical parameters of both As_2S_3 and As_2Se_3 thin films from ultraviolet to the near-infrared via variable-angle spectroscopic ellipsometer. *Semiconductors*. 2020. **54**, No 11. P. 1430–1438. https://doi.org/10.1134/S1063782620110020.

28. Sakaguchi Y., Asaoka H., Uozumi Y. *et al*. Silver photo-diffusion and photo-induced macroscopic surface deformation of $Ge_{33}S_{67}$/Ag/Si substrate. *J. Appl. Phys*. 2016. **120**. 055103. https://doi.org/10.1063/1.4959207.
29. Janai M. Photodissolution of silver in amorphous As_2S_3 films. *Phys. Rev. Lett.* 1981. **47**. P. 726–729. https://doi.org/10.1103/PhysRevLett.47.726.

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Вплив поверхневих плазмон-поляритонів на фотостимульовану дифузію в світлочутливих структурах Ag–$As_4Ge_{30}S_{66}$

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Анотація. Досліджено вплив поверхневих плазмон-поляритонів (ППП), збуджених на межі поділу між профільованою поверхнею шару срібла (у вигляді дифракційної решітки) та шаром $As_4Ge_{30}S_{66}$, на фотостимульовану дифузію срібла у халькогенід. Решітки з періодом a = 519 нм і глибиною модуляції $h/a \approx$ 0,037 (де h – глибина решітки) були сформовані на халькогенідних плівках фоторезисту за допомогою інтерференційної літографії та покриті шаром алюмінію товщиною 80 нм, шаром срібла 85 нм і тонким шаром $As_4Ge_{30}S_{66}$. Досліджено фотостимульовані зміни цієї структури шляхом вимірювання кутових залежностей дзеркального відбиття (R_p) p-поляризованого світла з довжиною хвилі 632,8 нм. Було виявлено, що в результаті опромінення «деградація» (розширення, збільшення відбиття в мінімумі) мінімуму в кутовій залежності R_p (яка пов'язана з резонансом ППП) відбувається швидше, коли зразки опромінюються під кутом, при якому збуджується ППП. Це спостереження свідчить про прискорення процесу фотостимульованої дифузії в цій структурі під дією плазмонного поля.

Ключові слова: поверхневий плазмон-поляритон, фотостимульована дифузія, халькогенідне скло, Ag, $As_4Ge_{30}S_{66}$.