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Germanium Wetting Layers' Dimensional Effect in Structural and Optical Properties of Silver Films

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The peculiarities of light absorption in silver films of different thickness (2–20 nm) deposited on germanium underlayers of different mass thickness are experimentally investigated. The conditions of percolation transition in 5 nm thick silver films deposited on germanium underlayers in the range of 1 nm are studied. The influence of germanium underlayers with a mass thickness up to 1 nm with a step of 0.2 nm in the visible and near-infrared wavelength range (300–2500 nm) on the above-mentioned properties of silver films is investigated. Optical percolation in silver films is associated with the peculiarities of growth mechanisms and modes of formation of metal condensate on an amorphous glass substrate. As shown, the germanium underlayers previously applied to the glass substrate reduce the threshold thickness of the optical percolation transition in the silver film and increase their absorbency compared to similar films formed on a clean glass surface. The increase in the absorption capacity of films deposited on the surface of the germanium underlayer is due to a decrease in the average linear size of crystallites compared to similar samples formed on a clean glass surface, and thus, an increase in the number of scattering metal centres per unit surface area.

Експериментально досліджено особливості вбирання світла в плівках срібла різної товщини (2–20 нм), осаджених на підшари ґерманію різної масової товщини. Досліджено умови перколяційного переходу в плівках срібла товщиною у 5 нм, осаджених на підшари ґерманію в інтервалі до 1 нм. Вивчено вплив підшарів ґерманію масовою товщиною до 1 нм із кроком у 0,2 нм у видимому та близькому інфрачервоному діяпазонах довжин хвиль (300–2500 нм) на оптичні властивості плівок срібла. Оптична перколяція у плівках срібла пов'язана з особливостями механізмів росту та режимів формування конденсату металу

на поверхні підкладинки. Показано, що попередньо нанесені на скляну підкладинку підшари ґерманію зменшують порогову товщину оптичного перколяційного переходу у плівці срібла та збільшують їхню вбирну здатність порівняно з аналогічними плівками, сформованими на чистій поверхні підкладинки. Зростання вбирної здатности плівок, нанесених на поверхню підшару ґерманію, зумовлене зменшенням середніх лінійних розмірів кристалітів порівняно з аналогічними зразками, сформованими на чистій поверхні скла, а тому і збільшенням кількости розсіювальних металевих центрів на одиниці площі поверхні підкладинки.

Key words: thin metal films, optical percolation, absorbency of film.

Ключові слова: тонкі металеві плівки, оптична перколяція, вбирна здатність плівок.

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1. INTRODUCTION

Nanometre metal films are basic systems of modern micro- and nanoelectronics elements as ohmic conductors with high transparency coefficient in the visible and infrared ranges of wavelengths [1]. The study of the features of the nanoscale layers' interaction with electromagnetic radiation in the vicinity of the percolation transition is promising in search for materials with new electrooptical properties under development of modern transparent electronics [1, 2]. There is an important problem to find the peculiarities of electrical and optical metal film parameters near its structure transition from dispersed phase to solid one as its mass thickness on the substrate surface increases. It is known that, in vicinity of the percolation transition, nanoscale metal film exhibits anomalous optical and electrical properties. Therefore, at viewpoint of prediction of its properties, it is necessary to establish the layer critical thickness d_c, at which this phase transition shows itself. One of the promising theories for d_c evaluation is percolation approach [3, 4]. That theory allows for the assessment and mode forecast of metal film growth in the vicinity of the percolation transition. It also predicts the electrooptical properties of percolation metal films. According to results highlighted in our previous works, the wetting underlayers (Ge, Si, Sb, *etc.*) application allows to impact on d_c value and helps to grow metal films with the predicted structure and its electrooptical parameters. That problem was discussed and actively applied in the study of electron-transport phenomena in gold [5] and silver [6] films in the vicinity of the percolation transition [3, 4].

This paper analyses the peculiarities of the germanium wetting effect on optical absorption of silver films with thickness from 2

nm to 20 nm. Peculiarities of the percolation transition due to the dimensional effect of the mass thickness of germanium underlayers were studied in silver films with 5 nm thickness deposited on 1 nm germanium underlayers. In order to predict the peculiarities of structure and optical percolation transition, the transmission and reflection spectra in the visible and near-infrared wavelength ranges (200–1800 nm) were investigated.

2. EXPERIMENTS

Silver films' deposition was carried out under ultrahigh vacuum conditions (the pressure of residual gas components did not exceed 10^{-6} Pa) [4, 5]. Silver films were obtained by condensation of thermally evaporated metal vapour at deposition rate of about 0.01 nm/s on substrate at 78 K. After that, investigated films were spontaneously stabilized at room temperature ($T = 300$ K) during 24 hours. Nanosize germanium underlayers of different mass thickness were deposited on the substrate before the deposition of the metal films. The described regime of metal films' preparation corresponds to the 'quench condensed' mode [7], in which condensation of the metal vapour and temporary thermal stabilization take place at temperatures T not exceeding $\leq (0.2–0.3)T_{melt}$, where T_{melt} is the melting temperature of metal [8]. For structural and optical studies, metal films of different thicknesses were applied simultaneously in the form of parallel strips with alternate closing of them from the continuous flow of metal with a shutter in order to achieve a metal film of a given thickness. At the end of the film deposition process, the film was thermostabilized spontaneously in a vacuum at room temperature ($T = 300$ K) during 24 hours. The substrate with films were removed from the vacuum system immediately before optical or electron microscopic studies.

The dimensional evolution of the microstructure of different thicknesses silver films was studied in PEM-100M transmission electron microscope. The main problem of investigation of metal films in the thickness range of 1–20 nm is their fragility; therefore, it is necessary to use supporting amorphous layer made by special technology of molecular condensation of carbon vapour on the surface of a chipped NaCl single crystal at the temperature of liquid nitrogen. Note that the carbon films were produced under conditions of reduced carbon evaporation temperature ($\cong 1770°C$) due to the presence of catalyst at area of carbon evaporation. It made possible to produce high quality, stable, amorphous carbon films with a thickness of 10–15 nm on the surface of the NaCl chip transparent for electron beam. Germanium wetting layers were deposited on surface of carbon film immediately before deposition of

silver films in one technological cycle in order to ensure identical formation conditions for all the studied samples.

Mass thickness of films was estimated by shift of resonant frequency of calibrated quartz vibrator placed in flow of evaporated metal vapour with sensitivity of 90–100 Hz/nm.

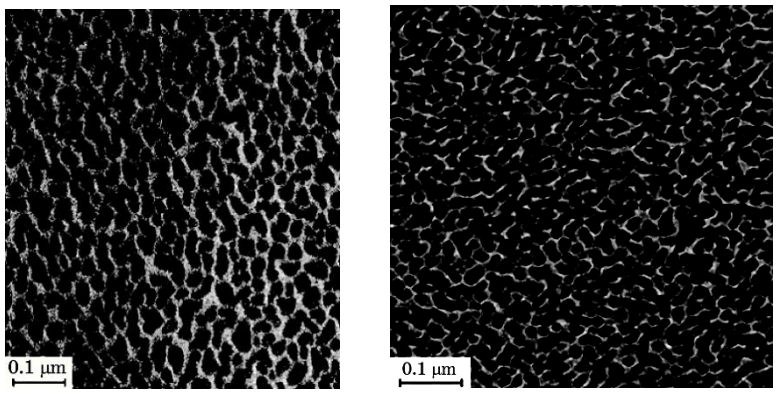
The study of the transmission $T(\lambda)$ and reflection $R(\lambda)$ spectra of silver films was carried out on Shimadzu UV-3600-VIS-NIR in the visible and near-infrared region of 300–2500 nm. In this study, it is assumed that the germanium underlayers do not affect the spectral characteristics of films, but change metal film structure and its growing conditions on the surface.

3. STRUCTURE OF THIN Ag FILMS

The results of electron-microscopy studies showed that silver films grown with above-described method are homogeneous polycrystalline metal layers without predominant crystallites' orientation. The parameters of silver films crystal lattice are similar with parameters of massive silver.

From the analysis of the results of electronographic studies, it can also be concluded that there are no impurity and non-equilibrium phases in investigated silver films as well as products of silver with germanium. The last result is well consistent with data of films' structure studies of simple metals deposited on the surface of germanium layers in the range of temperatures $T \leq (0.2–0.3)T_{\text{melt}}$ [7, 8].

Figure 1 shows microstructure of 12 nm silver films deposited on



a *b*

Fig. 1. Microstructure of 12 nm Ag films deposited on surface of amorphous carbon substrate (*a*) and carbon substrate precoated with 1 nm germanium wetting layers (*b*).

clean surface of carbon substrate (Fig. 1, *a*) and on the substrate precoated with 1 nm germanium underlayer (Fig. 1, *b*), respectively. It can be seen that linear dimensions of the crystallites on the surface with germanium underlayers are smaller than the similar crystallites' sizes of Ag film deposited on the pure amorphous surface.

At the same time, the concentration of isolated clusters on the substrate surface is increased in 1.6 times. Determination of the average linear sizes of crystallites D in the plane parallel to the substrate was carried out with analysis of clusters' statistical data of crystallites' sizes.

The histograms of crystallites' number distribution on linear dimensions of the crystallites shown in Fig. 2. According to the shift of the maximum distribution of crystallites to region of smaller D, we can state that the presence of 1 nm germanium underlayers decreases metal films' crystallites' linear dimensions in 2.2 times. It can conclude that the presence of additional crystallization centres in the form of germanium adatoms on the surface of amorphous substrate contributes to a more uniform filling of the substrate surface with metal crystallites of almost the same linear size and causes the growth of metal film of more developed polycrystalline structure.

The study of the microstructure of silver films of different thicknesses shows that the 'quench condensed' technique [5, 6] ensures the growth of metal films of the investigated thickness. The average linear dimensions of metal film crystallites depend on the mass thickness of germanium wetting layers.

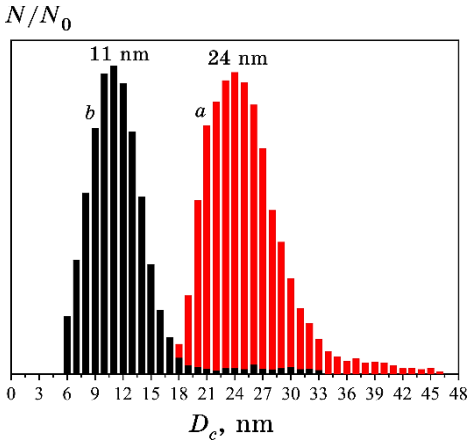


Fig. 2. Histogram of crystallites distribution on the surface of substrate covered with 12 nm silver films deposited on pure carbon substrate (*a*) and on carbon substrate precoated with 1 nm germanium wetting (*b*).

4. OPTICS OF THIN Ag FILMS

The analysis of the size-spectral dependences of reflection coefficient $R(\lambda)$ for silver films indicates fundamental difference in $R(\lambda)$ behaviour at infrared spectrum region (Fig. 3, *a*, *b*). In Figure 3, *a*, *b*, we observe simultaneous decrease (curve *3*, Fig. 3, *a*) and increase (curves *3*, Fig. 3, *b*) of R with λ for 10 nm silver film. The

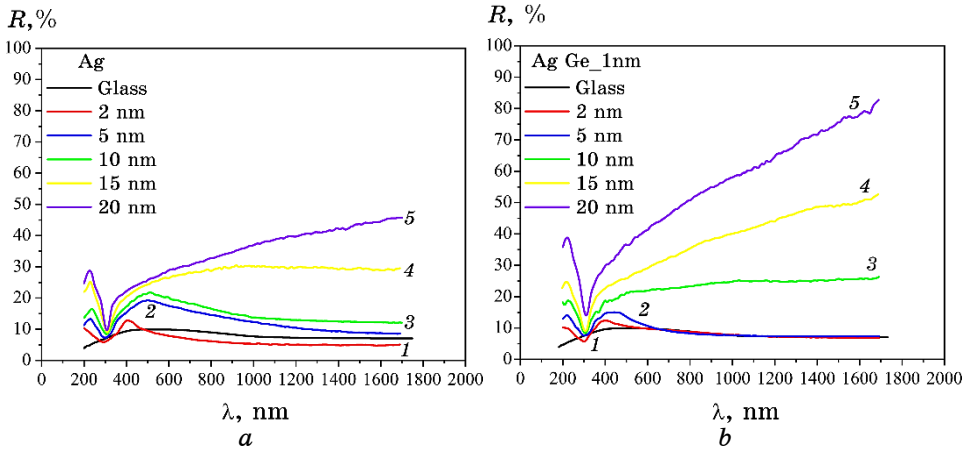


Fig. 3. Reflection spectra of silver films with mass thickness of 2, 5, 10, 15, 20 nm deposited on clean glass substrate (*a*) and glass substrate precoated with 1 nm germanium underlayer (*b*).

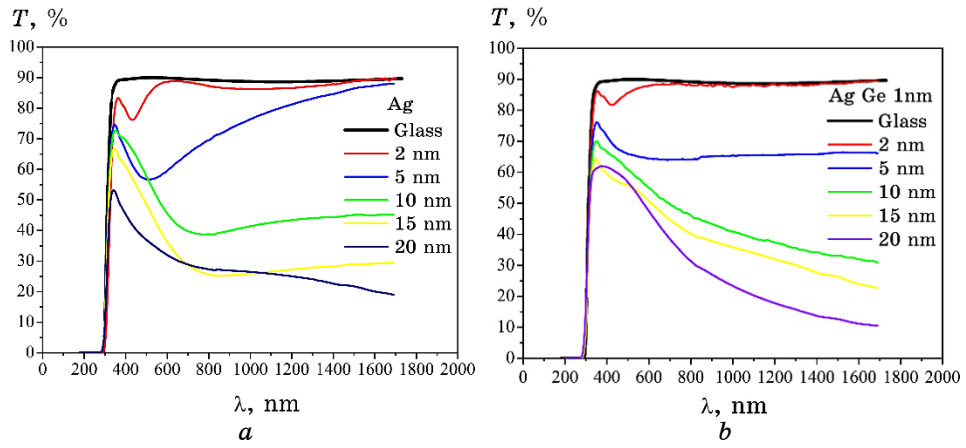


Fig. 4. Transmission spectra of silver films with mass thickness of 2, 5, 10, 15, 20 nm deposited on clean glass substrate (*a*) and glass substrate precoated with 1 nm germanium underlayer (*b*).

observed spectral $R(\lambda)$ behaviour is caused by difference film structure of same thickness metal films deposited on clean glass surface substrate and substrate precovered with 1 nm germanium underlayer. Silver films with thickness of several nanometers (Fig. 3, *a*, curve *1* and Fig. 3, *b*, curves *1* and *2*) have lower reflectivity R compared to the reflectivity R of a pure glass substrate (Fig. 3, *a*, *b*, curve *Glass*). It is because of metal clusters' network growing on the surface of glass substrate, which, due to geometry, increases particles' sizes and amplitude of surface inhomogeneities; therefore, the light scattering ability of dispersed film system increases (foggy mirror effect).

Changing the direction of optical coefficients $R(\lambda)$ and $T(\lambda)$ size-spectral dependence (Fig. 3 and Fig. 4) of silver films can be carried out with percolation theory [3, 4]. According to this approach, the slope of $T(\lambda)$ spectral dependences on different λ values in the infrared region of the spectrum is manifested at the certain d_c point of $T(d)$ curves' intersection dependences. Point of curves' intersection corresponds to percolation critical thickness d_c at the mode of the layer-by-layer metal film growth (2*D* mode or Frank–van der Merwe mode). According to [3, 4], during layer-by-layer formation, relation $(p - p_c) \propto (d - d_c)$ is valid in the vicinity of the percolation transition, where p is the surface filling degree $(0 < p < 1)$, p_c is the surface filling degree of substrate at the vicinity of percolation transition.

According to silver film structural transformations near d_c, silver islands form cluster of infinite size due to physical convergence with each other. Percolation approach considers that cluster of infinite size is one whose boundaries reach from one edge of the substrate to other one. In the point of electrical conductivity, the created metal cluster is called first ohmic-conducting metal percolation cluster. Despite the presence of solid metal cluster, structure of the metal film is mixed. It is consists of two subphases: dispersed (isolated metal islands) phase and solid percolation one. This structure, as the manifestation of physical properties of mixed metal systems, shows that reflection R, transmission T and absorption A in the infrared region of electromagnetic wavelengths are spectrally independent on λ [3]. When impact of each subphase is known, the grown metallic nanoscale network with given physical properties is controllable. Structures with compensated properties are especially valuable, since their parameters show independence from external factors and allow them to be separated depending on the set technological tasks. Understanding the regularities of this process with possibility of choose the conditions for the creation of percolation cluster in a dispersed metal system is of great importance for modern transparent electronics with given parameters [1].

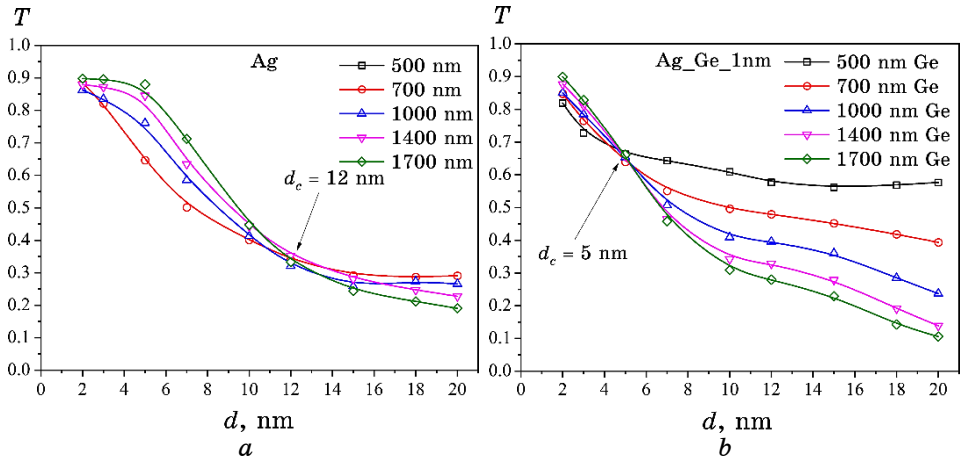


Fig. 5. Size dependences of silver films' transmission spectra T for different wavelengths. The point of intersection of the curves corresponds to the critical thickness d_c. (*a*) Silver films deposited on a clean glass substrate; (*b*) silver films deposited on a glass substrate precoated with 1 nm germanium underlayer.

Figure 5 shows the transmittance T–dimensional d dependence for the Ag films deposited on clean glass substrate and substrate precoated with 1 nm germanium underlayer, according to data in Fig. 3 and Fig. 4. For silver films deposited on a clean glass substrate, $d_c = 12$ nm, and for films deposited on 1 nm germanium underlayers, $d_c = 5$ nm. The d_c decrease is in a good agreement with structural data, according to which the decrease in the crystallites' average linear sizes on the substrate surface also leads to the increase of the concentration of isolated clusters on it. As the result, the accelerations of Ag film metallization and d_c percolation cluster formation at smaller thickness manifest themselves.

Analysis of silver films' absorption spectra A (Fig. 6) shows the act of dimensional effect in the wide spectral range of $A(\lambda)$. According to the percolation approach [3, 4], the spectral dependences of the absorption coefficient in the vicinity of the percolation transition are spectrally independent and are determined only by the film material and its structural features on the substrate surface. The value of the absorption coefficient for silver percolation films in infrared range of wavelengths varies in the range of 0.43–0.45, while, for similar percolation films deposited on 1 nm germanium underlayer, the value of the absorption coefficient varies in the range of 0.25–0.28, that corresponds to 73% decrease in absorption. The observed effect opens the possibility of manufacturing passive infrared filters based on silver films. The thickness and ab-

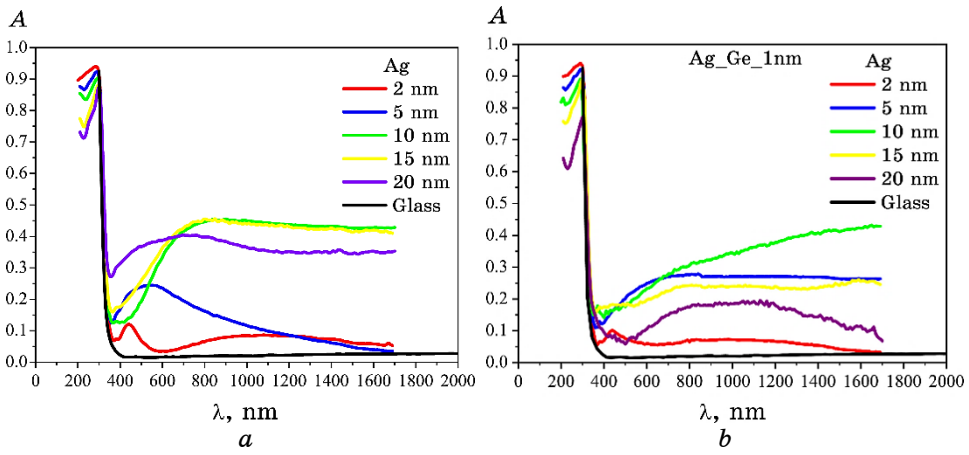


Fig. 6. Absorption spectra A for different thicknesses' silver films. (*a*) Silver films deposited on a clear glass substrate; (*b*) silver films deposited on a glass substrate covered with 1 nm germanium underlayer.

sorption coefficient of it can be changed by mass thickness of germanium underlayers. Analysis of dimensional dependence of plasmon absorption in dispersed silver films can be performed based on consideration of the 2 nm and 5 nm curves (Fig. 6, *a*), which correspond to films with a dispersed structure. According to data in Fig. 6, for 2 nm silver film, the value of plasmon wavelength λ_P is of 440 nm, and for 5 nm silver films, the plasmon wavelength λ_P is of 550 nm. The observed shift to longer wavelengths can be consequence of both the increase in the average linear size of crystallites and the change in interaction conditions of isolated silver clusters because of increase in their surface concentration.

Figure 7 shows the dependence $\ln(T - T_c) = f(\ln(\lambda))$, where $T_c \approx 40$ is the critical transparency near percolation transition [2, 3]. The angles of inclination of the silver films' linear approximation for the vicinity of percolation transition are $\mathrm{tg}(\alpha) = 0.8$ and $\mathrm{tg}(\alpha) = 0.6$, respectively. The value of the percolation index $\gamma = 1/\mathrm{tg}(\alpha)$ is $\gamma_{12\ \mathrm{nm}} = 1.25$ and $\gamma_{5\ \mathrm{nm}} = 1.67$, respectively. The fractal dimension indicator $D_f = 2 - 1/(2-\gamma)$, according to the percolation approach [2, 3], is of 1.6 and 1.97, respectively.

The calculated percolation parameters within the percolation theoretical models in two-dimensional percolation clusters and Ising model are given in Table.

A comparative analysis of the critical parameter γ for the investigated 12 nm silver films indicates that γ value is between the values predicted by the Ising models and the $2D$ percolation model, while, for silver films with thickness of 5 nm deposited on 1 nm

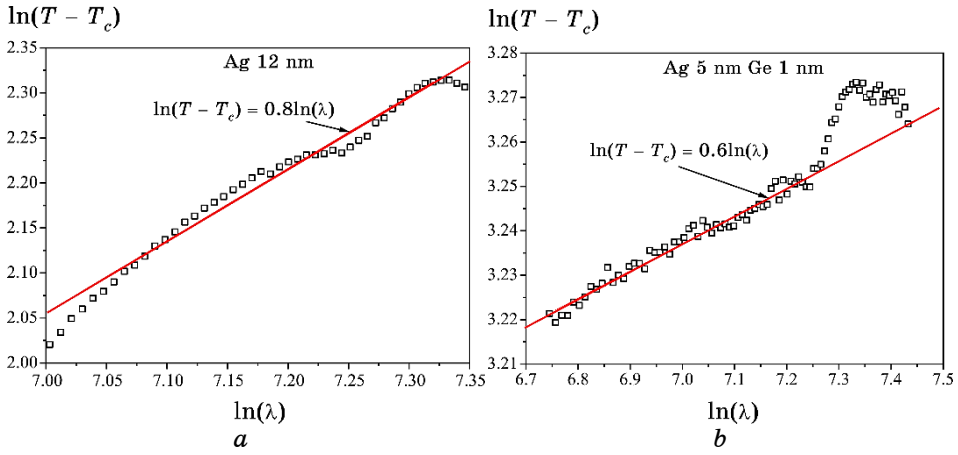


Fig. 7. Dependences of $\ln(T - T_c) = f(\ln(\lambda))$ near percolation transition for 12 nm silver films deposited on a clean substrate (*a*) and 5 nm silver films deposited on 1 nm germanium underlayer (*b*).

TABLE. Critical coefficients of silver films in the vicinity of the percolation transition.

	D_f	γ	d_c, nm
2*D*-percolation model	1.896	1.33	
2*D*-Ising model	1.875	1.00	
Ag 12 nm	1.6	1.25	12 nm
Ag 5 nm on Ge 1 nm	1.97	1.67	5 nm

germanium underlayer, this value is greater than the model predictions.

The fractal parameter in the case of 12 nm silver film is smaller compared to the predictions of the two-dimensional model that indicates the presence of significant number of empty places on the surface of the substrate, which is in good agreement with the results of structural studies [9, 10]. In the case of silver film on a germanium underlayer, the value of the fractal parameter is greater than the value predicted by the two-dimensional percolation model, which indicates high occupancy of surface substrate with isolated metal clusters as a result of germanium underlayer impact. Such data results are consistent with the tests of structural studies of silver films deposited on 1 nm germanium underlayer. It was found that the concentration of isolated metal clusters on the surface by 2.4 times higher, and the average distance between the isolated clusters is decreased by 2 times compared to similar films deposited

on bare surface. Reducing the distance between isolated clusters significantly increases the interaction between their electronic subsystems during interaction with electromagnetic waves that will significantly change the conditions for the percolation transition to smaller metal film mass thicknesses.

5. CONCLUSIONS

1. It was found that the mass thickness of germanium underlayers can change the absorption capacity of silver films of given thickness in the region of the percolation transition due to changes in the size of crystallites and the conditions of their growth on the surface of substrate.
2. It is shown that the percolation thickness d_c decreases from 12 nm to 5 nm, when silver film is grown on 1 nm germanium wetting layers.

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