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Impact of Germanium Wetting Nanolayers on the Optical Properties of Silver Films

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Light absorption and optical percolation in nanosized silver films with a thickness of 5 and 10 nm are investigated experimentally. 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 studied. 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. It has been shown that germanium underlayers predeposited on 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 absorbency of the films deposited on the surface of the germanium sublayer is due to a decrease in the average linear size of the crystallites compared to similar samples formed on a clean glass surface, and thus an increase in the number of scattering metal centers per unit surface area.

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

Експериментально досліджено поглинання світла та оптичну перколяцію у нанорозмірних плівках срібла товщиною 5 та 10 нм. Вивчено вплив підшарів ґерманію масовою товщиною до 1 нм з кроком 0,2 нм у видимому і ближньому інфрачервоному діапазоні довжин хвиль (300–2500 нм) на вищезгадані властивості плівок срібла. Оптична перколяція у плівках срібла пов'язана з особливостями механізмів росту та режимів формування конденсату металу на аморфній скляній підкладці. Показано, що попередньо нанесені на скляну підкладку підшари ґерманію зменшують порогову товщину оптичного перколяційного переходу у плівці срібла та збільшують їхню поглинальну здатність порівняно з аналогічними плівками, сформованими на чистій поверхні скла. Зростання поглинальної здатності плівок, нанесених на поверхню підшару ґерманію, обумовлене зменшенням середніх лінійних розмірів кристалітів порівняно з аналогічними зразками, сформованими на чистій поверхні скла, а відтак і збільшенням кількості розсіювальних металевих центрів на одиниці площі поверхні підкладки.

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

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1. INTRODUCTION

Metal films with a thickness of several nanometers are the main in the formation of elements of modern micro- and nanoelectronics as ohmic conductors with a high coefficient of transparency in the visible and infrared ranges of light waves [1].

The study of the electrical properties of nanosized layers and the study of the peculiarities of their interaction with electromagnetic radiation is relevant due to the possibility of production a material with new properties. In this regard, an important problem is to establish the features of the change of electrical and optical parameters of the metal film in the process of transition of its structure from the dispersed to the solid phase with increasing thickness. It is known that in the vicinity of this transition the film exhibits anomalous optical and electrical properties due to changes in the mechanisms of relaxation of current carriers.

An important problem is to establish the critical layer thickness d_c, at which the mentioned transition is manifested. The estimation of the d_c value is possible using percolation transition model [2, 3]. It is known from the literature that due to the use of underlayers of surfactants (Ge, Si, Sb) it is possible to change the value of d_c and produce metal films with the desired structure, electrical and optical parameters. This issue has been actively discussed and used in the study of

gold films deposited on the germanium sublayers [4] and silver films on the silicon underlayers [5].

In order to predict and estimate the critical thickness of the optical percolation transition d_c, we investigated the transmission and reflection spectra in the visible and near-infrared wavelength ranges (200–1800 nm) of thin layers of silver with a thickness of 5 and 10 nm deposited on a clean glass surface and glass surface pre-coated with a layer of germanium up to 1 nm thick in steps of 0.2 nm. We also considered the correlation between optical and electrical percolation transition in the studied silver films.

2. EXPERIMENTAL TECHNIQUE

Vacuum condensates of silver are prepared under conditions of static ultra-high vacuum condition (pressure of residual gas components did not exceed 10^{-7} Torr) in glass experimental devices. Note that the metal films are produced by condensing steam of thermally evaporated metal on a glass substrate cooled to 78 K using the technique of 'quench condensed' followed by thermal stabilization at room temperature ($T_{\text{room}} = 293$ K) for one day. This precluded the diffusion of the germanium inside film volume of the investigated silver film.

Germanium underlayers are applied to the substrate immediately before the condensation of test metal.

The results of study of the structure of the studied films by electron microscopy showed that at the rate of condensation of metal vapor and germanium underlayers on amorphous substrate less than 0.01 nm/s, it is possible to obtain stable, isotropic, homogeneous metal films with controlled structure.

It should be noted that the method of forming metal films on the substrate took place at a temperature $T_{\text{substrate}} \leq 0.3T_{\text{melting}}$ [6–7], where T_{melting} is the melting temperature of the metal, allows to obtain polycrystalline metal films with a lattice period similar to the crystal lattice of solid metal with average linear dimensions crystallites D, independent of the film thickness of the metal [4–5]. The obtained results are consistent with the data [8–10], which show the results of electron microscopic study of the evolution of dimensional dependences of the structure of films of a number of metals in the process of changing the temperature of the substrate. The mass thickness of the films is estimated by shifting the resonant frequency of the piezoquartz vibrator with a sensitivity not worse than 98–100 Hz/nm. The study of the transmission $T(\lambda)$ and the reflection $R(\lambda)$ spectra of silver films is performed with Shimadzu UV-3600-VIS-NIR in the visible and near-infrared region of wavelengths in the range of 200 nm $\leq \lambda \leq$ 1800 nm. The reflection spectra are investigated at a close to normal angle of incidence of electromagnetic radiation $\alpha = 8°$.

3. EXPERIMENT

The paper presents the results of the study of the transmission and reflection spectra of thin silver films obtained by the 'quench condensed' method. In order to establish the characteristics of the influence of germanium underlayers on the structure, the degree of filling of the substrate surface with silver film, and hence the reflection and transmission spectra, we studied silver films with a mass thickness of 5 and 10 nm deposited on germanium underlayers with a mass thickness of 0.2, 0.4, 0.6, 0.8 and 1 nm. These mass thicknesses are chosen not by chance, because the studied region of mass thicknesses is critical from the point of view of modern relevance and the need for further microminiaturization of the leading elements of modern electronics. It is known that the investigated region is a characteristic dimensional region of thicknesses, because the free path of the electron in investigated films at room temperature and polycrystalline structures of the metal film varies in the range from 10 to 20 nm. Note that all explanations of the obtained experimental data we will make in the approximation of the effective environment. The effective environment approximation assumes that the film is a homogeneous, isotropic system that fills the surface of the substrate. Let us analyse the spectral behaviour of the reflection coefficient of the studied silver films.

In Figure 1 shows the spectral dependences of the reflection coefficient of 5 nm thick silver films deposited on germanium underlayers with a mass thickness of 0.2, 0.4, 0.6, 0.8 and 1 nm, respectively (Fig. 1, *a*) and 10 nm thick silver films deposited on germanium underlayers with a

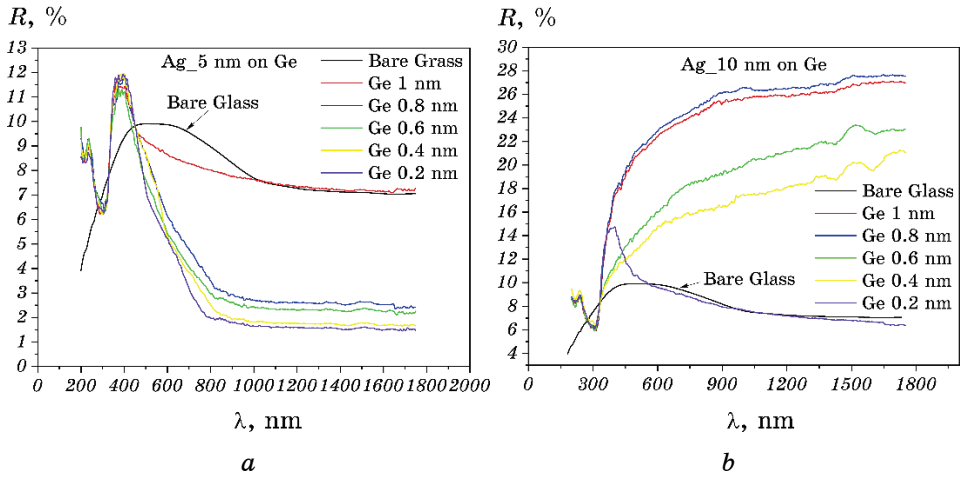

Fig. 1. The reflection spectra of silver films of different thicknesses of 5 nm (*a*) and 10 nm (*b*) are deposited on germanium underlayers with mass thicknesses of 0.2, 0.4, 0.6, 0.8, and 1 nm.

mass thickness of 0.2, 0.4, 0.6, 0.8, and 1 nm, respectively (Fig. 1, *b*). As we can see in Fig. 1, *a*, the reflection coefficient of a silver film with a mass thickness of 5 nm is smaller in comparison with the reflection coefficient from a clean glass surface (Fig. 1, *a* bare glass).

The observed behaviour of the reflection spectra may be due to the fact that the glass surface covered with a silver film becomes more inhomogeneous in the plane of the substrate, because on its surface are formed metal islands of teardrop shape (effect of 'misty glass') consequence of weak wetting) as a result the contribution to scattering of electromagnetic waves by an island phase increases. Note that germanium sublayers attenuate this effect (surfactant effect) and in particular at a thickness of 1 nm in the infrared wavelength range, the reflection coefficients of the metal film are proportional to the reflection coefficient of the pure glass substrate (Fig. 1, *a* Glass substrate) [11].

In the range of change of the germanium sublayer from 0.2 to 1 nm, the majestic reflection coefficient increases almost 4 times. Similar considerations are valid for silver films with a mass thickness of 10 nm (Fig. 1, *b*). However, due to the doubling of the mass thickness of silver, the picture changes radically, both in terms of the spectral dependence of the reflection coefficient and the values of its value. As we can see, 10 nm-thick silver films deposited on germanium underlayers with a mass thickness greater than 0.2 nm tend to increase the value of the reflection coefficient T with increasing λ. While the reflection coefficient for a silver film on germanium underlayer is 0.2 nm, similarly to a pure glass substrate (Fig. 1, *b* Glass substrate), the value of R of the metal film decreases with increasing electromagnetic wavelength λ. Note that the observed behaviour is characteristic of the properties of dielectric materials [2], and since we are dealing with metallic condensates of silver, we are talking about the dispersed phase (island film) of the investigated metal film.

We analyse the behaviour of the transmission spectra of the studied silver films. According to the percolation model, under the condition only free electrons of the metal subsystem [2] are involved in the region of mass thicknesses corresponding to the percolation transition of the reflection spectra R show independence from the wavelength λ. The effect is especially pronounced in the middle and infrared regions of electromagnetic wavelengths (approximation of free electrons). For the case when the spectral dependence T shows an increase in wavelength in the infrared region, which indicates an increase in optical transparency. We say that the metal film has a percolation structure and consists of separate isolated metal clusters (dispersed condensate phase). For the case of reverse trend course of the spectral dependence of the reflection coefficient, namely the decrease in the value of the transmission spectrum T with increasing wavelength λ, according to the percolation approach [2] we see the post-percolation the behaviour

of the optical properties of the investigated silver film.

The analysis of the spectral curve of the transmittance of a silver film with a mass thickness of 5 and 10 nm is given in Fig. 2, *a* and Fig. 2, *b*. From the figures we can see that the considered spectral dependence of the transmittance for silver films with a mass thickness of 5 nm shows pre-percolation behaviour for all values of germanium wetting layers (Fig. 2, *a*). At the same time, silver films with a mass thickness of 10 nm exhibit all three types of T spectral behaviour for different mass thickness of the germanium layers. Germanium underlayers with a mass thickness of 0.8 nm accelerate the appearance of a percolation channel in the silver film, because in the range $\lambda > 1000$ nm the transmittance is weakly dependent on λ. On the other hand, in the range of mass thickness of the germanium $d_{Ge} < 0.8$ nm, the silver film exhibits a percolation behave [2]. Let us analyse the obtained spectral dependences of the transmission coefficient within the percolation approach [2]. To achieve this goal, we need to analyse the graphs of the dimensional dependences of the transmittance T for different values of the electromagnetic wavelength λ in the infrared region of wavelengths (approximation of free electrons) (Fig. 3).

According to the percolation model, the dimensional dependences of the transmission spectra of thin metal films for different wavelengths in the infrared region tend to intersect at some point, which corresponds to the mass thickness of the metal films for which the percolation transition is observed. The analysis of the corresponding dimen-

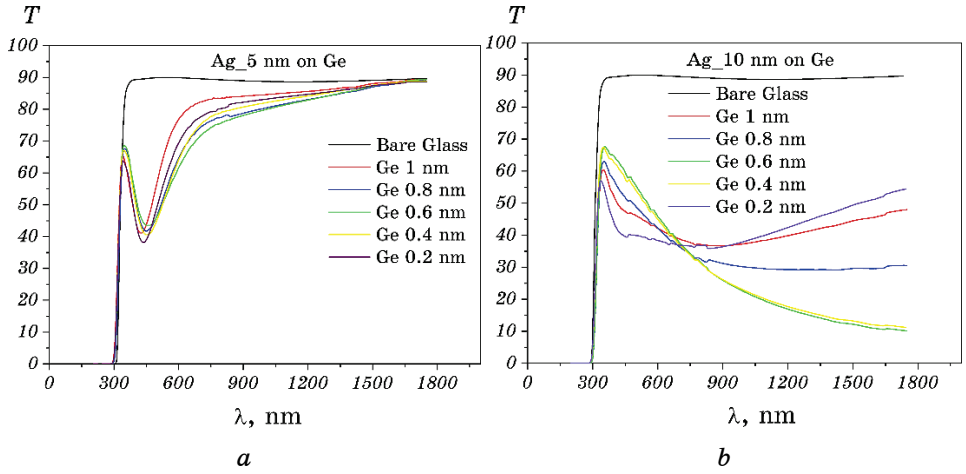

Fig. 2. Transmission spectra of silver films of different thickness. *a*—silver films with a mass thickness of 5 nm deposited on underlayers of germanium with a mass thickness of 0.2, 0.4, 0.6, 0.8, and 1 nm; *b*—silver films with a mass thickness of 10 nm deposited on underlayers of germanium with a mass thickness of 0.2, 0.4, 0.6, 0.8, and 1 nm.

sional dependences given for the wavelengths of 900, 1000, 1500, and 1700 nm is given on Fig. 3. From the obtained dimensional dependences, we observe a characteristic feature of the behaviour for the studied silver films. In particular, both for 5 nm films and for 10 nm films there is a characteristic dimensional dependence of T with a minimum, the magnitude of which manifests itself depends us λ. The course of these dependences also shows a tendency to intersect the dimensional curves T at the points of the predicted percolation transition of the studied silver films. We observe this behaviour especially vividly for films with a mass thickness of 10 nm (Fig. 3, *b*). The mass thickness of the germanium underlayer corresponding to the percolation transition condition in silver films with a mass thickness of 10 nm is 0.825 nm of the mass thickness of the germanium underlayer.

Other characteristic points of intersection of the curves do not give an unambiguous interpretation and physical explanation of the predicted values of d_c. Analysis of the absorption spectra of the studied films shown in Fig. 4 confirm the fact that silver films with a mass thickness of 5 nm (Fig. 4, *a*) are dispersed, because the absorption maxima correspond to the plasmon resonance in the studied samples around 450 nm. The germanium underlayers also change the half-width of the spectral distribution and shift the maximum distribution to the region of smaller λ, which can also cause stronger bonds (covalent type) between the silver film and the germanium underlayers and reduce the average linear dimensions of metal islands. In the case of 10

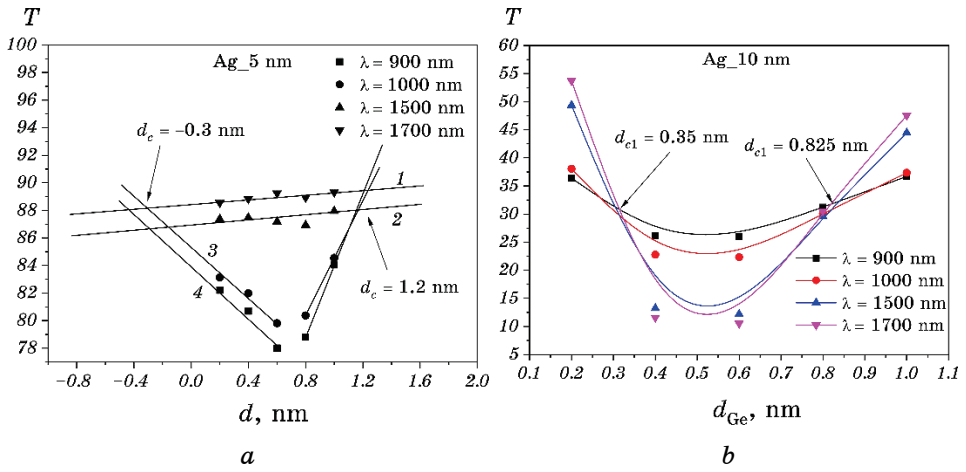

Fig. 3. Dimensional dependences of the transmission spectra of T films of silver for different values of wavelengths: 900, 1000, 1500, and 2000 nm. The point of intersection of the lines corresponds to the mass thickness of the percolation transition: *a*—silver films with a mass thickness of 5 nm; *b*—silver films with a mass thickness of 10 nm.

nm silver films, the maxima are more blurred, which may be the reason for the existence of both metallic and dispersed phases at the same time.

Note that additional information can be obtained by analysing the relationship between the size of the islands and their plasmon frequencies of the electronic subsystem [12].

According to the percolation model [2], the percolation threshold in the film corresponds to the critical film thickness d_c, at which the first ohmic conductivity channel occurs. In the vicinity of the transition from the islet to the appearance of the first conductive channel with an ohmic mechanism of charge transfer in the film, the dependence of the resistance R of the metal film on its thickness d can be represented by some universal thickness function:

$$R(d) \sim (d - d_c)^{-\gamma}. \tag{1}$$

Expression (1) is obtained from the assumption that $(d - d_c) \sim (x - x_c)$ [2], where x is a parameter that characterizes the degree of filling of the substrate with metal, x_c is the percolation parameter that corresponds to the degree of filling of the substrate surface, at which islands (crystallites) will form the first conductive channel. The exponent in expression (1) depends on the mechanism of film formation and growth. With two-dimensional film growth (2D percolation), the value of the exponent γ varies in the interval from 1 to 1.3, and in the case of

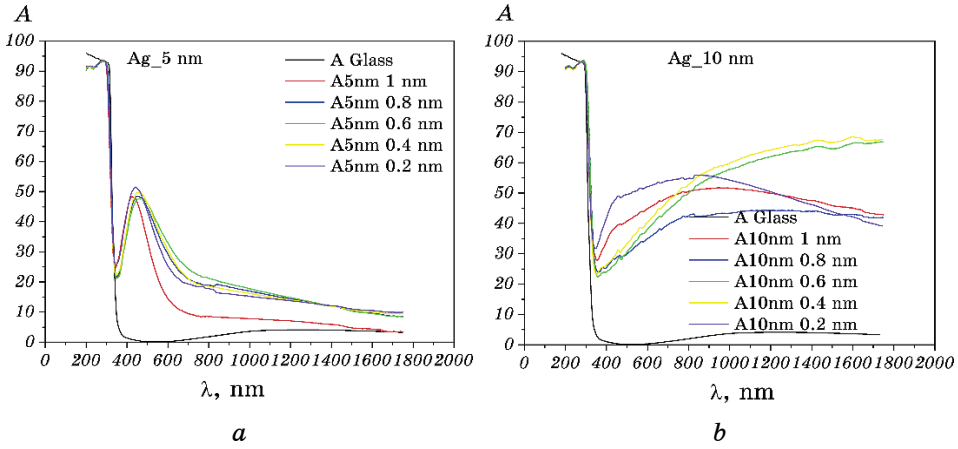

Fig. 4. Absorption spectra of silver films of different thickness. *a*—silver films with a mass thickness of 5 nm deposited on underlayers of germanium with a mass thickness of 0.2, 0.4, 0.6, 0.8, and 1 nm; *b*—silver films with a mass thickness of 10 nm deposited on underlayers of germanium with a mass thickness of 0.2, 0.4, 0.6, 0.8, and 1 nm.

$3D$ percolation, the value of γ usually exceeds the value of 1.5. Accordingly, the degree of filling of the surface with crystallites $x_c \geq 0.3$ at $2D$ percolation, and for $3D$ growth mode $x_c \geq 0.5$.

Analysis of the dimensional dependences of the resistance on the square of thin films of silver (Fig. 5) indicates a $2D$ mode of condensate formation on the substrate surface is predominant mode of layer-by-layer condensate formation, because the parameter $\gamma > 1.14–1.16$. On the other hand, the percolation coefficient d_c, which is responsible for the critical thickness of the occurrence of first ohmically conductive channel in the silver film, is 1.2 and 0.9 nm, respectively. The value of d_c agrees well with similar experimental data for optical percolation data shown on Fig. 3, which are 1.2 and 0.825 nm, respectively. The obtained result testifies to the consistency between the optical and electrical properties of the investigated silver films, because the structure of the condensate of the silver film on the surface of the substrate is responsible for the properties of the silver films.

Based on the obtained results, we can say that germanium underlayers change the conditions of condensation and mechanism formation of silver film deposited on top of germanium layers. By changing the mass thickness of the germanium wetting layers, it is possible to control the peculiarities of the conditions of formation of metal condensate on the surface of the substrate. The technique of surfactant layers [4, 5] allows to form metal samples with given electro-optical properties in the studied region of thicknesses. The observed effect requires further study in order to establish criteria for the influence of germanium layers on the

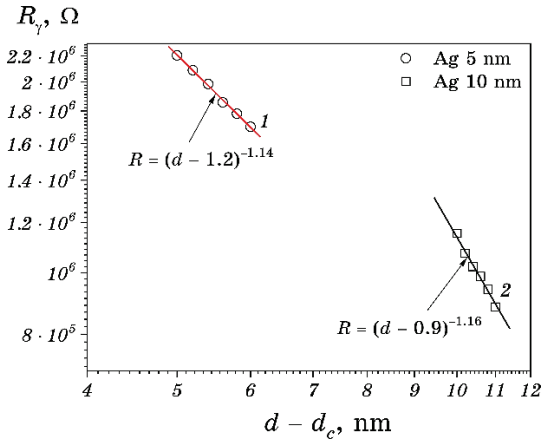

Fig. 5. Dimensional dependences of resistance per square of silver films of 5 nm (curve *1*) and 10 nm (curve *2*) deposited on germanium underlayers of 0.2 nm, 0.4, 0.6, 0.8, and 1 nm, respectively. Points are experimental data, linear lines are approximation functions of type $R_\gamma \sim (d - d_c)^{-\gamma}$ [5].

structure and optical properties of silver films of different mass thicknesses.

We emphasize that for the first time the possibility of predicting the critical value of the mass thickness of the surfactant underlayer for the formation of the percolation structure in silver films of different mass thickness is presented. The obtained result agrees with the results of the study of the influence of the dimensional effect on the kinetic properties of silver films with a thickness of 5 and 10 nm deposited on germanium underlayers of different thickness. The study of the influence of dimensional effect and surfactant underlayer on electrical and optical properties of 5 and 10 nm thick silver films and confirms the high sensitivity of physical properties of silver films to the mass thickness of germanium underlayer.

4. CONCLUSIONS

1. It is established that the numerical values of the thickness d_c, which corresponds to the optical percolation in thin films of silver, agree well with the quantitative data of the thickness of the percolation transition d_c calculated from the dimensional dependences of the resistance of silver films.
2. Germanium underlayers reduce the threshold thickness of the percolation transition d_c in the film and allow the formation of silver films with the desired electro-optical properties.
3. It is shown that the absorption capacity of silver films of a given thickness deposited on germanium underlayers is greater than the absorption capacity of similar samples formed on a clean glass surface. The observed properties are a consequence of the formation of a finer-grained structure of the silver film and an increase in the concentration of insulated metal islands on the surface of the glass substrate.

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