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SYNTHESIS OF SURFACE STRUCTURES DURING LASER-STIMULATED EVAPORATION OF A COPPER SULFATE SOLUTION IN DISTILLED WATER

The methodology, technique, and results of studies of the formation of films on the glass surface during the irradiation of water solutions of copper sulfate with the laser radiation are presented. We used the nanosecond radiation of an yttrium-aluminum garnet laser with the generation wavelength $\lambda = 1.06$ μm. The studies used solutions with different concentrations of copper sulfate. The structure of the films obtained in this case is compared with the structure of the films obtained as a result of drying the solutions without exposure to a laser radiation. The resulting films have both ordered and disordered structures. The characteristic dimensions of the structural elements of the films are 0.5–2 μm. The transmission of films in the 300–1200 nm spectral region is studied. In general, the resulting films are transparent in this area. Their transmission practically does not depend on the wavelength, but is different for different concentrations of the solution of copper sulfate.

Keywords: laser-stimulated evaporation, yttrium-aluminum garnet laser radiation, aqueous solution of copper sulfate, films, ordered structure, transmission spectra.

1. Introduction

Micro- and nanostructures synthesized on the surface of solid structures are currently widely used in highly dispersed systems, in particular, adsorbents, catalysts, fillers of composite materials, membranes, and in a number of other small-scale systems with quantum effects [1]. The creation of such structures on the surface of dielectrics and metals is carried out by various chemical and physical methods [2–14]. Among the physical methods of structuring the surface of metals, dielectrics, and semiconductors, a special place is occupied by laser methods, whose radiation of nano-pico- or femtosecond duration directly acts on the surface of a solid structure in air or another gaseous medium [10–13]. Another application of the laser radiation for surface nanostructuring can be laser-stimulated deposition from a salt solution placed on the surface of a solid [14].

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It should be noted that the characteristics of the structured and modified surface and the mechanisms of its structuring when applying the laser-stimulated evaporation of salt solutions from the surface of solid structures, in particular, under the action of defocused laser beams of the infrared range of the spectrum, are currently poorly researched and are of interest for a more detailed study with the aim of their practical use. Of particular interest are such studies, which can be carried out using widely available solid-state lasers with the duration of generation pulses in the interval of 5–50 ns. In this regard, we conducted studies of the formation of surface structures and their optical characteristics during the laser-stimulated evaporation of $CuSO_4$ salt solutions in distilled water from the surface of a glass substrate in air at atmospheric pressure.

The methodology, technique, and results of these studies are presented in this article.

2. Experiment Technique and Results

To create films from an aqueous solution of copper sulphate ($CuSO_4$), the laser radiation on yttrium-aluminum garnet (LIAG) was used. The scheme of the experiment is shown in Fig. 1. The main node of the experimental setup is an optical quantum generator with the modulated Q-factor of resonator (*1*). It emitted pulses of infrared light with the wavelength $\lambda = 1.06$ μm. The duration of a laser pulse was 40 ns. The tracking frequency of laser pulses was 1 Hz. The generation was carried out in one transverse and many longitudinal modes. At the same time, the laser pulse had the Gaussian spatial and temporal distributions.

Radiation from the generator was sent to amplifying stage (*2*), which consisted of three single-pass amplifiers of laser radiation. The energy in a laser pulse after the amplification was 0.05 J. The polarization of laser radiation was linear. After exiting the amplifying stage, the laser radiation was directed vertically down onto stage (*5*) with the help of rotating prism (*4*). On it was placed glass plastic (*6*) with two drops (*7*) and (*8*) of an aqueous solution of copper sulfate of the same concentration, almost identical in volume and size. During the experiment, one of these drops (*7*) was irradiated with laser radiation, and the other (*8*) remained a control (it was not irradiated with laser radiation and dried under normal atmospheric conditions). Diffusing lens (*3*) was used in the experiment to increase the diameter of the laser beam (4 mm) to the diameter of the solution drops (15 mm).

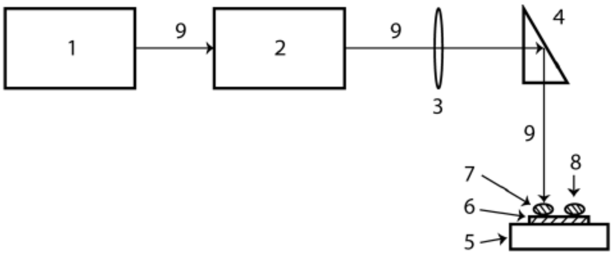
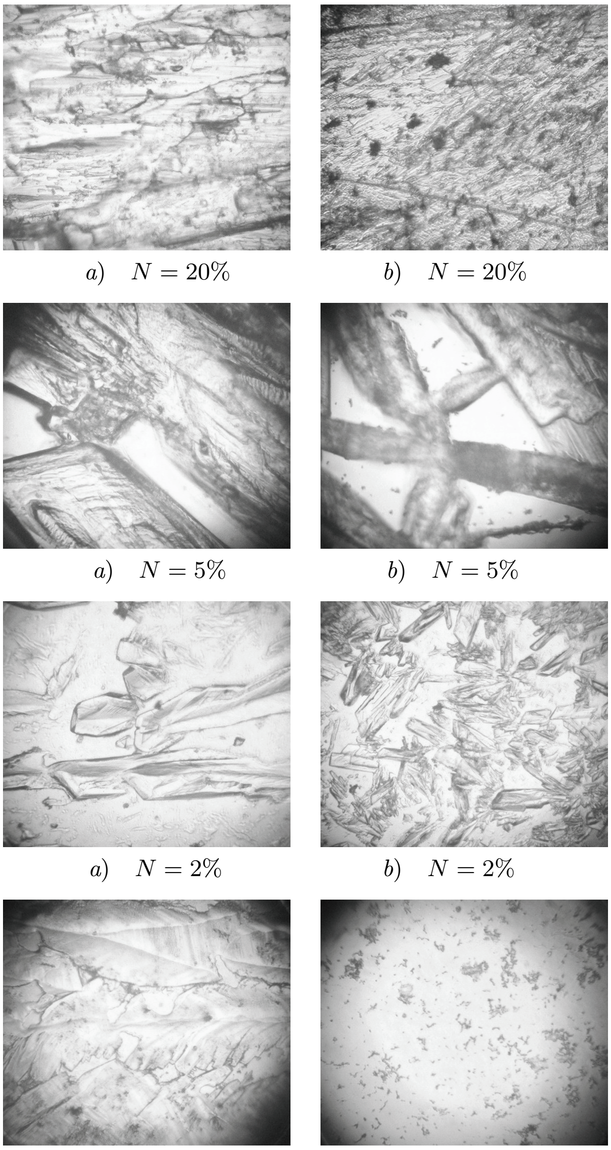


Fig. 1. Scheme of the experimental setup: *1* – optical quantum generator on yttrium-aluminum garnet; *2* – a cascade of three laser radiation amplifiers; *3* – diffusing lens; *4* – turn prism; *5* – item table; *6* – glass plate; *7* and *8* – identical drops of copper sulfate solution; *9* – laser radiation

The above energy and geometric characteristics of laser radiation indicate that the average power density of laser radiation on the surface of the studied solution drop was approximately 1.8×10^{10} W/m^2. In the experiment, drops with different concentrations of copper sulfate solution in distilled water were studied – N = 1%, 2%, 5% and 20%. In all studies, 6 drops of these solutions were used. The duration of the laser irradiation of the studied drops was equal to the duration of the complete drying of the control drops, which was an average of 200 minutes. Note that the drops that were irradiated with laser radiation dried faster (approximately in 120–150 minutes). So, during the rest of the time, the laser radiation already acted on the dry spots.

With the help of a device consisting of an optical microscope and a camera, photographs were taken of films that were formed from spots under the action of laser radiation, as well as films that were formed as a result of the drying of control spots. 20 photographs of different areas corresponding to the central parts of the obtained films were taken. In the case of films obtained under the action of laser radiation, radiation with maximum intensities fell into these parts. Illumination of the films in a microscope was carried out by an incandescent lamp. In Fig. 2 are given photos that contain the characteristic features. The total magnification of the used photo device was equal to 1500. The widths shown in Fig. 2 correspond to a size of 2 μm for the corresponding films.



a) $N = 20\%$ *b*) $N = 20\%$

a) $N = 5\%$ *b*) $N = 5\%$

a) $N = 2\%$ *b*) $N = 2\%$

a) $N = 1\%$ *b*) $N = 1\%$

Fig. 2. Photomicrographs of films obtained under the action of laser radiation (*a*) and control films (*b*) when using an aqueous solution of copper sulfate with different concentrations of N

Let us consider the main features of the structures of the obtained films. Thus, the control film obtained for the maximum concentration of copper sulfate solution used by us ($N = 20\%$) consists of randomly placed relatively small crystals. At the same time, the surface of the glass substrate is completely covered with these crystals. Let us now consider the film obtained for this solution concentration under the influence of laser radiation. This film is non-uniform. It does not contain clear rectilinear forms characteristic of crystalline structures. The density of the coating of the glass substrate in this case is also high – the entire surface of the glass is covered with a film.

For the solution concentration $N = 5\%$, both films have a clear crystalline structure. At the same time, the crystals are significantly larger than in the previous case. Moreover, for the film obtained under the action of laser radiation, the crystals have slightly larger sizes than for the control film. The density of the coating of the substrate in this case is much less than in the previous case – there are areas on the glass that are not covered by crystals.

In the case of a solution of copper sulfate with $N = 2\%$, there is a significant difference in the structures of the control film and the film obtained under the action of laser radiation. Thus, in the case of the control film, the surface of the glass is uniformly covered with randomly arranged small crystals. The density of the glass surface coating is approximately 50%. The structure of the film obtained under the action of laser radiation contains significantly larger crystals. Relatively long crystals stand out. They have a trough-like shape – depressions run along these crystals almost along their entire length. The orientation of these long crystals draws attention – they are placed almost parallel to one another. The density of the coating of the glass surface with these crystals is small as compared to the coating in the case of the control film.

At a concentration of 1% of the copper sulfate solution, the resulting films differ in structure even more significantly. Their structure is also significantly different from the structure of films obtained for higher concentrations of the copper sulphate solution. Thus, the control film does not contain any crystalline structure. It is quite uniform with very small inclusions of dark-colored particles. Judging by the color, these inclusions are probably microscopic particles of copper oxides.

As for the film obtained under the action of laser radiation, unlike the control film, it is highly heterogeneous and has a clearly manifested structure. The coating of the glass surface for this film is quite dense. A characteristic feature of the structure of this film is the absence of objects with clear rectilinear forms, which are characteristic of crystalline structures, and which are manifested in our films obtained for higher concentrations of the solution. Instead, the structure of this film consists of a series of leaf-shaped spots, which are separated by clear dark curvilinear boundaries. The main part of the leaf-shaped spots is elongated along the length. This is clearly visible on the example of two leaf-shaped spots shown in the photo. In turn, some spots have clearly identified ordered structures. This is quite clearly visible on the stain located in the lower part of the corresponding photo in Fig. 2.

These ordered structures consist of dark and light lines and stripes, which, within the same spot, are placed in parallel to one another, and, at the same time, at different angles to the structures corresponding to the neighboring spots. The dimensions of the elements of both ordered and disordered structures are about 0.5–2 μm.

We conducted a detailed study of the transmission spectra of the obtained films. The measurements of these spectra were carried out on the spectral complex based on the monochromator in the wavelength interval 300–1200 nm. For these studies, the installation was used, the scheme of which is shown in Fig. 3.

The radiation from the light source was collected by quartz condenser (*4*) and focused on the entrance slit of monochromator (*6*). Monochromatic light fell on sample (*1*) fixed in a holder which was placed in measuring chamber (*2*). The intensity of the light transmitted by the sample was determined by photomultiplier (*7*) using registration system (*8*). The registration of experimental data at the output of the photomultiplier was ensured by the use of a program that sets the required number of photon counts at each point of a given spectral range, the step of scanning the spectrum, and the initial and final values of the wavelength. In more details, the method of researching the transmission of light through films on this installation is given in [15].

We investigated the integrated transmission of films – the transmission of areas of films with a diameter of approximately 3–4 mm, which correspond to the central parts of the films. It is obvious that a significant number of objects of the film structure, which are shown in Fig. 2. The research was conducted for three areas of the spectrum that partially overlap: 300–500 nm; 400–800 nm, and 700–1200 nm. This is due to the use of various lamps (hydrogen lamp and incandescent lamp), as well as different types of diffraction gratings and photomultipliers for conducting the research in different areas of the radiation spectrum. In these studies, the step of changing the wavelength was 2 nm, and the width of the spectrum of the radiation incident on the sample was 0.2 nm. The results of these studies of the transmission spectra are shown in Fig. 4.

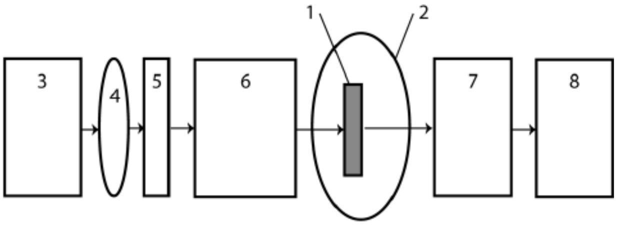
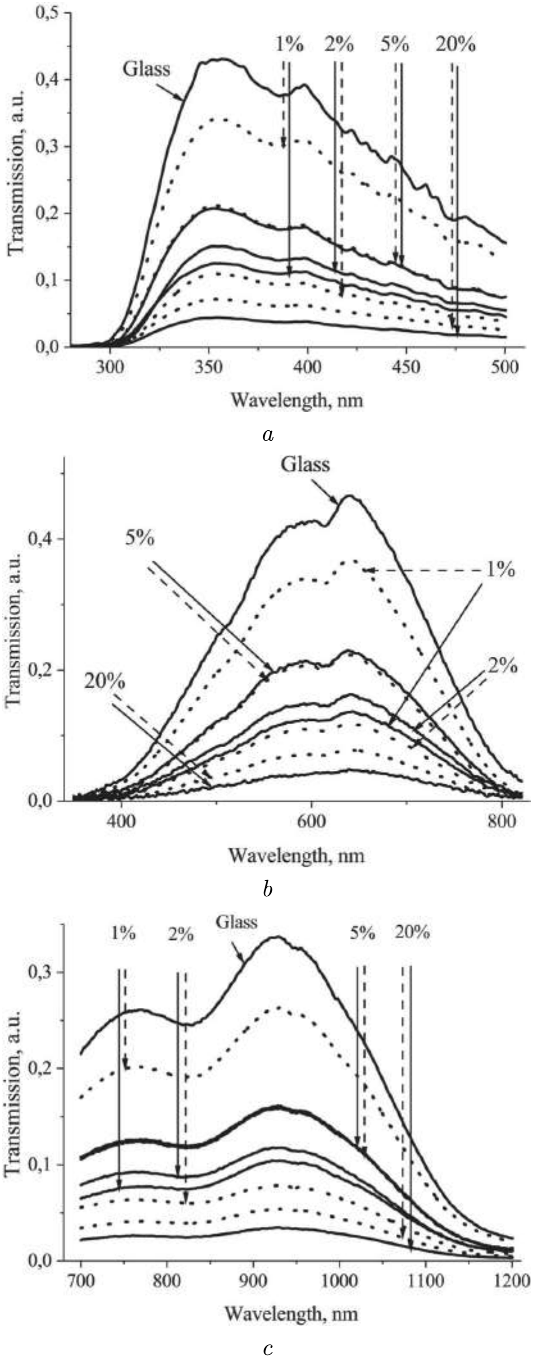


Fig. 3. The optical system of the installation for researching the transmission spectra of films: *1* – sample; *2* – measuring chamber; *3* – light source, *4* – condenser; *5* – light filters; *6* – monochromator; *7* – photoelectronic multiplier; *8* – radiation registration system

It is obvious that the spectra for the films presented in Fig. 4 include both the transmittance of the films themselves and the transmittance of the glass, the emission spectrum of the light source, and the sensitivity of the photomultiplier, while the spectrum corresponding to the glass substrate includes the transmittance of the glass, the emission spectrum of the light source, and the sensitivity of the photomultiplier. Therefore, to obtain the transmission spectra of the films themselves, it is necessary to substract, from the data on the transmission spectra of the films on the glass, the data on the transmission spectrum of the glass. The transmission spectra of the films obtained as a result of this procedure are presented in Fig. 5. “Stitching” of the data obtained for three sections of the spectrum into one dependence was carried out for wavelengths of 500 and 750 nm. Based on the given procedure for processing the obtained results, the transmission level equal to 1 in Fig. 5 corresponds to the transmission level of the glass substrate. Accordingly, the data for the films in this figure are given relative to the transmittance of the glass substrate.

As can be seen from Fig. 5, the transmittances of both control films and films obtained under the action of laser radiation, in general, do not strongly depend on the wavelength. Thus, for all films, there is a slight increase in the transmittance (approximately



a

b

c

Fig. 4. Transmittance of films on glass substrates obtained by using the solutions of copper sulfate with different concentrations, as well as a glass substrate for different areas of the spectrum. Dashed curves and arrows correspond to control films, and solid ones to films formed under the action of laser radiation and a glass substrate. The numbers in the figures correspond to the concentration of the used solution

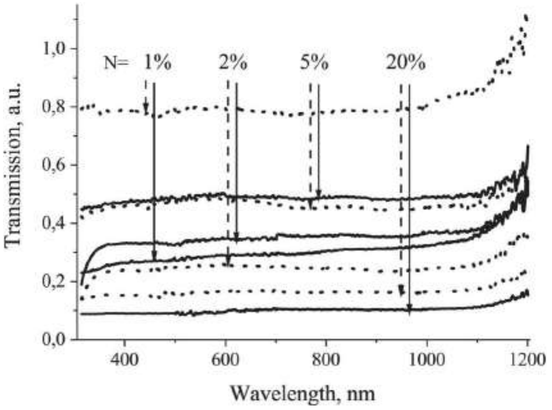


Fig. 5. The transmission spectrum of the films themselves (when excluding the transmission of glass substrates). Dashed curves and arrows correspond to control films, and solid ones to films formed under the action of laser radiation

by 1.5 times) for the region $\lambda > 1000$ nm. In addition, for both films obtained for $N = 2\%$, there is a slight decrease in the transmittance in the ultraviolet region $\lambda < 350$ nm. In all other cases, the transmission of films practically does not depend on the wavelength. The exception is the film obtained under the action of laser radiation for $N = 1\%$. For it, there is a monotonous increase in the transmittance with increasing the wavelength.

However, the average values of transmission coefficients differ significantly for different films. It should be noted that, for the obtained results, no correlation between the concentration of the used solution and the transmission of the corresponding films was found.

It is obvious that, for films that contain crystal structures, the main reasons for the loss of the intensity of incident radiation, along with the absorption, are the reflection and refraction of light at the faces of the crystals. Therefore, the transmittance of such films should depend on the size of the crystals and the density of these crystals covering the surface of glass substrates. It should be noted that the data on the transmission spectra of films with a crystalline structure, which are shown in Fig. 4 and Fig. 5, generally agree well with the features of their crystal structures, including those shown in Fig. 2.

For example, let us consider the spectra obtained for films corresponding to a solution of copper sulfate with the concentration $N = 2\%$. As can be seen from Fig. 2, the density of a coating with crystals of the film obtained under the action of laser radiation in this case is significantly lower than the density of the coating of the control film. Accordingly, the transmission of the first film is greater than the transmission of the control film. In addition, the density of a coating of the glass substrate with crystals for both films obtained from a solution of sulfate with the concentration $N = 5\%$ is approximately the same and relatively small. Accordingly, in this case, the transmission of both films is approximately the same and greater than the transmission of films corresponding to a solution with the concentration $N = 2\%$.

In general, as can be seen from Fig. 5, in cases where the films contain crystalline structures, the transmittances of the control films and the films obtained under the action of laser radiation do not differ much from one another. As for films that do not contain clear crystal structures (films obtained for copper sulfate solutions with the concentrations $N = 1$ and 20%), it is obvious that the main reason for the loss of the radiation intensity must be the absorption. In this case, there is a significant difference in the transmissions of control films and films obtained under the influence of laser radiation. Thus, the transmissions of the film obtained under the influence of laser radiation in the case of $N = 20\%$ approximately by 2 times and, in the case of $N = 1,\%$ approximately by 3 times are less than the transmissions of the corresponding control films.

3. Conclusions

We have investigated the process of film formation as a result of the exposure to a solution of copper sulfate in distilled water with different concentrations of powerful infrared nanosecond laser radiation. At the same time, a number of films were obtained. The structure of the films obtained by us under the influence of laser radiation mainly differ from the structures of the control films. Some of the obtained films have clear crystal structures, while some of the films have no crystal structure. The size of the elements of the film structures is 0.5–2 microns.

Control films and films obtained under the influence of laser radiation are transparent for the visible range of the spectrum. Their transmittance depends weakly on the wavelength of light. However, the transmission coefficients of the films differ significantly for different films. Moreover, no correlation between the permeability of the films and the concentration of the corresponding solutions is found. For films that contain crystalline structures, the ratio for transmission coefficients is consistent with the features of these structures. The transmission of films that do not contain crystalline structures is significantly less as compared to the transmission of the corresponding control films.

In general, the results of our research indicate the fundamental possibility to obtain relatively transparent structured films with different optical properties by the method of irradiation with powerful nanosecond laser irradiation of solutions of chemical compounds.

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СИНТЕЗ ПОВЕРХНЕВИХ СТРУКТУР ПРИ ЛАЗЕРНО-СТИМУЛЬОВАНОМУ ВИПАРОВУВАННІ РОЗЧИНУ МІДНОГО КУПОРОСУ У ДИСТИЛЬОВАНІЙ ВОДІ

Викладено методику, техніку і результати досліджень утворення плівок на поверхні скла при опроміненні водних розчинів мідного купоросу лазерним випромінюванням. Використовувалося наносекундне випромінювання ітрій-алюмінієвого гранатового лазера з довжиною хвилі генерації $\lambda = 1{,}06$ мкм. У дослідженнях використовувалися розчини із різною концентрацією мідного купоросу. Структура отриманих при цьому плівок порівнюється зі структурою плівок, отриманих у результаті висихання розчинів без дії лазерного випромінювання. Отримані плівки мають як впорядковану, так і невпорядковану структуру. Характерні розміри структурних елементів плівок становлять 0,5–2 мкм. Досліджувалося пропускання плівок в області спектра 300–1200 нм. Отримані плівки є прозорими у цій області. Їх пропускання слабко залежить від довжини хвилі, однак є різним для різної концентрації використовуваного розчину мідного купоросу.

Ключові слова: лазерно-стимульоване випаровування, випромінювання ітрій-алюмінієвого гранатового лазера, водний розчин мідного купоросу, плівки, упорядкована структура, спектри пропускання.