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Obtaining Films by Irradiation of an Aqueous Solution of Copper Sulfate by Infrared Laser Radiation

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Abstract—The methodology, technique, and results of studying the formation of films on the glass surface during laser irradiation of water solutions of copper sulfate with radiation are presented. The nanosecond radiation of an yttrium-aluminum garnet laser with a generation wavelength $\lambda = 1.06$ μm was used. Solutions with different concentrations of copper sulfate were applied. The structure of the films obtained in this case was compared with the structure of the films obtained as a result of drying solutions without exposure to laser radiation. The resulting films have both ordered and disordered structures. The characteristic dimensions of the structural elements of the films are 0.5–10 μm. The transmission of films in the visible spectral region (400–800 nm) was studied. In general, the resulting films are transparent in this area. Their transmission hardly depends on the wavelength, but it is different for different concentrations of the used solutions of copper sulfate.

Keywords: formation of structured films, yttrium-aluminum garnet laser radiation, copper sulfate aqueous solution, microphotographs of films, transmission spectra

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INTRODUCTION

Surface nanostructures have a future practical application in highly dispersed systems, in particular, adsorbents, catalysts, fillers of composite materials, membranes, and a number of other low-dimensional systems with quantum effects [1]. The formation of such structures on the surface of solids is carried out by various chemical and physical methods [2–4]. Thus, in [2], the main achievements in the field of electrochemical synthesis of nanostructured oxide coatings on aluminum, titanium, and niobium are analyzed and experimental data on studies of the morphology and physicochemical characteristics of nanostructured oxide coatings on valve metals, as well as their possible practical applications, are considered.

The study of imprints on the surface of electrodes of a high-current nanosecond discharge in air at atmospheric pressure, initiated by runaway electrons, showed that various surface structures with micro- and nanodimensions are formed on the anode surface, which makes it possible to modify and structure its surface [3].

The use of an overvoltage bipolar discharge of nanosecond duration in air at atmospheric pressure between copper, zinc, and stainless-steel electrodes made it possible to obtain surface nanostructures of transition metal oxides, which were deposited on a dielectric substrate placed near the electrode system [4–6].

In [7], the achievements in the field of technologies for obtaining periodic structures on the surface of semiconductors, metals, and dielectrics, mainly under the influence of laser radiation of nano-, pico- and femptosecond durations, are considered, and it is noted that periodic surface structures can be used in the manufacture of new types of MIS-transistors of liquid crystal displays and cells of solar elements.

In addition to surface nanostructures with sizes in the range of nano-, picometers, the synthesis of surface formations with sizes at the level of ten to one hundred micrometers during the interaction of radiation from a high-power CO_2 laser and a solid-state laser with 1 ms generation pulses was reported in [8].

The production of a thin nanostructured iron oxide film on a sapphire substrate under the action of laser radiation with a wavelength of $\lambda = 1064$ nm was reported in [9]. The film was probably in a superparamagnetic state, which is important for use in gas-sensitive sensors and various magnetic devices in medicine and biophysics.

The characteristics of a structured and modified surface and the mechanisms of its structuring when using laser-stimulated evaporation of salt solutions from the surface of solids, in particular, under the

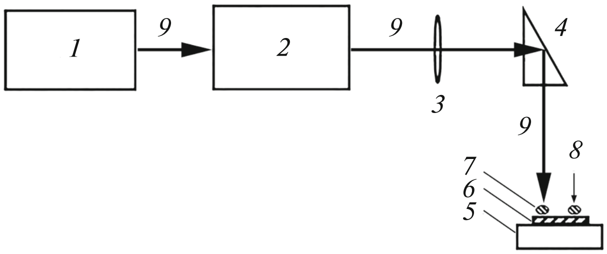


Fig. 1. Scheme of the experimental setup for creating films: (*1*) optical quantum generator based on yttrium-aluminum garnet; (*2*) cascade of three laser radiation amplifiers; (*3*) diverging lens; (*4*) rotary prism; (*5*) object table; (*6*) glass plate; (*7*, *8*) identical drops of copper sulfate solution; (*9*) laser radiation.

action of laser radiation in the infrared range of the spectrum, are currently poorly understood and are of interest for a more detailed study with the aim of their practical application. Of particular interest are such studies that can be carried out using widely used solid-state lasers with generation pulse durations in the range of 5–50 ns.

This paper presents the methodology, technique, and results of studies of structuring on the surface of glass during laser-stimulated evaporation of aqueous solutions of copper sulfate ($CuSO_4$) from a glass substrate in air of atmospheric pressure.

EXPERIMENTAL TECHNIQUE AND RESULTS OF RESEARCH

To create films on the surface of glass substrates from an aqueous solution of copper sulfate, radiation from an yttrium aluminum garnet laser was used. The scheme of the experimental setup is shown in Fig. 1. The main unit of the used installation was an optical quantum generator with a Q-switched resonator (*1*). It emitted pulses of infrared light with a wavelength of 1.06 μm. The duration of the laser pulse was 40 ns. The laser pulse repetition rate was 1 Hz. Generation was carried out on one transverse and many longitudinal modes. In this case, the laser pulse had Gaussian spatial and temporal distributions.

Radiation from the generator was directed to an amplifying stage (*2*), which consisted of three single-pass laser radiation amplifiers. The energy in the laser pulse after amplification was 0.05 J. The polarization of the laser radiation was linear. After exiting the amplifying stage, the laser radiation was directed vertically down to the object stage (*5*) using a rotating prism (*4*). A glass plate (*6*) was placed on it 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 one remained the control one (it was not irradiated with laser radiation and dried up under normal atmospheric conditions). To increase the diameter of the laser beam (4 mm), a diverging lens (*3*) was used in the experiment to the diameter of the droplets of the solution (15 mm).

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 an aqueous solution of copper sulfate were used: $N = 1$; 2; 5; and 20%. Six drops of the appropriate solutions were used in all studies. The experiments were carried out at room temperature and atmospheric pressure.

The duration of laser irradiation of the studied drops was equal to the duration of complete drying of the control drops, which averaged 200 min. Note that the drops that were irradiated with laser radiation dried out faster (approximately in 120–150 min). Thus, the laser radiation was already acting on the dried films the rest of the time.

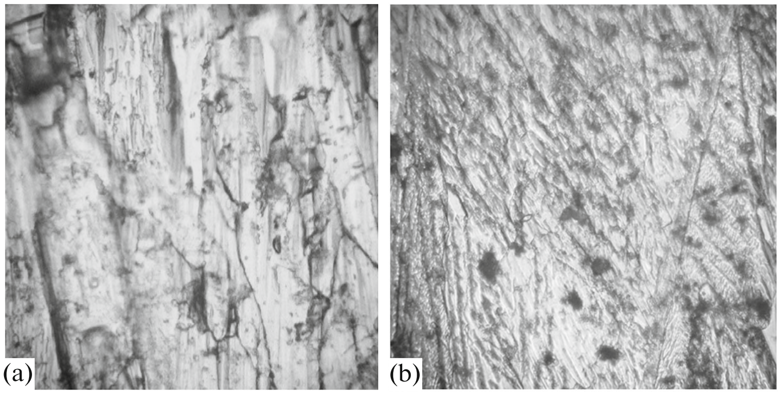
Using a device assembled from an optical microscope and a camera, we photographed films formed as a result of drying of control spots as well as the films formed from spots under the action of laser radiation. In this case, approximately 20 photos of various sections were taken corresponding to the central parts of the obtained films. In the case of films obtained under the action of laser radiation, radiation with maximum intensities fell into these parts. The films were illuminated in the microscope with an incandescent lamp. The total magnification of the photographic device was 300.

Figure 2 shows photographs that contain the characteristic features of the obtained films. The width of photographs shown in Fig. 2 correspond to the size of 10 μm on the corresponding films. As follows from Fig. 2, the characteristic dimensions of the structural elements of the resulting films are 0.5–10 μm.

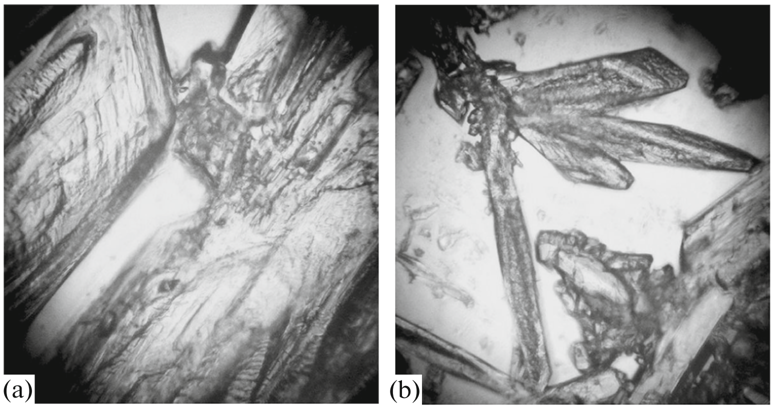
Let us consider the main features of the structures of the obtained films.

Thus, the control film obtained at the maximum concentration of copper sulfate solution we used ($N =$ 20%) consists of chaotically scattered relatively small crystals. The surface of the glass is completely covered with these crystals. Let us now consider a film obtained at this concentration of the solution under the action of laser radiation. This film is inhomogeneous. It does not contain clear rectilinear forms characteristic of crystalline structures. The coating density of the glass substrate in this case is also high: the entire surface of the glass is covered with a film.

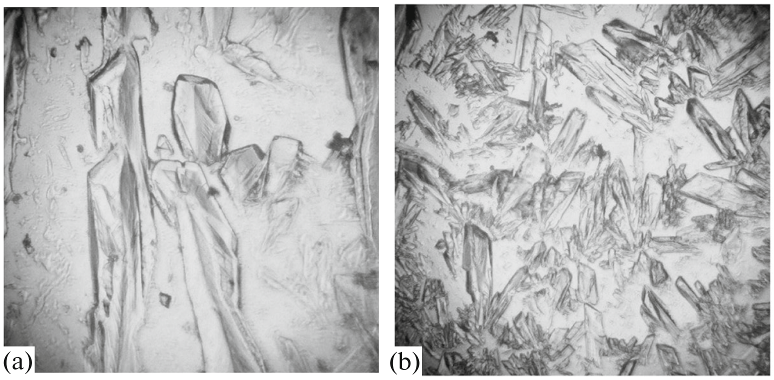
At the solution concentration of $N = 5\%$, both films have a distinct crystalline structure. In this case, the crystals are much larger than in the previous case. Moreover, on the film obtained under the action of laser radiation, the crystals are somewhat larger than on the control film. The density of the substrate coating in this case is much less than in the previous case:



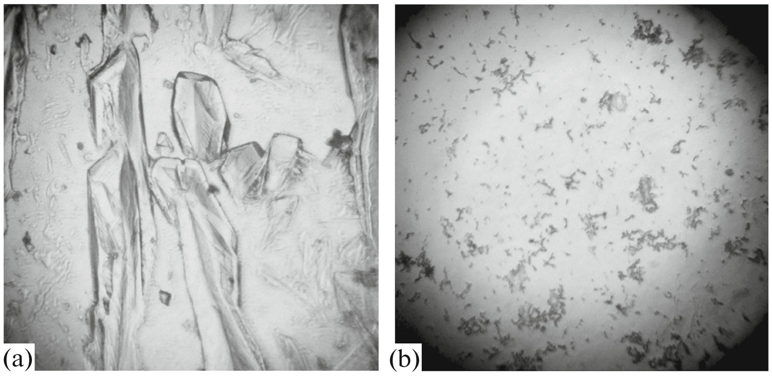
$N = 20\%$



$N = 5\%$



$N = 2\%$



$N = 1\%$

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

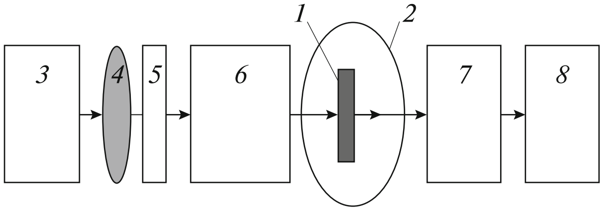


Fig. 3. Optical system of the setup for studying transmission spectra of the films: (*1*) sample; (*2*) measuring chamber; (*3*) light source; (*4*) condenser; (*5*) light filters; (*6*) MDR-23 monochromator; (*7*) photomultiplier; (*8*) radiation registration system.

there are areas on the glass that are not covered with 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 glass surface is uniformly covered with randomly arranged small crystals. The coating density of the glass surface is approximately 50%. The structure of the film obtained under the action of laser radiation contains crystals that are much larger in size. Relatively long crystals stand out. They have a trough-like shape; depressions run along these crystals almost along the entire length. Attention is drawn to the orientation of these long crystals: they are placed almost parallel to each other. Their orientation is perpendicular to the electric field strength vector of the laser radiation. The coating density of the glass surface with these crystals is small in comparison with the coating of the control film.

At the concentration of 1% solution of copper sulfate, the resulting films differ even more in structure from each other. Their structure also differs significantly from the structure of films obtained for high concentrations of copper sulfate solution. Thus, the control film does not contain a crystalline structure. It is fairly homogeneous with very small inclusions of dark red-brown 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 (Fig. 2b), unlike the control film, it is strongly inhomogeneous and has a clearly manifested structure. The coating of the glass surface with this film is quite dense. A characteristic feature of the structure of this film is the absence of objects with clear rectilinear shapes, which are characteristic of crystalline structures and appear in our films obtained for high solution concentrations. On the other hand, the structure of this film consists of a number of leaf-shaped spots separated by clear dark curvilinear boundaries.

The main part of the leaf-shaped spots is elongated and has an orientation perpendicular to the electric vector of the laser radiation. This is clearly seen in the example of two leaf-shaped spots, which are shown in the photo. In turn, some leaf-shaped spots have clearly manifested ordered structures. These ordered structures consist of dark and light lines and stripes, which are located within the same spot parallel to each other and at the same time at different angles to the structures corresponding to neighboring spots. This is clearly seen in the spot at the bottom of the corresponding photograph in Fig. 2.

We have carried out detailed studies of the transmission spectra of the obtained films in the visible region. These spectra were measured using a spectral complex assembled on the basis of an MDR-23 monochromator. In the studies, radiation with wavelengths $\lambda = 400-800$ nm and a setup whose is shown in Fig. 3 were used.

In these studies, the radiation of an incandescent lamp was used, which was collected by a quartz condenser (*4*) and focused on the entrance slit of an MDR-23 monochromator (*6*). Monochromatic light fell on a sample (*1*) fixed in a holder, which was placed in the measuring chamber (*2*). The intensity of the light transmitted by the sample was determined by a photomultiplier tube (PMT) (*7*) using a registration system (*8*). A photomultiplier of the FEU-100 type served as the radiation receiver. Registration of experimental data at the PMT output was provided using a program that specified the required number of photon counts at each point of the given spectral range, the spectrum scanning step, and the initial and final wavelengths. This program also controls the stepper motor of the monochromator. A more detailed procedure for studying light transmission by films using this setup is given in [10].

Note that we studied the integrated transmission of the films, i.e., transmission of regions with a diameter of approximately 2–3 mm, corresponding to the central parts of the films. It is obvious that a significant number of film structure objects, which are shown in Fig. 2, fall into these areas. The results of the studies of the transmission spectra are shown in Fig. 4.

Obviously, the spectra of the films shown in Fig. 4 include the transmission of the films themselves and the transmission of glass, the emission spectrum of the light source, and the sensitivity of the PMT, while the spectrum corresponding to the glass substrate includes transmission of the glass, the emission spectrum of the light source, and the sensitivity of the PMT. Therefore, to obtain data on the transmission spectra of the films themselves, it is necessary to divide the data on the transmission spectra of films on glass by the data on the transmission spectrum of glass.

The analysis of the results shown in Fig. 4 show that the application of the above procedure gives reliable results in the region of 420–770 nm. The transmission spectra of the films themselves, obtained as a result of such a procedure, are shown in Fig. 5.

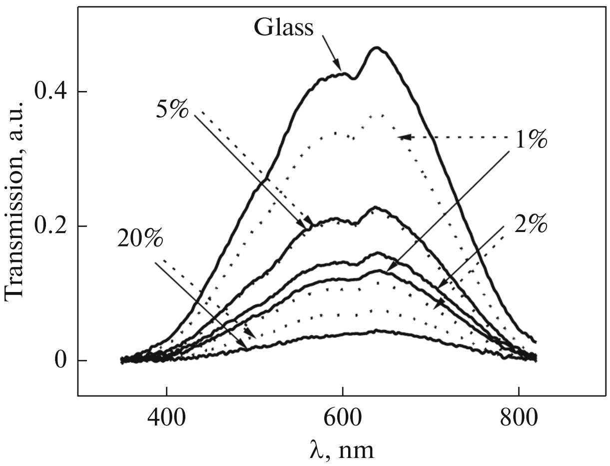


Fig. 4. Transmission spectra of the films on glass substrates as well as glass substrates. The dashed curves with an arrow correspond to the control films, and the solid curves correspond to the films formed under the action of laser radiation and the glass substrate.

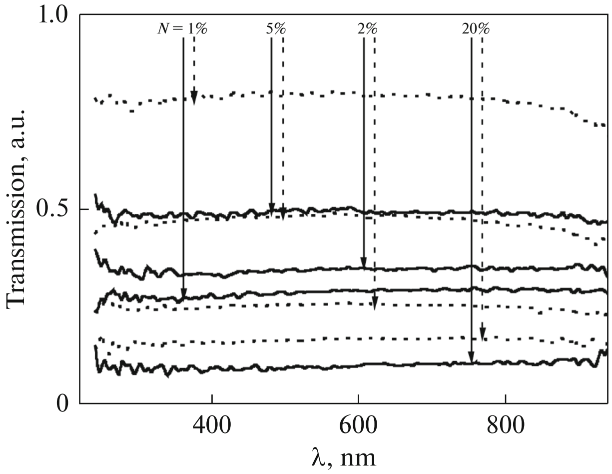


Fig. 5. Transmission spectra of the films themselves (excluding transmission of glass substrates). Dashed curves with an arrow correspond to control films, and solid curves correspond to the films formed under the action of laser radiation.

As follows from Fig. 5, transmission of control films and films obtained under the action of laser radiation within the scatter of experimental points, practically in the entire investigated spectral range, does not depend on the wavelength. At the same time, the value of the transmittance is different for different films. It should be noted that, for the results obtained, no correlation was found between the concentration of the used solution and the transmission of the respective films.

Obviously, for the films containing crystalline structures, the main reasons for the loss of incident radiation intensity, along with absorption, are the reflection and refraction of light on the crystal faces. Therefore, transmission of such films should depend on the size of the crystals and the density of coverage of the surface of glass substrates by these crystals.

It should be noted that the data on the transmission spectra of films with a crystal structure, which are shown in Figs. 4 and 5, are generally in good agreement with the features of their crystal structures, including those shown in Fig. 2.

As an example, we will consider data on the spectra obtained on the films corresponding to the solution of copper sulfate with a concentration of $N = 2\%$. As follows from Fig. 2, density of the coating by crystals of the film obtained under the action of laser radiation, in this case, is significantly less than the coating density of the control film. Accordingly, transmission of the first film is greater than transmission of the control film.

In addition, density of the coating by crystals of the glass substrate for both films obtained from a solution of vitriol with a concentration of $N = 5\%$ is approximately the same and relatively small. Accordingly, in this case, transmission of both films is approximately the same and greater than the transmission of films corresponding to the solution with a concentration of $N = 2\%$.

In general, as follows from Fig. 5, in cases when the films contain crystalline structures, transmission of control films and films obtained under the action of laser radiation do not differ much from each other. As for films that do not contain distinct crystal structures (films obtained using solutions of copper sulfate with concentrations of $N = 1$ and 20%), it is obvious that the main reason for the loss of radiation intensity should be absorption. In this case, there is a significant difference in the transmission of control films and films obtained under the influence of laser radiation. Thus, light transmission of the film obtained under the action of laser radiation in the case of $N = 20\%$ is approximately two times, while that in the case of $N = 1\%$ is approximately three times less than transmission of the corresponding control films (Fig. 5).

CONCLUSIONS

We studied the process of the film formation as a result of exposure of high-power infrared nanosecond laser radiation to the solution of copper sulfate in distilled water with different concentrations. In this case, a number of films were obtained. Some of the obtained films have a clearly manifested crystalline structure, while some of the films have no crystalline structure. The dimensions of the film structure elements are 0.5–10 μm. The structures of the films obtained by us under the action of laser radiation mainly differ from the structures of the control films. On the films obtained under the influence of laser radiation from the solutions with low concentrations of copper sulfate

(1 and 2%), a distinguished orientation of the elements of the structure of the films with respect to the polarization of the used radiation appears.

Control films and films obtained under the influence of laser radiation are transparent for the visible range of the spectrum. Their transmission does not depend on the wavelength of light. However, transmittance of the films is different for different films. Moreover, no correlation was found between transmission of the films and the concentration of the corresponding solutions. On the films containing crystalline structures, the ratio of transmission coefficients is consistent with the features of these structures. Transmission of the films that do not contain crystalline structures is much lower in comparison with the transmission of the corresponding control films.

In general, the results of our studies presented in this work indicate the fundamental possibility of obtaining relatively transparent structured films with different optical properties by irradiating solutions of chemical compounds with high-power nanosecond laser radiation.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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