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Synthesis of Surface Structures at Laser-Stimulated Evaporation of a Copper Sulfate Solution in Distilled Water

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A methodology, technique, and research results for the synthesis of films on a glass surface upon irradiation of aqueous solutions of copper sulfate with laser radiation are presented. The studies used the radiation of a yttrium-aluminum garnet laser, its second harmonic and the radiation of a semiconductor laser. Solutions with different concentrations of copper sulfate were used. The structure and and characteristics of the control films obtained as a result of drying solutions without exposure to laser radiation. Films synthesized under the action of laser optical characteristics of the films obtained in this case are compared with the structure radiation have both ordered and disordered structures. The characteristic dimensions of the structural elements of these films are 0.5-2 microns. For solutions with low concentrations, the density of the coating of glass substrates with films obtained under the action of laser radiation is much higher than the density of the coating with control films. The transmissions of the films were studied in the spectral range 300-1200 nm. It was found that the transmission of films obtained under the action of laser radiation and control films differ.

Keywords: Laser-stimulated evaporation, Laser radiation, Aqueous solution of copper sulfate, Films, Orderly structure, Transmission spectra.

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1. INTRODUCTION

Micro- and nanostructures synthesized on the surface of solids are now widely used 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 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 for structuring the surface of metals, dielectrics, and semiconductors, a special place is occupied by laser methods, when nano-, pico- or femptosecond radiation directly acts on the surface of a solid body in air or other gaseous medium [10-13]. Another application of a laser for surface nanostructuring can be laser-assisted deposition from a salt solution, which is placed on the surface of a solid [14].

It should be noted that 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 are currently poorly studied and are of interest for a more detailed study with a view to their practical use.

In this regard, we studied the process of formation of surface structures and their optical characteristics during 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. EXPERIMENTAL METHOD AND TECHNIQUE

For the synthesis of films from an aqueous solution of copper sulphate ($CuSO_4$), a setup was used, the scheme of which is shown in Fig. 1.

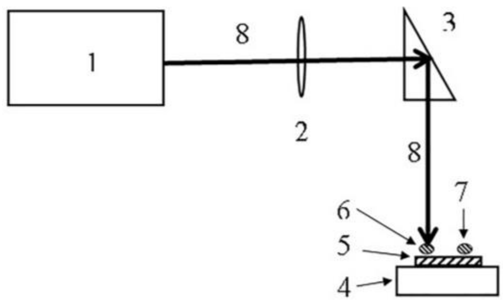

Fig. 1 – Scheme of the experimental setup: 1 – Source of laser radiation; 2 – Diffusing lens; 3 – Turn prism; 4 – Piece table; 5 – Glass plate; 6 and 7 – Identical drops of copper sulphate solution; 8 – Laser radiation

After leaving the laser source 1, the radiation was directed vertically down to the object stage 4 using a rotary prism 3. Glass plate 5 was placed on it with two drops 6 and 7 of an aqueous solution of $CuSO_4$ of the same concentration, almost identical in volume and size. During the experiment, one of these drops (6) was irradiated with laser radiation, while the other (7) remained the control one (it was not irradiated with laser radiation and dried up under normal atmospheric conditions). Diffusing lens 2 was used in the experiment to increase the diameter of the laser beam to the diameter of the solution spots on the

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glass substrate.

In various studies, we used the fundamental radiation of a yttrium aluminum garnet laser (LIAG), its second harmonic (SGLIAG), as well as radiation of a semiconductor laser (SL). The yttrium-aluminum garnet laser emitted pulses of infrared light with a wavelength of $\lambda = 1060$ nm. The laser pulse duration 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 space and time distributions. The radiation from the generator was directed to an amplifying stage, which consisted of three single-pass laser radiation amplifiers. The energy in the laser pulse after amplification was 5×10^{-2} J. The polarization of the laser radiation was linear.

The second harmonic ($\lambda = 530$ nm) was obtained from the fundamental radiation of the LIAG using a KDP crystal. The conversion efficiency was 15 %. In this case, the energy in the pulse was 7.5×10^{-4} J, and the pulse duration was 30 ns.

A continuous-wave semiconductor laser emitted blue light with a wavelength of $\lambda = 445$ nm with an average power of 500 mW.

The conditions for conducting research are summarized in Table 1.

Table 1 – Conditions for experimental studies of film synthesis: P is the average power density of laser radiation on the surface of the sample under study (for LIAG and SGLIAG radiation, within a pulse of 40 and 30 ns, respectively); N is the concentration of the solution; n is the number of solution drops in the samples under study

Conditions	Radiation	λ, nm	P, W/m^2	N, %	n
A	SGLIAG	530	2.2×10^9	20	8
B	SL	445	50	1,5	5
C	SL	445	50	1,5	2
D	LIAG	1060	1.5×10^{10}	1	5

3. STRUCTURE OF FILMS

Using a device consisting of an optical microscope and a camera, photographs were taken of films formed as a result of the drying of control spots, as well as films formed from spots under the action of laser radiation. About 20 photographs were taken of different parts of the surface, corresponding to the central parts of the films. In the case of films synthesized under the action of laser radiation, radiation with a maximum intensity hit in these parts. The films were illuminated in the microscope by the radiation of incandescent lamp.

Fig. 2 shows photographs containing the characteristic features of the respective films. The total magnification of the photographic device used was 1500. The widths of the photographs shown in Fig. 2. corresponding to the size of 2 μm on the respective films.

As follows from Fig. 2, in all cases the structure of the films obtained under the action of laser radiation differs significantly from the structures of the control films. Let us consider the main features of the structures of the acquired films.

Let us first consider the films obtained for a solution concentration of 20 % (experimental conditions A in Table 1). The control film (b) consists of randomly distributed relatively small crystals. In this case, the surface of the glass substrate is completely covered with these crystals. Let us now consider a film obtained for the same solution concentration under the influence of laser radiation (a). To obtain it, SGLIAG radiation was used. This film consists of fairly large crystals. In this case, the coating density of the glass substrate is relatively insignificant – there are rather large areas on the glass surface that are not covered with crystals.

As for the films obtained for low solution concentrations (see conditions B; C; D in Table 1), in all cases the control films contain relatively small crystals. The smallest crystal sizes occur for solution concentration $N = 1$ % (case D). The coating density of glass substrates in these cases is negligible.

The films that were synthesized under the action of laser radiation for these solution concentrations contain flat elongated leaf-shaped structures of rather large sizes. The sizes of these structures are 0.5-3 μm. The coating density of glass substrates with these structures is much higher than for control films.

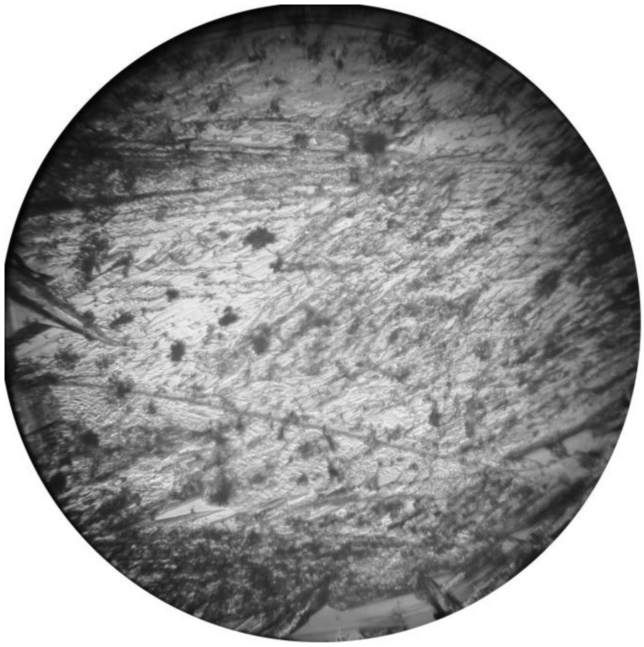
4. TRANSMISSION SPECTRA OF THE FILMS

We have studied the transmission spectra of the obtained films. These spectra were measured in the wavelength range of 300-1200 nm using a spectral complex assembled on the basis of an MDR-23 monochromator. A detailed procedure for studying light transmission by films using this setup is given in [15].

We have studied the integrated transmission of films – the transmission of sections of films with a diameter of approximately 3-4 mm, which correspond to the central parts of the films. It is obvious that a large number of objects of the film structure, shown in Fig. 2, fall into these areas.

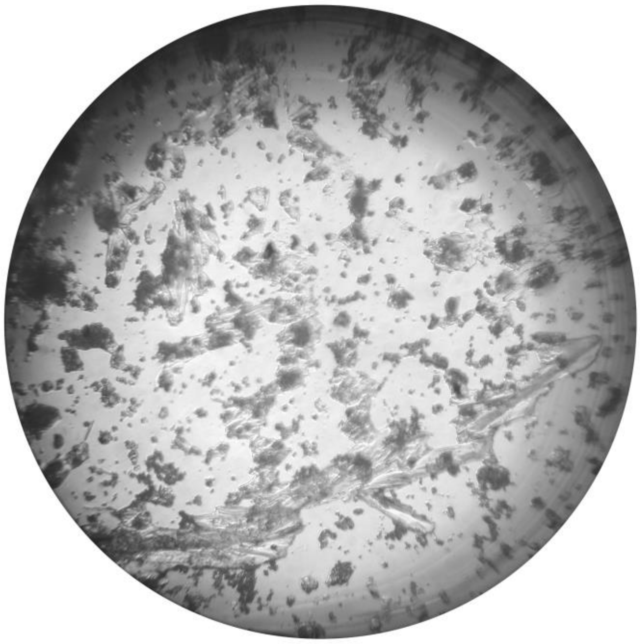
Studies were carried out for four sections of the spectrum, partially overlapping with each other: 300-500 nm; 400-800 nm; 700-1000 nm and 900-1200 nm. This is due to the use of various lamps (hydrogen lamps and incandescent lamps), as well as various types of diffraction gratings and photomultiplier tubes (PMT) for research in different parts of the radiation spectrum. In these studies, the wavelength step was 2 nm, and the width of the spectrum of the incident type of radiation was 0.2 nm. The results of these investigations of the transmission spectra are shown in Fig. 3.

Obviously, shown in Fig. 3 spectra include both the transmission of the films themselves and the transmission of glass, the emission spectrum of the light source and the sensitivity of the PMT, and the spectrum of the corresponding glass substrate – the 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 transmission spectra of the films themselves obtained as a result of such a procedure are shown in Fig. 4. "Stitching" of the data obtained for four parts of the spectrum into one dependence was carried out for wavelengths of 450; 750 and 950 nm.

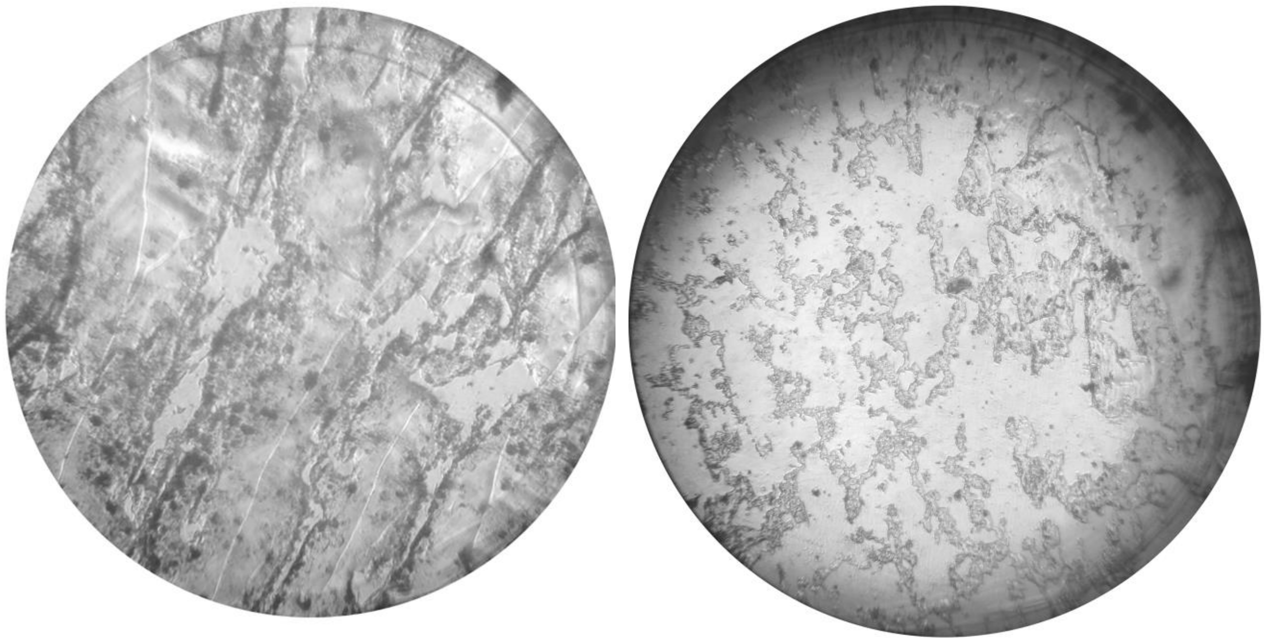
a b

A

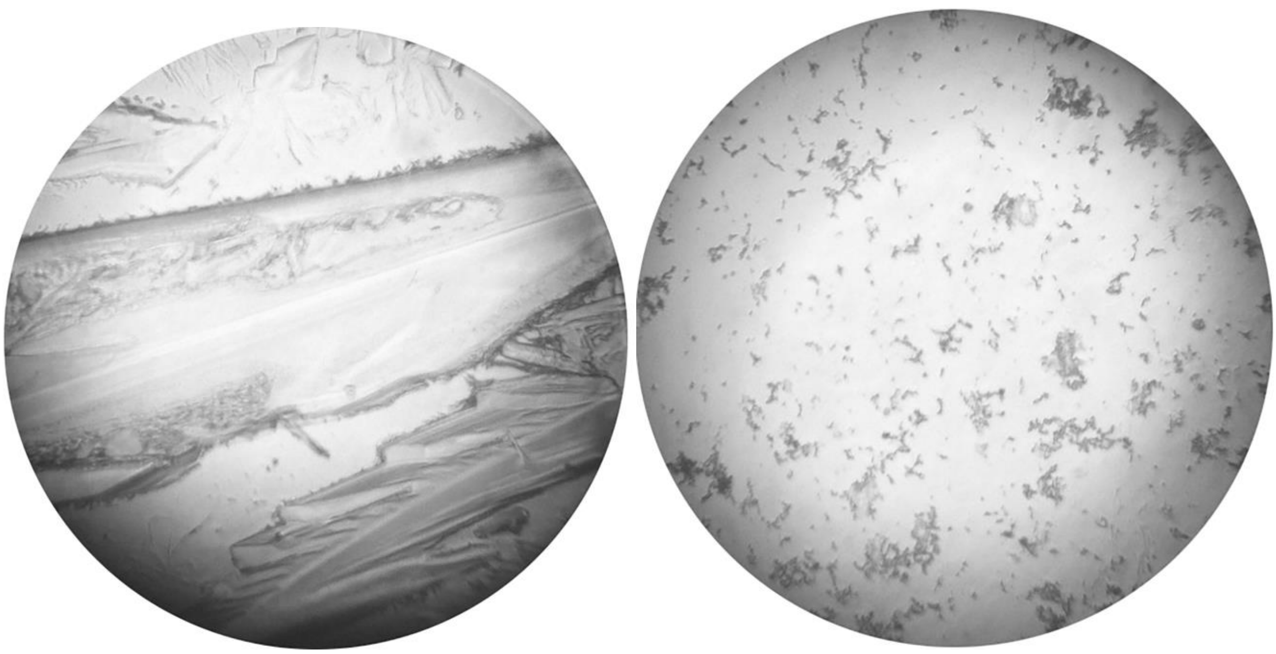
a b

B



a b

C



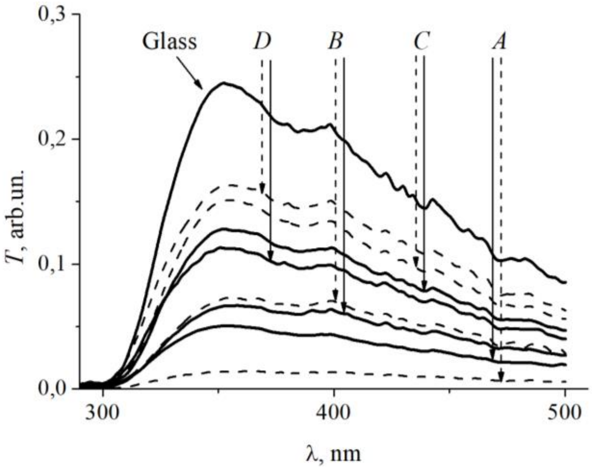
a b

D

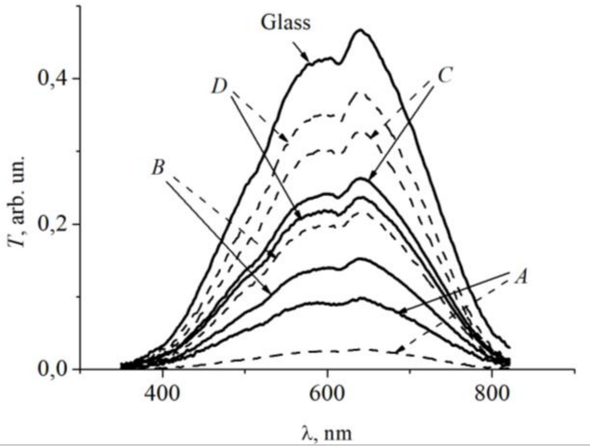
Fig. 2 – Photographs of films synthesized under the action of laser radiation (a) and control films (b). Oblique uppercase letters correspond to the experimental conditions in which the films were obtained (see Table 1)

Based on the above procedure for processing the obtained results, the transmission level equal to 1 in Fig. 4 corresponds to the transmission level of the glass substrate. Accordingly, the data for the films in this figure are given in relation to the transmission of the glass substrate.

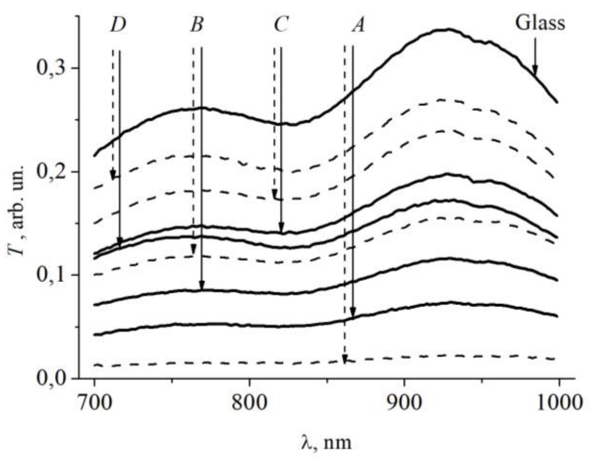
As follows from Fig. 4, the transmission of both control films and films obtained under the action of laser radiation in most of the studied spectral range is



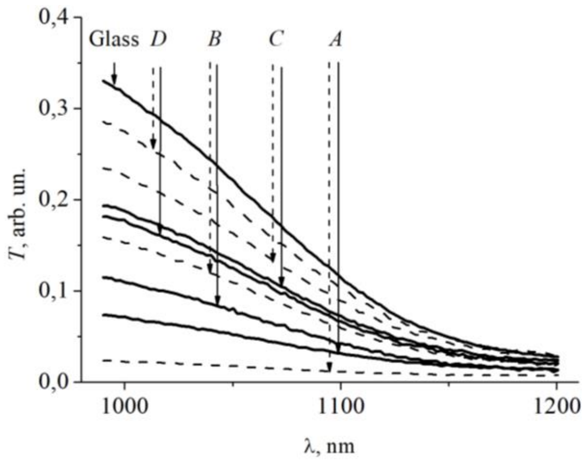
a



b



c



d

Fig. 3 – Dependences of the transmission (T) of films on glass substrates, as well as glass substrates, on the wavelength (λ) of radiation for different parts of the spectrum. Dashed curves and arrows correspond to control films, and solid curves correspond to films formed under the action of laser radiation and a glass substrate. Oblique uppercase letters correspond to the experimental conditions in which the films were obtained (see Table 1)

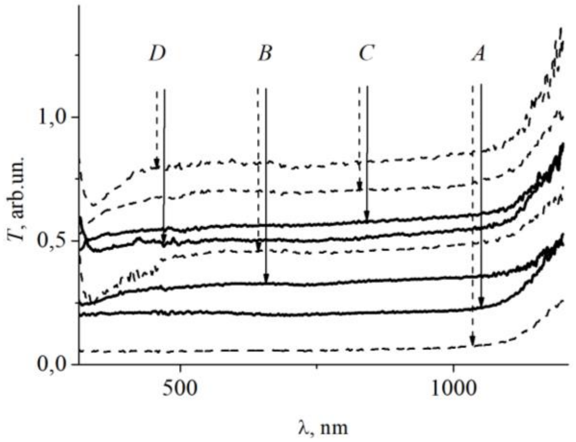


Fig. 4 – Transmission spectra of films. Dashed curves and arrows correspond to control films, and solid curves correspond to films formed under the action of laser radiation. Oblique uppercase Latin letters correspond to the experimental conditions in which the films were obtained (see Table 1)

practically independent of the wavelength. Only in the regions $\lambda < 500$ nm and $\lambda > 1000$ nm is there a significant dependence of the transmission on the wavelength.

In the region $\lambda > 1000$ nm, the transmission of all films increases with increasing wavelength. In the region $\lambda < 500$ nm, the nature of the dependences of the transmission on the wavelength is different for the films obtained under different conditions.

Thus, the transmission of both films obtained for the solution concentration $N = 20$ % (A) in the region $\lambda < 500$ nm does not depend on the wavelength. For films obtained under conditions C, in the indicated region of the spectrum, a monotonous increase in transmission occurs with increasing wavelength, and in the transmission of films obtained under conditions B and D, minima occur in the vicinity of $\lambda = 340$ nm. It should be noted that for the films obtained under the action of laser radiation, these minima are smoothed in comparison with the minima corresponding to the control films.

A comparison of the transmission of control films and synthesized films under the action of laser radiation also showed the following. For conditions A (N = 20 %), the transmission of the film obtained under the action of laser radiation in the entire spectral region under study was significantly (approximately 2-3 times) greater than the transmission of the control films.

For all other conditions (for low solution concentrations), the transmission of the films synthesized under the action of laser radiation was lower than the transmission of the control films. The greatest difference (by a factor of 1.5) took place for films obtained on the basis of a solution with a concentration of N = 1 % (conditions D).

This situation with the transmission of control films and films obtained under the action of laser radiation is in good agreement with the structure of the corresponding films (Fig. 2). Thus, for conditions A, the coating density of the glass substrate in the case of the control film was significantly higher than in the case of the film synthesized under the action of laser radiation. And, accordingly, the transmission of the control film is much less than the transmission of the film formed under the action of laser radiation. For all other conditions (B, C and D), the density of the substrate coating in the case of control films is much less than in the case of films obtained under the action of laser radiation. Accordingly, the transmission of control films for these conditions is greater than the transmission of films formed under the action of laser radiation.

5. CONCLUSIONS

We studied the process of film synthesis as a result of exposure to a solution of copper sulphate in distilled water with different concentrations of radiation from different lasers. In this case, a number of films were obtained. The structure of the films obtained under the influence of laser radiation differed from the structure of the control films. It was found that the coating density of glass substrates with films obtained under the action of laser radiation from solutions with a low salt concentration was significantly higher than the coating density with control films. The size of the elements of the film structures obtained under the action of laser radiation was 0.5-2 μm.

Studies of the transmission spectra for the spectral region 300-1200 nm showed that both the control films and the films synthesized under the action of laser radiation were generally transparent. Their transmission weakly depended on the wavelength of light. At the same time, the average transmission values of the films obtained under the action of laser radiation and the control films differed significantly from each other. So, for a high concentration of the solution (20 %), the transmission of the film obtained under the action of laser radiation is greater than the transmission of the control film, and for low concentrations of the solution, on the contrary, the transmission of the films obtained under the action of laser radiation is less than the transmission of the control films. Such behavior of the transmission of films correlates well with the density of coating of glass substrates by these films.

On the whole, 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 laser radiation.

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Синтез поверхневих структур при лазерно-стимульованому випаровуванні розчину мідного купоросу в дистильованій воді

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Наведено методику, техніку, і результати досліджень синтезу плівок на поверхні скла при опроміненні водних розчинів мідного купоросу лазерним випромінюванням. В дослідженнях використовувалося випромінювання лазера на ітрій-алюмінієвому гранаті, його друга гармоніка та випромінювання напівпровідникового лазера. Застосовувалися розчини з різною концентрацією мідного купоросу. Структура та оптичні характеристики отриманих при цьому плівок порівнюються зі структурою та характеристиками контрольних плівок, отриманих в результаті висихання розчинів без впливу лазерного випромінювання. Синтезовані під дією лазерного випромінювання плівки мають як впорядковану, так і невпорядковану структуру. Характерні розміри структурних елементів цих плівок складають 0,5-2 мкм. Для розчинів з невеликими концентраціями щільність покриття скляних підкладок плівками отриманими під дією лазерного випромінювання значно більша ніж щільність покриття контрольними плівками. Досліджено пропускання плівок в області спектру 300-1200 нм. Виявлено, що пропускання плівок, отриманих під дією лазерного випромінювання та контрольних плівок відрізняються між собою.

Ключові слова: Лазерно-стимульоване випаровування, Лазерне випромінювання, Водний розчин мідного купоросу, Плівки, Упорядкована структура, Спектри пропускання.