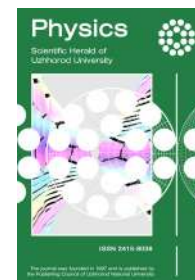


# Scientific Herald of Uzhhorod University Series “Physics”

Journal homepage: <https://physics.uz.ua/en>

Issue 49, 43-47

Received: 11.01.2021. Revised: 02.03.2021. Accepted: 10.06.2021



УДК 535:621.373.8:539

PACS 79.20.Ds; 79.20.Eb; 81.07.b; 81.16.c; 81.16.Rf

DOI: 10.24144/2415-8038.2021.49.43-47

## Formation of Structured Films Upon Irradiation of an Aqueous Solution of Copper Sulphate with High-Power Laser Radiation

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### Abstract

**Relevance.** Among the physical methods of structuring the surface of metals, dielectrics, and semiconductors, a special place is occupied by laser methods, when laser radiation acts directly on the surface of a solid body.

**Purpose.** The purpose of this study is to elucidate the possibility of obtaining a structured surface by laser-stimulated evaporation of salt solutions placed on the surface of a solid body.

**Methods.** Thus, the process of film formation on the glass surface was studied when a one-percent aqueous solution of copper sulphate was irradiated with powerful laser radiation on a yttrium-aluminium garnet with a generation wavelength of 1.06 microns and a pulse duration of 40 ns.

**Results.** The structure and properties of the film obtained under such conditions are compared with the structure and properties of the control film formed by drying the same volume of copper sulphate solution of the same concentration, but without exposure to laser radiation. This control film is uniform, without any structural elements. The film formed under the influence of laser radiation is structured – it contains characteristic leaf-like elements with dimensions of 0.5-2 microns. The transmission spectra of both films in the range of 300-800 nm were studied.

**Conclusions.** It was found that the transmission of the control film decreases slightly with increasing wavelength of incident light. The transmission of the film obtained under the action of laser radiation is practically independent of the wavelength, but approximately 3-2.5 times less than the transmission of the control film

**Keywords:** formation of structured films, laser radiation on yttrium-aluminium garnet, aqueous solution of copper sulphate, photomicrographs of films, transmission spectra

### Introduction

Surface nanostructures have promising practical applications in highly dispersed systems, in particular, adsorbents, catalysts, composite material cores, membranes and a number of other low-dimensional systems with quantum effects. The formation of such structures on the surface of solids is carried out by various chemical and physical methods [1-6]. Thus, in [1] the main achievements in the field of electrochemical synthesis of nanostructured oxide

coatings on aluminium, titanium and niobium are analysed, experimental data from studies of the morphology and physical-chemical characteristics of nanostructured oxide coatings on valve metals are considered, as well as their possible practical applications.

The study of reflections on the surface of electrodes of a high-current nanosecond discharge in atmospheric pressure air initiated by escaping electrons showed that

### Suggested Citation:

Bondar II, Suran VV, Mynya OY, Shuaibov OK, Shevera IV, Krasilinets VM. Formation of structured films upon irradiation of an aqueous solution of copper sulphate with high-power laser radiation. *Scientific Herald of Uzhhorod University. Series “Physics”*. 2021;(49):43-47.

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various surface structures of micro- and nanoscale dimensions are formed on the surface of the anode, which allows modifying and structure its surface [2].

In [7-12], achievements in the field of technologies for obtaining periodic structures on the surface of semiconductors, metals and dielectrics are considered, mainly under the action of laser radiation of femto-picosecond duration, and it is noted that periodic surface structures can be used in the manufacture of new types of MDN transistors, liquid crystal displays, and solar cells.

In [13], it was reported that a thin nanostructured iron oxide film was obtained on a sapphire substrate under the action of laser radiation with a wavelength of 1064 nm. The dimensions of the film structures were 0.1x0.3 microns. The film was probably in a superparamagnetic state, which is important for use in gas-sensitive sensors and various magnetic devices of medicine and biophysics.

Characteristics of the structured and modified surface and mechanisms of its structuring during the use of laser-stimulated evaporation of salt solutions from the surface of solids, in particular, under the influence of defocused laser beams of the infrared spectrum, which are currently poorly studied and are of interest for more detailed study with the aim of their practical use. Of particular interest are such studies that can be conducted using widely available solid-state lasers with a generation pulse duration in the range of 5-50 ns.

*The purpose of the study* was to develop a method for structuring the glass surface by laser-stimulated evaporation of aqueous salt solutions of  $\text{CuSO}_4$  from the surface of the glass substrate under standard pressure.

## Materials and Methods

To create films from an aqueous solution of copper sulphate ( $\text{CuSO}_4$ ), the radiation of a yttrium-aluminium garnet (LIAG) laser was used. The main node of the experimental setup was an optical quantum generator with a modulated Q-factor of the resonator. It emitted pulses of infrared light with a wavelength of 1.06 microns. The duration of the laser pulse was 40 ns. The frequency of the laser pulses was 1 Hz. Generation was carried out on one transverse and many longitudinal modes. At the same time, the laser pulse had Gaussian spatial and temporal distributions.

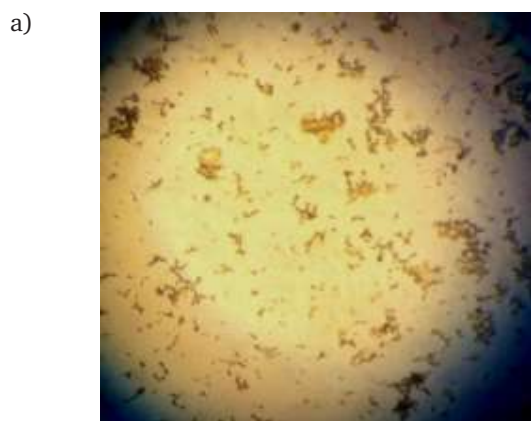
The radiation from the generator was directed to an amplifier stage consisting of three single-pass laser radiation amplifiers. The energy in the laser pulse after amplification was 0.05 J. After leaving the amplifying stage, it was sent to a slide table, on which was placed a glass plate with two almost identical drops of an aqueous solution of copper sulphate. During the experiment, one of these droplets was irradiated with laser radiation, while the other remained a control (it was not irradiated and dried out under normal atmospheric conditions). To increase the diameter of the laser beam (4 mm) to the diameter of the solution droplets (15 mm), a scattering lens was used in the experiment. The above energy and geometric characteristics of laser radiation indicate that the average power density of laser radiation on the surface of the solution drop under study was approximately  $1.8 \times 10^{10} \text{ W/m}^2$ .

The experiment used a one percent aqueous solution of copper sulphate. The duration of laser irradiation of the test drop was equal to the duration of complete drying of the control drop, which is 210 minutes. Notably, the drop that was irradiated with laser radiation dried up in about 150 minutes. During the remaining time, the laser radiation was acting on the dried spot. At the same time, both drops formed films on the glass surface, which differed significantly in structure.

## Results and Discussion

Using an optical microscope, both films were photographed. At the same time, about 20 photos of various sections corresponding to the central parts of the resulting films were taken. In the case of films obtained under the action of laser radiation, radiation of maximum intensities fell into these parts.

Figure 1 shows the characteristic features of the structures of the resulting films. Illumination of films in a microscope was carried out by an incandescent lamp. The magnification of the microscope was 1500. The width of the photos shown in Figure 1 corresponds to a size of 2 microns on the corresponding films. According to Figure 1, the resulting films are very different in structure. Thus, the control film (a) does not contain a crystal structure. It is quite uniform with very small inclusions of dark red-brown particles. Judging by the colour, these inclusions are probably microscopic particles of copper oxides.

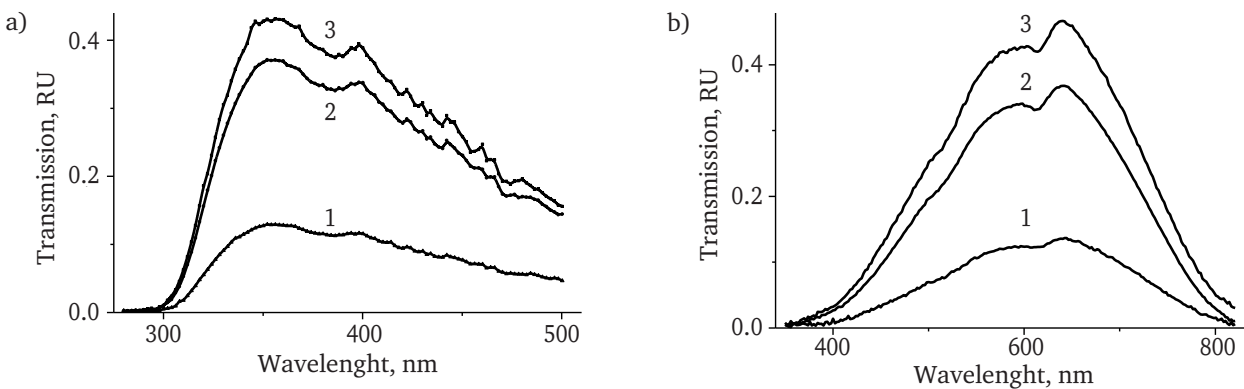


**Figure 1.** Micrographs of the control film (a) and the film obtained under the action of laser radiation (b)

As for the film obtained under the action of laser radiation (Fig. 1 (b)), then unlike the control one, it is very heterogeneous and has a clearly defined structure. The cover on the glass surface with this film is quite dense. This film, like the control film, does not contain objects with clear rectilinear shapes that are characteristic of crystal structures. However, a characteristic feature of the structure of this film is that its structure consists of a series of elongated leaf-shaped spots separated by clear dark curved borders. For their part, some spots have clearly defined ordered structures. These ordered structures consist of dark and light lines and stripes that are located parallel to each other within the same spot, and at the same time, at different angles to the structures corresponding to neighbouring spots. This is clearly visible in the spot at the top of the corresponding photo in Figure 1 (b).

These structures are located parallel to each other.

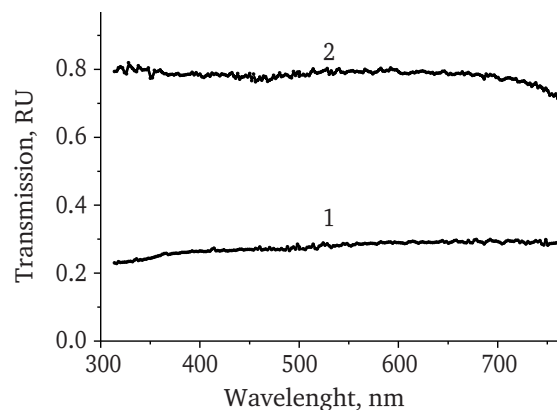
The dimensions of elements of both ordered and disordered structures are about 0.5-2 microns. The authors conducted detailed studies of the transmission spectra of the obtained films in the near ultraviolet and visible regions of the spectrum. The total wavelength range was 300-800 nm. Measurements of these spectra were carried out on the KSWU-23 spectral complex based on the MDR-23 monochromator at room temperature. A detailed method for studying the transmission of light by films on this installation is given in [14-15]. Integrated film transmission – the transmission of sections of films with a diameter of approximately 2-3 mm corresponding to the central parts of the films – was also studied. Admittedly, a significant number of film structure objects, which are shown in Figure 1, fall into these areas. The results of studies of transmission spectra are shown in Figure 2.



**Figure 2.** Transmission spectra formed under the action of laser radiation (1) and control (2) films on a glass substrate and the glass substrate itself (3) obtained using radiation from a hydrogen lamp (a) and an incandescent lamp (b)

Spectra (1) and (2) shown in Figure 2 include both the transmission of the films themselves and the transmission of glass, the radiation spectrum of the light source and the sensitivity of the photoelectronic converter (FEC), and the spectrum (3) – the transmission of glass, the spectrum of the radiation source and the sensitivity of the FEC. Therefore, to obtain the transmission spectra of the films themselves, it is necessary to divide the data of spectra (1) and (2) by the data of spectra (3). Analysis of

the results shown in Figure 2 suggests that the application of this procedure gives reliable results for the regions of 320-500 nm (for a hydrogen lamp) and 420-770 nm (for an incandescent lamp). The transmission spectra of the films themselves obtained as a result of this procedure are shown in Figure 3. At the same time, the “crosslinking” of the data obtained for the two lamps was carried out for a wavelength of 450 nm.



**Figure 3.** Transmission spectra of films formed under the action of laser radiation (1) and control (2)

According to Figure 3, it is clear that the transmission of the control film decreases slightly during the transition to light waves with large wavelengths. As for the film formed under the action of laser radiation, its transmission, depending on the wavelength, is approximately 2.5-3 times less than the transmission of the control film. At the same time, its transmission in the entire spectral range under study practically does not depend on the wavelength of light.

## Conclusions

The authors investigated the process of film formation due to exposure of powerful infrared nanosecond laser

radiation to a 1% solution of copper sulphate in distilled water. At the same time, a structured film with a characteristic structure size of 0.5-2 microns was obtained. The resulting film is transparent in the visible range of the light wave spectrum (300-800 nm). Its transmission in this spectrum range does not depend on the wavelength of light, but is 2.5-3 times less than the transmission of the control film.

In general, the findings presented in this paper indicate the fundamental possibility of obtaining relatively transparent films with ordered structures by irradiating solutions of chemical compounds with powerful nanosecond laser radiation.

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## Утворення структурованих плівок при опроміненні водного розчину мідного купоросу потужним лазерним випромінюванням

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### Анотація

**Актуальність.** Серед фізичних методів структурування поверхні металів, діелектриків та напівпровідників особливе місце займають лазерні методи, коли безпосередньо лазерне випромінювання діє на поверхню твердого тіла.

**Мета.** Метою цієї роботи є з'ясування можливості отримання структурованої поверхні методом лазерно-стимульованого випаровування розчинів солей, розміщених на поверхні твердого тіла.

**Методи.** Для цього здійснено дослідження процесу формування плівок на поверхні скла при опроміненні однопроцентного водного розчину мідного купоросу потужним випромінюванням лазера на ітрій-алюмінієвому гранаті з довжиною хвилі генерації 1,06 мкм і тривалістю імпульсу 40 нс.

**Результати.** Структура й властивості отриманої за таких умов плівки порівнюються зі структурою та властивостями контрольної плівки, утвореної внаслідок висихання такого ж об'єму розчину мідного купоросу однакової концентрації, але без впливу лазерного випромінювання. Ця контрольна плівка є однорідною, без будь-яких структурних елементів. Плівка ж, яка утворилася під дією лазерного випромінювання є структурованою – вона містить характерні листкоподібні елементи з розмірами 0,5–2 мкм. Досліджено спектри пропускання обох плівок в області 300–800 нм.

**Висновки.** Виявлено, що пропускання контрольної плівки дещо зменшується під час збільшення довжини хвилі падаючого світла. Пропускання ж плівки, отриманої під дією лазерного випромінювання, практично не залежить від довжини хвилі, однак приблизно у 3–2,5 рази менше пропускання контрольної плівки

**Ключові слова:** утворення структурованих плівок, випромінювання лазера на ітрій-алюмінієвому гранаті, водний розчин мідного купоросу, мікрофотографії плівок, спектри пропускання