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Optical and Photocatalytic Properties of Chemically Deposited Cu_xS Layers

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Abstract. Thin films and layers of copper sulfide with Cu_xS composition were obtained by chemical deposition from aqueous medium on substrates of matted and unmatted quartz. Using scanning electron microscopy and EDX analysis, the features of the morphology and composition of layers on different substrates were revealed. An excess of copper was found in the semiconductor layer. For the films grown on unmatted quartz, the transmission spectra were determined, as well as the optical band gap by processing the Tauc equation. The layers deposited on matted quartz were investigated for photocatalytic activity by oxidation in their presence of hydroquinone under the action of UV radiation.

INTRODUCTION

Recently, photocatalysis on semiconductor materials has attracted attention of researchers as a promising environmentally friendly way of direct use of solar energy to obtain hydrogen from water [1, 2], as well as the destruction of organic pollutants in aqueous media [3, 4]. The efficiency of photocatalysis as a heterogeneous process depends on the specific surface area of the catalyst on which oxidation takes place [5]; however, the use of dispersed semiconductor systems in practice is complicated by the impossibility of extracting the spent dispersion from the reservoir. Only a small number of works [6, 7] were devoted to the fixing of photoactive material on the surface of a floating substrate. When the photocatalyst is fixed on a floating substrate, the specific surface area is lost, which can negatively affect the catalytic properties of the material. An alternative can be the creation of photocatalysts based on materials with magnetic properties [8].

One of the compounds in demand for photocatalysis are copper sulfides Cu_xS ($x = 1 \div 2$), which have *p*-type conductivity. A feature of these compounds is the ability to control the band gap in a wide range from 1.0 eV to 3.0 eV by varying the composition and structure, which is confirmed by [9–12]. The composition, structure, and morphology of the material, and hence its optical properties and photocatalytic activity, depend on the method and conditions of synthesis [13–15].

This article is devoted to the production of nanosized photosensitive Cu_xS layers on the surface of matted and unmatted quartz substrates by chemical bath deposition method, and to the study of their optical and photocatalytic properties on the hydroquinone oxidation under the action of UV radiation.

EXPERIMENTAL DETAILS

Nanosized layers of Cu_xS were synthesized by chemical deposition from an acetate reaction system at pH = 5.4 using the following solutions: copper sulfate CuSO_4 with concentration of 0.03 mol/L, sodium acetate CH_3COONa with concentration of 2.0 mol/L, and thiocarbamide $\text{N}_2\text{H}_4\text{CS}$ with concentration of 0.02 mol/L. The acidity of the reaction medium was controlled by dropwise addition of a solution of concentrated acetic acid CH_3COOH .

The plates of matted and unmatted quartz with a size of $(25 \times 25) \text{ mm}^2$ were used as a substrate material for deposition. The substrates were previously degreased. A substrate made of unmatted quartz was also etched for 20 sec

in a solution of hydrofluoric acid HF diluted with water in a ratio of 1:20, after which it was activated in solutions of tin hydrochloric acid SnCl_2 (0.03 mol/L) and thiocarbamide (1.5 mol/L) by 3 minutes each.

The treated substrates, fixed in fluoroplastic holders, were immersed in hermetically sealed molybdenum glass reactors, which were placed in a TS-TB-10 thermostat for 45, 60, and 90 minutes at 353 K.

The thickness of the layers was estimated using an MII-4M Linnik's microinterferometer with a measurement accuracy of up to 22%.

The microstructure and morphology of the layers were studied on a TESCAN MIRA 3 LMU field emission electron microscope using a high-brightness Schottky cathode to obtain high-resolution, high-contrast, low-noise images at an electron beam accelerating voltage of 10 kV. The magnification range was from 100 to 500,000 times. Elemental analysis was performed using an Oxford Instruments INCA Energy 350 X-max 80 X-ray energy dispersive microanalysis system with an X-max 80 Standart nitrogen-free detector.

The particles forming crystallites were measured using the Measurer software.

To study the optical properties of transparent Cu_xS films, a PE-5300 VI spectrophotometer with specially designed cuvettes was used. The transmission and absorption spectra were recorded in the wavelength range from 325 to 1000 nm.

The mathematical and graphic processing of the experimental data was carried out using the Microsoft Office Excel and Origin software packages.

RESULTS AND DISCUSSION

The objects of study were copper sulfide layers Cu_xS ~120 nm thick. Externally, the substrates with films were transparent dark brown coatings interfering with light in the violet region of the spectrum. The layers obtained on matted quartz were distinguished by better adhesion to the substrate surface. Figure 1 shows electron microscopic images of layers obtained on the surface of matted (a) and unmatted (b) quartz after 45 min of synthesis.

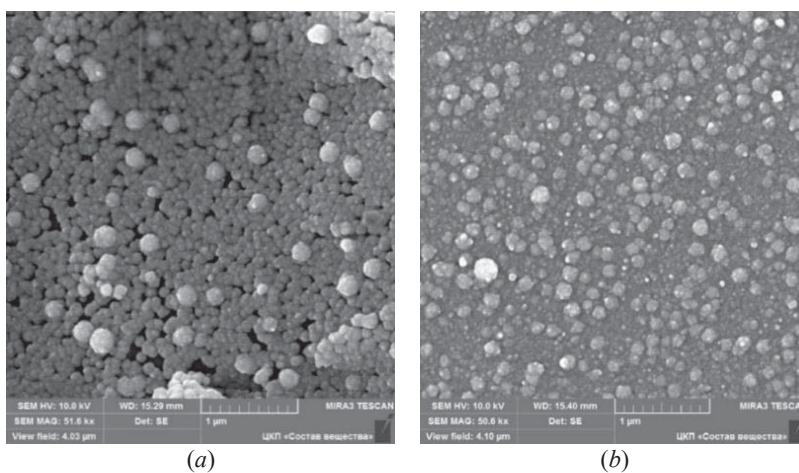


FIGURE 1. Electron microscopic images of Cu_xS films synthesized after 45 min at 353 K on matted (a) and unmatted (b) quartz substrates. Magnification 50,000 times.

The results of experiments on the deposition of copper sulfide from the acetate system at $\text{pH} = 5.4$ on various substrates showed that without surface activation with tin chloride and thiocarbamide, the semiconductor layer can be fixed only on the surface of matted quartz, which may be due to the larger specific surface area of this substrate, which promotes adhesion of the formed in the volume of the solution of copper sulfide nuclei. In addition, analysis of electron microscopic images showed that surface activation affects the morphology of the resulting layers. Thus, a continuous film of copper sulfide forms on the surface of unmatted quartz (Figure 1b). Presumably, as a result of the activation of the substrate surface in solutions of tin chloride and thiocarbamide, a hydroxide or sulfide layer of the activator metal is formed on its surface, which has a greater affinity (in comparison with untreated quartz) for copper sulfide nuclei formed at the substrate surface, which facilitates their consolidation.

In turn, copper sulfide deposited on matted quartz is a loose monolayer of globules, ~80 % of which lies in the range of 140–240 nm, and the maximum distribution falls on particles with a diameter of 140–200 nm, which is ~50 % of their total number (Figure 2a).

The film deposited on unmatted quartz is also formed by large globules, but the space between them is filled with a uniform layer of copper sulfide particles, the size of which cannot be reliably determined due to the absence of clear boundaries between grains. Large globules of the film are characterized by a smaller scatter in size compared to the layer obtained on matted quartz, and their diameter in 90 % of cases lies within 140–220 nm (Figure 2b).

The obtained values of the particle diameters exceed the measured film thickness (120 nm), which may indicate that the main body of the film on unmatted quartz is formed precisely by a uniform layer of copper sulfide particles filling the space between large globules.

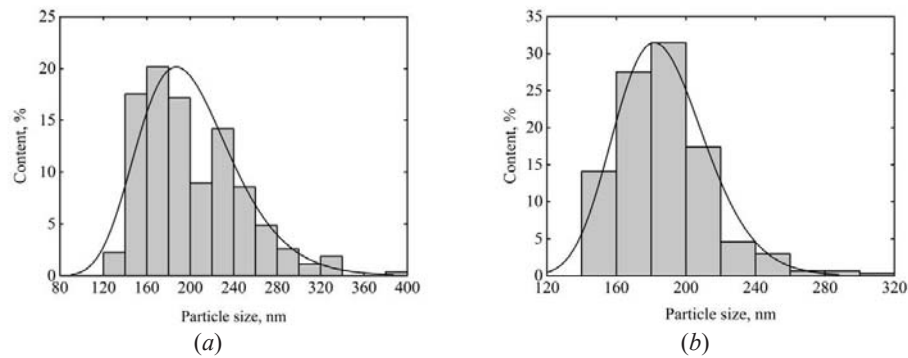


FIGURE 2. Histograms of the size distribution of Cu_xS particles on substrates of matted (a) and unmatted (b) quartz after 45 min and a temperature of 353 K.

To determine the elemental composition of the synthesized layers, a local energy dispersive analysis of the sample surface was carried out at least at five points. The layers were analyzed for sulfur and copper contents. The elemental analysis results shown in Table 1 demonstrate that the activation of the substrate material affects the composition of the forming copper sulfide layers. The resulting discrepancy in the composition of the semiconductor coating to bivalent copper sulfide CuS is explained by the manifestation of reducing properties by thiocarbamide towards copper (II) ions Cu^{2+} [16, 17]. Moreover, we can conclude that, apparently, the formation of an interglobular layer on unmatted quartz occurs at the late stages of synthesis, when most of the Cu^{2+} ions are reduced in the solution.

TABLE 1. Elemental composition of Cu_xS films obtained after 45 min of synthesis at 353 K.

Substrate material	Content of elements, at. %		Cu/S
	Cu	S	
Matted quartz	45.03 ± 1.54	54.97 ± 1.54	1.22 ± 0.08
Unmatted quartz	42.24 ± 1.87	57.76 ± 1.87	1.37 ± 0.11

The most important characteristic of an optical semiconductor material, which determines the suitability of its use in a certain wavelength range, is the optical band gap. Therefore, studies of the optical properties of copper sulfide layers obtained on unmatted quartz were carried out in the wavelength range from 325 to 1000 nm.

The optical band gap was determined graphically by extrapolation to the abscissa axis of the straight-line section of the dependence constructed by the Tauc equation for the band gap of the direct transition [18]:

$$\alpha h\nu = A \cdot (h\nu - E_g)^{\frac{1}{2}}, \quad (1)$$

where α — absorption coefficient; A — constant; $h\nu$ — photon energy; E_g — optical band gap.

$$\alpha = \frac{1}{d} \cdot \ln \frac{1}{T}, \quad (2)$$

where d — layer thickness, cm^{-1} ; T — transmittance coefficient, %.

The results of measuring the optical transmittance and calculation of the band gap of copper sulfide thin film on unmatted quartz substrate are shown in Figure 3.

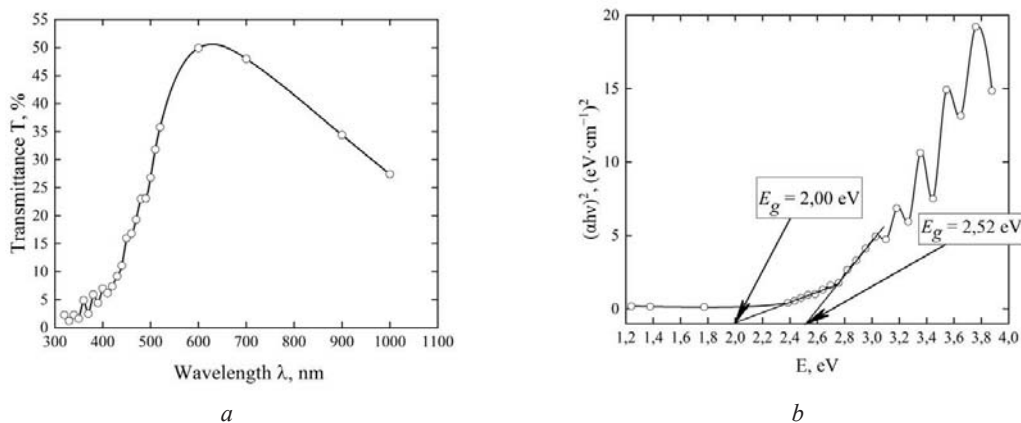


FIGURE 3. Results of optical studies of copper sulfide thin film obtained on unmatted quartz substrate after 45 min of synthesis at 353 K. Transmittance spectra (a). Determination of the optical band gap (b).

The oscillating nature of the dependence of the optical transmission value on the wavelength of the radiation passing through the film indicates the interference of light in the film (Figure 3 a) due to its small thickness. The intrinsic absorption edge of the film is in the range of 300–400 nm. The maximum transmission of the film is at 620 nm and is 52 % of the incident radiation. The dependence shown in the figure above (Figure 3 b) has two straight sections, indicating the presence in the film of two copper sulfide phases with different band gap. The optical gap value of 2.00 eV corresponds to the phase of monovalent copper sulfide Cu_2S , and the value of 2.52 eV corresponds to the phase of divalent copper sulfide CuS , which corresponds to the previously obtained results of other researchers [18–20].

The photocatalytic activity of the samples obtained on matted quartz was studied under the action of ultraviolet (BUV-15 lamp, wavelength 253 nm) radiation. The efficiency of the photocatalyst was evaluated by the rate of hydroquinone oxidation (HQ). At discrete time intervals (1–2 h), the HQ concentration was determined by voltammetry on a PU-1 polarograph. To study the stability and photocatalytic activity of Cu_xS films, HQ oxidation in 3 cycles of UV irradiation of freshly prepared HQ solutions in the presence of the same film sample was investigated (Figure 4).

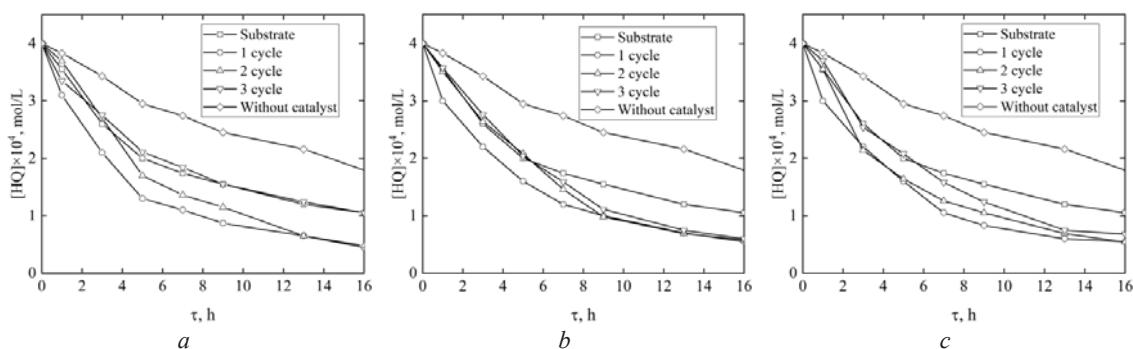


FIGURE 4. The change in the concentration of hydroquinone over time under the influence of ultraviolet radiation without catalyst, with an empty substrate of matted quartz and matted quartz with copper sulfide layer obtained after 45 (a), 60 (b) and 90 (c) min of synthesis.

In ultraviolet light without a catalyst, a slight decrease in the concentration of hydroquinone was observed in solution, due to its destruction under the influence of radiation itself. When a pure matted quartz substrate is immersed in a solution, a noticeable acceleration of the reaction is observed, which may indicate the catalytic activity of the substrate material itself and the presence of active oxidation centers on its surface. Immersion in a solution of a substrate coated with a layer of copper sulfide further accelerates the oxidation reaction of hydroquinone. A noticeable acceleration of the reaction is observed in the first cycle of photocatalysis. The second and the third cycles proceed more slowly, close to the rate of oxidation on the surface of a clean substrate. Films obtained within 60 and 90 minutes of synthesis demonstrated the best suitability for reuse (Fig. 4 *b, c*).

CONCLUSIONS

Copper sulfide layers were obtained by chemical deposition from aqueous media on quartz and matted quartz substrates. It was found that the films were formed by a monolayer of globules, the diameter of which lies within 140–240 nm, and the space between the globules on unmatted quartz is filled with a continuous layer of smaller particles of copper sulfide, which is associated with the activation of the surface of this substrate by solutions of tin chloride and thiourea.

Elemental analysis showed the predominance of copper over sulfur in the composition of the layers, and the copper content of the film on unmatted quartz is higher than that of the film on matted quartz, which can be related with activation of unmatted substrate surface.

According to the results of optical studies, two values of the band gap (2.00 and 2.52 eV) were established for the film synthesized on unmatted quartz, which corresponds to the band gap values for the phases of monovalent and bivalent copper sulfides, respectively.

Studies of the oxidation of hydroquinone by UV radiation in the presence of a copper sulfide layer obtained on matted quartz demonstrated the photocatalytic activity of the deposited material. At the same time, the layers obtained within 60 and 90 minutes of synthesis demonstrated a greater depth of the reaction and the possibility for reuse.

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