

Multifunctional spectrophotometric sensor based on photosensitive capacitor

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Abstract. The work demonstrates the possibility of using a structure, which is similar to the structure of a powder photosensitive capacitor, as a spectrophotometric sensor. For creating an active photosensitive layer of the sensor, a suspension of ZnS:Cu:Al:Cl particles uniformly distributed in a dielectric matrix $C_3H_5(C_{18}H_{33}O_3)_3$ was used as a dielectric layer between the capacitor plates. It was shown that, depending on the characteristics of the active layer material (particle size and material, dielectric matrix properties) and the configuration of the electrical circuit, the sensor can effectively operate both in the capacitive element mode and in the voltage generator mode.

Keywords: spectrophotometric sensor, photosensitive powder capacitor, ZnS:Cu:Al:Cl particles.

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1. Introduction

Development of high-tech production methods determines the improvement of methods and means of the scientific base of experimental research, which, in turn, leads to the need to enhance the sensors for monitoring the technological premises, the environment, *etc.*

Radiation and optical monitoring methods play an important role in solving this problem [1, 2]. These methods are primarily distinguished by the absence of material contacts with the research object and, therefore, by the possibility of obtaining the most reliable data characterizing radiation or optical emission.

Photoelectric sensors are separated into several types according to the method of modulating the recorded signal (amplitude [3], frequency [4], phase [5]), design (diffuse [6], opposed [7], with a retroreflector [8], slotted [9], fiber optic [10]), signal type (discrete [11], analog [12]), presence of a screen [13] (to protect the receiver and sensor from extraneous light), type of radiation being detected [14] (UV, IR and visible radiation), and explosion safety [15]. In addition to the main types, there are also specialized photoelectric sensors

designed to solve specific problems (gamma probes [16], scintillator structures [17], *etc.*). Choice of a sensor type depends on the task, measuring range, operation conditions, dimensions, weight and cost.

Sensor is a mandatory element of measuring instruments, control and regulation systems, *etc.* Creating sensors uses multiple physical effects and principles such as the photoelectric effect [18], piezoelectric effect [19], thermoelectric effect [20] and others. These effects are at the core of the operation of various sensor types allowing conversion of external influences of various natures into electrical signals for further analysis and processing.

However, widespread use of sensors often faces the problem of their high cost [21]. This is due to the complex design of many sensors, which makes them difficult to manufacture. Manufacturing highly accurate and reliable sensors often requires advanced technology and equipment, which are expensive themselves. Moreover, some sensor types require use of special materials with unique properties, which increase the sensor cost.

At the same time, wider use of well-known physical effects can significantly simplify sensor manufacturing technologies. For example, using standard semiconductor

technologies or application of common materials can reduce the manufacturing costs. Simplification of the technological process and reduction in the material costs reduces the overall production costs, making sensors more accessible to users. This also allows for increased production volumes to meet the growing demand for sensors and improve their competitiveness in the market. Cheaper and easier-to-manufacture sensors can take a leading position in various fields such as industrial, medical, environmental and consumer electronics.

Photoelectric sensors play an important role in the development of light-emitting diode (LED) technology [22], providing high efficiency, accuracy and control in various applications [23]. With the development of technology, LED lighting and devices are increasingly used in a wide variety of areas, from household lighting to complex industrial and medical systems, as well as phytolighting systems. Photoelectric sensors make it possible to measure LED emission parameters such as intensity, spectral composition and color temperature [24]. This is important to ensure consistent product quality, compliance with standards and improved energy efficiency of LED devices. Introduction of LED lighting systems with advanced functionality (high-power LED lighting systems [25], phytolighting systems [26], systems with adjustable spectral composition [27], *etc.*) into production makes the use of photoelectric sensors for these systems extremely important. Such sensors provide automatic lighting control depending on the level of natural light, presence of people and other factors. This allows one to significantly save energy and improve indoor comfort.

In security and monitoring systems, photoelectric sensors are used for detecting motion and presence as well as for environmental monitoring [28]. LED technologies in combination with photoelectric sensors make it possible to create highly accurate and reliable security systems. In medicine, photoelectric sensors and LEDs are used in diagnostic and therapeutic devices such as for measuring pulse and blood oxygen saturation (pulse oximeters) in phototherapy devices [29].

In industrial and scientific research, photoelectric sensors are used for process analysis, product quality control, and in various sensor systems [30]. In combination with LED light sources, they enable highly accurate measurements and observations. Photoelectric sensors in LED lighting systems help in environmental monitoring, such as urban light control, and monitoring water and air pollution.

Therefore, photosensors are the most important elements of the development and improvement of the LED technology. They provide high accuracy, efficiency and reliability of lighting and control systems, which contributes to their widespread use in various spheres of life [31]. Therefore, introduction of cost-effective methods of manufacturing photoelectric sensors and use of proven physical principles can significantly expand sensor application. This will not only reduce the cost of sensors, but also make them available for various purposes.

The goal of this work is to study the parameters of a structure similar to the one of a powder electro-luminescent capacitor used as an ultraviolet radiation sensor. Use of such a structure may become an example of successful application of simple and cost-effective solutions in production of high-performance sensors.

2. Material and methods

The schema of the experimental setup is shown in Fig. 1. A radiation source (LED XPGDWT-B1-0000-00KE7) (1) was placed in a box (2) coated with matte black paint. The structure under study was located at the bottom of the box. The structure had a form of a “device for rapid analysis” (indicated by a dashed line in Fig. 1), obtained by the standard for powder phosphors technology [32]. This structure consisted of two glasses (3) with a conductive optically transparent layer (ITO) (4), located one above the other. Between the glasses, there was a photo-sensitive layer ($\sim 70 \mu\text{m}$) (5) of a suspension of phosphor powder uniformly distributed in a $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{33}\text{O}_3)_3$ dielectric matrix. The layer thickness was adjusted by changing the thickness of the polymer film (6).

The phosphor was a ZnS powder (ETO.035.295 TU) activated with copper and co-activated with aluminum and chlorine. It was annealed in a quartz test tube at a temperature of 800°C during 180 min. The charge composition was: 94.0 g of zinc sulfide, 1.0...3.2 g of elemental sulfur, 0.8 g of ammonium bromide, and 0.45 g of copper chloride. To limit contact with the atmosphere during annealing, a gas seal made of granular activated carbon was used.

To record the potential difference across the contacts of the structure and the structure capacitive characteristics, a Keithley 2635B precision source-meter was used. The measurement modes of the Keithley 2635B source were controlled using a computer. To power the LED, a stabilized linear power supply Tektronix PWS2326 was used (the output voltage from 0 to 30 V, the output current from 0 to 5 A).

The measurements were carried out under pulsed illumination of the structure by a LED with $\lambda_{\text{max}} \sim 450 \text{ nm}$ at different intensities (8.8 and 91.5 W/m^2). Before the measurements, the charge existing in the structure was

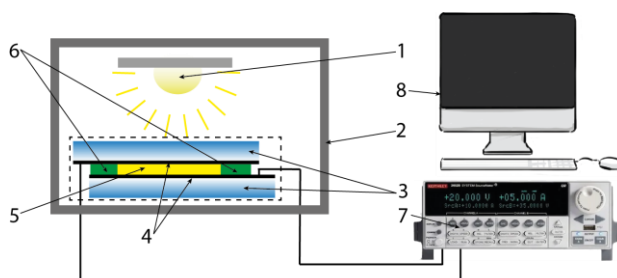


Fig. 1. Schema of the experimental setup: 1 – radiation source (LED XPGDWT-B1-0000-00KE7), 2 – box, 3 – optical glass, 4 – ITO layer, 5 – photosensitive layer, 6 – polymer film, 7 – source-meter Keithley 2635B, 8 – PC.

compensated. To measure the parameters of absorption of radiation with $380 < \lambda_{\max} < 780$ nm by the powder of a phosphor, an Everfine Haas-2000 spectrometer and LED with $\lambda_{\max} \sim 450$ nm were used as radiation sources. The study showed the absorption by the phosphor of about 99.7% for the radiation power of 8.8 W/m^2 .

3. Results and discussion

The structure under study is a capacitor whose capacitance changes under illumination. Fig. 2a shows the dependences of the capacitance of the structure under illumination by pulsed light with different intensities for 300 s. As can be seen from this figure, the dark capacitance is $5.9 \cdot 10^{-10}$ F. Fig. 2b shows the dependence of the change in the capacitance on the intensity of the incident radiation. When the structure is illuminated with the light intensity of 8.8 W/m^2 , the capacitance of the structure increases to $6.1 \cdot 10^{-10}$ F. When the illumination intensity increases by almost 10 times, to 91.5 W/m^2 , the capacitance of the structure increases to $6.3 \cdot 10^{-10}$ F and reaches almost saturation. Since the geometric parameters of the capacitor do not change, a change in its capacitance is only due to a change in the dielectric constant of the material between the plates of the capacitor. The dielectric constant of the binder ($\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{33}\text{O}_3)_3$) also does not change under illumination. Consequently, the main processes affecting the change in the dielectric constant in the capacitor being considered occur in the particles of the powder localized in the binder ($\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{33}\text{O}_3)_3$), *i.e.* in the ZnS:Cu:Al:Cl particles. Moreover, the change in the dielectric constant takes place mainly in the layer of the particles, which is located directly next to the illuminated transparent contact, *i.e.* in the particles which absorb the incident radiation. In these particles, electron-hole pairs are generated under the influence of radiation, sharply increasing the concentration of minority charge carriers. In the particles, which are located further away from the illuminated contact and do not absorb light, the concentration of charge carriers is essentially lower. Nevertheless, depending on the particle material, the processes associated with reabsorption of the luminescent radiation from the layers, involved in absorption of the external radiation, by subsequent particle layers may be observed.

Figs 3a, 3b show the dependences of the potential difference at the contacts of the structure on time at lighting on and off. As can be seen from these figures, when the structure is illuminated, a potential difference appears at its contacts. It should be noted that, despite the change in the magnitude of the incident light flow, the potential difference across the contacts changes very slightly (Fig. 3c). This is probably a consequence of the fact that due to their relative position, the set of the ZnS:Cu:Al:Cl particles in the dielectric matrix acts as a set of capacitors, mainly connected in parallel. In this case, the total charge for such capacitors set may be represented as $q = q_1 + q_2 + q_3 + \dots + q_n$, and the voltage at their contacts as $U = U_1 = U_2 = U_3 = \dots = U_n$.

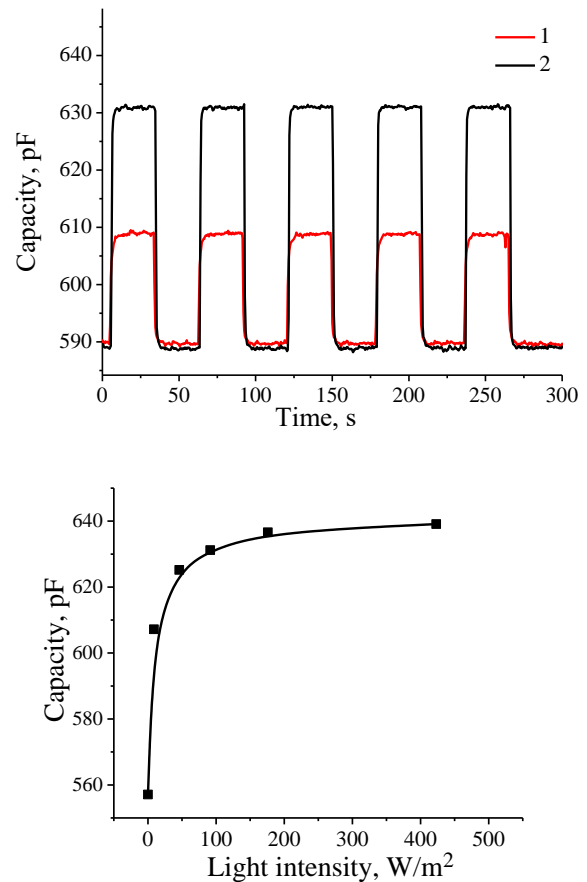


Fig. 2. Dependence of the structure capacitance on (a) time under illumination of different intensities turned off and on. The intensity of the incident radiation is 8.8 W/m^2 (1), 91.5 W/m^2 (2). (b) dependence on the lighting intensity.

It should be noted that the voltage at the contacts of the structure changes non-monotonously with time when the lighting is turned on and off. The dependence of the voltage at the contacts on time after turning on the lighting can be separated into three sections (see Fig. 3b). The first section duration is about 0.1 s after the starting illuminating the structure, the second section lasts ~ 10 s when the lighting is on, and the third section lasts ~ 10 s with the lights off.

As can be seen from Fig. 3b, at the first moment of time of the order of ~ 0.04 s, the voltage rises abruptly to a value of ~ 0.85 mV, and at almost the same velocity during the next ~ 0.05 s it drops to a value of ~ 0.4 mV. This behavior of the dependence of the voltage at the structure contacts on time when the lighting is turned on and off is caused by the fact that illumination of the surface of the ZnS:Cu:Al:Cl particles generates electron-hole pairs, which is accompanied by a sharp increase in the concentration of non-equilibrium charge carriers on the particle surfaces. Since the excess concentration of non-equilibrium charge carriers on the surface of the particles is higher than that in the bulk, since only a small part of the incident light reaches the bulk, electrons and holes migrate from the surface inside the particles.

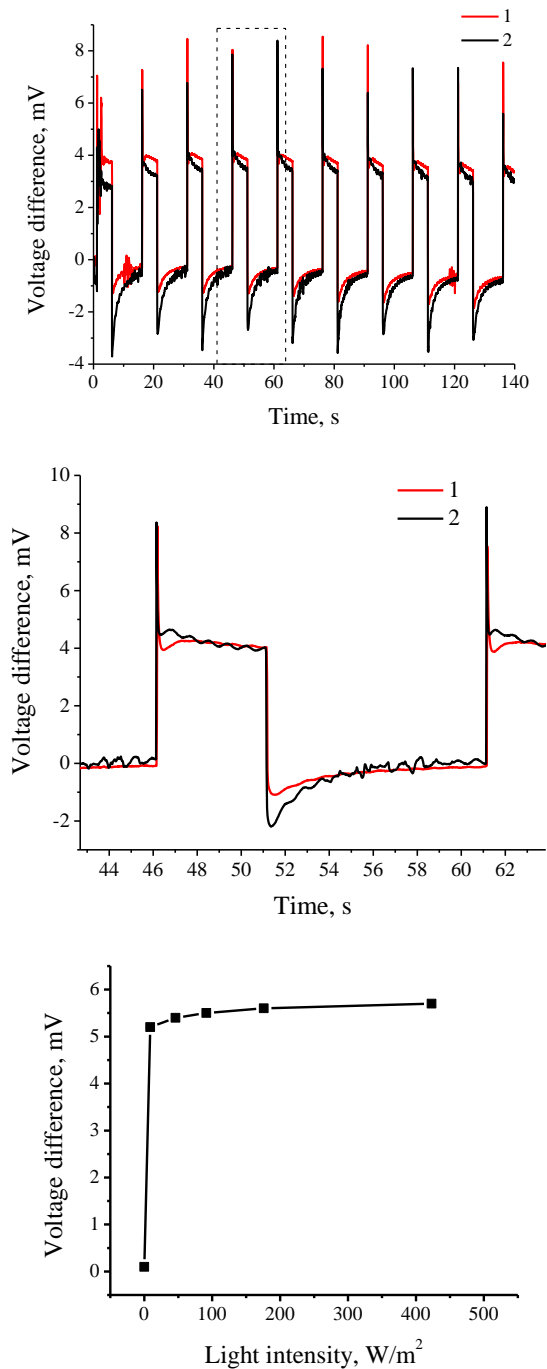


Fig. 3. Dependence of the potential difference at the contacts of the structure (a), (b) on time (a – within the interval of 0...140 s, b – within the interval of 0...20 s) under illumination of different intensities turned off and on. The intensity of the incident radiation is 8.8 W/m²(1), 91.5 W/m²(2). (c) dependence on the incident radiation intensity.

Considering the fact that the mobility of electrons is higher than that of holes, the electrons are ahead of the holes, which leads to charge separation. A positive charge on an illuminated surface and a negative charge on an unlit surface is created. As a result, a photoelectromotive force (EMF) or Dember EMF [33] arises, which compensates the difference in the diffusion flows

of electrons and holes. In turn, the positive charge of the illuminated surface of the particles induces a charge of the opposite sign at the contact.

It should be noted that the charge carrier recombination velocity in ZnS:Cu:Al:Cl is significant as compared to the electron migration velocity into the bulk. In this regard, within ~ 0.04 s, the potential reaches its maximum value (~ 0.85 mV). During the next time interval of ~ 0.05 s, when recombination processes start, the lifetime of the photoexcited carriers drops sharply, which in turn leads to a decrease in the surface potential. In Fig. 3b, this corresponds to a sharp drop in the potential in the first section to ~ 0.4 mV, since the carrier concentration under illumination still exceeds its “dark” value despite the recombination processes.

These processes take place until a certain quasi-equilibrium state is established in the entire structure, in which the generation G_0 and recombination R_0 velocities become equal. The second section of about 10 s corresponds exactly to this steady state at a given illumination level.

It should be also noted that the structure under consideration is a capacitor. Therefore, the type of the dependence in the first section will be also influenced by the parameters of this capacitor.

When the lighting is turned off, the potential difference across the contacts sharply drops and takes negative values of the order of -0.11 mV at the first moment of time. Then within 5 s it monotonically approaches zero. Recharging of the structure and its subsequent long-term discharge are probably associated with the presence of ZnS:Cu:Al:Cl electron acceptor traps in the band gap. Under illumination, these traps are filled with non-equilibrium charge carriers. After turning off the illumination, it takes some time to empty (release) them. This time is longer, the greater is the depth of these traps level. As mentioned above, illumination of one side of the structure creates a carrier concentration gradient in it. Turning off the lighting leads to rapid migration of the carriers to the depletion zone. Therefore, the main role in the formation of the potential at the contacts passes from the carriers localized on the surface to the carriers captured by the traps.

4. Conclusions

As can be seen from the presented results, the structure with an active photosensitive layer that contains ZnS:Cu:Al:Cl particles has significant potential for use as a multifunctional sensor. Its ability to change electrical characteristics in response to exposure to radiation, ultraviolet and optical radiation allows its use in a variety of fields, from environmental monitoring to medical diagnostics. Depending on the characteristics of the active layer material and the electrical circuit configuration, the sensor can effectively operate in both capacitive element mode and voltage generation mode, providing flexibility and versatility in use, mainly due to generating charge carriers in the photosensitive

material at low irradiation intensity to ensure high sensitivity of the sensor. Use of a structure with an active photosensitive layer containing ZnS:Cu:Al:Cl particles will also provide an advantage of the sensor fast-acting, since the change in the voltage across the contacts of the structure when the lighting is turned on and off demonstrates its ability to quickly respond to changing conditions.

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Багатофункціональний спектрофотометричний датчик на основі фоточутливого конденсатора

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Анотація. У роботі продемонстрована можливість використання структури, що є подібною до структури порошкового фоточутливого конденсатора як спектрофотометричного датчика. Для створення активного світлочутливого шару сенсора як діелектричний шар між пластинами конденсатора використовувалася суспензія частинок ZnS:Cu:Al:Cl, які були рівномірно розподілені в діелектричній матриці $C_3H_5(C_{18}H_{33}O_3)_3$. Показано, що в залежності від характеристик матеріалу активного шару (розміру і матеріалу частинок, властивостей діелектричної матриці) і конфігурації електричної схеми датчик може ефективно працювати як у режимі ємнісного елемента, так і в режимі генератора напруги.

Ключові слова: спектрофотометричний датчик, фоточутливий порошковий конденсатор, ZnS:Cu:Al:Cl частинки.