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Correlation between photographic and electrical properties of the polymer–semiconductor–salt of metal photosensitive composition

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ABSTRACT

In the current paper experimental data about changes in the electrical properties (relative permittivity) of the PVA–ZnO–$BiCl_3$ photosensitive composition under UV radiation are presented. Also the correlation between dielectric constant and density of optical blackening are investigated.

1. Introduction

Photosensitive compositions, which consist of a polymer with dispersed in it semiconductor and sensitized by salt of a metal, are exhibit sensitivity to the UV- and X-ray irradiation [1]. Sensitivity appears to change the color of the surface of the photosensitive composition under the influence of initiating radiation (Fig. 1). This darkening shown in Fig. 1 occurs directly under the influence of light (without additional display or other treatment), i.e. the composition of this class implements a direct blackening.

Photostimulated processes in the compositions of this class the most detailed study on the example of polyvinyl alcohol–zinc oxide–bismuth chloride compositions (PVA–ZnO–$BiCl_3$) [1–8] and polyvinyl alcohol–zinc oxide/titanium oxide–lead acetate composition (PVA–ZnO/TiO_2–$Pb(Ac)_2$) [9,10]. The form wherein the sensitizer (metal salt) is present in a such photosensitive compositions is strongly influence on photographic properties of it [3], as well as the concentration of the acetate groups in the polymer matrix structure [4–6].

During the direct blackening processes in the PVA–ZnO–$BiCl_3$ photosensitive composition the formation of metallic bismuth and polyene structures $(-C{=}C-)_n$ occur [1,2]. Both the metallic bismuth and polyene structures are exhibit sufficiently high electron conductivity [11,12]. Therefore in [2] it was made an assumption, that irradiating of the PVA–ZnO–$BiCl_3$ photosensitive composition should lead to an increase of its electrical conductivity.

This paper provides the first experimental data on changes in the electrical properties of the PVA–ZnO–$BiCl_3$ photosensitive composition irradiated by UV light. Also, the correlation between the photographic and electrical properties of the photosensitive composition is investigated.

2. Materials, experimental methods and equipment

For the manufacture of the photosensitive composition chemically pure polyvinyl alcohol 11/2 grade, pure zinc oxide and anhydrous, chemically pure bismuth chloride are used.

The photosensitive layer is achieved by the following method: 10 g of the PVA is mixed with 100 g of distilled water and left to draw for up to 10 h. During this time the polyvinyl alcohol granules swell in the water. Then the 10% PVA aqueous solution thus obtained is heated at 80–90 °C for 45 min until the solution becomes homogeneous. After that, 12 g of the zinc oxide is added to 100 ml of the PVA aqueous solution. The resulting compound is mixed up and poured out on to a glass plate. This used no more than 2/3 of the total compound. This means that the heaviest fractions of ZnO were left in the container making the photosensitive composition more homogeneous.

Bismuth chloride unimolar aqueous solution is prepared singly. To make it, 31.5 g of anhydrous bismuth chloride is dissolved in water. Intense hydrolysis takes place during the dissolving. The completely hydrolyzed bismuth chloride – $Bi(OH)_3$ – falls as a white

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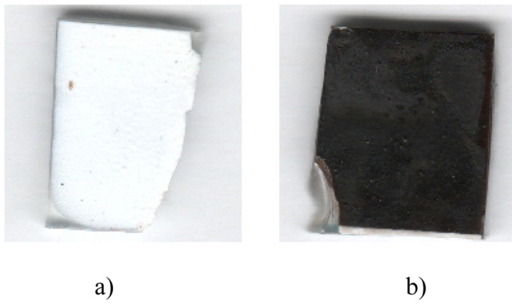

Fig. 1. The PVA–ZnO–$BiCl_3$ photosensitive composition surface coloration changes during the UV-irradiation. (a) – photosensitive composition before irradiation, (b) – photosensitive composition after irradiation (duration 60 s, illumination 0.105 W/sm^2).

sediment, and the bismuth chloride complexes $BiCl^{3-}$ ($n = 0 \ldots 6$ [14]) basically stay in solution.

After the polyvinyl alcohol filmed with dispersed zinc oxide for 12–15 h drying at normal conditions, the bismuth-containing compound –bismuth chloride aqueous solutions– is added by dipping the filmed bismuth chloride aqueous solutions for 30 s. After that, the surplus moisture is removed from the surface by a warm air flow for 5 min. Measurement shows that as a result of such treatment nearly 9 mass% of the bismuth chloride gets into the photosensitive composition [13].

It is known [1], that photostimulated transformations in the photosensitive composition occur mainly in the surface layer. To determine the depth at which the composition components are changing during the UV irradiation, it was investigated by scanning electron microscopy with Evo 40 (Carl Zeiss) electron microscope. To define the photographic characteristics of the photosensitive composition was used the method of construction of characteristic curves. The density of the optical blackening was measured by the author's hardware–software equipment.

The exposure of the resulting photosensitive composition was made by mercury-vapor lamp DRT-125 integral light. The energy of UV-irradiation is basically allocated between the spectral ranges: 230–280 nm (9–11%), 280–315 nm (22–25%), 315–400 nm (21–22%). The total luminous flux of the DRT-125 lamp is 1730–1850 lm. The illumination near the photosensitive composition surface during the experiments is 0.105 W/sm^2.

The experiment consisted of illumination of the PVA–ZnO–$BiCl_3$ photosensitive composition by the UV light for a specific time, with simultaneous determination of optical blackening and relative permittivity.

To define electric properties (relative permittivity) of the photosensitive composition the method of the resonance frequencies in the resonant circuit was used. In Fig. 2 the scheme of the voltage resonance investigation is present. As the source was used the GZ-112 sinusoidal signal generator (SSG on Fig. 2) with the ability to continuously adjust the frequency from 10 Hz to 10 MHz. In this experimental setup photosensitive composition is subjected to UV irradiation, installed between the flat plates of the capacitor with a known area of the plates (S). The distance between the plates of a capacitor (D), equal to the thickness of the photosensitive composition, was measured with a micrometer. The resonance frequency (ν) of the oscillation circuit was determined by the maximum value of the current in the voltage resonance mode. In addition to the capacitor of variable capacity (C) in the resonant circuit it was used the constant $L = 16.4$ mH. The resonant frequency is related to the parameters of the oscillation circuit by the Thompson's ratio:

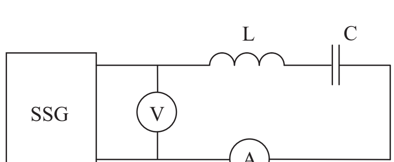

Fig. 2. The experimental scheme for determining the electrical characteristics of the photosensitive composition.

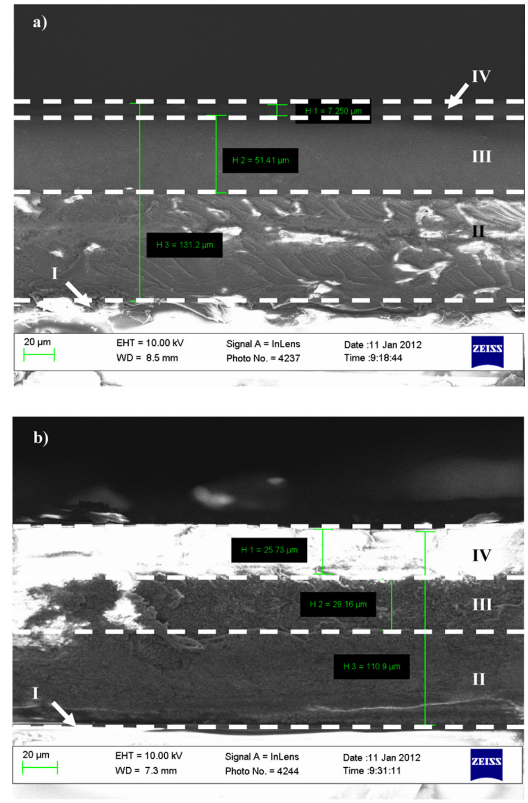

Fig. 3. The SEM images of the PVA–ZnO–$BiCl_3$ photosensitive composition cross sections before (a) and after (b) UV irradiation during 120 s. I – the glass substrate, II – the zinc oxide layer, III – the polyvinyl alcohol layer, IV – the PVA layer, impregnated by bismuth chloride (before irradiation) or by photolysis products (after irradiation).

$$\nu = \frac{1}{2\pi\sqrt{LC}}. \quad (1)$$

In turn, the flat capacitor capacity can be determined from following equation:

$$C = \frac{\varepsilon\varepsilon_0 S}{D}, \quad (2)$$

where ε_0–electric constant, ε–relative permittivity of a dielectric separating the plates of a capacitor (in our case-relative permittivity of a photosensitive composition).

From the Eqs. (1) and (2) the PVA–ZnO–$BiCl_3$ photosensitive composition relative permittivity can be expressed:

$$\varepsilon = \frac{DL}{\varepsilon_0 S(2\pi\upsilon)^2}. \quad (3)$$

3. Results

The above-described manufacturing process involves obtaining a photosensitive composition layer structure: till drying zinc oxide is settles down, wherein the bismuth chloride sensitization impregnated only the upper part of the composition. On Fig. 3 shows the SEM images of the cross sections of the PVA–ZnO–$BiCl_3$ photosensitive composition before irradiation (Fig. 3a) and after exposure for 120 s (Fig. 3b). From these figures it is seen that