

# Surface photoconductivity of anodically grown ZnO layers

R. DRAGON

Physical Laboratory, Institute of Mathematics, Physics and Chemistry, Technical University of Opole, ul. Ozimska 75, 45-370 Opole, Poland.

Surface photoconductivity of thin, anodically grown ZnO layers, separated from the maternal zinc substrate and glued onto a slice of organic glass, has been investigated. The effect of spectral sensitization with erythrosin on the photoconductivity of anodic ZnO layers has also been studied. The width of the forbidden energy gap in investigated material, estimated from the experimentally determined spectral distribution of the photosensitivity equals 3.3. eV.

## 1. Introduction

Zinc oxide, being a n-type semiconductor, is the subject of very intensive investigations. Among others, the photoelectric properties of polycrystalline powders and ceramics, monocrystals and thin thermally grown ZnO layers are systematically studied [1].

The effect of UV-radiation on the electrical conductivity of anodically grown ZnO layers in contact with electrolyte was first studied by VESELOVSKII [2] and then by SCHWABE [3]. The author of the present paper revealed the internal photoeffect in dry anodic ZnO layers, occurring in the sandwich-type cells: zinc substrate-anodic ZnO layer-semitransparent metallic electrode [4], but was unable to determine the spectral distribution of photosensitivity of the investigated materials because of the difficulties connected with the absorption of light in the semitransparent metallic electrode evaporated onto the surface of the ZnO layer.

In order to overcome these difficulties, in the present investigation the surface photoconductivity of anodically grown ZnO layers was studied. This enabled determining the spectral distribution of photosensitivity of the investigated material. Additionally, the effect of sensitization with erythrosin on the photoconductivity of anodic ZnO layers has been investigated. The aim of this paper is to present the results of these studies and to compare the photoelectric properties of anodically formed ZnO layers with those for ZnO layers thermally grown on the zinc substrate [1], [5]-[9].

## 2. Experimental conditions

Zinc platelets cut from a sheet of the purity of 99.98% were chemically cleaned and then electrolytically oxidized in the electrolyte prepared from 0.5 M Na<sub>2</sub>CO<sub>3</sub> and

1.0 M NaOH water solutions mixed in the volume proportion of 7:1. In the process of electrolytical oxidation the zinc platelets were used as anodes. A platinum platelet was used as the cathode. The electrolytical deposition of ZnO layers was carried out at 0.5 h, at a constant voltage of 40 V. Under these conditions the ZnO layers of the thickness of 0.8  $\mu\text{m}$  were grown [10].

The oxidized zinc platelets were rinsed in running water and next in distilled water, and finally dried in a stream of hot air.

The surface photoconductivity of anodically grown ZnO layers was measured using the gap type cells shown in Fig. 1. They were prepared as follows. Oxidized zinc platelets were glued to the slice of an organic glass with the glue prepared by dissolving the organic glass in chloroform. The ZnO layer covering the opposite side of the zinc platelet was removed mechanically and the zinc substrate was dissolved in mercury by the method described by HUBER [11].

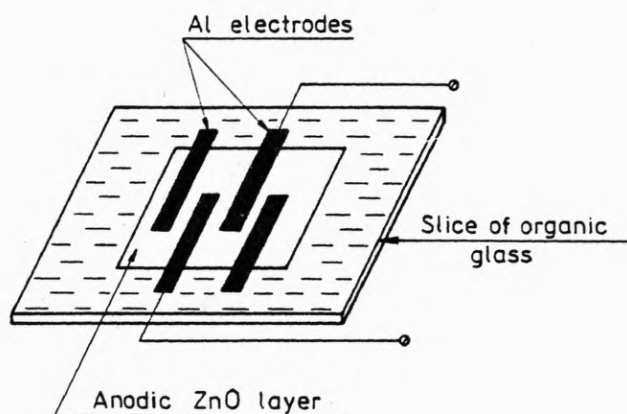


Fig. 1. Sketch of the cell used for measurements of the surface photoconductivity

Part of the ZnO layers were coloured (sensitized) with erythrosin ( $\text{C}_{20}\text{N}_8\text{I}_4\text{O}_5$ ) by dipping a slice of the organic glass with glued ZnO layer for a few hours in an ethanol solution of erythrosin ( $10^{-4}$  M/litre).

The aluminium electrodes were deposited by vacuum evaporation on the free surfaces of pure and coloured ZnO layer.

The photoconductivity was measured between two neighbouring electrodes. The illuminated area of the surface of investigated ZnO layers was  $\sim 0.4$   $\text{cm}^2$ . The samples were placed in a hermetically closed metallic container with a quartz window. The air inside the container was dried with phosphor pentoxide  $\text{P}_2\text{O}_5$ .

The sample surface was illuminated through a quartz window by the light emitted by a quartz lamp ABO 200 and monochromatized by means of the VSU-1 monochromator. The intensity of light at the output slit of the monochromator was measured by means of a vacuum thermoelement VTh-1.

The optical absorption measurements were performed with the aid of the spectrophotometer UV VIS Specord.

All the measurements were carried out in the atmospheric air at the room temperature.

### 3. Results and discussion

#### 3.1. Pure (non-coloured) anodic ZnO layers

Photocurrent of the anodically grown ZnO layers illuminated with UV radiation ( $\lambda = 365$  nm), measured at the constant voltage between the electrodes, monotonically increase with illumination time. As it is seen in Fig. 2, initially the increase rate of the photocurrent  $di/dt$  is constant and then slowly diminishes. After 30–40 minutes, the photocurrent reaches a saturation value. After switching the illumination off, the photocurrent gradually decays.

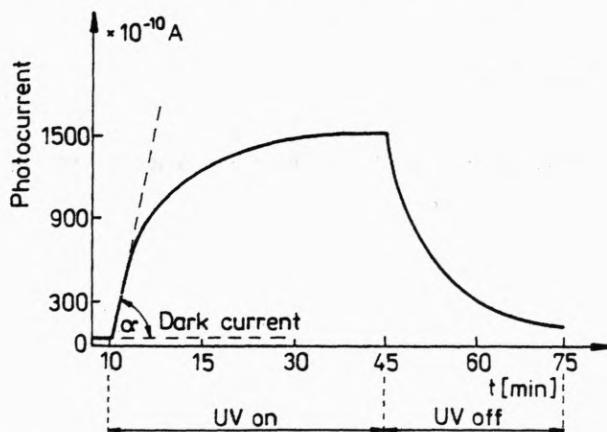


Fig. 2. Increase and decay curves of the photoconductivity of the surface cell ( $\lambda = 365$  nm)

Figure 3 represents the initial parts of the photocurrent increase curves measured at different, constant in time, illumination intensities. As may be seen, the initial parts of these curves are linear. The slope (photocurrent increase rate) of these curves increases with increasing intensity of illumination. The decay of the photocurrent after switching the illumination off is nonlinear and slower than the increase after switching the illumination on.

Figure 4 represents the dependence of the photocurrent increase rate, determined from the data shown in Fig. 3, on the intensity of illumination  $L$ . The initial photocurrent increase rate is directly proportional to the intensity of illumination of the sample. From the same figure, it follows that the reduced initial photocurrent increase rate (*i.e.* increase rate divided by the illumination intensity,  $(di/dt)(1/L)$ ) is constant for a given sample at a given wavelength of light illuminating the sample.

Figure 5 represents the results of measurements of the reduced initial photocurrent increase rate at various wavelengths of light illuminating the sample, ranging from 360 to 400 nm. The reduced initial photocurrent increase rate changes with changing the illumination wavelength. The curve shown in Fig. 5 can be treated as a

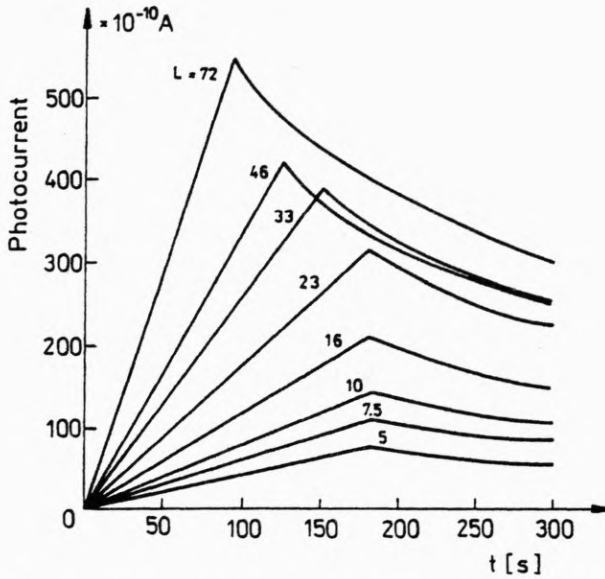


Fig. 3. Initial parts of the increase curves of the photocurrent  $i$  for different intensities of illumination  $L$  ( $\lambda = 365$  nm)

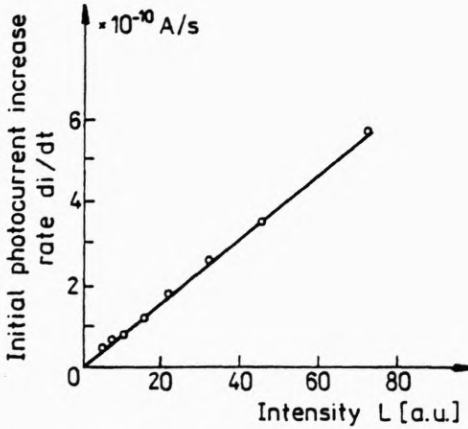


Fig. 4. Initial photocurrent increase rate  $di/dt$  vs. intensity of illumination  $L$

spectral distribution of the surface photosensitivity of anodic ZnO layers. The shape of this curve is very similar to that determined by WEISS [9] for the thermally grown ZnO layers.

Extrapolation of the linear part of the curve depicting the spectral distribution of photosensitivity of the investigated ZnO layers gives a cut-off wavelength of the illuminating light  $\lambda_g = 378$  nm which corresponds to the energy of photons of 3.28 eV. This wavelength determines the edge of the fundamental adsorption band and permits estimating the width of the forbidden energy gap in anodically grown ZnO layers at room temperature as being equal to 3.28 eV.

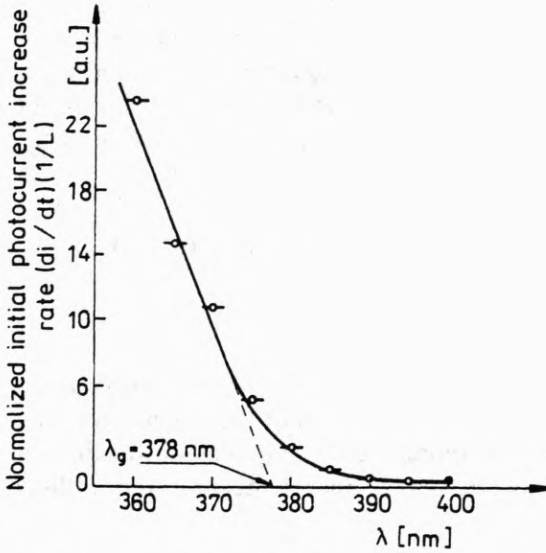


Fig. 5. Normalized initial photocurrent increase rate  $(di/dt)(1/L)$  vs. the wavelength of light  $\lambda$

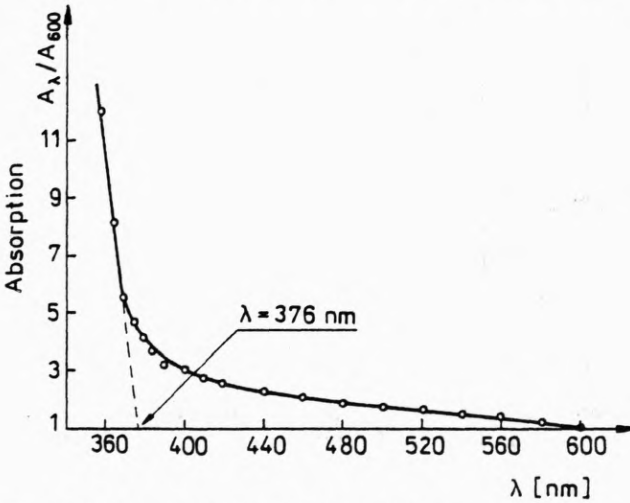


Fig. 6. Optical absorption spectrum of the anodically grown ZnO layers

In order to check this supposition, the optical adsorption of investigated ZnO layers has been measured. The results of these measurements are shown in Fig. 6. The results of the measurements were normalized by relating the value obtained at each wavelength to that obtained at  $\lambda = 600$  nm. Thus, the curve from Fig. 6 represents the spectral distribution of the ratio  $A_\lambda/A_{600}$ , where  $A_\lambda$  is the absorption at the wavelength  $\lambda$  and  $A_{600}$  denotes the absorption determined at the wavelength of 600 nm. As may be seen from Fig. 6, in the visible range of spectrum, the optical absorption of ZnO layers changes very slowly, whereas a sharp increase is observed on passing into UV range.

Comparison of the results of optical absorption (Fig. 6) and photosensitivity (Fig. 5) measurements shows that the rapid changes in both the curves occur in the same interval of wavelengths. Extrapolation of the steepest part of the absorption curve gives a cut-off wavelength of 376 nm, which agrees well with the result obtained from the photoconductivity measurements. Thus, the position of the edge of fundamental absorption band and the width of the forbidden energy gap in anodic ZnO layers equal, correspondingly,  $\lambda_k \approx 380$  nm and  $E_g \approx 3.3$  eV. These results agree well with the data reported in [1] for ZnO layers thermally grown on Zn substrates.

### 3.2. Anodic ZnO layers coloured with erythrosin

The first step in investigation of the anodic ZnO layers coloured with erythrosin was the determination of their optical absorption. The results of these measurements are shown in Fig. 7. Curve 1 in this figure represents the optical absorption of erythrosin dissolved in ethanol, whereas curves 2 and 3 display the optical

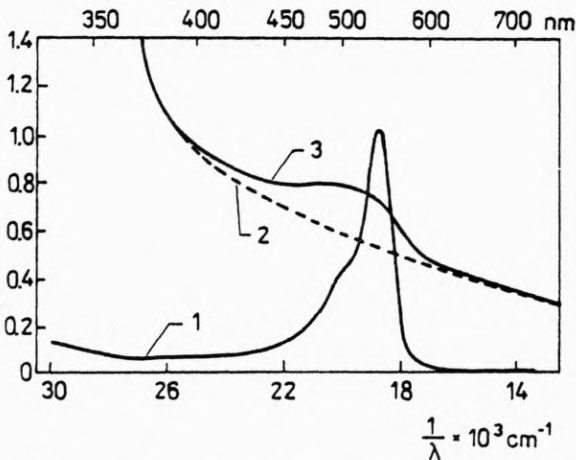


Fig. 7. Optical absorption spectra: 1 — ethanol solution of erythrosin ( $2 \times 10^{-5}$  M/litre), 2 — as-grown anodic ZnO layer, 3 — anodic oxide layer coloured during 5 hours in the ethanol solution of erythrosin ( $10^{-4}$  M/litre)

absorption for pure ZnO layer and for the same layer coloured with erythrosin. The optical absorption band of erythrosin lies in the visible range of spectrum and exhibits maxima in the vicinity of 500 and 530 nm. The as-grown (pure) anodic ZnO layers are transparent and their adsorption in the visible range slowly increases with decreasing wavelength. In the UV range of spectrum optical absorption of pure ZnO layer rapidly increases. Optical absorption of ZnO layer coloured with erythrosin is a combination of the absorption spectra of erythrosin and pure (non-coloured) ZnO. Therefore, the ZnO layers coloured with erythrosin display photoconductivity in both the visible and UV range of spectrum. Photoconductivity of coloured ZnO layers illuminated with light from the UV range (365 nm) is similar to that observed for pure ZnO layers.

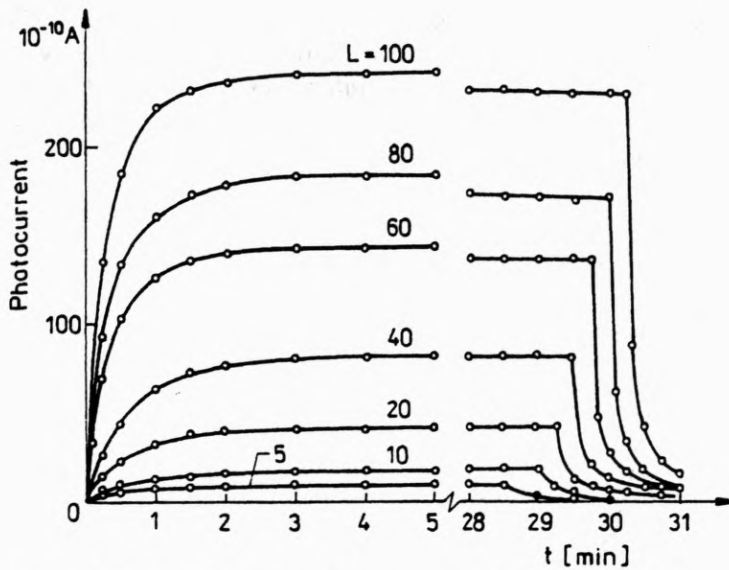


Fig. 8. Photocurrent growth and decay curves at different intensities of illumination  $L$  ( $\lambda = 537$  nm) for the ZnO sample coloured with erythrosin

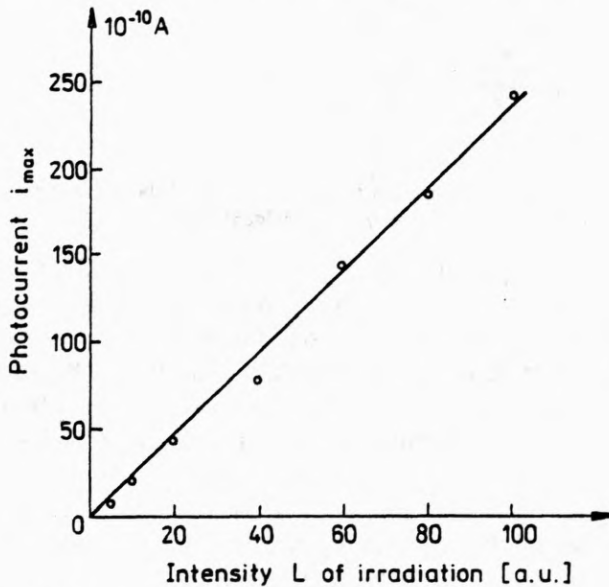


Fig. 9. Maximum values of the photocurrent  $i_{max}$  from Fig. 8 vs. intensity of illumination  $L$  ( $\lambda = 537$  nm)

Photoconductivity of coloured ZnO layers in the visible range of spectrum was investigated at the wavelength of 537 nm. Figure 8 represents the photocurrent increase and decay curves for these layers measured at different (constant in time) intensities of illumination  $L$ . The shape of these curves is similar to that observed in

the case of illumination with UV radiation ( $\lambda = 365$  nm). It can be assumed that the electrons responsible for erythrosin induced photoconductivity originate from the molecules of erythrosin and the kinetics of this photoconductivity is governed by the ZnO matrix. As it follows from Fig. 8, at larger intensities of illumination the photoconductivity displays "fatigue effect" — after reaching the saturation value photocurrent intensity starts to decrease with time.

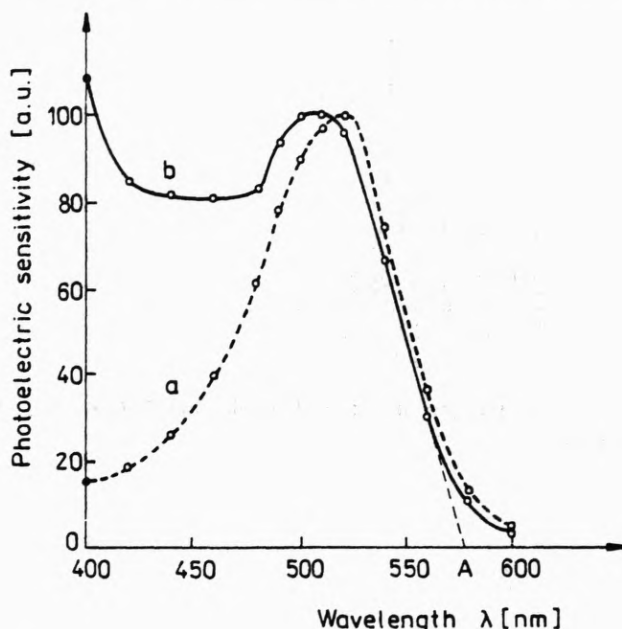


Fig. 10. Spectral photosensitivity of ZnO samples: a — from the maximum values of the photocurrent, b — maximum values of the photocurrent divided by the energy of incident light

Maximum value of photocurrent  $i_{\max}$  is directly proportional to the illumination intensity  $L$  (Fig. 9). Measurements of the maximum photocurrent values at different wavelengths enabled determining the spectral distribution of the erythrosin induced photosensitivity. The results of these measurements are shown in Fig. 10. Curve a in this figure represents the dependence of the maximum photocurrent value  $i_{\max}$  on the wavelength of light illuminating the sample. Curve b displays a similar dependence for maximum photocurrent value  $i_{\max}$  divided by the energy quanta of the incident light. Thus, the curve b can be interpreted as the spectral distribution of the photosensitivity induced by erythrosin. Extrapolation of the long wavelength decaying part of this curve (Fig. 10, point A at  $\lambda = 580$  nm) gives the value of the optical activation energy of the erythrosin induced photoconductivity equal to 2.14 eV. This agrees well with the value of the optical activation energy for pure erythrosin (2.12 eV) determined in [12].

Concluding, it can be stated that the optical and photoelectric properties of anodically formed ZnO are very similar to the properties of ZnO layers thermally grown on the Zn substrate. The properties of anodic ZnO layers and the ease



of their preparation makes them a very promising material for various practical applications (*e.g.* electrophotography and electronics).

## References

- [1] HEILAND G., MOLLWO E., STÖCKMAN F., *Electronic processes in zinc oxide*, [In] *Solid State Physics*, Vol. 8, Academic Press, New York 1959.
- [2] VESELOVSKII V. I., *Zh. Fiz. Khim.* **21** (1947), 983.
- [3] SCHWABE K., *Z. Phys. Chem.* **205** (1956), 304.
- [4] DRAGON R., *Zeszyty Naukowe WSP w Opolu, Fizyka* **4** (1964), 45 (in Polish).
- [5] PUTZEIKO E. K., TERENIN A. N., *Zh. Fiz. Khim.* **23** (1949), 676; *DAN SSSR* **90** (1953), 1005.
- [6] PUTZEIKO E. K., *DAN SSSR* **91** (1953), 1071.
- [7] KORSUNOVSKII G. A., *DAN SSSR* **134** (1960), 1394.
- [8] HAUFE K. H., *Photographic Sci. Eng.* **20** (1976), 124.
- [9] WEISS H., *Z. Physik* **132** (1952), 335.
- [10] DRAGON R., *Opt. Appl.* **13** (1983), 47.
- [11] HUBER K., *Helv. Chim. Acta* **27** (1944), 1443.
- [12] TOPCZIEW A. W. [Ed.] *Organicheskie poluprovodniki* (in Russian), Izd. AN SSSR, Moskva 1963.

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