

The kinetic of photoreactions in zinc oxide microrods

M Fiedot, O Rac, P Suchorska-Woźniak, W Nawrot, H Teterycz

Wrocław University of Technology, Faculty of Microsystem Electronics and Photonics, Janiszewskiego 11/17, Wrocław, Poland

E-mail: marta.fiedot@pwr.edu.pl

Abstract. Zinc oxide is the oldest sensing material used in the chemical resistive gas sensors which allow to detect many gases, such as carbon oxide, nitrogen oxides and other. This material is also widely used in medicine and daily life as antibacterial agent. For this reason this semiconductor is often synthesized on the polymer substrates such as foils and textiles. In presented results zinc oxide was deposited on the surface of poly(ethylene terephthalate) foil to obtain antibacterial material. As synthesis method chemical bath deposition was chosen. The growth of zinc oxide structures was carried out in water solution of zinc nitrate (V) and hexamethylenetetramine in 90°C during 9 h. Because antibacterial properties of ZnO are strongly depended on photocatalytic and electric properties of this semiconductor impedance spectroscopy measurements were carried out. During the measurements material was tested with and without UV light to determinate the kinetic of photoreactions in zinc oxide. Moreover the composite was analyzed by XRD diffraction and scanning electron microscope. The X-ray analysis indicated that obtained material has the structure of wurtzite which is typical of zinc oxide. SEM images showed that on the PET foil microrods of ZnO were formed. The impedance spectroscopy measurements of ZnO layer showed that in UV light significant changes in the conductivity of the material are observed.

1. Introduction

Zinc oxide is a white semiconductor that is widely used in medicine as an antifungal and antibacterial material, which is associated with its high biological activity, lack of toxicity and low price [1]. Moreover, this oxide is widely used in electronics for production of various components, such as gas sensors [2], varistors [3] or solar cells [4]. It has many useful properties such as refractive index of $n = 1.95\text{--}2.10$ [5], a direct band gap of 3.3 eV [6], piezoelectric coupling coefficient of 1.19 C/m² [7] and good photocatalytic properties [8].

The photocatalytic properties of this material are some of the causes of their good biological activity. As a result of the processes occurring on the surface of the semiconductor, the photocatalytic generation of free radicals [9-11] and the release of the Zn²⁺ ions [12-14] takes place.

In the literature, there are many studies which show that the exposure of ZnO to ultraviolet radiation leads to a significant improvement in its biological activity [15]. Therefore, it can be assumed that the mechanism associated with the photocatalysis is more important than the release of ions.

Good photocatalytic properties of ZnO are directly related to photogeneration of electric charge carriers in the material under the influence of electromagnetic radiation with an energy equal to or greater than the width of the band gap. In the case of this semiconductor, radiation is within the UV range [16].



Research conducted by Ann et al. demonstrated that exposure of zinc oxide rods to UV radiation for 20 minutes reduced the survivability of *E. coli* by 18% and *S. aureus* by 22% in comparison with the test with no additional lighting [17].

In order to better understand the antibacterial activity of ZnO and explain the effect of UV radiation on its properties, the kinetics of photoinduced electron transfer occurring in the microrods of zinc oxide deposited on a polymer film were studied in this article. Measurements were performed using impedance spectroscopy.

2. Experimental part

As a method of the surface modification of the poly(ethylene terephthalate) (PET) film, the chemical bath deposition (CBD) technique was applied. The growth of the ZnO structures was carried out in an equimolar aqueous solution of zinc nitrate (V) $\text{Zn}(\text{NO}_3)_2$ and hexamethylenetetramine (HMT) at a concentration of 100 mM. The obtained solution was stirred on a magnetic stirrer for 24 hours, after which it was filtered. Then the previously prepared polymer film sized 4 x 2 cm was placed in a beaker with the prepared solution. The mixture was heated at 90°C for 9 hours. After the deposition process, the obtained sample was rinsed to remove by-products and the excess of the modifying agent, which had not permanently bound to the surface of the test material.

The prepared sample was examined by X-ray diffraction (XRD) to determine the crystalline structure of deposited layer and define the size of crystallites. The crystallographic structure of zinc oxide was determined using Philips Materials Research Diffractometer (MRD) by means of $\text{CuK}\alpha$ radiation.

The microstructure of sample was examined with the use of electron scanning microscope (SEM) JSM 5800 LV of Jeol company. The microscope is equipped in ISIS 300 system for X-ray analysis of Oxford company.

The AC measurement was performed across the test structure, between the upper electrode and the lower electrode (the test material was placed between two copper electrodes). To obtain appropriate contact between sample and electrons the measuring system was pressed with 462.5 g/cm². The Solartron SI 1260 impedance analyser was used in the tests. The measurements of polymer composite impedance were performed in a frequency range from 10 Hz to 1 MHz, stimulating the structures by the sinusoidal voltage signal with an amplitude of 500 mV. In addition, the sample was exposed to light with a UV radiation wavelength. The radiation source was produced by MICROTHERM company.

3. Results

In order to determine the crystalline structure of deposited layer, XRD measurements were performed. The obtained diffractogram show patterns corresponding to the PET substrate and zinc oxide with the wurtzite structure (Figure 1).

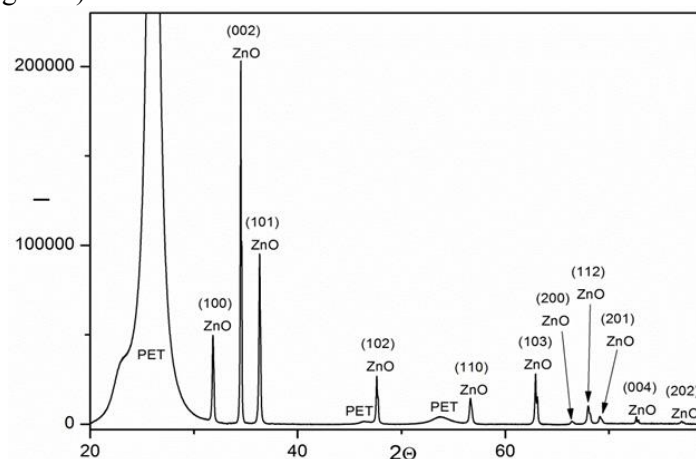


Figure 1. XRD test of the sample.

Furthermore the average size of the obtained ZnO crystallites ($L_{(002)}$) (1) was determined using the Scherrer's equation. The apparatus broadening was 0.05° . On the basis of literature data, it was assumed that the value of constant K was 0.9 [18]. By substituting relevant data to the equation, it was found that the mean size of the ZnO crystallites formed on the PET substrate was approximately 62.1 nm.

$$L_{(101)} = \frac{K \cdot \lambda}{B \cdot \cos \Theta} \quad (1)$$

where: K – Scherrer constant,

λ – length of an X-ray radiation beam [\AA],

B – integral width (FWHM) of the peak (002) [rad],

θ – glancing angle a given interference band [rad];

The SEM analysis of the pure polymer substrate as well as shape and size of ZnO structures obtained in the deposition process were carried out. The PET substrate surface analysis showed it to be smooth, although there were visible spherical structures, which might be spherulitic semicrystals in polymer or post-production impurities (Figure 2a). The SEM image of the sample after the deposition process shows apparent hexagonal rods of zinc oxide with an average width of 550 nm and a height of 2 μm (Figure 2b).

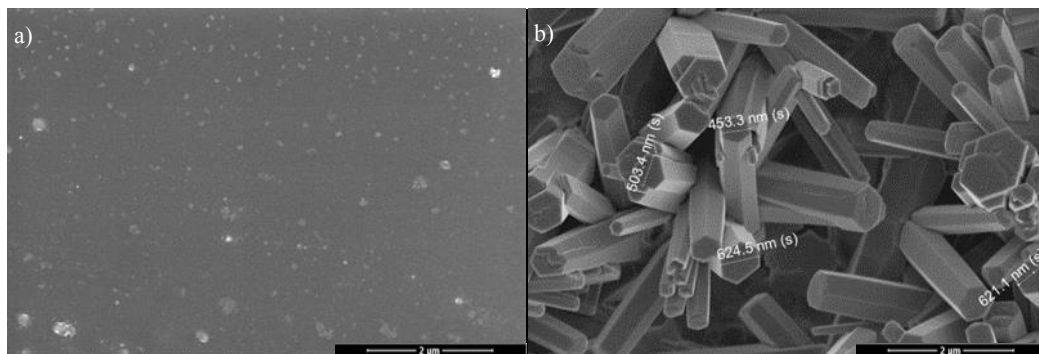


Figure 2. SEM image of (a) pure polymeric films, (b) polymeric films after deposition.

Many authors associate the antibacterial properties of ZnO with its photocatalytic properties. If the oxide is exposed to radiation with energy greater than or equal to its band gap, then the transfer of electrons from the valence band to the conduction band takes place. As a result of this process, holes (h^+) migrate to the surface of material and react with water molecules (moisture) from the environment, leading to the formation of hydroxyl radicals (OH^\bullet). These radicals present very strong oxidizing properties, thus they are capable of degrading all kinds of organic compounds, from which the microorganisms or biological impurities are composed. As a result of these reactions, various kinds of organic substances are decomposed into water and carbon dioxide [19,20].

Moreover it is known from the literature that during zinc oxide exposure to air, the oxygen adsorption occurs on its surface. In this process oxygen molecules react with electrons present in the material (2). In result chemically adsorbed oxygen ions are formed on the surface and the superficial depletion layer with lower conductivity than in the bulk of zinc oxide emerges. During exposure of the semiconductor to UV radiation, the holes present on the ZnO surface react with the adsorbed ions, causing release of the gaseous oxygen, which desorbs from the surface (2) [21].





In order to analyze behavior of the tested materials under the influence of UV radiation, the transportation kinetics of carriers generated by radiation was analysed. For this purpose, the sample was placed between two electrodes, one of which had a hole for exposing the sample (Figure 3).

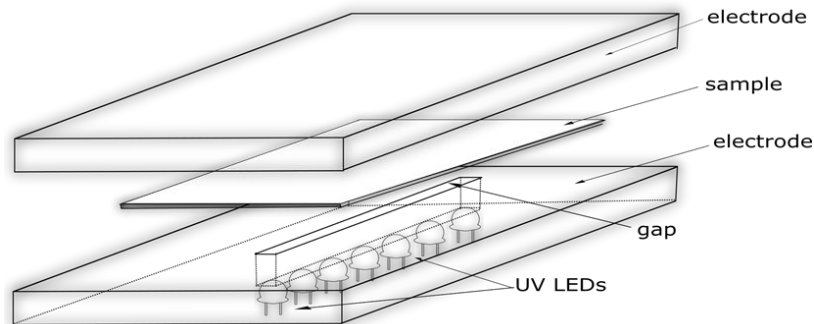


Figure 3. Diagram of the measuring system.

The electrical parameters of samples were determined by impedance spectroscopy during and after radiation. Measurement - both in the presence of UV radiation and after it was turned off - was performed every two minutes. Analysis of Nyquist plots showed that the system impedance decreases rapidly during exposure and it stabilizes after approximately 6 minutes (Figure 4). After switching off the lighting, the impedance of the sample gradually increases and approaches the baseline (Figure 5).

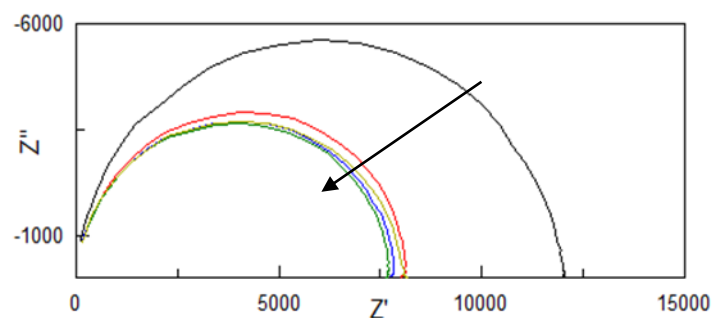


Figure 4. Nyquist plots for a sample during exposure to UV radiation.

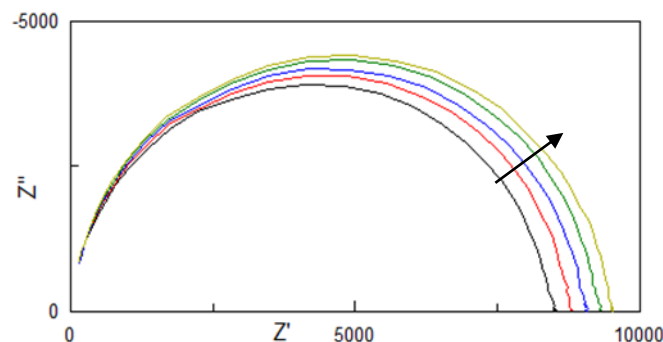


Figure 5. Nyquist plots for a sample after exposure to UV radiation.

Based on the literature data and the obtained test results, equivalent circuit model of the test object was determined. It consists of three resistors, one capacitor and two constant phase elements CPE (Figure 6) [21].

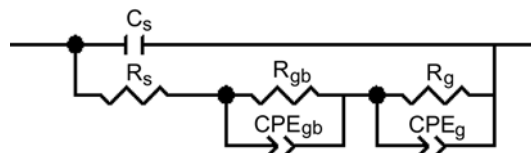


Figure 6. Equivalent circuit model of the test sample.

On the basis of the generally accepted model of zinc oxide photoconductivity, which takes into account the phenomena occurring in the bulk of material as well as on its surface, it can be concluded that C_s is substrate geometrical capacitance, R_s is contact resistance, R_{gb} and CPE_{gb} correspond to the electric parameters of the grain boundary, and R_g and CPE_g to the grain bulk.

On the basis of the Nyquist plots and using the above model, the changes in value of individual elements of the electrical equivalent circuit were determined. It was noted that the contact resistance oscillates around a constant value, which is approximately 150 Ω . In the case of surface and bulk resistance, evident changes occur under UV radiation. During radiation of the samples, both R_{gb} and R_g decrease. Decrease of bulk resistance is due to the generation of electron-hole pairs during radiation exposure. In contrast, the increase in ZnO grain boundary conductivity is due to the decrease in the width of the semiconductor depletion layer, which is formed in the surface area of ZnO in oxygen atmosphere. After switching off the radiation, as a result of the recombination of charge carriers and electric and readsorption of oxygen ions on the surface, both resistance values increase and the system returns to the state before exposure (Figs. 7, 9).

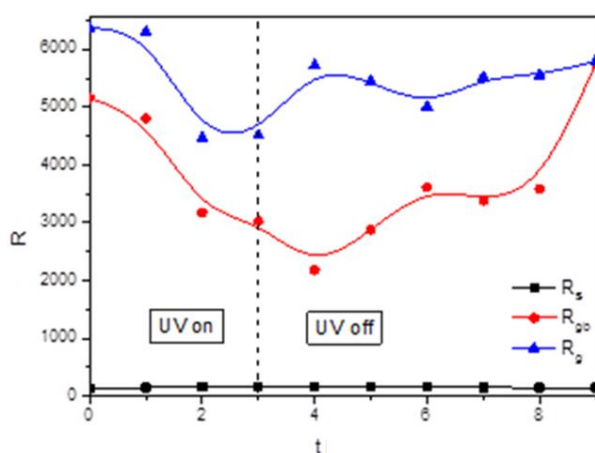


Figure 7. Changes in resistance of the system with UV and without UV.

During the radiation rapid changes in the capacitance of depletion layer along grain boundaries are also observed (Figure 8). This is due to desorption of oxygen ions from the surface of the material and decrease in thickness of the depletion layer and an increase in density of semiconductor carriers (Figure 8, 9). After turning off the UV radiation, the material gradually returns to the state before exposure and the CPE_{gb} value increases.

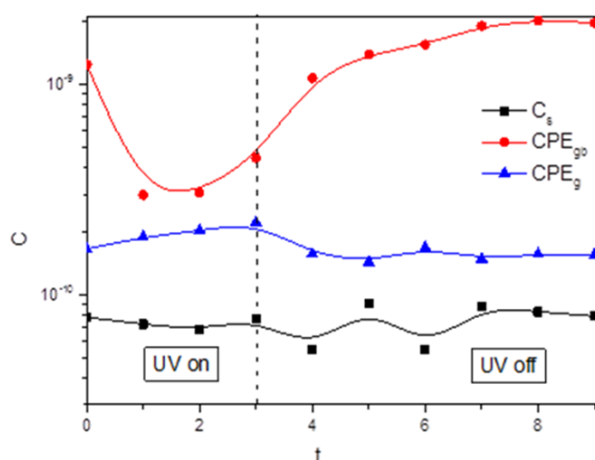


Figure 8. Changes in the system capacitance with UV and without UV.

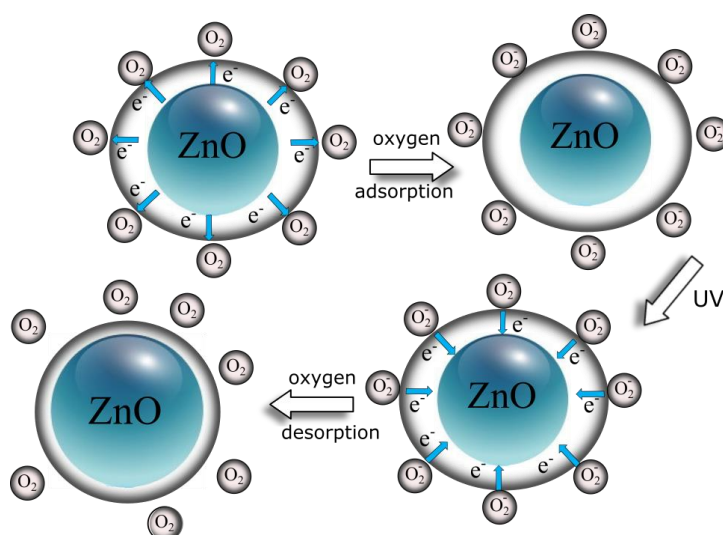


Figure 9. Changes occurring on the surface of ZnO under UV.

In conclusion, on the basis of the tests carried out using impedance spectroscopy on the rods of zinc oxide formed on the surface of the polymer film, it was found that under the influence of UV radiation, mainly resistance and capacitance of the depletion layer at the grain boundary is changed. It can therefore be assumed that the material will demonstrate high photocatalytic activity. It is further noted that separation speed of the carriers in the tested ZnO microrods is greater than their recombination rate. On this basis, authors of the publication believe that this effect can significantly contribute to increase of ZnO biological activity. Moreover, the long recombination time of the charge carriers in the system would likely result in improvement of antibacterial activity of the rods also after the radiation is stopped (up to approx. 10 minutes).

4. Conclusion

This article presents the results of research designed to analyse the phenomena occurring in microrods of zinc oxide under ultraviolet radiation.

The ZnO microrods were deposited on the polyester (PET) substrate in the hydrothermal process. The obtained structures have height of approx. 2 microns and width of 550 nm and wurtzite structure. The electrical characterization of the ZnO microrods subjected to UV irradiation, using impedance spectroscopy were carried out. A replacement model of the sample consisting of three resistors, one

capacitor and two constant phase elements was proposed. The analysis of each resistance value showed that both the value of bulk resistance R_g as well as grain boundary R_{gb} decrease during irradiation and after turning off the radiation source, they return to their baseline values. It is further noted that under UV, the capacity of the grain boundary decreases and increases after the radiation is finished.

All the observed changes are related to the interaction of the ZnO surface with oxygen present in the atmosphere which absorbs electrons while adsorbing on the surface of material and turns into the ion form. In the process, the depletion layer having a higher resistance than the bulk of material is formed on the zinc oxide surface. During ZnO exposure to UV radiation electron-hole pairs are formed and oxygen is desorbed, resulting in width reduction of the depletion layer. After turning off the radiation, oxygen readsorption occurs and the system returns to its original state.

Taking into account the test results, authors are planning further work to determine direct impact of UV radiation on the antibacterial properties of polymer films and polymer fabrics coated with zinc oxide bacteria by analysing the survivability of bacteria with and without radiation. This will allow identifying the determinants of the photocatalytic, electrical properties and biological activity of the zinc oxide microrods.

5. References

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