Dependence of the photoconductivity of nanofibers based on indium-zinc oxide on the concentration of components

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Abstract. The paper presents results of a study of indium-zinc oxide nanofibers sensitivity to ultraviolet radiation in the range 230-290 nm. Nanofibers are synthesized by electrospinning. It is shown that the largest increase in photoconductivity is observed at the indium to zinc concentration ratio of about 1:1.

1. Introduction
UV sensors are widely used for detecting radiation in many different applications from chemical industry and medical apparatus to sunlight UV meters and various scientific equipment tools. Recently, a company Rohm has developed a UV sensor using a thin film of zinc oxide [1]. Sensors based on nanowires should be in general more sensitive because of a higher free surface area. Zinc oxide is a wide gap semiconductor possessing unique electrical and optical properties; particularly, it belongs to the class of transparent conductive oxides. The low conductivity of undoped zinc oxide makes it difficult to use this material for producing transparent electrode, which leads to necessity to decrease the resistance of the functional material. Increased conductivity is achieved by introducing of donor impurities, such as group 3 elements, into zinc oxide. Embedding M$^{3+}$ cations in the ZnO structure increases the free charge carrier density [2]. Of all the group 3 elements, Ga$^{3+}$ and In$^{3+}$ have the closest values of the effective ion radius to the Zn$^{2+}$ radius, and these elements are mainly used as dopants for zinc oxide [2]. In the present paper, we report on the study of indium-zinc oxide (IZO) nanofiber photoconductivity in the UV spectral range with the aim to determine an optimum indium concentration providing a maximum photoresponse.

2. Experimental details
Fabrication of IZO fibers was performed by the electrospinning method. Formation of nanowires occurred in electrostatic field in the jet of polymer solution or molten polymer [3]. Fibers were formed from a mixture of solutions of zinc acetate dihydrate $\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O}$ and hydrated indium nitrate $\text{In(NO}_3)_3\cdot4.5\text{H}_2\text{O}$ in water and solution of high-molecular polyvinylpyrrolidone PVP ($\text{Mr} = 1.3\cdot10^6 \text{ g/mol}$) in ethanol. Solutions with various atomic content of In and Zn were prepared. The diameter of the obtained nanofibers ranged from 240 to 300 nm (Figure 1).

After the process of electrospinning, to remove polymer, annealing of the obtained fibers was carried out in a high-temperature vacuum furnace OTF-1200X in air at 600°C. After
annealing, the nanofibers’ sizes reduced down to 50-100 nm. To evaluate the PVP removal, elemental composition was investigated using a SEM equipped with an EDX system. Also, thermogravimetric analysis showed a loss of 80% weight of the fibers during annealing. Both techniques confirmed the absence of PVP in the samples after first annealing. To measure the current-voltage characteristics, nanofibers were deposited on SiO$_2$ substrate. Gold contacts with a diameter of 1 mm and with a distance between them of 1 - 1.5 mm were then deposited by thermal vacuum evaporation through a mask. I-V characteristics of the samples were measured using a Keithley 2410 source-meter. A device "Photon" served as the source of weak ultraviolet radiation in the wavelength range 230-290 nm. It was placed directly over the sample at a distance of 5 cm. In this case, the sample surface irradiance was 45 W/cm$^2$.

Figure 1. SEM images of nanofibers before annealing.

Figure 2. I-V characteristics of IZO nanofibers with different concentration of Zn without UV irradiation (UV-off) and under irradiation (UV-on).
3. Results and discussions

I-V characteristics of the samples with different atomic ratios of In and Zn, under UV irradiation and with natural light, are presented in Figure 2. It is found that the maximum conductivity increase, almost five orders of magnitude, is achieved when a ratio of In:Zn = 1:1 (i.e., ~50 at.% of In and, accordingly, 50 at.% of Zn) - see Figure 3.

The times of current rise and decline are about 100 and 500 sec., respectively (Figure 4). The slow increase and decline in the conductivity might be associated with photochemical processes of oxygen desorption and adsorption on the fibers’ surface. Oxygen molecules from the environment are easily absorbed on the surface of nanowires by capturing free electrons from the conduction band, and the molecules become negatively charged ions. When exposed to UV radiation, electron-hole pairs are generated in the IZO nanowires. Then, the photogenerated holes recombine with adsorbed oxygen ions to form oxygen molecules that desorb from the nanofiber surface [4]. Simultaneously, there is an increase in the number of electrons in the conduction band. Under the influence of the applied bias voltage, free electrons move to the anode, and the photocurrent thus appears. The larger the surface area of IZO nanofibers, the more oxygen molecules can adsorb and desorb from their surface at UV irradiation and therefore the higher is the photocurrent.

4. Conclusion

To summarize, IZO is a promising material for UV radiation sensing [2, 5]. In this work, by means of the electrospinning method, nanofibers of mixed indium (0-100%) and zinc oxide (IZO) are obtained. It is shown that the conductivity of the IZO nanofibers increases under irradiation with light in the range of $\lambda = 230$-290 nm. The maximum conductivity increase, almost five orders of magnitude, is achieved when the ratio of In:Zn is about 1:1. This effect can be used for development of efficient UV radiation sensors.
Figure 4. Photocurrent as a function of time at UV irradiation switching-on (1) and switching-off (2). Sample - IZO nanofibers with indium content of 50%.

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