Research Article

UV Sensitivity of Indium-Zinc Oxide Nanofibers

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Indium-zinc oxide (IZO) nanofiber matrices are synthesized on SiO$_2$-covered silicon substrates by the electrospinning method. The nanofibers’ dimensions, morphology, and crystalline structure are characterized by scanning electron microscopy, atomic force microscopy, and X-ray diffraction. The results of studying the electrical properties of nanofibers, as well as their sensitivity to UV radiation depending on the In-to-Zn concentration ratio, are presented. It is shown that the highest sensitivity to UV is observed at the indium content of about 50 atomic %. The photocurrent increment with respect to the dark current is more than 4 orders of magnitude. The response and recovery times are 60 and 500 sec, respectively. The results obtained suggest that IZO nanofibers can find application as UV sensors with improved characteristics.

1. Introduction

Metal oxide nanofibers have lately attracted considerable research interest due to their unique optical and electronic properties and the related applications [1, 2]. Among numerous semiconducting nanomaterials, ZnO with a wide band gap of $\sim 3.4$ eV and high electron mobility has many promising applications in optoelectronics, solar cells, and chemical and UV sensors [2]. However, a relatively low conductivity of undoped zinc oxide makes it difficult to use it as a functional material, and an increase in conductivity might be achieved by introducing donor impurities. Group III elements Al, Ga, and In as substitutional elements for Zn can be used as $n$-type dopants [3]. $M^{3+}$ cations are thus donor impurities, and their incorporation into the structure of zinc oxide in the cationic positions of zinc leads to an increase in the density of free charge carriers. The choice of the doping impurity is based on a comparison of the ionic radii of zinc and a trivalent cation. Of all the group III elements, Ga$^{3+}$ and In$^{3+}$ are most often used in practice because they possess the closest effective ionic radii to the Zn$^{2+}$ radius [4].

The UV photodetection performance of In-doped zinc oxide thin films has been studied in several papers [5–7]. For example, at a 290 nm illumination, In-Ti-Zn oxide (with $\sim 1\%$ Ti additive) sensing devices exhibit a photo-to-dark current ratio of over $10^4$ [7].

The effects of indium addition on the structural, optical, and electrical properties of the zinc oxide nanofiber matrices have been studied in the work [8]. It has been shown that indium-doped zinc oxide nanofibers undergo significant changes in their optical and electrical properties compared to undoped zinc oxide nanofibers. Because the optical properties strongly depend on the In concentration in mixed In-Zn oxide (IZO) [8, 9], one can suppose that the sensitivity of the material to UV radiation is also a function of that factor. Some preliminary results on the subject have been previously published in our work [10]. In this work, we report on the electrospinning synthesis, characterization and electrical properties of IZO nanofibers, and their sensitivity to UV radiation depending on the In-to-Zn concentration ratio.

2. Experimental Details

The samples under study were obtained by means of electrospinning [1, 2, 8, 10]. For the preparation of indium-zinc oxide nanofibers, the mixture of water solutions of hydrated indium nitrate (In(NO$_3$)$_3$·4.5H$_2$O) and zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O) was added to the solution of a
polymer in ethanol. High-molecular-weight polyvinylpyrrolidone (PVP) (Mr = 1.3·10^6 g/mol) was used as a polymer. The total mass of the salts in the solution was 0.6 g, the volume of ethanol was 8 ml, and the mass of PVP was 0.6 g. The mixture was stirred in a magnetic stirrer for two hours.

Seven solutions with different atomic contents of In and Zn were prepared, namely, with 95 (IZO2), 80 (IZO3), 60 (IZO4), 50 (IZO5), 40 (IZO6), 20 (IZO7), and 10% (IZO8) of indium; also, the pure In-containing (IZO1) and Zn-containing (IZO9) solutions were obtained. The pH of the solutions was almost independent of the In-to-Zn concentration ratio and varied from 6.4 for IZO1 to 6.9 for IZO9.

It was found that the higher the percentage of zinc in the solution was, the faster the solution became turbid and precipitated. For example, the IZO2 solution could be stored for several months, while the IZO7 solution precipitated in a few minutes after preparation.

One could prevent the precipitation by means of suppressing hydrolysis, for example, adding an acid. In our experiments, acetic acid was used to suppress hydrolysis. However, it was found that the presence of a precipitate did not interfere with the synthesis of fibers. Meanwhile, the addition of acetic acid during the synthesis somehow reduced the sensitivity of the ensuing samples to ultraviolet irradiation. Therefore, we did not use the acid-assisted hydrolysis suppression.

In the electrospinning setup, we used a syringe with a needle diameter of 0.7 mm. A liquid (prepared solutions) was fed from the syringe with an NE-300 syringe pump. A potential difference of 15–18 kV was created with an INVR-30/5 high-voltage source between the needle and the substrate. An aluminum foil was used as a collector for deposited nanofibers. The distance between the needle nozzle and the collector was 15 cm. The liquid flow rate was varied in the range 0.3 to 0.5 ml/h. Nanofibers were deposited onto Si-SiO₂ substrates with an area of 2 to 5 cm², which were located on the collector. After deposition, nanofibers were annealed in air at 600° for 5 h, with the 5°C/min heating and cooling rates, to remove the polymer binder and crystallize the IZO fibers. To evaluate the PVP removal, elemental composition was investigated using an SEM equipped with an EDX system. Also, TGA/DTA results showed a loss of 78% weight of the nanofibers during calcination. AFM results (Figure 3) show uniformity and smoothness of nanofibers, although the vertical dimension of the fiber is slightly smaller than the horizontal one (Figure 3(b)).

Figure 5 shows I-V curves of the nanofiber samples. One can see that the photocurrent is greater than the dark current (by more than 4 orders of magnitude for sample IZO5) as a function of illumination intensity distribution for ZnO nanofibers (sample IZO9) is presented. Qualitative phase analysis shows that a polycrystalline phase of hexagonal zinc oxide with the wurtzite structure is formed after annealing. The XRD pattern of In oxide nanofibers corresponds to the cubic In₂O₃ phase (Figure 4(b)), and sample IZO5 (In/Zn = 50/50) represents a mixture of the ZnO and In₂O₃ phases (Figure 4(c)). However, the In₂O₃ phase demonstrates fairly clear polycrystalline maxima, while the ZnO-phase XRD pattern in Figure 4(c) rather corresponds to an X-ray amorphous material, which might be due to a smaller average size of ZnO particles (crystallites), as compared to In₂O₃ grains, in IZO fibers.

Figure 6 demonstrates the relative sensitivity (the photocurrent I to the dark current I₀ ratio) as a function of IZO nanofiber composition, i.e., the zinc concentration. This curve shows a clearly pronounced maximum at 40–50 at.% of Zn. For these IZO nanofibers, the conductivity increases by 4 to 4.5 orders of magnitude with UV irradiation.

The characteristic time of photoresponse when the UV illumination is switched on and off is rather long. The times of current rise and fall are about 60 and 500 sec, respectively (Figure 7).

A slow rise and decline of the conductivity might be associated with the photochemical processes of oxygen...
desorption and adsorption on the fibers’ surface. Oxygen molecules from the environment are easily absorbed on the surface of nanofibers by capturing free electrons from the conduction band, and the molecules become negatively charged ions in this case. When exposed to UV radiation, electron-hole pairs are generated in the IZO nanofibers. Then, the photogenerated holes recombine with adsorbed $\text{O}_2^-$ ions to form oxygen molecules that desorb from the nanofibers’ surface [12]. Simultaneously, an increase in the number of electrons in the conduction band occurs. 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 higher the rate of adsorption (desorption) of oxygen molecules from their

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FIGURE 1: Nanofiber matrices on the Si-$\text{SiO}_2$ substrate with deposited Au contacts. Photos made with an optical microscope at magnification 4x (a) and 40x (b).
surface at UV irradiation and therefore the higher the photocurrent. When switching off the source of UV radiation, oxygen from air is adsorbed to the surface of the fibers and captures excess electrons from the conduction band and the resistance of the fibers gradually increases to the initial value.

To test the effect of oxygen on the conductivity, sample IZO3 has been placed in a vacuum chamber. Air evacuation does not lead to a significant change in the initial resistance, but under the influence of UV radiation, the final resistance of the sample in vacuum is much less than that when it is irradiated in air (Figure 8). This is accounted for by a higher rate of desorption of oxygen molecules from the surface in vacuum. When turning off the UV radiation, the resistance remains low until air is allowed to enter the chamber. Thus,

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**Figure 4:** XRD patterns of nanofibers after annealing for samples IZO9 (a), IZO1 (b), and IZO5 (c).

**Figure 5:** I-V characteristics of samples IZO1 (In$_2$O$_3$), IZO5 (InZn 1:1), and IZO9 (ZnO) when they are irradiated with UV ("on") and under natural illumination ("off").

**Figure 6:** UV sensitivity of IZO nanofibers as a function of zinc percentage.
experiments in vacuum confirm that the decrease in the resistance of the fibers is associated with the processes of desorption and adsorption of oxygen from their surface. The results obtained are consistent with the work [13], where the ZnO fibers have been synthesized by the sonochemical process. The response to UV (conductivity change) in this work is about 3 orders of magnitude, the response time is 33 seconds, and the recovery time is 244 seconds. In vacuum (2.4 × 10^{-3} Torr, i.e., 0.4 Pa), the recovery time increases to several tens of minutes [13].

Numerous studies of ZnO show an enhancement in UV sensing due to doping of the material with different elements, including indium [5, 6], vanadium [14], magnesium [15], aluminum [12, 16, 17], gallium [17], tin [18], manganese [19], nickel [20], and others. Different mechanisms have been proposed to account for these effects. In particular, the enhancement in UV sensitivity in vanadium-substituted ZnO is attributed to trapping and detrapping of electrons at V^{4+} - and V^{5+}-related defect states [14]. The enhanced response of Mg-doped ZnO nanoparticles is associated with unpaired electrons added to the photocurrent [15]. In the work [17], the high responsivity of Al- and Ga-doped ZnO-based photodetectors is attributed to their high photoconductivity, while Chongsri and Pecharapa [16] supposed that in Al-doped ZnO, a photocurrent increase is due to the excess of Al-produced defects which affect the electron mobility. In the work [18], the maximum photoresponse has been observed in 7 wt.% Sn-doped ZnO. It has been suggested that unsaturated bonds across the (101) ZnO crystallographic plane in such doped samples can act as better sites for adsorption of O_2 molecules displayed in higher UV photoresponse [18]. The question of which of these mechanisms are involved in the enhancement of the UV sensitivity in our case (Figure 6) seems to require an additional investigation. Also, the effects of phase separation for samples with high indium content should be taken into account, since segregation of indium is likely occurring in samples IZO4 and IZO5, perhaps as indium oxide in the grain boundaries [8], and the material of nano/fibers might thus be a mixture of phases including both In_2O_3 and heavily In-doped ZnO. This inference is supported by the XRD data in Figure 4(c).

4. Conclusion

Zn-In oxide nanofibers with different concentrations of In oxide (in a wide range from zero to 100%) have been synthesized by the electrospinning technique. The samples with the indium-to-zinc concentration ratio of about 1:1 show an enhanced UV sensitivity. In such IZO samples, the ratio of the photocurrent to the dark current reaches 4.5 orders of magnitude as against 0.5–1.5 orders of magnitude for ZnO and In_2O_3 samples. This value is of the order of or higher than the corresponding parameters reported in the literature for both ZnO nanofibers [2, 13] and doped ZnO thin films [5–7, 14–20].
The response and recovery have been measured to be about 60 and 500 sec, respectively. These relatively slow conductivity growth and decay are associated with the photochemical processes of oxygen desorption and adsorption on the fibers’ surface responsible for the IZO photoconductivity mechanism. An increased effective surface area of nanofibers as compared to that of thin films and bulk samples ensures their improved UV-sensing characteristics.

Electrospinning is a simple and low-cost method for producing mixed metal oxide nanofiber matrices, and IZO nanofibers, as the results presented show, can find application as UV sensors with improved characteristics.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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References