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Spectroscopy and kinetics of indium-zinc oxide nanowires UV sensitivity

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The results of studying the spectroscopy and kinetics of the sensitivity in air and vacuum of indium zinc oxide nanofibers to ultraviolet radiation at various ratios of In and Zn concentrations are presented. It has been shown that the greatest sensitivity is observed at an indium content of about 50 at.%. The increment of the photocurrent relative to the dark current during measurements in air is more than 4 orders of magnitude. In a vacuum, photosensitivity doubles. The mechanisms of photoconductivity of indium−zinc oxide nanofibers are considered.

Keywords: indium zinc oxide, nanowires, photosensitivity, photocurrent spectroscopy, photocurrent kinetics.

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Synthesis and study of nanostructured metal oxides — one of the important directions of modern nanoelectronics and nanophase materials science. In particular, one of the promising oxide nanomaterials are quasi-one-dimensional structures (nanorods, nanofilaments) based on indium zinc oxide− (IZO).

The initial components for the synthesis of IZO nanofilaments are zinc oxides (ZnO) and indium oxides (In_2O_3). They are direct- bandgap semiconductors belonging to the class of transparent conducting oxides. The bandgap width of zinc oxide is $E_g = 3.36$ eV; the monocrystalline indium oxide has a fundamental $E_g = 2.89$ eV and an optical one $E_g = 3.7$ eV [1]. In [2–4], it has been shown that IZO nanofilaments are a promising material for the development of UV sensors due to their high sensitivity to ultraviolet (UV).

This study aimed to capture the spectral dependence of the UV sensitivity of IZO nanofilaments with composition variation, in air and in vacuum, and to investigate the kinetics of the photocurrent when the UV source is switched on and off at the wavelength corresponding to the photosensitivity maximum. Strictly speaking, photosensitivity should be considered as the ratio of

$$S = (I_\mathrm{p} - I_0)/I_0,$$

where I_p — photocurrent, I_0 — dark current. But for our samples $I_0 \ll I_\mathrm{p}$ so we take $S = I_\mathrm{p}/I_0$ as the photosensitivity value.

The synthesis of IZO nanofilaments was carried out by electrospinning [2,3] method. The nanofilaments were deposited on a citalloy substrate, and after annealing, their diameter was 40−80 nm. Gold contacts with a diameter of 1 mm at a distance of ~ 1.5 mm from each other were sputtered onto the samples through a mask. Spectral dependences of the photocurrent were measured on samples with indium to zinc concentration ratio 50/50 at.%, showing the highest sensitivity to UV [2,3], 95/5 at.%, as well as on unalloyed In_2O_3 and ZnO samples.

A superhigh-pressure xenon lamp DKSSH 150-2 and a light-field monochromator MDR-23 with interchangeable diffraction gratings were used in the setup for spectral dependence of the photocurrent. Measurements in the 280−780 nm range were carried out on a diffraction lattice 1200 strokes/mm. A constant voltage of 5 V was applied to the samples during the experiments. The kinetics of current rise and fall when the light source was switched on and off was recorded using a precision calibrator — Keythley 2410 multimeter. The irradiation time for each sample was 20 min.

For measurements in vacuum, the samples were placed in a chamber with electrical taps, and continuous evacuation was performed using an oil-free SD-5D scroll forevacuum pump (the pumping speed 1.33 l/s, ultimate residual pressure 5 Pa). The sample was irradiated through a quartz window installed in the end of one of the vacuum connectors of the chamber.

Fig. 1 shows the averaged spectral dependences of different samples.

The spectra of pure samples agree well with the available literature data for nanocrystalline oxides of indium [5] and zinc [6]. The shift of the maximum spectrum of In_2O_3 nanofilaments to the short-wavelength region (higher photon energies) compared to ZnO (~ 3.6 eV in ZnO and ~ 3.8 eV in In_2O_3) is remarkable, which is explained by the larger optical bandgap width of indium (III) [1].

A small doping with zinc (5 at.%) of indium oxide nanofilaments (Fig. 1, *b*, curve *2*) leads to an increase in the photosensitivity at the maximum of the spectral dependence (~ 327 nm or 3.8 eV) by about 6−7 times. The

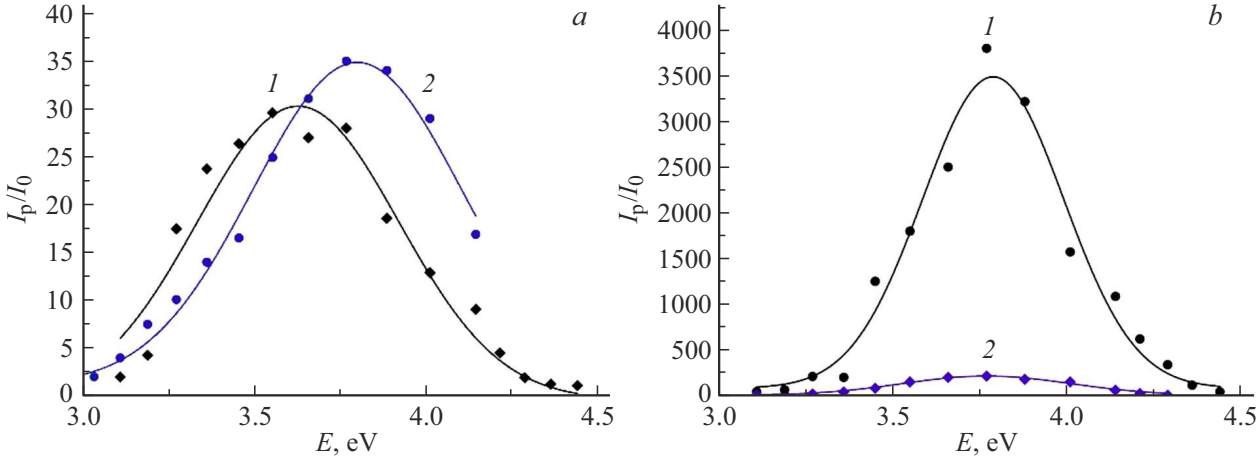

Figure 1. Spectral dependences of photosensitivity for (*a*) pure zinc oxide (*1*) and indium oxide (*2*) (*b*) nanofilaments with indium/zinc concentration ratios of 50/50% (*1*) and 95/5% (*2*). I_p — irradiation current, I_0 — dark current.

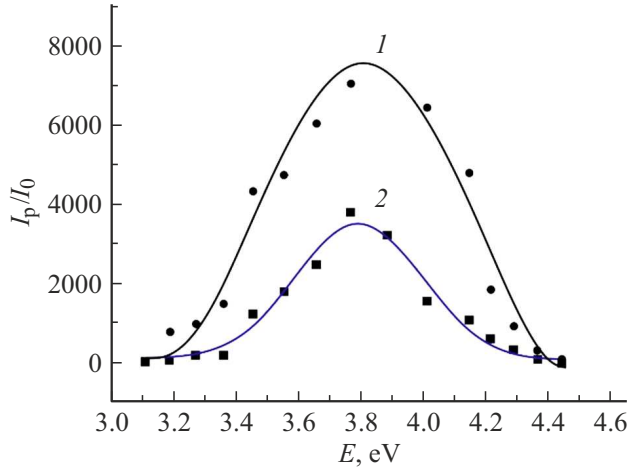

Figure 2. Spectral dependences of photocurrent in a 50/50 at.% sample placed in air (*2*) and in vacuum (*1*) ($p = 5$ Pa).

greatest increase in photosensitivity is observed in filaments with equal concentrations of indium and zinc (Fig. 1, *b*, curve *1*) — by about 2 order of magnitude compared to pure samples. At the same time, the position of the curve maximum in doped samples is approximately the same as in pure indium oxide (~ 3.8 eV).

If the sample is placed 50/50 at.% in a vacuum chamber, its photosensitivity in the maximum increases by a factor of two further compared to that measured in air (Fig. 2).

Simultaneously with the spectral characteristics, the time dependences of the rise and fall of the photocurrent at the wavelength 327 nm, corresponding to the maximum of the photosensitivity spectrum in air and in vacuum, were studied (Fig. 3). The UV source power was measured with a TKA-PKM 12 radiometer and was ~ 0.1 mW/cm^2.

Parameters of the photosensitivity rise and fall equations

Parameters		Pure oxides, air		Indium-zinc oxide, IZO 50/50 at.%	
		In_2O_3	ZnO	air	in vacuum
Current rise:	S_0	33	37	3900	10800
	S_1	29	34	3700	8000
	α_1, min^{-1}	0.24	0.21	0.11	0.05
Current fall: α_2, min^{-1}		0.23	0.20	0.11	0.05

The photosensitivity rise and fall curves are described, respectively, by the equations

$$S(t) = \begin{cases} S_0(1 - \exp(-\alpha_1 t)), & \text{current rist,} \\ S_1 \exp[(-\alpha_2 t)^\beta], & \text{current fall,} \end{cases}$$

where S_0 — photosensitivity at current saturation, S_1 — photosensitivity at the moment of switching off the UV source, α_1 and α_2 — inverse lifetimes of nonequilibrium carriers excited by UV. Note that α_1 and α_2 should ideally be equal, but may differ slightly due to local heating of filaments under UV or other factors. The parameters of the equations are summarised in the table. The value of the parameter β is almost the same for all samples and is of the order of 0.5.

The UV photocurrent kinetics of the UV sensor based on indium-zinc oxide nanofilaments was analysed in more detail in [7], but at wavelengths 230–290 nm and at higher intensities (1 mW/cm^2). The data shown in Fig. 3, *b* confirm that the transition to the equilibrium state after switching off the illumination is slower the lower the partial pressure of oxygen on the surface of the filaments [7].

In our case, the key role in the mechanism of nanofilament UV response is attributed to the adsorption-desorption

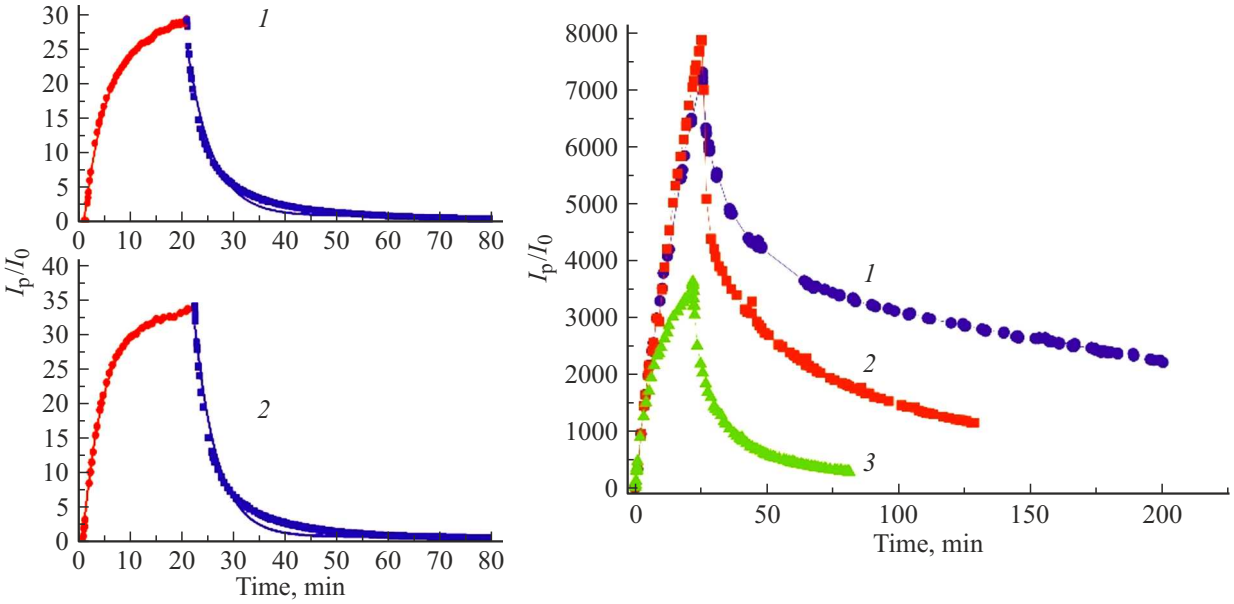

Figure 3. Current rise and fall kinetics: (*a*) for Zn O (*2*) and In_2O_3 (*1*) samples in air, (*b*) for IZO 50/50% sample: *1* — sample placed in vacuum chamber, irradiation and current drop at $p = 5$ Pa, *2* — irradiation in vacuum, recovery occurs in air, *3* — irradiation/recovery occur in air. The irradiation time is 20 min

of oxygen on the surface of the filaments, which was mentioned in [6–9]. Under UV exposure, electron-hole pairs are generated in the nanofilaments, holes restore the neutral state of oxygen ions, the latter associate into molecules and desorb into the surrounding atmosphere. As a result, additional free electrons remain in the nanofilaments, which participate in the UV-photocurrent [7–9].

In the air, desorption of oxygen from the depth is likely to be virtually nonexistent, since no concentration gradient occurs due to adsorption of oxygen from the air. In a vacuum there is no adsorption of oxygen to the surface, so after photogeneration of free carriers and desorption of oxygen from the surface there is a rather slow diffusion of oxygen from the depth and its desorption from the surface, so for 20 min illumination of the sample there is no saturation of the photocurrent.

The photocurrent has a saturation state corresponding to the ionisation of all impurity centres and the departure into the environment of all the excess oxygen accumulated (absorbed) on the surface and in the depth of the filaments in the equilibrium state (before UV exposure). Its rise time depends primarily on the mobility of ionised vacancies at which they diffuse to the filament surface [5,7].

When unalloyed filaments and filaments with small impurity concentrations are irradiated in air, an equilibrium between adsorption and desorption for 15–25 min is apparently established, depending on the oxygen concentration and defects in the depth of the filaments. For a 50/50% sample both in air and even more so in vacuum, saturation of the photocurrent in 20 min does not occur. In such filaments there are more defects or more oxygen ions on intergrain boundaries, for 20 min the formed oxygen molecules do not have time to reach the surface at low radiation power.

The high rise and fall times of photocurrent (Fig. 3) indicate, rather, the leading role in the time response characteristics of mass transfer mechanisms (diffusion, absorption) than optoelectronic effects such as ionisation and recombination processes. But under UV-exposure not only free carriers are created „zone–zone“, but also impurity centres are ionised inside the bandgap of IZO. In IZO-nanofilaments with a phase composition of 50/50% of such potential for UV response impurity centres are an order of magnitude more than in pure oxides, so the UV sensitivity is much higher. The nanofilament UV-sensitivity analysed in this study generally confirms the above hypothesis.

The photocurrent decay time, which is also the equilibrium state recovery time, depends very strongly on the oxygen concentration in the surrounding atmosphere. Therefore, its value for nanofilaments in vacuum can be many hours (Fig. 3, *b*).

It was found that the maximum photosensitivity in doped nanofilament samples was observed at UV wavelength ~ 327 nm (or 3.8 eV). In unalloyed ZnO ~ 345 nm (or 3.6 eV), In_2O_3 ~ 327 nm (or 3.8 eV). The photosensitivity is highest in nanofilaments with the ratio of zinc and indium oxides 50/50%, which can be explained by the highest concentration of impurity centres and the presence of a larger number of intergranular boundaries. The significant increase in sensitivity in vacuum is most likely due to the absence of oxygen adsorption on the surface of nanofilaments, and the long rise and attenuation times

of photocurrent — with slow diffusion of oxygen from the depth of nanofilaments with its subsequent desorption.

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Conflict of interest

The authors declare that they have no conflict of interest.

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