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PHOTOELECTRIC PROPERTIES OF SCREEN-PRINTED Al-DOPED ZnO FILMS

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The potential of cheap semiconductor materials in the area of solar energy use is illustrated by the example of zinc oxide (pure and Al-doped in various concentrations). Under investigation was the electric conductivity and photoelectric properties of ZnO thin films. The samples were prepared using screen-printing technique. The results of measurements point to non-linear relationships between Al concentration, photosensitivity and electrical conductivity of thin ZnO films. Optimal Al concentration for practical use of ZnO in photovoltaic devices is found to be ~ 1%. The experimental methods, technologies and results described in the paper could be used for further investigations in this area.

Key words: *Al-doped ZnO films, screen printing technique*.

1. INTRODUCTION

The current world energy crisis is forcing the scientific community to search for cheaper and more efficient ways of energy production. One of them is the use of monocrystalline solar cells (COP ~23% [1]); however, their manufacturing cost is very high, and is not repaid by the electricity produced during their operation. For this reason, alternative semiconductor structures such as zinc oxide are investigated worldwide. As compared with other semiconductor materials, ZnO has much higher excitation energy of excitons; it is more resistant to radiation and is a multifunctional material, with piezoelectric, ferroelectric and ferromagnetic properties [2]. Zinc oxide is a semiconductor with a wide bandgap (E = 3.37 eV), and can be used in semiconductor lasers and UV-LED technologies [3]. This material is applied in solar cells, piezoelectric transducers as well as in the form of catalytic particles and sensors [4] for determination of the molecular composition of gases. Zinc oxide is also ecologically clean and biocompatible material, which is important in medical applications [5]. The main problem in the use of impurity-free ZnO is that this material has an immense specific resistance. This peculiarity complicates the practical application of pure zinc oxide. For electrical resistance reduction purpose, the doping of ZnO is applied using different chemical combinations [6]. For studying a semiconductor material of the kind the screen-printing technique has been proved to be very convenient. This technique is cheap and technologically simple.

2. EXPERIMENTAL

2.1. Preparation of the substrate

The substrates (25×35 mm in size) were made from ordinary glass. After ultrasonic surface cleaning, they were placed in a high-vacuum camera "УСУ-4" for sputtering a thin conducting nickel electrode. The sputtering was performed using a specially made mask shaped as a system of parallel electrodes (total nine on each substrate), with a width of 0.5 mm and a height of 25 mm. The minimum distance between two electrodes was 0.5 mm, the maximum – 4 mm. Such location of electrodes allows different areas of thin ZnO film to be checked for homogeneity.

2.2. Preparation of the mixture

Micro-fine powder of zinc oxide was mechanically mixed with aluminium chloride to obtain Al_2O_3 doped ZnO powders of different weight percentage (1, 3, 5 and 7 wt.%) [1]. The prepared powder was calcined at 900 ^oC for 5 h in air and ball-milled to ensure a sufficiently fine particle size. Such a long calcination time is necessary to get rid of chlorine.

2.3. Preparation of the samples

The doped ZnO was mixed with 2-phenoxyethanol ($C_8H_{10}O_2$) in proportion 70:30 to provide a binder of the desired viscosity. The binder was deposited on the glass substrates with electrodes using the screen-printing technique. The prepared samples were annealed at 180 ^oC for 1 h in air to evaporate 2-phenoxyethanol from the samples.

3. RESULTS AND DISCUSSION

3.1. Structure and chemical composition of the thin films.

The microstructure and chemical composition of the film surface were analyzed using a scanning electron microscope (SEM, Tescan Vega LMU) coupled with an energy dispersive spectrometer (INCA X-Ray Microanalysis). The X-ray powder diffraction analysis was performed using an X-ray diffractometer (Rigaku Smartlab).

Figure 1 shows the SEM image of Al-doped ZnO film. It is seen that the film contains voids and grains. Their sizes are found to range from 100 to 400 nm.

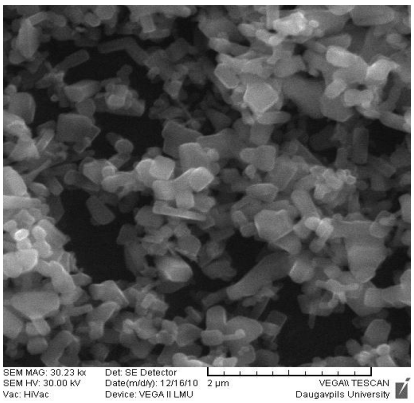

Fig. 1. The screen-printed Al (1 wt.%) doped ZnO surface.

The quantitative elemental compositions of the pure and doped ZnO films were analyzed using an energy dispersive spectrometer. The mass % of Al in each sample was not in the stoichiometric proportion. Table 1 shows the Al concentration in the samples.

Table 1

The Al concentration in the samples

Number of sample	1	2	3	4
Measured Al concentration, %	0.15	0.45	0.89	1.18

The crystalline structure and chemical composition of the films were analyzed by means of an X-ray diffractometer (Rigaku Smartlab) using CuKά - 1.544 Å emission. Figure 2 depicts an XRD pattern of non-modified (pure) and Al-doped ZnO films. The peaks seen in Fig. 1*a* are matching well with the PDXL database reported data on ZnO [7]. The peaks of XRD pattern in Fig. 1*b* correspond to the ZnO, $ZnAl_2O_4$ materials, which are considered to be microcrystalline in nature. The peaks of ZnO and $ZnAl_2O_4$ are designated by X and Y.

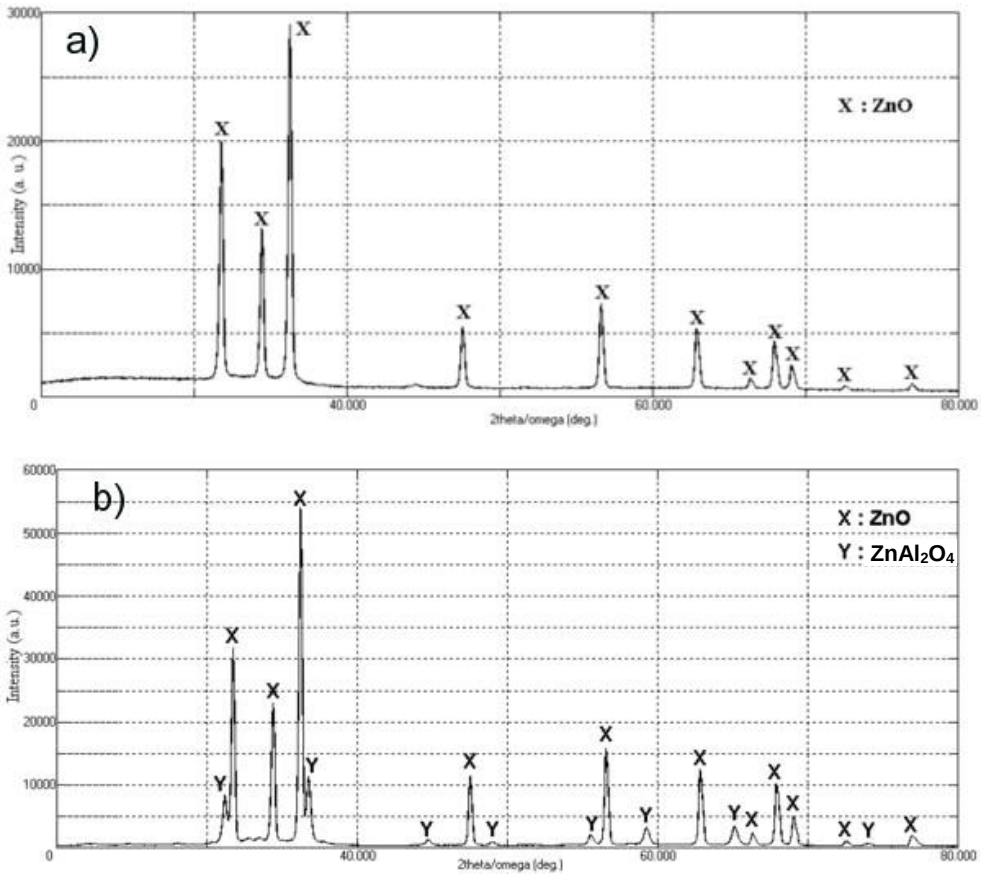

Fig. 2. XRD of (*a*) non-modified ZnO and (*b*) Al-doped (0.89 wt.%) ZnO.

3.2. Photoelectric properties of thin films.

Photoelectric parameters of pure and Al-doped ZnO films were measured by the device consisting of a 405nm laser source, a laser power meter (*Ophir Nova II*), a multimeter (*Picotest M3500A*), a laptop and the optical system. Measurements of electric resistance were performed at a constant laser beam power. For preparation of samples the areas 3mm ×3mm in size were deposited at the 0.2 W/cm^2 laser beam intensity. The corresponding group of nickel electrodes on the glass substrate were connected to the multimeter in the resistance measurement mode. The duration of data reading was 0.5 s. The full measurement cycle for each sample took 210 s. Figure 3 shows the electric resistance variations for the pure and Al-doped (0.15 wt.%) ZnO samples. In the figure, domain 1−2 corresponds to the start-end of measurements, domain 2−3 − to the saturation of electric resistance under laser deposition, and domain 3−4 − to its relaxation after deposition. In the case of pure ZnO the initial electric resistance steeply decreases from R_{init} = 1.1×10^8 Ohm to R_{min} = 0.45×10^6 Ohm within 1 s. After the end of deposition, the electric resistance restores to its initial level in 1 s. As seen in the figure, much lower initial electric resistance R_{init} = 5×10^7 Ohm and longer relaxation time are observed for the 0.15% Al doped ZnO in comparison with the pure ZnO sample.

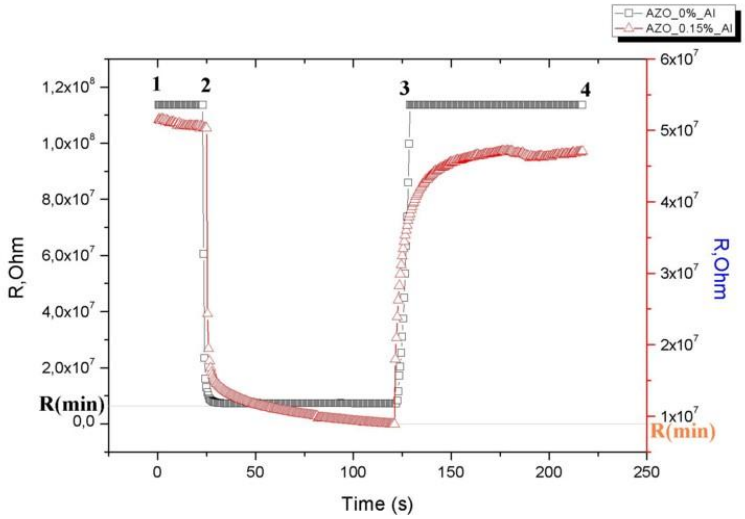

Fig. 3. Variations in the electric resistance of pure and 0.15% Al-doped ZnO samples in a full cycle of deposition-relaxation.

Significant increase in the relaxation time of electric resistance is observed for 0.89% Al doped ZnO sample (see Fig. 4, domain 3−4).

Figure 5 shows the comparative relaxation time of electric resistance for pure and Al-doped ZnO films. The curves describe a relative variation in the electric resistance, R_1/R_o and R_2/R_o (R_o being the resistance of samples before deposition, R_1 and R_2 – after 150 and 200 s relaxation). Laser deposition was stopped at the 120th second of the experiment.

In Fig. 5 it is seen that at Al % < 1 the relaxation time of electric resistance is much greater than the time of its saturation under 405 nm laser deposition; *vice versa*, if Al concentration exceeds 1% the time of saturation is much longer than

that of relaxation. With increasing Al concentration the dark (initial) resistance of samples decreases proportionally. At Al % > 1.5% a very low dark resistance is observed but the samples are practically insensitive to the 405nm laser radiation. It could be suggested that the Al atoms cause an increase in the total concentration of free charge carriers and in the lifetime of photoinduced charge carriers in ZnO.

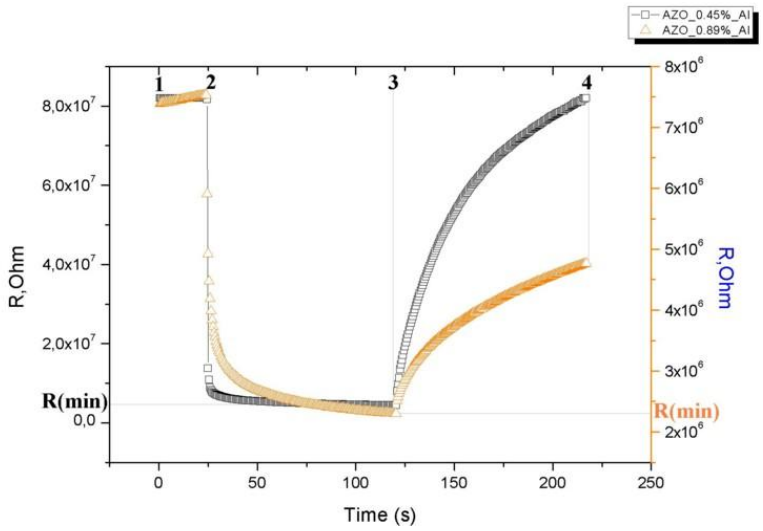

Fig. 4. Variations in the electric resistance of 0.45% and 0.89% Al-doped ZnO samples in a full cycle of deposition-relaxation.

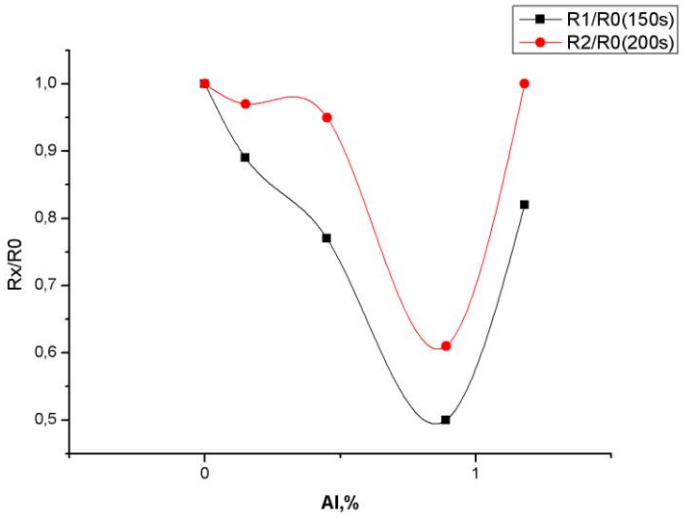

Fig.5. Relative variation in the electric resistance of ZnO thin-film samples *vs.*Al dopant concentration.

4. CONCLUSIONS

The study of Al-doped screen-printed ZnO thin films has made it possible to determine their photosensitivity and to reveal the total conductivity of the samples is increasing with Al concentration. The experiments have shown that the best ratio between the conductivity and the photosensitivity is achieved with 1% Al concen-

tration. This result could be considered of the key significance for raising the efficiency of ZnO-based photosensitive semiconductor devices.

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7. PDXL Software. Version 1.8.1.0 Copyright 2007-2011 Rigaku Corporation.

AR SIETSPIEDES DRUKAS IEGŪTO Al ZnO KĀRTIŅU FOTOELEKTRISKĀS ĪPAŠĪBAS

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K o p s a v i l k u m s

Galvenais uzsvars ir likts uz cinka oksīda elektriskās vadāmības un gaismjutības regulēšanu leģēšanas ceļā, kā arī plānu kārtiņu iegūšanas vienkāršošanu, izmantojot sietspiedes drukas tehnoloģiju. Autoru aprakstītās eksperimentālās metodes un tehnoloģijas sniedz plašu darbības lauku tālākiem pētījumiem šajā jomā.

14.03. 2012.