

# Photoelectric and spectral properties of ZnO thin films

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An optimization of transparent conductive coatings to increase efficiency is very important for solar cell applications. The developed technique has allowed to obtain both transparent high conductive and dielectric ZnO films doped by different impurities. Measurements of dark and photoconductivity were carried out in a wide frequency range. Photoelectric property studies have shown that with Li doping it is possible to achieve a significant increase of the photoconductivity. The current-voltage characteristics, current-optical power sensitivity and kinetics of rise and decay times of slow and fast components of the photoresponse were studied. It was found that the dark current and photocurrent in Li doped ZnO films have different conductivity mechanisms: hopping mechanism or charge transfer in a Hubbard-model impurity band for dark conductivity current, and drift mechanism of charge transfer in the conduction band for photoconductivity current.

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## 1. Introduction

ZnO films are *n*-type semiconductors and useful wide-band gap materials for optoelectronic applications, e.g., gas sensors, UV detectors, light emission devices, and transparent electrodes used for solar cells [1-6]. It is also known that ZnO doping by different elements is possible, allowing to obtain films with new interesting electrical properties. For example, doping ZnO with Al, Ga or F increases film conductivity without impairing the optical transmission, whereas doping by Li ions increases its resistivity. With suitable codoping [7], resulting in p-type ZnO is possible to form p-n junctions [8]. ZnO films can be prepared by variety deposition methods such as sputtering, spray pyrolysis, chemical vapour deposition and others.

There are two mechanisms of charge transport [9] in semiconductors: charge transport in the conduction band due to the drift of carriers, and charge transport by carriers excited to the localized states near to Fermi level in an impurity conduction band. Both types of charge transport can give a contribution to the conductivity (dc and ac).

In this work the results of investigations of the electrical and photoelectric properties of pure and lithium doped ZnO films are reported, including the research of the conductivity processes for direct and alternating currents. Based on the obtained results, the mechanisms of charge transport responsible for dark and photoconductivity are suggested.

## 2. Experimental procedures

Pure and lithium doped ZnO films for optical and electric measurements were obtained by electron beam vacuum deposition [10] and sol-gel methods; (0002) sapphire plates were used as substrates. The photoconductivity of films was measured with the help of Al electrodes, which were deposited by vacuum deposition

on the ZnO surface in a planar configuration using parallel strips with dimensions of 7×20 mm<sup>2</sup> and distance 3 mm. Thus a planar structure Al-ZnO:Li-Al was prepared. To study the photoconductivity we used UV radiation in a spectral range of 360-400 nm. Different illumination geometries were used to measure the photocurrents and photoinjection currents, including front-side illumination of the region between Al electrodes and backside illumination through the sapphire substrate. The light intensity was varied in the range 0÷2 mW/cm<sup>2</sup> using a disk optical attenuator. The direct current photoconductivity measurements were carried out at the fixed bias voltage  $U_{DC}$  (from -160V to 160V). The alternating-current (ac) measurements of photoconductivity in the range 10<sup>2</sup>÷10<sup>3</sup> Hz were carried out with a bridge circuit, and in the higher frequency-range (50·10<sup>3</sup>÷3·10<sup>8</sup> Hz) with a Q-meter (E4-7, E4-11). The equivalent circuit consisting of parallel-connected capacitors and series-connected resistors was used to calculate the real and imaginary part of dark conductivity and photoconductivity.

The electric signal was recorded by a data acquisition system ("National Instruments"). Specific software was developed, i.e. virtual instruments for measurements of photoresponse kinetics, current-optical power (I-W) and current-voltage (I-V) characteristics.

## 3. Results and discussion

Some results of photo and dark conductivity investigations in pure and lithium doped ZnO films are given in [10, 11, 12]. The typical spectral dependence of the photoconductivity has a peak at 3.33 eV for all lithium-doped (0.5, 0.6, 0.8, 1, 5 and 10 at.%) ZnO films. Only in the film doped with 0.8 at.% of Li the photoinjection current was observed (maximum at ~3.23eV). This film had highest resistivity, ~10<sup>6</sup> Ωcm and has also showed the largest photoresponse. Therefore, in

this work special attention is given to investigation of the ZnO film with 0.8 at.% lithium doping.

Treating the metal-semiconductor (Al-ZnO:Li) as a Schottky barrier, in which the thermionic emission component of current prevails above the tunnel component, it is possible to estimate barrier height  $\Phi_d$  from expression for an ohmic contact with resistivity  $R_C$  [13]:

$$R_C = (k/qA^{**}) \exp(\Phi_d/KT), \quad (1)$$

where  $T$  is the absolute temperature;  $A^{**}$  - the effective Richardson coefficient;  $k$  - the Boltzmann constant and  $q$  - the electron charge. The Richardson coefficient can be obtained from the equation:

$$A^{**} = 4\pi q m^* k^2 / h^3, \quad (2)$$

where  $m^* \sim 0.27m$  [14] is effective mass of charge carrier (we assume that  $m^*$  does not depend on lithium concentration).

For ZnO films  $A^{**}$  is estimated to be about  $35 \text{ A/cm}^2\text{K}^2$ . The measured value of the resistivity of the ohmic contact Al-ZnO:Li is  $R_C = 0.09 \Omega$ . The Schottky barrier height  $\Phi_d$  was determined to equal to 0.42 eV for the dark current.

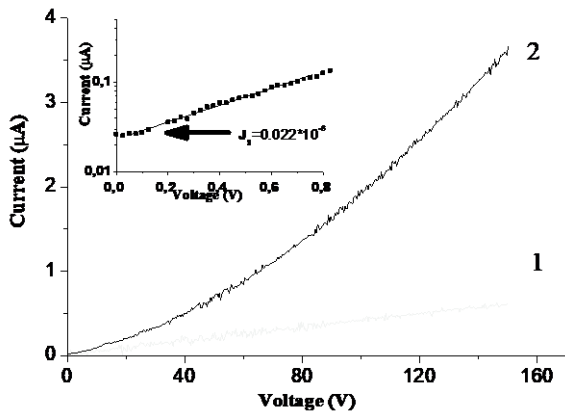


Fig. 1. Current-voltage characteristic for dark conductivity (1) and photoconductivity (2). The inset I-V characteristic shows the determination of  $J_s$  saturation current value.

Fig. 1 shows the current-voltage characteristic in the planar Al-ZnO:Li-Al (Li-0.8 at.%) structure for the dark conductivity (curve 1) and the photoconductivity (curve 2). In both cases I-V characteristics are symmetrical for positive and negative voltages, therefore only positive branches are shown. The dark I-V characteristic has linear behaviour, i.e. there is an ohmic contact with a small barrier height. The photo I-V characteristic shown in Fig. 1 was obtained with UV illumination having an intensity of  $200 \mu\text{W/cm}^2$ . This characteristic has exponential behaviour, i.e., there is the Schottky barrier with significant height  $\Phi_{ph}$ . It is possible to calculate the Schottky barrier height  $\Phi_{ph}$  from the expression:

$$J_s = A^{**} T^2 \exp(-\Phi_{ph}/kT). \quad (3)$$

The saturation current  $J_s$  is determined from an I-V plot on semi-logarithmic scale (inset of Fig. 1). The intersection of a straight-line fit line with the I axis gives a saturation current  $J_s = 0.022 \cdot 10^{-6} \text{ A}$  ( $5 \cdot 10^{-12} \text{ A/cm}^2$ ). So the Schottky barrier height is equal to  $\Phi_{ph} = 0.98 \text{ eV}$ .

The different values of the Schottky barrier heights for dark current ( $\Phi_d = 0.42 \text{ eV}$ ) and photocurrent ( $\Phi_{ph} = 0.98 \text{ eV}$ ) can be explained if we assume the existence of different mechanisms for charge carrier transport. In the case of photocurrent the charge transport is carried out in conduction band by a drift mechanism, and in the case of dark current the charge transport is carried out in the Hubbard-model impurity band located in a forbidden band by a hopping mechanism.

Experiments have also shown that the magnitude of photocurrent is a linear function of UV radiation intensity for the range  $0 \div 200 \mu\text{W/cm}^2$ . The photoresponse  $M(\text{A/W})$  calculated by the formula  $M = (I_{ph} - I_{dark})/P$ , where  $P$  is the power of UV radiation, is equal to  $0.02 \text{ A/W}$ .

Fig. 2 illustrates the spectral dependencies of the photocurrent and the photoinjection current for planar Al-ZnO:Li-Al (Li-0.8 at.%) structure. The spectral dependence of the photoconductivity has allowed us to define an activation energy for the photoconductivity ( $\sim 3.15 \text{ eV}$ ), and the spectral dependence of the photoinjection current has allowed to estimate the energy of the Fermi level. The difference between these values determines the Schottky barrier height. It is necessary to remark here that ZnO:Li film has energy band gap  $\sim 3.33 \text{ eV}$  [11]. So when the photon energy exceeds the band gap energy, i.e.  $h\nu > E_g$ , generation of electron-hole pairs to the valence and conduction bands takes place. A photoinjection current occurs if the photon energy exceeds the Schottky barrier value, i.e.  $h\nu > \Phi_{ph}$ , then electrons in the metal electrode with energy sufficient for overcoming the Schottky barrier are excited and injected into the conduction band of the semiconductor [15]. In the theory developed by Fowler [13] the dependence of a quantum yield  $R$  from the photon energy  $h\nu$  for photoelectrons is given by the formula  $R \sim (h\nu - \Phi_{ph})^2$ . To obtain an activation energy of the photoconductivity ( $3.15 \text{ eV}$ ) and the energy of the Fermi level ( $0.12 \text{ eV}$ ), the dependencies (square root) of the photocurrent and photoinjection current versus the photon energy are plotted and then the long-wavelength edges of these dependencies are fitted by straight lines to intersect the energy axis (Fig. 2) for a determination of the activation energies.

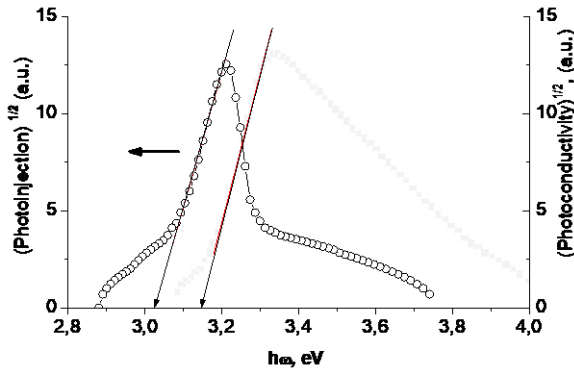


Fig. 2. Spectral dependencies of photocurrent and photoinjection current in Al-ZnO:Li-Al structure.

Fig. 3 shows the time-dependence of the  $Q$ -factor variation in the planar Al-ZnO:Li-Al structure as the UV radiation is switched on and off. The measurements are carried out at the frequency  $5 \times 10^4$  Hz. Switching the UV light on promotes an increase of photoconductivity and accordingly the decrease of  $Q$ -factor. As can be seen from the figure, the rise time of photoresponse is composed of two components. Tentatively, they can be divided into fast ( $\tau_{fast}$ ) and slow ( $\tau_{slow}$ ) components. Similar two-component dependencies (but for decay times of dc-photoconductivity) were observed previously [5]. In our present measurements, the decay time of the photoresponse at the high frequencies occurs following a more complicate (non exponential) dependence (Fig. 3b), in contrast to the direct current measurements.

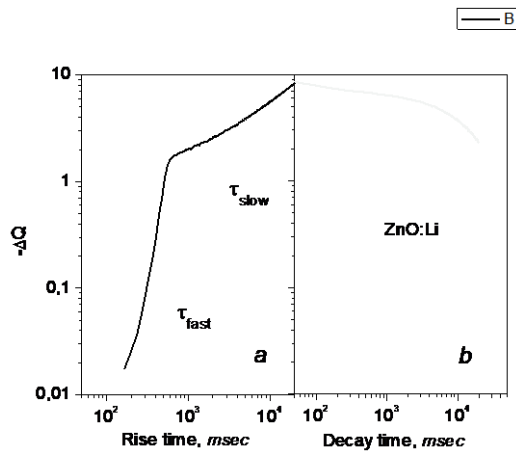


Fig. 3. Kinetics of rise time (a) and decay time (b) of  $Q$ -factor variation in Al-ZnO:Li-Al structure.

Fig. 4 indicates the dependencies of  $\tau_{fast}$ ,  $\tau_{slow}$  and Maxwell relaxation time ( $\tau_M$ ) at  $10^3$  Hz frequency as functions of the Li-impurity concentration. It is seen that the abrupt changes of  $\tau_M$  and  $\tau_{fast}$  for Li concentrations  $\sim 0.8$  at.% take place. This is similar and corresponds to changes in lattice parameter, energy band gap and electrical resistivity reported earlier [11] for Li doped ZnO films. For semiconductors in which the photoelectrons and

thermoelectrons drift in a conduction band, both the rise time and Maxwell relaxation time of photoresponse will coincide [15]. The essential different behaviour of these parameters in the ZnO:Li films also can be taken as indirect confirmation of the existence of different bands for charge transport by photo and dark carriers.

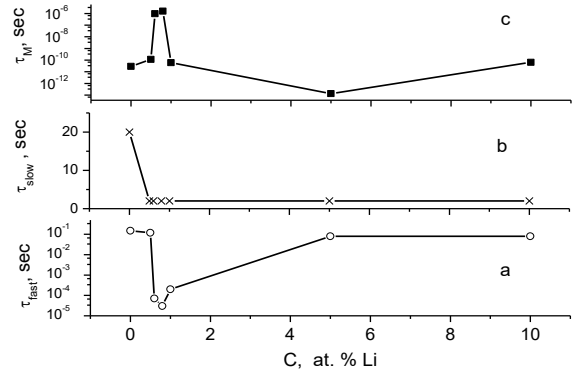


Fig. 4. Dependencies of the fast (a) and slow (b) components of rise time and Maxwell relaxation time (c) on Li concentration in ZnO film.

Fig. 5 illustrates the frequency dependencies of dark conductivity for ZnO and ZnO:Li films plotted on logarithmic scales. From experimental data obtained we can approximate the mechanism of charge carrier transport by variable-range hopping transport between donors:

$$\sigma(\omega) = \sigma(0) + A\omega^s, \quad (4)$$

where theoretical value  $s$  is close to 0.8,  $A$  - constant,  $\omega$  - cyclic frequency of an electric field. In pure films the measured value  $s = 0.68$ , and in Li doped films  $s = 0.51$ . In both cases obtained values are close to 0.8 (for dark current). Therefore it is possible to explain the charge carrier transport for dark conductivity by the hopping mechanism or electron transfer via a Hubbard-model impurity band located near to Fermi level provided that the occupation value of this level  $N(E_F)$  is finite.

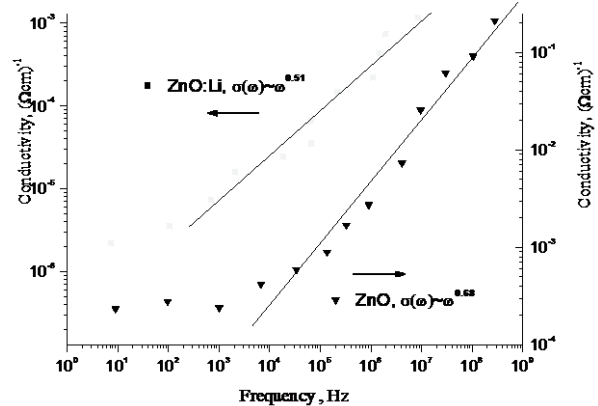


Fig. 5. Frequency dependencies of dark conductivity in pure and 0.8 at.% Li doped ZnO films.

Fig. 6 shows the frequency dependence of photoconductivity for Al-ZnO-Al and Al-ZnO:Li-Al planar structures. Supposing the drift mechanism of charge

transport by the photoelectrons, the obtained experimental data can be approximated by the Drude formula:

$$\sigma(\omega) = \sigma(0)/(1 + \omega^2 \tau_D^2), \quad (5)$$

we deduce values for  $\tau_D$  of  $\sim 4 \times 10^{-6}$  sec for pure ZnO, and  $\sim 9 \times 10^{-6}$  sec for lithium doped.

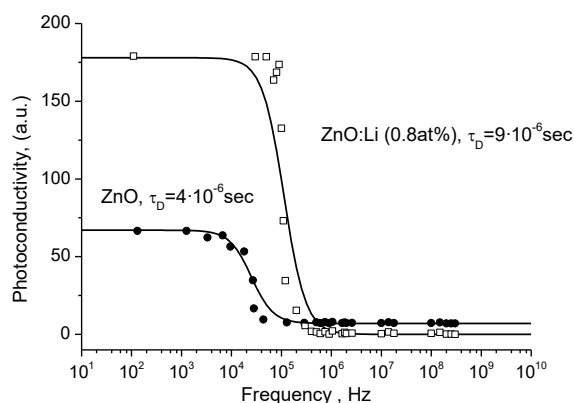


Fig. 6. Frequency dependencies of photoconductivity in pure and Li (0.8 at.%) doped ZnO films.

It is necessary to note that values of the Drude relaxation times for photocurrents in ZnO films significantly exceed the values of Drude relaxation times derived for dark currents, exceeding traditional semiconductor values ( $\tau_D = 10^{-10} \div 10^{-13}$  s). It is possible to explain this observation in terms of photoelectron transport phenomena that account not only for phonons affecting transport in a conduction band but also their recombination. Therefore, for photoelectrons the Drude relaxation time can be greater. As it is seen from Fig. 6, the photoconductivity does not depend on frequency in the range  $0 \div 10^5$  Hz since photoelectrons are moved by the drift mechanism and do not interact with carriers moving in the impurity band of the Hubbard-model.

#### 4. Conclusions

High-resistive lithium doped ZnO films showing high photosensitivity with UV illumination were investigated. From the current-voltage characteristics of dark and photocurrents, the Schottky barrier heights for Al-ZnO:Li junction were calculated. Different heights of the Schottky barriers for dark currents ( $\Phi_d = 0.42$  eV) and photocurrents ( $\Phi_{ph} = 0.98$  eV) are explained by postulating the existence of different bands dominating the charge transport for photo and dark carriers. Based on results of the frequency-dependencies of dark and photocurrents, the conclusion is made that the photoconductivity currents in ZnO films are caused by a drift mechanism by photoexcited electrons in the conduction band, whereas the dark conductivity current is caused by a hopping mechanism via localized states near to the Fermi level, according to Hubbard-model impurity band transport. As a proposed application,

ZnO:Li films can be used as UV photodetectors and also as resistive buffer layers in solar cells with high UV transmission.

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