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Photosensitization of ZnO nanostructured thin films with organic dyes

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We report in this contribution on the photosensitization effect of ZnO nanostructured thin films with copper-phthalocyanine (CuPc). ZnO films were prepared by pulsed laser deposition (PLD), on optical glass substrates, covered with 300 nm thick ITO films. The structure and morphology of ZnO films were optimized for photovoltaic-cell applications by controlling the growing conditions. ZnO films (wurtzite type) were (001) preferentially oriented in the growth direction. Organic dyes were vacuum sublimated on ZnO films, and subsequently a 300 nm thick copper film was vacuum sublimated on top of the structure, acting as an ohmic contact. Action spectra of ITO/ZnO/CuPc/Cu photovoltaic structures were recorded and a well defined response was observed in the range of absorption bands of organic dyes. The dark I-V characteristics were also recorded, and electrical characterizations of the photovoltaic structures are given. The measured fourth quadrant I-V characteristics under integral illumination (photoelement regime), allowed us to extract the typical photovoltaic cells parameters.

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1. Introduction

A promising route towards the fabrication of efficient, low-cost solar cells, followed in the past decade, points to the fabrication of hybrid cells based on inorganic nanostructured materials and organic semiconductors. Several approaches were proposed, starting with Grätzel's structures, having a liquid electrolyte [1,2], to bulk-heterojunction structures, based on the blends of strongly light absorbing semiconducting polymers and inorganic nanostructured compounds [3-5].

The strategy is to create an extremely rough interface between the components in order to achieve improved charge transfer, and also to improve the charge collection at electrodes. Although some promising results have been obtained, more work has to be done, especially to improve the charge collection.

Generally, oxides of transitional metals (TiO_2, ZnO) were used as the inorganic component of the heterostructures. ZnO is a very promising material for the fabrication of thin film solar cells, due to its high absorption coefficient in the UV region of the spectrum, its large exciton binding energy (60 meV) [6], and good radiation stability. In addition of being transparent in the visible region, ZnO can be made electrically conductive if doped with appropriate dopants [7]. On the other hand, as organic counter-part of the heterostructure, CuPc is recommended by its high absorption coefficient in the visible region of the spectrum [8].

In the present work we report on the fabrication and characterization of a hybrid ITO/ZnO/CuPc/Cu photovoltaic cell. ZnO nanostructured film was deposited on optical glass substrate covered with indium-tin oxide (ITO) film (300 nm thick) by pulsed-laser deposition (PLD). That technique was proved to be a versatile one for making thin solid films with complex chemical compositions and various structural and morphological characteristics. The main thing about PLD is that it provides good control over several parameters during deposition. ZnO film was optimized, to achieve a rough surface and a good transparency. CuPc film was grown on top of ZnO by thermal vacuum deposition. I-V characteristics of the heterostructure were recorded, and also the spectral photovoltaic response was measured.

2. Experimental details

ZnO thin films were synthesized by pulsed KrF* (λ = 248 nm and $\tau_{FWHM} \approx 7$ ns) laser ablation of ZnO targets on optical glass substrates and optical glass coated with 300 nm - thick ITO film. The reaction chamber was evacuated to a residual gas pressure below 10^{-4} Pa. Data regarding preparation conditions of the films analyzed in this paper are collected in Table 1.

Table 1. ZnO films parameters.

Sample	Target	Substrate	Deposition Temperature [º C]	Oxygen Pressure [Pa]	Film thickness [nm]	Measured band-gap [eV]
ZSC3	ZnO	300 nm ITO coated optical glass	200	13	293	3.24
ZSC5	ZnO	300 nm ITO coated optical glass	200	6.5	510	3.26
ZSC7	ZnO	300 nm ITO coated optical glass	200	40	537	-
ZSC9	ZnO	300 nm ITO coated optical glass	350	13	388	3.24

X-ray diffraction (XRD) data were collected at room temperature, using a DRON UM1 diffractometer. A horizontal powder goniometer in Bragg–Brentano focusing geometry with graphite monochromator was used. XRD spectra were recorded by using Cu-Kα line, λ = 1.54178 Å. Optical absorption spectra of the ZnO films were recorded at room temperature, using a Perkin-Elmer Lambda 35 spectrometer.

CuPc was grown on top of ZnO by thermal vacuum deposition, at a residual pressure of 6×10^{-3} Pa. The evaporator consisted of a quartz container heated to 350 °C. The substrates were maintained at 50 °C during the deposition. To improve the structural and chemical homogeneity of the films, they were subsequently thermally treated in vacuum at 80 °C, for 10 min. Finally, a copper back-electrode was vacuum sublimated on top of the structure.

I-V characteristics of ITO/ZnO/CuPc/Cu structure were recorded by using a Keithley 2400 SourceMeter.

3. Results

A. *ZnO films characterization*

Structural analysis of the samples by X-ray diffraction revealed that the films consist of a hexagonal-close-packed wurtzite type phase ZnO, (001) preferentially oriented in the growth direction (Fig. 1).

One can easily observe that on increasing the substrate temperature and the oxygen pressure during deposition, the film texture and crystalline quality got more pronounced. Samples ZSC5 and ZSC7 were grown at the same substrate temperature, but at different oxygen pressure (see Table 1). By increasing oxygen pressure, the (002) peak narrows while its intensity increases. Also (103) peak disappears, which confirms that the film is more textured. By increasing substrate temperature, (002) peak gets narrower (see sample ZSC9, Table 1) but (103) peak is again present in the XRD pattern, although narrower. However, the oxygen pressure was lower in the case of ZSC9 sample, as compared with ZSC7. A lattice constant c=5.212 Å was obtained, compared with the reported bulk value c_{bulk}=5.206 Å.

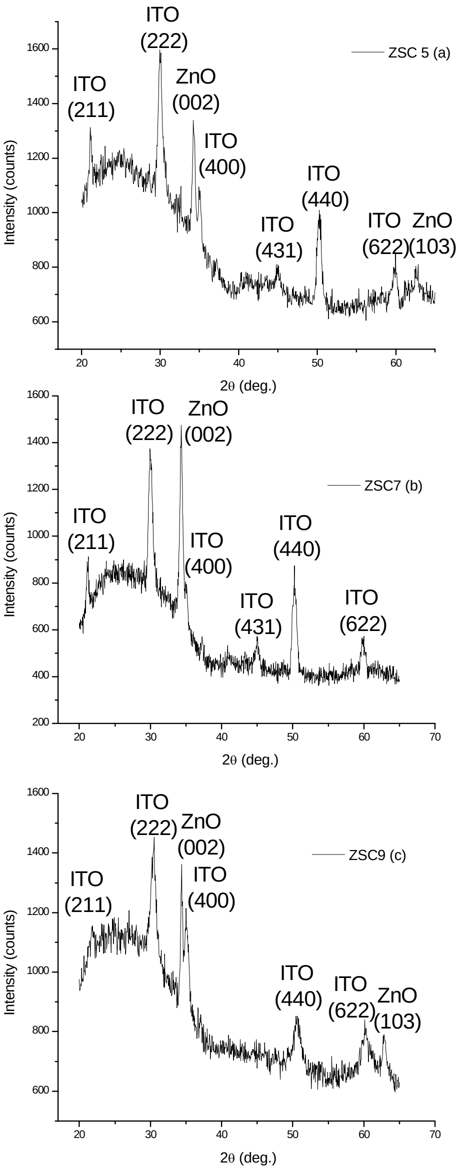

Fig. 1. XRD patterns of PLD deposited ZnO films; the films are indexed as indicated in Table 1.

Fig. 2 shows optical absorption spectra of ZnO films indexed as indicated in Table 1. The optical band-gap, E_g, was determined from the well-known dependence of the absorption coefficient, α, on the incident photons energy, $h\nu$, in direct-band semiconductors [9]:

$$\alpha(h\nu) = A\frac{\left(h\nu - E_g\right)^{1/2}}{h\nu}, \tag{1}$$

where A is a constant depending on the refractive index of the material and on the electron and hole effective masses (Fig. 2(b)).

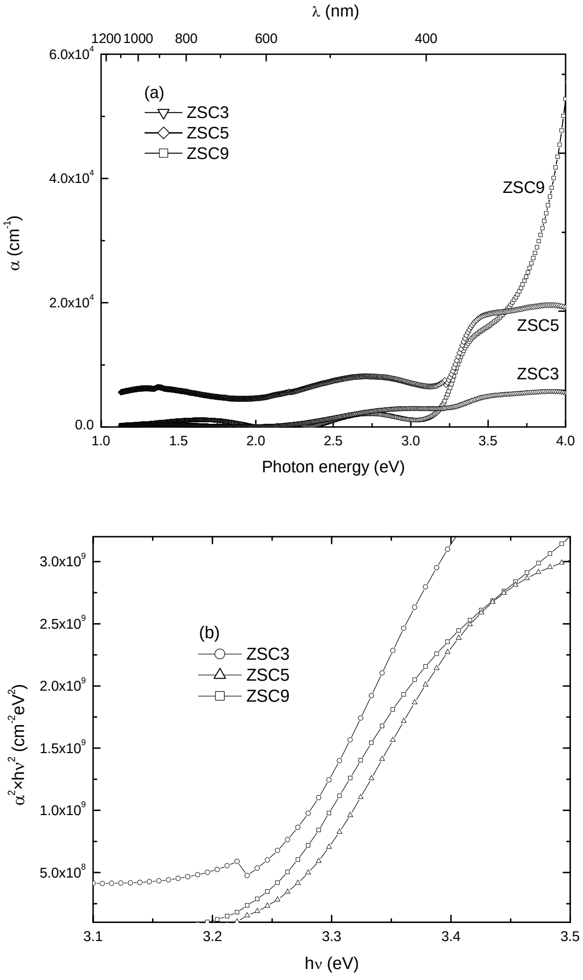

Fig. 2. Optical absorption spectra of ZnO films, indexed as indicated in Table 1 (a) and optical threshold region (b).

In the near band-edge region, the dependence of the absorption coefficient on photons energy is well described by Urbach's exponential law (Fig. 3):

$$\alpha(h\nu) = B\exp\left(\frac{h\nu}{E_0}\right), \text{ with } h\nu < E_g. \tag{2}$$

Such a behavior was also reported in Ref. [10]. Usually Urbach's law is explained by assuming an exponential tail in the density of states in the band-gap, although it is difficult to find a model of disorder inducing that tail. In Ref. [11] arguments are given to show that Urbach's law is related to electric microfields associated to defects and to exciton effects. We believe this is the explanation for the observed near-band edge absorption, given the important exciton effects in ZnO.

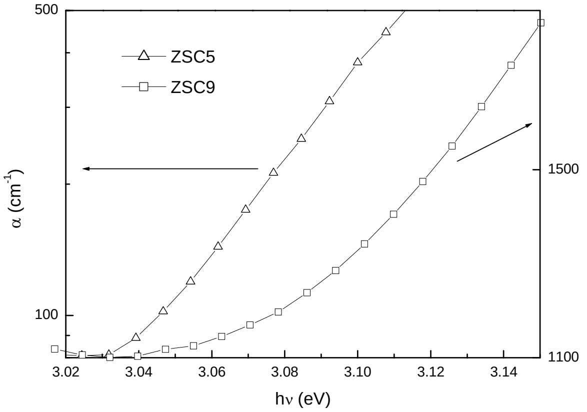

Fig. 3. Near-band-edge absorption spectra (Urbach's tails) of ZnO films indexed as indicated in Table 1.

Photoluminescence spectra of the films, recorded at room temperature using a Perkin-Elmer PL4 spectrometer, are shown in Fig. 4. The emission was excited with 325 nm light. For all films, near-band-emission, due to free exciton recombination, dominates. It shows a broadened peak, with some structure in the case of ZSC3 sample. Again, as observed also in the case of XRD investigation, the substrate temperature during deposition has the most important effect on PL. The deep-level emission (DLE) is present, but its intensity is much lower. DLE appears in the green region of the spectra (a shoulder can be observed at 512 – 515 nm). It comes probably from oxygen vacancies or zinc in interstitial positions [12].

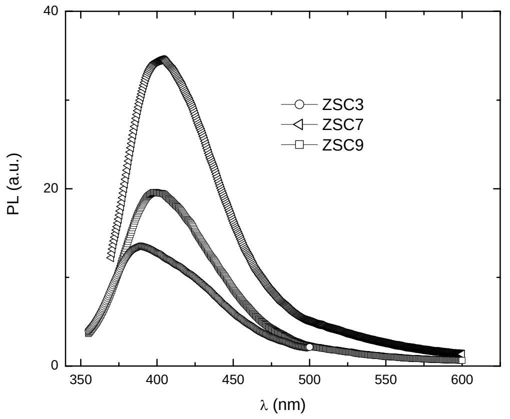

Fig. 4. PL spectra of ZnO films, indexed as indicated in Table 1.

B. Characterization of ITO/ZnO/CuPc/Cu structures

Fig. 5 shows I-V characteristics recorded at room temperature (298 K) for one of the ITO/ZnO/CuPc/Cu structures. It was obtained by growing a 1700 nm thick CuPc film on the ZSC7 ZnO film. The copper back-contact was 350 nm thick. Dark I-V characteristics show a rectifying behavior. Under illumination (white light from a incandescence lamp, 1.34 mW integral optical power incident to ITO electrode of the structure) the current-voltage characteristics, shown as solid line in Fig. 6, was obtained. Although the open-circuit voltage value looks promising, the short-circuit current is very small and the series resistance of the structure is large. The measured fill-factor was 29.8%.

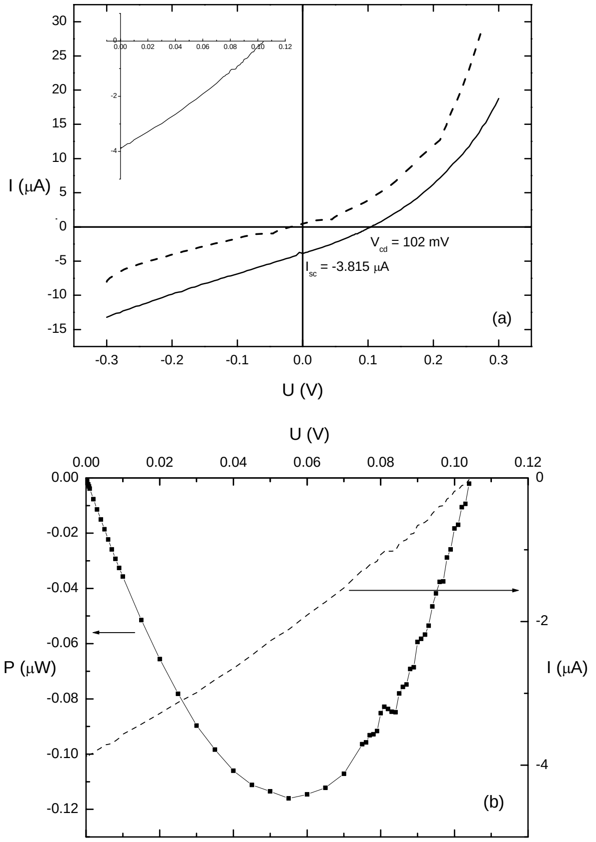

Fig. 5. (a) I-V characteristics (dark and under white light illumination). In the inset the fourth quadrant is shown; (b) Power-voltage dependence in the fourth quadrant (solid line). The I-V characteristics is also shown (broken line).

The spectral response of the structure is shown in Fig. 6(a). By comparing with the absorption spectrum of CuPc film (Fig. 6(b)), it is obvious that the charge separation occurs at the ZnO/CuPc interface, through the dissociation of molecular excitons generated in the organic semiconductor.

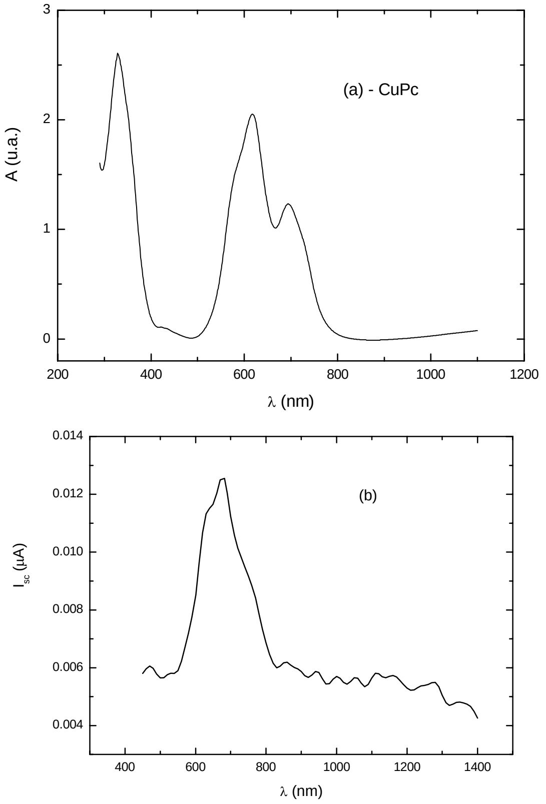

Fig. 6. Optical absorption spectrum of the CuPc film (a) and action spectrum of the cell (b).

4. Conclusions

Hybrid organic/inorganic semiconductor photovoltaic cells, of the type ITO/ZnO/CuPc/Cu were produced. ZnO thin films optimized for use in optoelectronic applications (high transparency in the visible region of the spectrum) were deposited on glass substrates covered with ITO (300 nm thick). Structural characterization of ZnO films was performed, indicating only the presence of the wurtzite phase. The films are (001) preferentially oriented in the growth direction. The texture and crystalline quality of the films is very sensitive to the oxygen pressure in the reaction chamber during the deposition. Increasing the oxygen pressure results in improved crystalline quality and texture.

The measured optical band-gaps of ZnO films were in 3.24 – 3.26 eV range, as compared to 3.3 – 3.4 eV reported for bulk samples. Room-temperature PL spectra show near-band-edge emission broadened peaks, with some structure in the 425 – 450 nm range. Also deep-level emission exists in the green region of the spectra, but its intensity is much lower.

The measured I-V characteristics of a ITO/ZnO/CuPc/Cu cell are of rectifying type. Under illumination, a photovoltaic effect at the ZnO/CuPc interface was measured. The fill-factor of the cell was

29.8%. Although the open-circuit voltage is promising, improvements need to be done in the direction of reducing the series resistance and increasing the short-circuit photocurrent.

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