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# Organic Photovoltaic Cells Based on ZnO Thin Film Electrodes

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Due to its wide band-gap (ca. 3.4 eV), ZnO is a possible candidate material to be used as transparent electrode for a new class of photovoltaic (PV) cells. Also, an increased interest for the photovoltaic properties of several organic monomers and polymers (merocyanines, phthalocyanines and porphyrins) was noticed, because of their high optical absorption in the visible region of the spectrum allowing them to be used as potential inexpensive materials for solar cells. Preparation and properties of CuPc (copper phthalocyanine) based photovoltaic cells using ZnO thin films as transparent conductor electrodes are presented in this paper. ZnO layers are grown by pulsed laser deposition, while the organic layers are obtained by thermal evaporation. Structural characterization is performed by electron microscopy. Optical and transport properties of the mutilayered structures are obtained by electrical and spectro-photometric measurements. The influence of the ZnO-polymer interface on the external quantum efficiency (EQE) of the photovoltaic cell is clearly evidenced by our measurements.

**Keywords:** Photovoltaic Cells, ZnO Films, PLD, Surface Morphology, EQE.

## 1. INTRODUCTION

The constantly growing costs of the conventional fossil fuel based energy represents a strong enough reason to channel the research towards alternative renewable resources such as wind or solar energy. Studies concerning the solar cell efficiency aiming at reducing the costs for the energy unit lead to already two generations of solar cells based on two different technologies. The first generation (1G) of solar cells is completely based on the silicon technology, using single crystal or multi-crystalline silicon. Commercially available PV devices of the first generation are in the 18–21% efficiency range for single crystal devices and 13–14% but at lower manufacturing costs for the multi-crystalline silicon. The second generation (2G) photovoltaic cells are based on thin films instead of bulk materials, using amorphous silicon (a-Si), polycrystalline Si, CdTe, CdS, etc. thin films deposited on low cost transparent substrate (glass). Efficiency up to 16–18% has been experimentally proven for such devices.[1] A third generation (3G) of PV cells is currently developing researches in two parallel technologies. The first one intends to extend the 2G single junction devices to multiple junction devices. The second direction, involving dye sensitized and hybrid organic–inorganic layered devices, became a very promising alternative after the successful results of Grätzel in 2001.[2] During the last years a special attention has been paid to the PV properties of the organic semiconductors as low cost highly absorbent materials in the visible range. Among the intensely studied organic materials we can mention the merocyanines, prophirines, phthalocyanines[3–5] etc.

This work presents some optical and electrical results in relation with the structural aspects of PV cells based on copper phthalocyanine (CuPc) as optically absorbent layer and ZnO thin films as transparent conductor oxide (TCO) front electrode.

## 2. EXPERIMENTAL DETAILS

Photovoltaic cells with the following multilayer sequence Al/CuPc/ZnO/glass have been prepared using ZnO:Al (AZO) as TCO front electrode deposited on the glass substrate. The AZO layers have been grown by pulsed laser deposition from a ceramic sintered target made up of a mixture of ZnO and 1 wt% $Al_2O_3$. We used as laser source the fourth-harmonic ($\lambda = 266$ nm) of a solid state Nd-YAG

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laser. The substrate (Si or glass) has been maintained at 400 °C, while the $O_2$ pressure, as working gas in the deposition chamber, has been varied in the 1–10 Pa range. The as-prepared AZO/glass substrates have been used to further deposit the photosensitive CuPc layer and the Al back electrode by vacuum thermal evaporation. The residual pressure in the deposition chamber was $10^{-3}$ Pa. The CuPc powder (provided by Aldrich) has been slowly evaporated at 400 °C from a quartz crucible covered with quartz wool in order to prevent explosive evaporation. The substrate has been maintained at 40 °C. After deposition, an *in-situ* thermal treatment at 100 °C for 10 minutes has been applied for structural homogenization. The Al back electrode (200 nm thick) has been also deposited by thermal evaporation.

Morphological and structural characterization has been carried out by transmission electron microscopy (TEM) using a JEOL 200 CX microscope and scanning electron microscopy (SEM) using a JEOL JSM 5510 microscope. Specimens for TEM analysis have been prepared by mechanical thinning via the tripod method followed by ion milling using a Gatan PIPS installation. To ease the cross-section specimen preparation for TEM, Si substrates instead of glass were used for the AZO films PLD depositions. Electrical and photoelectrical characterization were performed with an Oriel Cornerstone 130 monochromator, a Keithley 2400 sourcemeter and a Keithley 6517a electrometer connected to PC via a GPIB interface.

## 3. RESULTS AND DISCUSSION

The typical cross-section TEM (XTEM) image of a PLD deposited AZO layer on Si substrate (Fig. 1(a)) shows a columnar growth mode. Next to the interface with the substrate, a polycrystalline layer can be noticed from which elongated grains develop along a direction almost normal to the substrate. The film is compact showing no cracks or pores between the crystal grains. The corresponding selected area electron diffraction (SAED) pattern is presented in Figure 1(b). The main diffraction maxima of the ZnO wurtzite structure are indicated by arrows. The discontinued diffraction rings of the SAED pattern reveal a strong structural texturing around the $[001]_{\text{ZnO}}$ crystallographic direction oriented almost perpendicular to the substrate, in a range of ±20° around the normal to the substrate. The unequal growth of the constituent grains along the $c$-axis, which represents the rapid growth direction for ZnO, corroborated with the misalignment of the $c$-axis from the substrate normal, leads to a surface roughness around 30–50 nm, as noticed on the XTEM image.

The electrical and optical characteristics of the AZO front electrode are presented in Figure 2. For the electrical measurements at low temperature the samples have been placed in a cryostat under vacuum at $10^{-1}$ Pa. The electrical resistivity of the AZO layers has been measured by the van der Pauw method,[6] with the four contacts disposed in line. The electrical resistivity measures less than $3 \times 10^{-4}$ Ωm at room temperature and saturates around $3.6 \times 10^{-4}$ Ωm below 30 K.

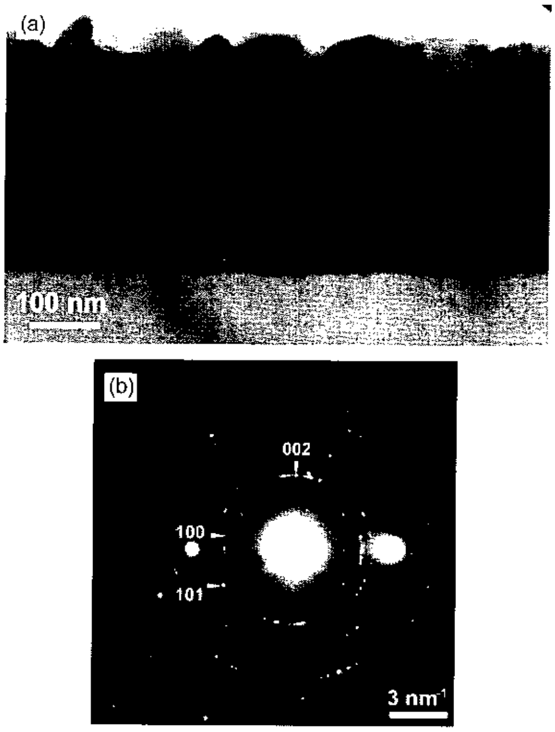

Fig. 1. (a) XTEM image of a typical AZO thin film deposited by PLD, used as front electrode in our PV cells; (b) SAED pattern of the AZO layer showing texturing around the [002] crystallographic direction oriented almost perpendicular to the substrate.

For the optical measurements at room temperature we used a Perkin-Elmer Lambda 35 spectrophotometer. The AZO layer shows good optical qualities to be used as front electrodes, meaning low optical absorption in the 400–800 nm range, as shown by the graphs in Figure 2(b). The width of the optical band gap $E_g = 3.42$ eV was determined from the dependence of the absorption coefficient on the energy of the incident photons for semiconductors with direct band gap.[7]

The as-deposited AZO layers have been used as front electrodes for PV cells with the Al/CuPc/ZnO/glass structure. Several samples have been prepared varying the deposition conditions of the AZO layer while keeping unchanged the experimental conditions for the CuPc and Al layers in order to reveal the influence of the AZO-CuPc interface on the PV characteristics of the obtained cells. In Figure 3 we show the SEM images of two AZO layers deposited by PLD at two different oxygen pressures: 1 Pa for sample 1 and 10 Pa for sample 2. The SEM images have been recorded prior to the CuPc and Al films deposition. One can immediately observe a notable difference in terms of surface roughness between the two samples. We have already seen on the XTEM image that a contribution to the surface roughness in the range 30–50 nm

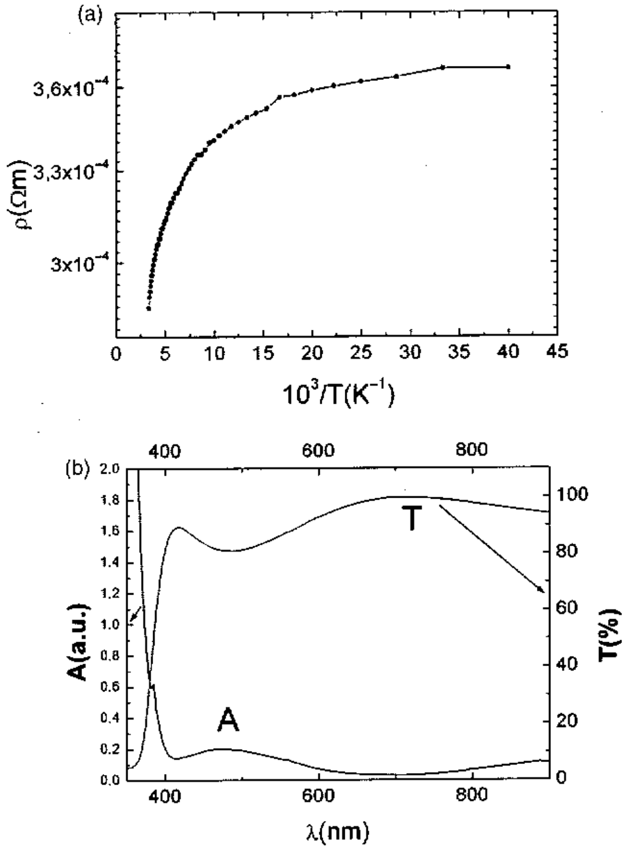

**Fig. 2.** (a) Temperature dependence of the electrical resistivity of the AZO layer deposited on the glass substrate. (b) Optical absorption (A) and transmittance (T) curves of the AZO layer.

comes from the ZnO grains growth process. There is a second contribution revealed by the SEM images, due to the presence of particulates on the films surface. This matter has been considered one of the major drawbacks of the PLD method and, therefore, it attracted a great deal of attention during decades. In principle, it is widely accepted that there are two mechanisms responsible for the presence of these particulates on the film surface.[8–10] The large (micrometric size) particulates are microdroplets of melted substance coming from the target. Their number on the film surface is strongly influenced by the laser wavelength, thermal characteristics of the target and, also, the morphological characteristics of the target (surface roughness, porosity, etc.). Small particulates, in the range of 100–1000 nm, are formed during the laser plasma expansion in the space between the target and the collector, and their presence is greatly influenced by the pressure and nature of the working gas.

In our case both of these mechanisms may be evocated to explain the increased roughness of sample 2. On one hand, the oxygen pressure was 10 times larger during the deposition of this film, leading to a higher density of droplets with sizes of hundreds of nm.

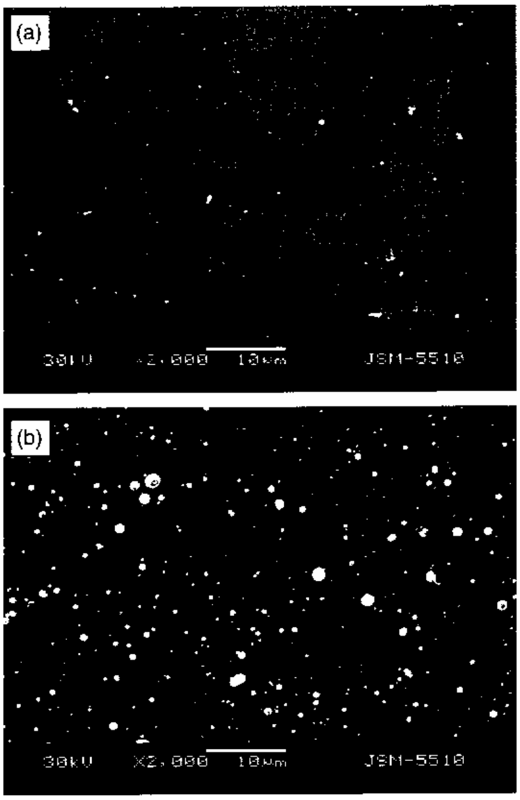

**Fig. 3.** SEM images of the as-deposited AZO layers, samples 1 and 2 in (a) and (b), respectively, obtained by PLD in different experimental conditions.

On the other hand, the same ZnO:$Al_2O_3$ target has been used first for the sample 1 and then for the sample 2 without any surface polishing in between. Therefore, the surface of the target was degraded to a certain degree when the film 2 was deposited. This would explain the presence of the large droplets (up to 3 $\mu$m size) on the surface of sample 2.

The two AZO/glass layers described have been used for the fabrication of PV cells by further depositing the CuPc and Al layers. The current–voltage characteristics without illumination of the two cells presented in Figure 4 show only a slight rectifying behavior especially for the structure based on the AZO 2 layer.

The two $I$–$V$ characteristics are described by the following relation:

$$I = I_0\left\{\exp\left[\frac{q(U - IR_S)}{nk_BT}\right] - 1\right\} + \frac{U - IR_S}{R_{sh}}$$

where $I$ represents the current for the applied voltage $U$, $I_0$ is the saturation reverse current, $R_s$ is the series resistance of the structure (corresponding to the neutral regions), $R_{sh}$ is the shunt resistance (associated with the leak currents), $q$ is the electron electrical charge, $k_B$ the Boltzmann constant and $n$ is the junction factor induced by the charge generation-recombination phenomena in the space charge region. After the appropriate approximations

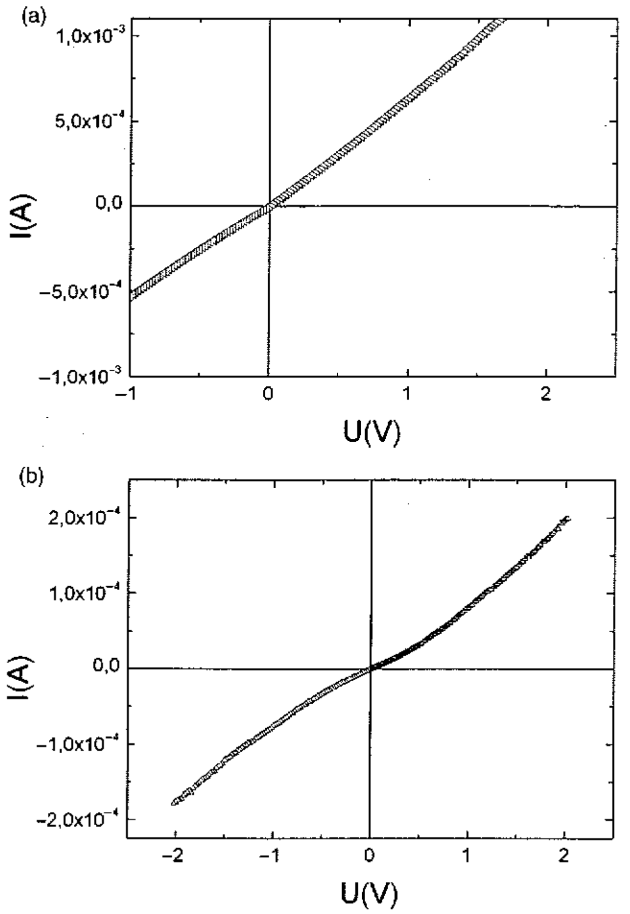

**Fig. 4.** Dark $I$–$V$ characteristics of the Al/CuPc/ZnO/glass structure at room temperature in the case of the AZO 1 layer (a) and the AZO 2 layer (b).

for high voltage and low voltage polarization regimes, the mentioned junction parameters have been derived to fit the experimental curves as follows: $I_0 = 2.79 \times 10^{-4}$ A, $n = 7.12$, $R_S = 412\ \Omega$, $R_{sh} = 1.72$ k$\Omega$ in case of sample 1 and $I_0 = 3.45 \times 10^{-6}$ A, $n = 4.22$, $R_S = 8087\ \Omega$, $R_{sh} = 17.21$ k$\Omega$ for sample 2. The reduced value of the shunt resistance $R_{sh}$ is in agreement with the slight rectifying character of the two structures.

The external quantum efficiency (EQE) curves measured at room temperature for the two PV structures are comparatively shown in Figure 5. As a reference, the optical absorption spectrum of CuPc is added to the graphs (solid line). The absorption spectrum of the ZnO layer is also shown in the insets. EQE measures the efficiency of generating charge carriers by the absorbed photons, including the photons absorption efficiency, exciton diffusion efficiency and charge collection efficiency. In our case, we measured the flux of incident photons using a calibrated differential p-i-n Si photodetector. The EQE in the Q region of the CuPc absorbent (500–800 nm), where ZnO shows no significant absorption, measures 6–10% for sample 1. At higher photon energies, the photo generation processes become important not only in CuPc, but in ZnO,

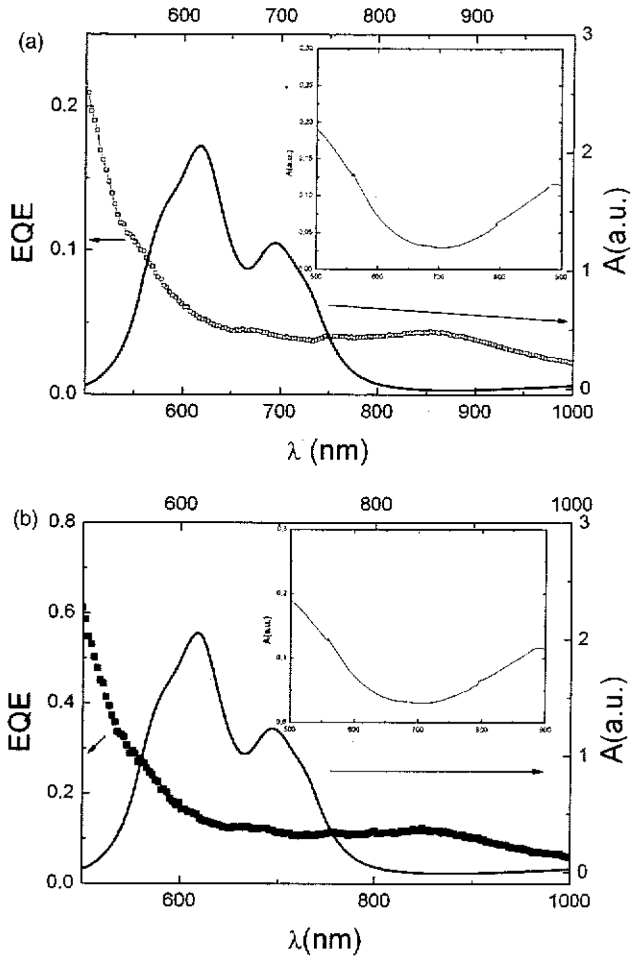

**Fig. 5.** Spectral dependence of the external quantum efficiency (EQE) of the Al/CuPc/ZnO/glass structure in the case of the AZO 1 layer (a) and the AZO 2 layer (b). The solid line shows the absorption spectrum of CuPc. The absorption spectrum of the ZnO layer is shown in the inset.

also, which explains the accentuated EQE increase up to 30% at wavelengths below 500 nm. The same characteristics of the EQE spectral dependence are noticed in case of sample 2, only this time the EQE value raises up to 14–25% in the spectral range corresponding to the CuPc absorption Q-band.

Considering the experimental conditions used for the PV cell fabrication in the two analyzed cases, the difference consists in the PLD deposition parameters for the AZO films growth. The increased oxygen pressure in the case of sample 2 lead to an AZO film with an increased surface roughness. The rough interface between the AZO and CuPc layers determined a higher value for the EQE. The explanation for this significant increase comes from two aspects. On one hand, a rough interface means a higher specific surface and, hence, a higher charge collection efficiency at the AZO electrode. On the other hand, the rough interface determines diffuse scattering of light incident on this interface back into the CuPc absorbing layer, increasing this way the absorption efficiency. The benefic role of the rough interfaces in the particular case of PV cells has been evidenced by other authors, also, who demonstrated better PV characteristics for the cells built up on chemically etched TCO electrodes with increased surface roughness.[11] In the case of PLD layers, surface roughness comes somehow naturally, originating both from the deposition conditions and the film growth process, as described earlier. This is one of the few situations in the case of the PLD thin films, where the presence of particulates on the film surface turns out from a major drawback of the deposition method into a desirable benefic effect regarding the quality of the obtained PV cells.

## 4. CONCLUSIONS

The photovoltaic effect has been successfully evidenced in Al/CuPc/ZnO/glass structures obtained in different experimental conditions. The amplitude of the effect is strongly influenced by the roughness of the ZnO-CuPc interface. The EQE increases from 5–10% in the 500–800 nm spectral range for a smooth interface (sample 1) to about 14–25% in the same spectral range for a rough interface (sample 2). Our results confirm the positive role played by a rough interface between the electrode and the active layer in improving the EQE by the mechanism of light entrapping. The roughness of the PLD obtained ZnO thin film comes from the presence of micro-droplets on the surface. The deposition conditions can be adjusted in order to obtain an optimal interface roughness to increase the EQE.

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