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Photovoltaic cells based on nickel phthalocyanine and zinc oxide formed by atomic layer deposition

Research Article

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Abstract: The introduction of an ultrathin zinc oxide (ZnO) layer formed by the atomic layer deposition (ALD) technique was found to improve the operation parameters of nickel phthalocyanine (NiPc) based photovoltaic cells with a transparent bottom electrode, indium tin oxide (ITO). This improvement is attributed to several reasons, such as i) increase of photovoltaic yield in ITO/$p-$NiPc/$n-$ZnO/Al cells incorporating a hybrid heterojunction as compared to single-layer ITO/NiPc/Al cells, ii) enhancement of the overall spectral response in the double-layer cells and iii) extension of long-term operational stability.

1. Introduction

Progress in the development of organic–based solar cells is associated, in most cases, with use of the layered (or bulk) heterojunctions, as well as with their protection against atmospheric conditions [1–3]. This particularly concerns various prototypes of solar cells employing ph–

thalocyanines (Pc) as photoactive materials [1]. Due to high sensitivity of these compounds to absorbed gases (sensitivity of electrical parameters of solids or thin films, but not molecular destruction), isolation from ambient air is highly desired. Additionally, problems arise at the in–terface between the Pc layer and the top–deposited metal–lic electrode. The device life time suffers much from in–stability of this interface, which can roughly be realized as chemical (possible reactions, diffusion of components *etc.*) and physical degradation, that is alteration in bar–rier properties.

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One way to solve this problem is the insertion of an ultra-thin layer, organic or inorganic, before depositing the top contact [4–6]. This may either prevent penetration of admixtures into the Pc layer or facilitate injection of charge carriers from the contact, or both. The present work investigates the effect of the introduction of a zinc oxide (ZnO) ultrathin layer on the operation of photovoltaic cells based on nickel phthalocyanine (NiPc). Phthalocyanine complexes are known for their exceptional chemical and thermal stability, providing compatibility even with, for example, chemical vapor deposition process [7]. Therefore, direct atomic layer deposition (ALD) of ZnO is not expected to cause significant damage to the underlying molecular film. ZnO is a transition metal oxide semiconductor, which is very promising for use in solar cells. Owing to certain technological advantages, it is frequently used as inorganic component of hybrid heterostructures [8–11].

2. Experimental

Thin polycrystalline NiPc films were deposited by thermal evaporation of initial powder (Aldrich, used as received) from a molybdenum boat resistively heated up to $\sim$400°C in vacuum $< 10^{-3}$ Pa on the standard glass/ITO (indium tin oxide) substrates. Such conditions provide high thickness uniformity with a molecular content of a film that is equivalent to that of the powder before sublimation [12, 13]. The resulting films thickness (400 nm for NiPc) was measured using an interference microscope MII-2.

In order to elevate the photoconversion activity of the cells, NiPc films were intentionally doped with oxygen [12, 13]. For this, freshly made films have been stored in sealed quartz ampoules filled with pure oxygen for 7 days.

Some samples were then placed in a commercial ALD reactor (Cambridge Nanotech S100) [14, 15] to make double-layer cells, whereas others were used for making the single-layer cells that serve as reference. ZnO was grown on top of the pre-patterned NiPc films in low temperature conditions ($\sim$100°C) from diethyl zinc (Zn(CH$_3$CH$_2$)$_2$) and deionized water precursors. Using the ALD method a 26 nm thick ZnO layer was deposited, and the following parameters were measured: carrier concentration was 10^{16} cm^{-3} (n-type); mobility was 2.9 cm^2/Vs; and conductivity was 0.01 Ω^{-1}cm^{-1}.

Finally, a 200 nm thick aluminum layer (metallic cathode) was thermally evaporated onto the top of all samples to complete the fabrication of photovoltaic cells in the same conditions as for evaporation of NiPc films. The active area of these devices, both ITO/NiPc/Al and ITO/NiPc/ZnO/Al series, was 10x10 mm^2.

The photoelectrical characterization was carried out immediately after fabrication and repeated after one-month storage of samples under normal conditions. Current-vs-voltage ($J-V$) characteristics were obtained using an AUTOLAB measuring station (Eco Chemie) controlled by a GPES software. The sweep rate was set at 0.025 V/s with the forward bias corresponding to positively charged ITO contact. The sweeping started from zero voltage up to the maximum positive voltage (+2 V), then proceeded in the opposite direction down to the maximum negative voltage (-2 V), and then returned back to the initial zero value. Some hysteresis was detected for the ITO/NiPc/Al cells [16], in contrast to the ITO/NiPc/ZnO/Al cells, but it will not be discussed in this work.

Optical absorption spectra and photocurrent action spectra were obtained using a "SPECORD M-40" spectrometer (Carl Zeiss) in the wavelength range of 350-900 nm at room temperature. In the latter case, the samples were illuminated with monochromatic light through the transparent ITO electrode and the resulting photocurrent was measured by an electrometer with high input resistance (that is nearly J_{sc}). The photocurrent spectra were corrected to equal amount of incident photons. A xenon lamp was used for illumination of cells in a broad spectral range, with the intensity of incident light 75 mW/cm^2 (P_{in}). All measurements were done in air at room temperature.

3. Results and discussion

3.1. Dark currents

Dark $J-V$ characteristics for two types of cells are plotted in Fig. 1A (linear scale). Only weak rectifying behavior is seen in the ITO/NiPc/Al cells in the dark. Rectification ratio (RR=$J^{forward}/J_{reverse}$ at 1 V) is equal to 1,7. At forward bias, the $J-V$ curve consists of three sections (marked as **I**, **II** and **III** in Fig. 1A). This suggests that there are different mechanisms that control the charge transport, depending on the applied voltage [1, 13, 17–21]. Few initial points ($0 < U < 0,5$ V) constitute the first section, which is nearly ohmic. Within section **II**, experimental points were found to follow the power law dependence $J \sim U^n$, where $n=2$, whereas in section **III**, index n is equal to 2.9 (with correlation coefficients better than 0.997). This implies transition to the space charge limited currents with exponential distribution of traps [13, 17–21]. Hence, considering section **III**, one can write the current density as function of applied bias in the following form:

$$I = q\mu N_v \left(\frac{\varepsilon}{qP_0 k_B T_t} \right)^l \frac{V^{l+1}}{d^{2l+1}}, \tag{1}$$

where N_v is effective density of states, P_o is the trap den-

sity per unit energy range at the valence band, ε is dielectric permittivity, d is film thickness, k_B is the Boltzmann constant, q is electronic charge, μ is mobility, the ratio $l = T_t/T$, T_t is the temperature parameter characterizing the exponential trap distribution, and T is absolute temperature. Then, the total trap concentration $N_{t(e)}$ is described as $N_{t(e)} = P_0 k T_t$. Using μ, N_v and ε values

taken from the literature [17, 20], an approximation of experimental points (see Supplementary file) in the section III of Fig. 1A with eq. 1 gives the following parameters: $l=1.9$, $T_t =570$ K at $T= 300$ K, $P_o = 7.6\times10^{45}$ J^{-1}m^{-3}, $N_{t(e)} =5.98\times10^{25}$ m^{-3}. These parameters are in reasonable agreement with those published earlier [13, 17–20] for Au/NiPc/Al cells.
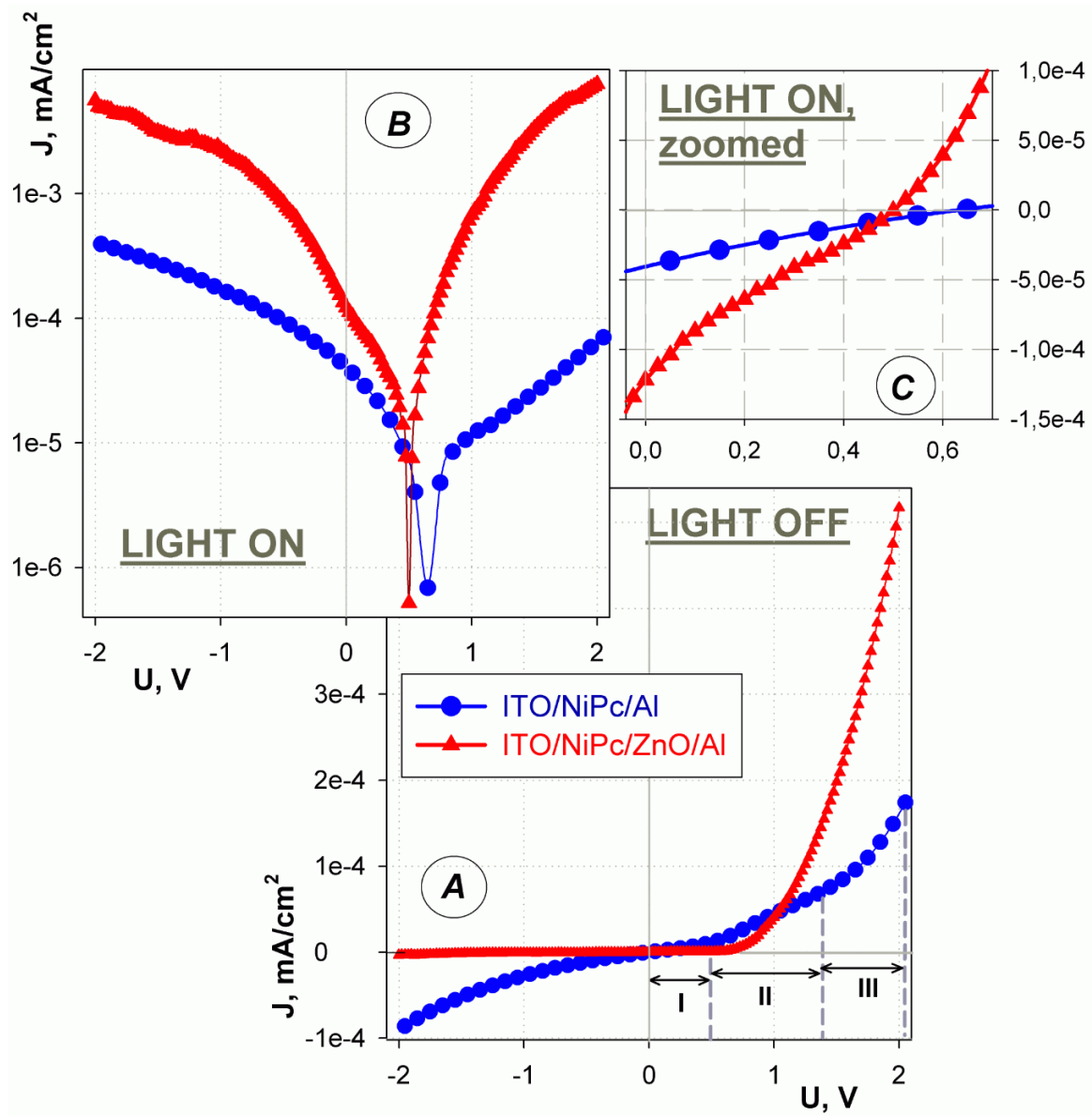

Figure 1. J-V plots for single (blue curves with circles) and double-layer cells (brown curves with triangle) in the dark (A) and under illumination (B). Zoomed data for illuminated cells are shown in the inset (C).
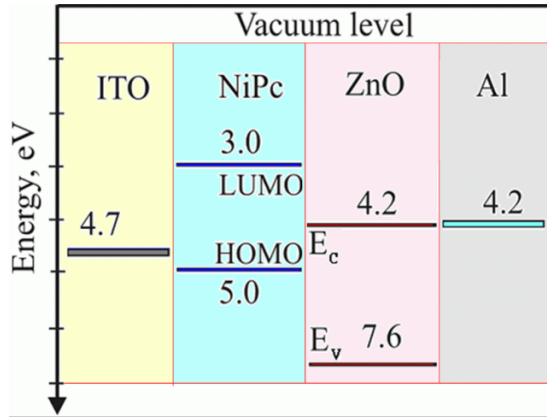
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Figure 2. Diagram of energy levels (all values are in electron-volts). The layout of the structures corresponds to the "layer-by-layer" deposition of materials going from glass/ITO substrate to top aluminum contact, *i.e.*, from the left to the right in the picture.

Diode properties of the ITO/NiPc/ZnO/Al cells in the dark are more pronounced (see, Fig. 1A); the RR value in this case is equal to 42 (*cf.* [17, 20]). This is apparently caused by lowering of the interfacial resistance by insertion of conductive ZnO interlayer. In addition, ZnO protects the soft surface of a molecular NiPc film against the hot vapor-deposited metallic atoms that can get into the bulk film. This is similar to recently elucidated role of interlayers in the electrical properties of light-emitting diodes [6, 22]. Note that metallic atoms or particles that have penetrated inside of the active layer, may serve as exciton quenching sites or even react with organic materials leading to its degradation [6].

The energy level diagram of this heterostructure, considering isolated materials, based on the values adopted from Refs. [8, 10, 23] is represented in Fig. 2.

It is assumed that Al forms a quasi-ohmic contact with the ZnO layer [24], therefore, the rectification takes place at the $p-$NiPc$/n-$ZnO heterojunction (Fig. 2). Since the concentration of free carriers in ZnO is almost six orders of magnitude larger than that in NiPc, the space charge region will be localized within the NiPc layer. Consequently, generation–recombination processes will be mostly controlled by phtalocyanine. Concentration of traps in the NiPc layer in the ITO/NiPc/ZnO/Al heterostructure can also be estimated from eq.(1) using experimental points in Fig. 1A. This gives $N_{t(e)} = 7 \times 10^{26}$ m^{-3}, whereas $l = 2, 4$, $T_t = 720$ K at $T = 300$ K and $P_o = 7 \times 10^{46}$ J^{-1} m^{-3}. The increased trap concentration by about order of magnitude is obviously caused by unintentional doping of NiPc during the ALD procedure. The doping occurs due to diffusion during the first stages of

ZnO growth, of the Zn precursor and water towards NiPc, facilitated by the natural porosity of the organic film as described earlier [15].

The $J - V$ dependence for the ITO/NiPc/Al cells is linear at a reverse bias above 1 V in the $\log(J) \sim \sqrt{U}$ coordinates, which implies conduction process either of the Schottky or of the Poole-Frenkel type [13, 17–21]. For the ITO/NiPc/ZnO/Al structures, the reverse bias $J - V$ curve has a complex profile (approximately N-like). A more detailed study of conduction mechanisms in these cells by impedance spectroscopy will be published elsewhere.

3.2. Light currents

Both types of cells are light sensitive, with the light-induced currents being considerably higher for the cells containing the heterojunction (Fig. 1B, log scale). The 4th quadrant of the $J - V$ graph is re-plotted in Fig. 1C on a linear scale, for proper comparison. The corresponding photovoltaic parameters are listed in Tab. 1. There, the fill factor was calculated as

$$FF = \frac{U_{MPP} \cdot J_{MPP}}{U_{oc} \cdot J_{sc}},$$

where U_{mpp} and J_{mpp} are experimental points corresponding to the maximum power output of the cell. Power conversion efficiency is given by [1, 3, 13, 21]:

$$\eta = \frac{FF \cdot J_{sc} \cdot U_{oc}}{P_{in}}.$$

Very low values of power conversion efficiency (η) are not surprising since the cells were not optimized (thickness, addition of transporting layers, adaptation of cathode material, encapsulation *etc.*). Nevertheless, our results indicate that η increases by 2.5 times after the introduction of a ZnO layer, as seen from Tab. 1. Open circuit voltage V_{oc} becomes slightly lower, which is likely due to the changing difference in actual positions of the energy levels of contacting materials (see Fig. 2). Some decrease of the fill factor for double-layer ITO/NiPc/ZnO/Al cells can be explained by an increased contribution of parasitic resistances [1–3, 13, 21] (Fig. 1C). These may become more apparent after subjecting relatively friable NiPc films to the ALD procedure.

Therefore, the improved value of η should be a consequence of a strongly increased short circuit current J_{sc} (Tab. 1). It is, in turn, proportional to i) absorption efficiency in the active material, ii) efficiency of exciton dissociation and iii) collection efficiency of free carriers at the electrode [1, 3]. In our case the first reason, that is, an expanded coverage of the incident light spectrum, is believed to dominate over the last two.

Table 1. Table of parameters.

Parameter →	U_{oc} (V)	J_{sc} (mA/cm^2)	FF	η, %
ITO/NiPc/Al	0,61	$3,9 \times 10^{-5}$	0,23	$7,3 \times 10^{-6}$
ITO/NiPc/ZnO/Al	0,51	$1,3 \times 10^{-4}$	0,20	$1,8 \times 10^{-5}$
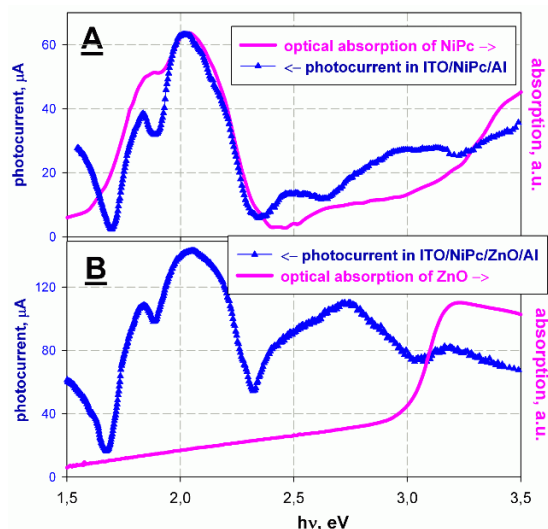
Figure 3. Photocurrent action spectra (blue curves with triangles) for single (A) and double-layer cells (B) compared to optical absorption (purple curves) of NiPc (A) and ZnO (B) layers.

3.3.   Spectral response

In order to compare the spectral sensitivity of the cells in more detail, the photocurrent action spectra were examined – Fig. 3A, B. One should keep in mind that efficiency of photoconversion in such sandwich cells is inevitably limited by inherent absorption of the glass/ITO substrate through which the light reaches the active layers. It becomes dominating at photon energies above 3.5 eV.

Both organic and inorganic semiconductors are optically active in their respective spectral domains. NiPc has two huge bands in the visible (around 620 nm [Fig. 3A]) and UV domain (around 340 nm). Since the latter is screened by the substrate, only the low-energy side of this band is seen in the right part of Fig. 3A. The former band (Q-band) at 2.0 eV is attributed to the first π–π^* electronic transition in the phthalocyanine macrocycle, that is from highest occupied (HOMO) to lowest unoccupied (LUMO) molecular orbital (see Fig. 2). This band is split in the crystalline state of phthalocyanines, giving an additional maximum at 1.8 eV [1, 13, 21, 25, 26]. As can be seen from Fig. 3A, the photocurrent action spectrum of the ITO/NiPc/Al cells al-

most entirely follows the molecular absorption. The origin of the small increase of photocurrent in the range of 2,5 and 2,9 eV is not completely understood.

ZnO strongly absorbs in the UV range but transmits visible light [8–11] (cf. Fig. 2; bandgap of ZnO is ~3.3–3.4 eV). The absorption edge is usually broad and extends to 2.9 eV (Fig. 3B). Again, most of the fundamental absorption of ZnO is cut off by the substrate, so that only some of the electrons excited from the valence band will contribute to the photocurrent.

The most prominent peak in the photocurrent action spectrum of the ITO/NiPc/ZnO/Al cell (Fig. 3B) is in the red part of the visible domain. From comparison with Fig. 3A, it reflects the contribution of molecular excitons created in NiPc upon absorption of photons. The broad photocurrent peak of low intensity at ~3.2 eV corresponds to the interband transition in ZnO [27]. The broad, middle intensity peak centered at ~2.7 eV is possibly associated with a defect structure of the ZnO layer [28], or with the presence of Zn(OH)$_2$ [29]. The rise of signal at wavelengths with energies <1.6 eV in Fig. 3B is most likely due to weakening of the photocurrent screening effect in highly absorptive NiPc pigment [25, 26]. Excitation of the trapped charge carriers or interfacial states cannot be ruled out.

3.4.   Long-term stability

Measurements made after aging of samples for 30 days reveal that the rectifying behavior of the ITO/NiPc/Al cells almost vanishes and RR is in the range of unity. This can be assigned to the degradation of the barrier properties of the NiPc/Al interface. In contrast, rectification properties of the ITO/NiPc/ZnO/Al cells deteriorate insignificantly, accompanied by some changes in the profile of the $J - V$ plot (see Supplementary file). RR is as high as 380, but becomes lower with increasing bias. The $J-V$ dependence at voltages higher than 0.3 V can be linearized in the full logarithmic scale.

Illumination causes a negligible photovoltaic effect in the ITO/NiPc/Al cells after aging. On the contrary, basic photovoltaic parameters remain almost on the same level in the aged ITO/NiPc/ZnO/Al cells. Therefore, adding a ZnO layer prevents degradation of electrical properties of the NiPc layer. Furthermore, the p−NiPc/n−ZnO heterojunction formed during ALD is expected to be more durable than the junction of NiPc with thermally evaporated aluminum.

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4. Conclusions

In this work, the applicability of the ALD technique to fabrication of hybrid photovoltaic cells based on nickel phthalocyanine was demonstrated for the first time. The double-layer structures containing a $p-$NiPc/$n-$ZnO heterojunction were obtained by sequential deposition of NiPc (thermal evaporation), ZnO (ALD) and Al (thermal evaporation); their dark and photo-induced electrical parameters have been analyzed. In comparison with the reference single-layer Schottky barrier cells (ITO/NiPc/Al), these cells exhibit much higher J_{sc}, which in turn results in the increase of overall power conversion efficiency by 2.5 times. Spectral measurements reveal that the principal reason for this is more effective capturing of incident photon flux in the double-layer structure. Moreover, the ultrathin ZnO interlayer plays an important role in protecting the phthalocyanine semiconductor and in stabilizing the output parameters of the photovoltaic cells in ambient conditions.

Acknowledgements

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