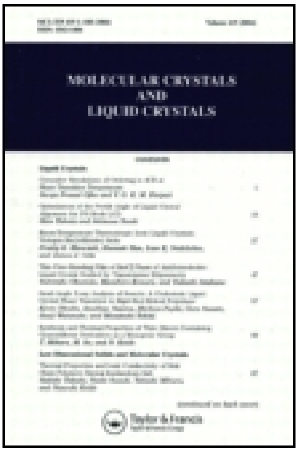

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Georgy L. Pakhomov [a] , Vlad V. Travkin [a] , Pavlo Y. Stakhira [b] , Vladislav V. Cherpak [b] & Dmitro Y. Volynyuk [b]

[a] Institute for Physics of Microstructures of the Russian Academy of Sciences, Russian Federation, Nizhny Novgorod, GSP

[b] Lviv Polytechnic National University, Lviv, Ukraine

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Electrical Properties of Phthalocyanine-Based Sandwich Cells with Embedded Ultrathin Metallic Layer

GEORGY L. PAKHOMOV,[1] VLAD V. TRAVKIN,[1]
PAVLO Y. STAKHIRA,[2] VLADISLAV V. CHERPAK,[2]
AND DMITRO Y. VOLYNYUK[2]

[1]Institute for Physics of Microstructures of the Russian Academy of Sciences, Russian Federation, Nizhny Novgorod, GSP
[2]Lviv Polytechnic National University, Lviv, Ukraine

This work describes the electrical characteristics of thin film sandwich cells with vanadyl phthalocyanine complex as a photoactive material in air and in water vapors. The characteristics are altered by the incorporation of an ultrathin metallic layer in phthalocyanine, so that the cells with the aluminum layer in the presence of mixed water/ammonia vapors may generate a significant output power in dark. The effect is assigned to the contribution of mobile ions appeared owing to electrochemical reactions at the metallic interlayer.

Keywords Conductivity; photovoltaic cells; phthalocyanines

Introduction

Recently [1], we have demonstrated how the environment modifies the electrical characteristics of single-layer cells based on vanadyl phthalocyanine (PcVO) photoconductor sandwiched between the indium tin oxide (ITO) anode and the top metallic cathode. The exposure of these cells to water vapors, or, more evidently, to a water/ammonia mixture, enables one to achieve an output electrical power in dark which is less but comparable to that produced due to the photovoltaic process. This effect was assigned to the chemical reactions running at the low work function metallic electrode, such as aluminum or indium. They are believed to be the reason for weak dark currents observed in cells of such a type which are often (most likely erroneously) regarded as the persistent or residual photoconductivity [2]. Next, it was found out that the insertion of an ultrathin zinc oxide interlayer under the cathode improves the photoconversion efficiency of the phthalocyanine-based cells and reduces their time degradation [3].

Address correspondence to Georgy L. Pakhomov, Institute for Physics of Microstructures of the Russian Academy of Sciences, Russian Federation, 603950 Nizhny Novgorod, GSP-105. E-mail: pakhomov@ipm.sci-nnov.ru

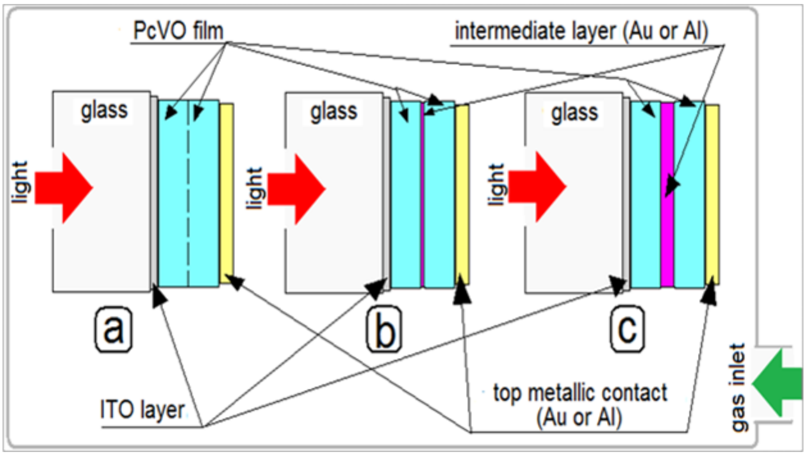


Figure 1. Schematic of samples.

To further investigate these processes, we have studied, in the present work, more complicated cells based on two equal PcVO layers with a thin metal layer (~10–20 nm) inserted in between (Fig. 1). The cells were then exposed to various gas or vapor atmospheres, and their current-vs-voltage (*J*-*V*) characteristics were measured in dark and under the white light illumination. There are reports in the literature on embedding ultrathin (non-continuous) metal layers in molecular films aimed at the improvement of a solar cell efficiency [4] or at the manufacturing of memory cells [5,6]. For instance, the aluminum interlayer thinner than 15 nm inserted in a tris(8-hydroxyquinolinato)aluminum (AlQ3) bilayer film was found to consist of individual clusters that further coalesce with increase in the thickness [5].

Experimental

The details of experimental procedures and measurements can be found elsewhere [1,3,7]. The interstitial metallic layer thickness was estimated by the white light interferometry using a non-contact optical profilometer TalySurf CCI2000 (Taylor&Hobson) and proved by a large-area atomic force microscope (Solver SMENA, NT-MDT).

Three types of cells were fabricated and tested: (a) reference cells without interstitial layer, (b) with an ultrathin layer ~10 nm thick and (c) with a thicker layer (~20 nm) (Fig. 1). As proved by optical spectroscopy, the transparency of such multilayered structures does markedly differ from that of the phthalocyanine layer alone. Only a slight increase of the spectral baseline was registered (about 10%), with no effect on positions of the basic absorption maxima in the electronic spectrum of a PcVO film.

Results and Discussion

Characteristics for the reference single-layer cells with Al and Au top electrodes in air are compared in Figure 2 (logarithmic coordinates). A typical diode-like dependence with the rectification ratio RR = 17 @1.6 V is observed for the cells with Al contacts, while ITO/PcVO/Au cells demonstrated almost symmetric dependences

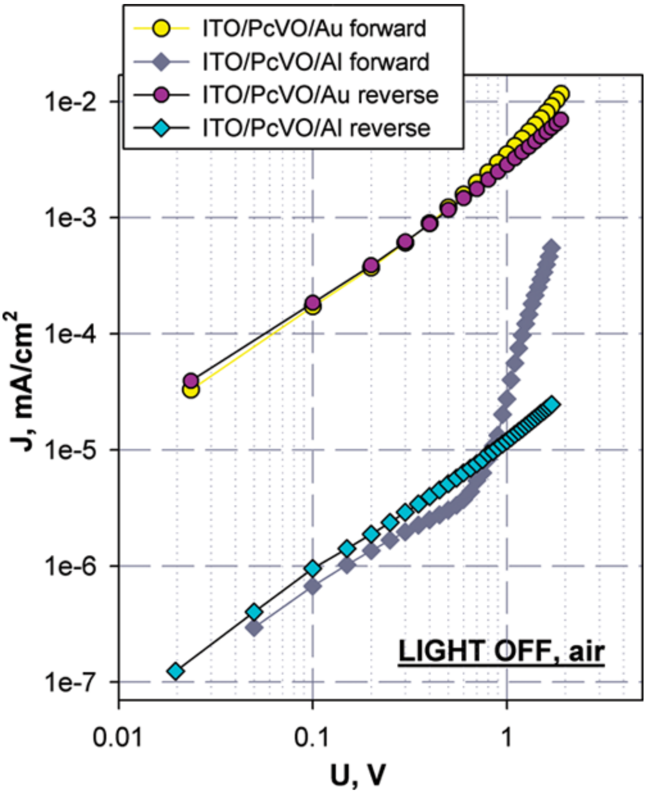


Figure 2. Comparison of dark *J-V* plots for single-layer cells with Al and Au top electrodes in air.

with RR = 1.4 (see Fig. 2). In the former case, the forward bias curves consist of two sections: the first section corresponds to ohmic currents, whereas the second section at voltages above 0.5 V conforms with the space charge limited current behavior (power index of 5.7). Reverse currents are always slightly non-linear – Figure 2.

Both dark and light-assisted conductivities of such cells in air are largely affected by embedding the metal layer into PcVO. Table 1 summarizes some output parameters. The ultrathin metallic layer ($\leq$10 nm, Al or Au) decreases the density of forward dark currents leaking through the cells, so that diode properties in dark practically vanish – Figure 3(a). However, under illumination, the presence of the Au interlayer becomes almost invisible: dependences of the cells with and without ultrathin gold layer are very similar – Figure 3(b). A probable reason may be the internal photoeffect or the scattering of light in gold nanoparticles composing the non-continuous metallic layer. The insertion of an Al interlayer simply deteriorates the cell's operation in air under illumination – Table 1 and Figure 3(b). It is not yet clear why the open circuit voltage is not constant as the cathode material remains unchanged – Table 1.

In the ITO/PcVO/Au cells, the dark current densities are about two orders of magnitude higher than those in similar cells with aluminum on top – Figure 2. Possibly, this can be caused by the diffusion of gold atoms inward the PcVO film depth and a partial carbonization of the interface, as revealed earlier in Ref. [7].

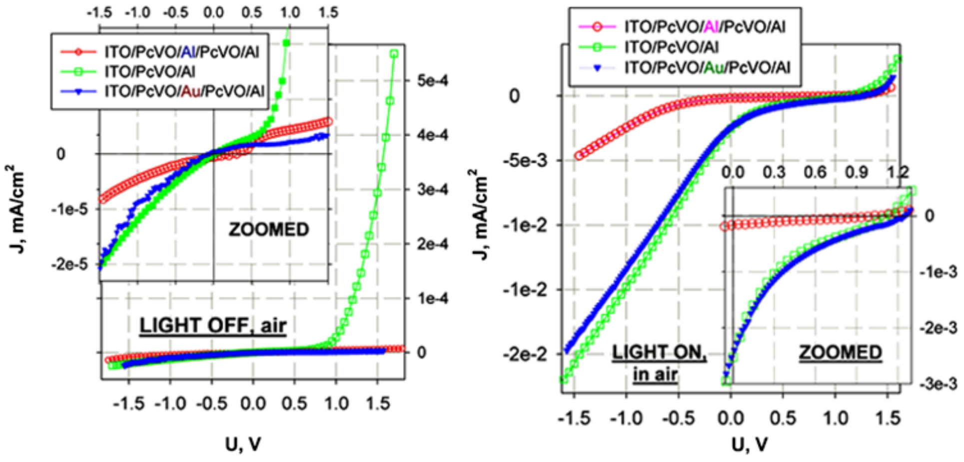
Table 1. Table of parameters

Cell structure	Conditions	U_{oc} (V)	J_{sc} (mA/cm^2)	FF	P_{out} (nW)	η (%)
ITO/PcVO/Al	In Air, light on	1.15	2.5e-3	0.11	320	4.2e-4
ITO/PcVO/Al/PcVO/Al	In Air, light on	1.06	1.7e-4	0.25	45	6.0e-5
ITO/PcVO/Al*/PcVO/Al	In Air, light on	0.62	7.9e-8	0.34	0.0017	2.2e-8
ITO/PcVO/Au/PcVO/Al	In Air, light on	1.25	2.5e-3	0.12	380	5.0e-4
ITO/PcVO/Al / PcVO/Al	H_2O, light on	1.16	2.5e-4	0.22	66	8.5e-5
ITO/PcVO/Al / PcVO/Al	H_2O, light off	0.95	2.2e-5	–	13	–
ITO/PcVO/Al / PcVO/Al	NH_3/H_2O, light on	0.47	1.3e-3	0.20	121	
ITO/PcVO/Al / PcVO/Al	NH_3/H_2O, light off	0.47	1.3e-3	–	120	–

$FF = U_{MPP} \cdot J_{MPP}/U_{oc} \cdot J_{sc}$ where U_{mpp}, J_{mpp} – experimental points corresponding to the maximum output power of the cell. Power conversion efficiency: $\eta = FF \cdot J_{sc} \cdot U_{oc}/P_{in} \times 100\%$.

$^*{\sim}20$ nm, in all other cases, the interlayer thickness is ≤ 10 nm (see the text).

Since neither a barrier nor oxide is formed in the case of a gold electrode, in contrast to Al, and the work functions of Au and ITO are similar, the *J-V* plots are almost symmetric and only slightly nonlinear – Figure 2. The ITO/PcVO/Au cells are light sensitive (photocurrent-to-dark current ratio is 20 @1.6 V), but the photovoltaic effect is, of course, absent.



(a) (b)

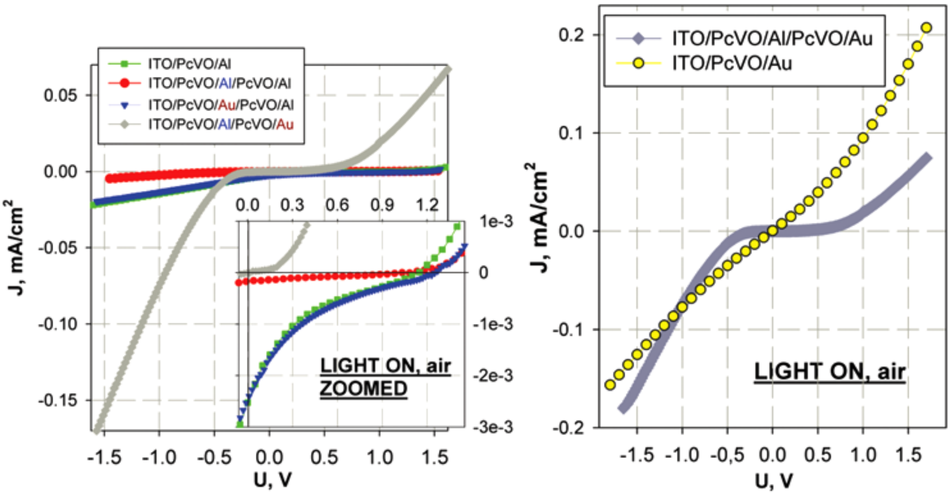
Figure 3. *J-V* plots measured in air for the cells having an Al or Au ultrathin interlayer, in dark (a) and under illumination (b).

The insertion of the Al interlayer into ITO/PcVO/Au cells leads to a change of the rectification direction and decreases the current densities – Figure 4(a). A very large hysteresis appears in dark (not seen in the same cells with Al top contact). It is presumably attributed to the trapping of charge carriers, whose contribution becomes visible in the cells with injecting Au-contacts.

Under illumination, the dependences are essentially nonlinear – Figure 4(b), but do not fit known equations. Again, no photovoltaic effect was detected. This implies that, indeed, the interlayer is insulated from any electrode, otherwise the cell would become asymmetric. The photocurrent is quite high (ratio to the dark current is 3500 @1.6 V at the reverse bias), and *J*-*V* plots of illuminated cells concur with those of the cells without Al layer, only the shape is different – Figure 4(b). Comparing this observation to [4], we can assume that the presence of a non-continuous gold layer leads to different optical field strengths (interference effects) in the photoactive regions of the thus modified PcVO cell.

The insertion of a thicker Al layer (~20 nm) results in the increase of the overall cell's resistance by about four orders of magnitude as compared to the single-layer cell and in the loss of photosensitivity (graphs not shown here).

Similarly to [1], in the presence of water vapor, all the studied cells demonstrate the battery effect in dark. This effect dramatically increases in mixed water + ammonia vapors, which may be explained by the action of ammonium and/or hydroxyl ions formed under such conditions. For the cells containing an ultrathin Al interlayer, the output power due to electrochemical reactions in dark is maximal – Table 1. Dark *J*-*V* plots of structures with an ultrathin Al layer are displaced from the point of origin in NH_3+H_2O vapors much stronger than under illumination in air and hence approach those measured due to the photovoltaic effect for the reference ITO/PcVO/Al cell – Figure 5. Notably, this displacement concerns basically the short circuit current.



(a) (b)

Figure 4. Dark *J*-*V* plots for the cells (Au on top) with and without ultrathin Al interlayer in air (a) and the same under illumination (b).

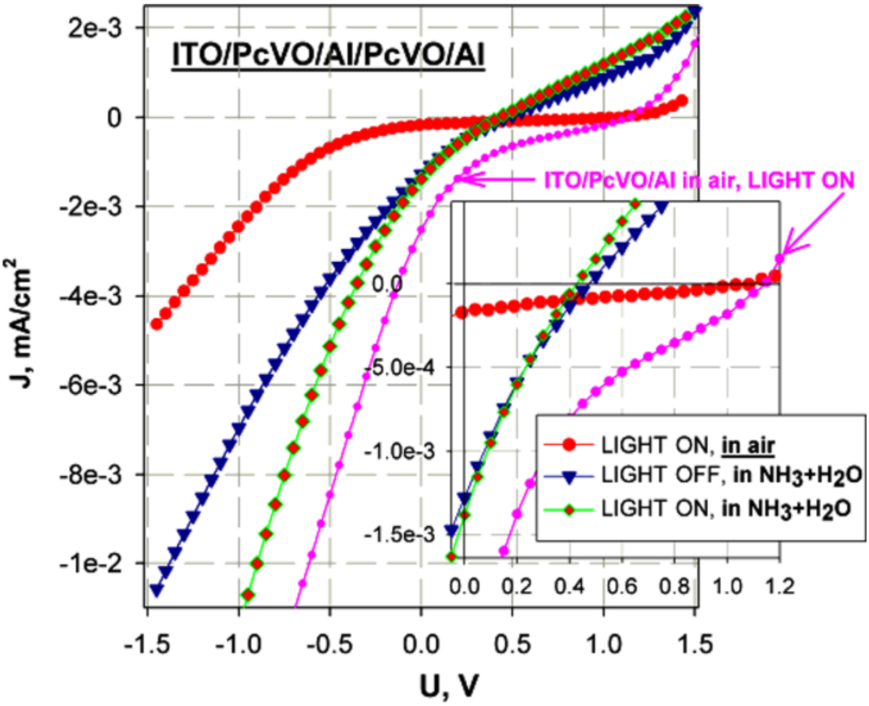


Figure 5. Comparison of *J-V* plots for the cells (Al on top) with ultrathin Al interlayer in $NH_3 + H_2O$ vapors in dark and under illumination with *J-V* plot of the same cell in air and with the reference ITO/PcVO/Al in air (for the last two, light is ON).

Therefore, in such a case, the ionic component of conductivity is reinforced by reactions at the intermediate Al layer. This component creates the independent parallel channel for the ionic current across the cell, which is, in contrast to the electronic current, light insensitive, thus making the action of external illumination negligible – Figure 5.

After the storage in $NH_3 + H_2O$ vapors overnight, the light sensitivity of these cells completely disappears (or even has the opposite sign), while the current density increases. This suggests that the ionic conductivity becomes the major mechanism. Additionally, reactions involving an ITO material cannot be ruled out [8].

Conclusions

In conclusion, we compared *J-V* plots for the phthalocyanine-based sandwich cells with and without an ultrathin interstitial layer (Al or Au), which is located in the middle of the PcVO film bulk and thus does not contact the bottom or top electrode. If the thickness of this interlayer is small enough, and the metal is Al, the output electrochemical power in dark in such cells exposed to saturated ammonia + water vapors exceeds that generated during the photovoltaic process under the 75 mW/cm^2 illumination in air. So, instead of being an obstacle for the charge transport across the PcVO film, the ultrathin Al interlayer serves as a source of mobile ions and hence facilitates the ionic conductivity. Additionally, we suggest that namely the battery effect [2] is most likely the origin of dark J_{sc} and U_{oc} [9]. This battery effect may however dominate over the electronic conductivity under certain conditions that are described in this work.

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