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Phthalocyanine-based photoelectrical cells: effect of environment on power conversion efficiency

Georgij L. Pakhomov · Lev G. Pakhomov ·
Vlad V. Travkin · Mikhail V. Abanin ·
Pavlo Y. Stakhira · Vladyslav V. Cherpak

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Abstract We have fabricated single-layer sandwich cells containing photoactive molecular layer (vanadyl phthalocyanine complex) and tested them in various environments. In contrast with dry gases, such as argon, oxygen, and ammonia, which cause the changes mainly in the first quadrant of *J*–*V* plots, addition of water vapor resulted in appearance of significant dark short-circuit currents and open circuit voltages. These values were amplified by the presence of mixed water and ammonia vapors. The observed effect is explained by the near-electrode reactions and by the existence of ionic component of conductivity in phthalocyanine layer, which give rise to generation of output electrical power in the dark. The power conversion efficiency under the white light illumination does not follow this trend being the highest in an inert atmosphere (argon). Changing the material of the top metal electrode from aluminum or indium to gold terminates both photovoltaic and dark power generating processes, though sensitivity of the current to vapors holds out.

Introduction

Photovoltaic effects in thin films of porphyrins and phthalocyanines (Pc) are mostly studied in the single-layer sandwich cells, where one electrode is transparent (like indium tin oxide, ITO), and another (top) electrode is evaporated metal of low work function (e.g., Al, In, Pb, Mg). This metallic layer is usually thin and reactive, so that the Pc/metal interface is chemically and morphologically unstable, being dependent on the sample history and environment. The diffusion rates of admixtures coming from ambient air (like oxygen, water [1]) are high enough to allow their free migration within the Pc layer and, hence, delivery of reactants to any interface within the time less or comparable with duration of measurements. This partly explains some dispersion of literature data obtained for such cells and urges to use either strongly controlled conditions (inert gases, vacuum) or encapsulation.

Actual conditions (oxidation, corrosion, interfacial reactions) at the Pc/metal junction, strongly affect (photo-)electrical properties of the Schottky type cells, as well as the cells containing a heterojunction [2–8]. As suggested in some reports, photovoltaic effects observed in different atmospheres may be accompanied, or even replaced, by electrode reactions [2–11], often leading to switching [9, 10, 12, 13]. Dark open circuit voltages and short-circuit currents were also observed in the Schottky type cells incorporating various porphyrins and phthalocyanine compounds [3, 5, 7]. However, these processes are not completely understood and require additional investigations in each particular case. In this work, we report on photovoltaic measurements on the glass/ITO/PcVO/Al cells in different gaseous atmospheres, where PcVO is vanadyl phthalocyanine complex ($C_{32}N_8H_{16}V{=}O$), a well-known molecular photoreceptor of porphyrin type [14].

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G. L. Pakhomov (✉) · L. G. Pakhomov ·
V. V. Travkin · M. V. Abanin
Institute for Physics of Microstructures of the Russian Academy of Sciences, GSP-105, 603950 Nizhny Novgorod, Russian Federation
e-mail: pakhomov@ipm.sci-nnov.ru

P. Y. Stakhira · V. V. Cherpak
Lviv Polytechnic National University, 12, S. Bandery Str., 79013 Lviv, Ukraine

Experimental

Initial PcVO powder of pigment grade was routinely sublimed in vacuum ($\sim 10^{-3}$ Pa, VUP-5M) onto the precleaned standard ITO covered glass substrates (Aldrich) under variable conditions, such as deposition rate and substrate temperature [11]. Thus, we obtained structurally dissimilar layers composed predominantly of monoclinic, triclinic, or amorphous phase [9, 10]. The structure of layers was verified by means of the X-ray diffraction, UV/Vis/NIR and FT-IR spectroscopy, and atomic force microscopy (will be published elsewhere). In the present work, we discuss mainly polycrystalline PcVO layers with monoclinic modification. Next, the VOPc films on the substrates were transferred to evaporator, where they were covered with metallic layer through the mask (cathode). We used basically Al, but Au and In cathodes were also evaporated for comparison. The working area of thus fabricated devices was $\sim 3 \times 10^{-2}$ cm^2. Experimental details were described earlier [11]. Immediately after fabrication, the devices were placed into a sealed steel cuvette filled with dry air, argon, oxygen, or ammonia for photoelectrical measurements at room temperature. In several experiments, samples were exposed to water- or water-saturated ammonia vapors (pressures: $P_{\mathrm{H_2O}} \approx 3.2$ kPa and $P_{\mathrm{NH_3/H_2O}} \approx 11$ kPa/2 kPa, respectively), under the same conditions. Use of strong oxidizing agents (like NO_2) causes changes in the redox state of phthalocyanine molecule. Consequently, in addition to the corrosion of electrodes, oxidizing gas largely affects conductivity (often irreversibly), visual color and, in general, chemical nature of the phthalocyanine layer (formation of ion-radical salt) making further comparison meaningless.

Current-versus-voltage (*J*–*V*) characteristics were recorded in the dark and under illumination from ITO side through the glass window in the cuvette. A 40 W tungsten lamp was used to illuminate the samples, which provides intensity of incident light of 70 mW/cm^2. The sweeping rate was intentionally set up to “quiet” regime (delay time of 2 s or more between successive readings) to avoid offset and hysteresis caused by re-charging of a double ionic layer capacitance at the PcVO/ITO interface [9, 10]. Several samples were measured in each series (atmosphere, light on/off switching) with particular care in the recovery of initial signal.

Results

As seen from Fig. 1, both the dark- and light-assisted currents in the ITO/PcVO/Al cells depend on the atmosphere. In the dark, the curves changes only in the first quadrant of *J*–*V* plot, whereas the dependences in the third quadrant remain almost unaltered. The highest rectification ratio (RR) was found in air (RR = 14 at 1.5 V), the lowest—in ammonia atmosphere (RR = 1.05). It should be noted that the characteristics of these cells degrade inevitably with time (during several hours, days), regardless of the atmosphere in which they have been kept, and also with number of sweeps recorded on them [3]. However, the irreversibility of *J*–*V* dependences shown in Fig. 1 (see, red line with triangles: samples exposed back to air after measurements in different gases) is thought to be caused by the gas treatment but not by natural aging of samples, which takes much longer period.

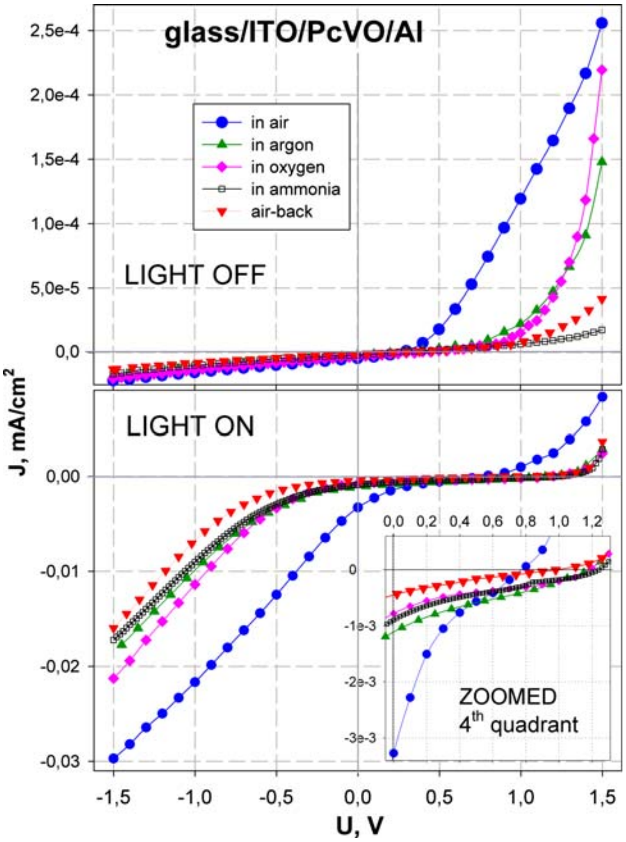

Fig. 1 Dark and light *J*–*V* plots for the cells with a 200-nm thick crystalline PcVO layer measured in different atmospheres (top-to-down sequence) and back in air at room temperature. Forward bias corresponds to the positively charged ITO electrode

Even in the dark, the *J*–*V* curves measured in various environments do not pass exactly through the point of origin in some cases (cf. [9, 10]), being slightly shifted toward the negative part of *y*-axis. However, these deviations are negligible and comparable with the level of noise or instrumental errors, so they will not be taken into account here.

For the cells in air, the dark forward *J*–*V* dependences can be linearized in full logarithmic scale at voltages above 1 V, with slope angle being equal to 2. This is what one would expect for phthalocyanine films with one ohmic contact when amount of charge carriers injected from the contact into the bulk exceeds the thermally generated ones, thus the space charge limited current dominates over Ohm's law [3, 14–16].

In contrast, for the cells tested in the Ar, O_2, or NH_3 atmospheres, a better straightness was been obtained in the semi-logarithmic coordinates. Therefore, the forward J–V dependences do not obey the power law under these conditions. Instead, they can be well fitted by exponential function suggesting diode-like behavior [17].

At the reverse bias, the dependences are nearly linear in any atmosphere (Fig. 1).

The ITO/PcVO/Al cells demonstrate strong photovoltaic effect under illumination. Gaseous atmosphere has little effect on light-assisted currents, especially in the first quadrant of the J–V plot, except for the samples measured in air (Fig. 1). In the latter case, the output characteristics of the cells seem to suffer from additional parasitic resistances that make fill factor (FF) lower, and from the decrease of open circuit voltage V_{oc} (Table 1). Generally, the ITO/PcVO/Al cells behave more like photodiodes than the power generating photoelements. The ratio of the light-assisted current to dark current (J_{light}/J_{dark}) at 1 V is about 10 under forward and above 1,500 under reverse bias for ITO/PcVO/Al cells in air. The resulting power conversion efficiency η is very low (Table 1), as expected for the non-optimized Schottky type cells [15, 16, 18]. In the best samples, the value of η around 0.001% was achieved.

The J–V curves in the fourth quadrant are re-plotted in the inset in Fig. 2, for clarity. The largest short-circuit current J_{sc} was detected for the cells in air, while the largest V_{oc}—in NH_3 gas (1.24 V), which determines nearly similar η (Table 1). Notably, the cells with indium cathode deposited under the same conditions instead of aluminum (i.e., ITO/PcVO/In) exhibit always lower RR in the dark. They are less efficient under the light, regardless of the atmosphere [3]. The latter tendency is mostly due to significantly decreased V_{oc}, whereas J_{sc} is slightly higher than that in the cells with Al top cathode.

In our previous work, the ITO/NiPc/Al cells were tested in the presence of saturated ammonia vapor in humid air [7]. We showed that redox reactions running at nickel phthalocyanine/aluminum interface are responsible for generation of electrical power. In order to elucidate this better, the cuvette with ITO/PcVO/Al(In) samples were filled with either saturated NH_3/H_2O or pure H_2O vapor, and the readings were taken (Figs. 2, 3). Under such conditions, profiles of the dark J–V dependences were completely modified, for both forward and reverse bias, as compared with previous experiments (see Fig. 1). Rectification practically disappears or even changes the direction (Figs. 2, 3). This switching of rectification appears to be conceptually similar to the observations in Refs. [12, 13].

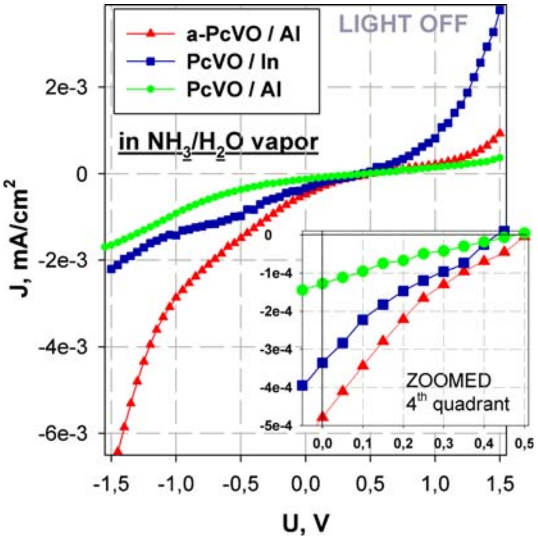

Fig. 2 J–V plots for the cells with a 200-nm thick PcVO layer and Al or In cathode, and with less crystalline (denoted as a-PcVO) layer [14], measured in the $NH_3 + H_2O$ vapor in the dark

Table 1 Table of parameters

Interface	Conditions	U_{oc} (V)	J_{sc} (mA/cm^2)	FF	P_{out} (nW)	η (%)
a-PcVO/Al	In Ar, light on	0.21	1.3e−2	0.21	16.0	8.1e−4
PcVO/Al	In air, light on	0.78	3.3e−3	0.13	9.2	4.7e−4
PcVO/Al	In NH_3, light on	1.24	9.0e−4	0.21	6.0	3.4e−4
PcVO/In	In air, light on	0.23	3.9e−3	0.30	7.7	3.9e−4
a-PcVO/Al	NH_3/H_2O vapor, light on	0.50	2.3e−3	0.25	8.1	4.1e−4
a-PcVO/Al	NH_3/H_2O vapor, light off	0.50	5.2e−4	–	1.2	–
PcVO/In	NH_3/H_2O vapor, light off	0.46	3.0e−4	–	0.8	–
PcVO/Al	H_2O vapor, light off	0.55	6.3e−5	–	0.2	–

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

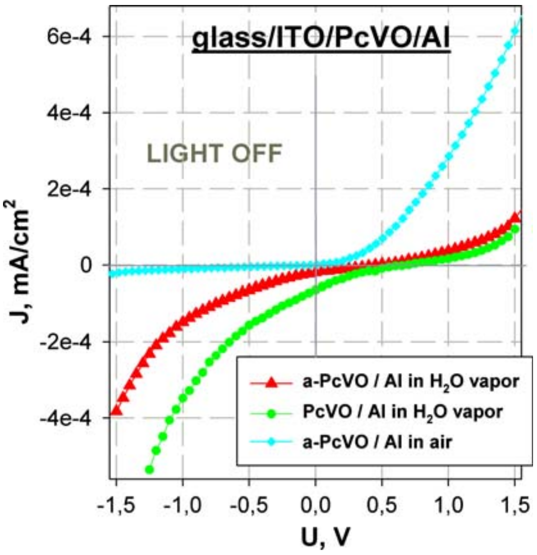

Fig. 3 *J*–*V* plots for the cells with a 200 nm thick PcVO layer with different morphology (see Fig. 2) measured in the dark in H_2O vapor and for the same cell in air, for comparison

In the presence of ammonia + water vapor, the cells generate electrical energy in the dark, which is only five times lower than the power converted from the light (Table 1). This effect is getting less intensive but still remains when indium top contact is used (Fig. 2). Therefore, appearance of dark-V_{oc} and dark-J_{sc} cannot be unambiguously attributed to the role of Al in electrochemical reactions or to the specific phthalocyanine compound, as suggested earlier [3, 7]. Most likely, output of the cells reflects electrochemical processes running at the reactive top electrode, in which the existence of built-in potential and formation of oxides [7] are prerequisites. This assumption is supported by the fact that the cells with noble metal top contact (i.e., ITO/PcVO/Au) showed almost symmetric *J*–*V* curves both in the dark and under illumination in any atmosphere, with no significant deviations from the point of origin (not shown here (see, supplementary data)).

Moreover, a weak but distinguishable electrical power is produced when the water vapor alone is inflated into the cuvette (Table 1). It means that the action of ammonia is important for getting a higher power yield in the dark, but not essential for changing the rectifying behavior of the cells, as can be concluded from Fig. 3. It is worth noticing, that the shape of *J*–*V* plots in the dark in the presence of humidity closely resembles that measured under illumination in a dry (or inert) atmosphere, therefore, they can easily be confused with persistent photoconductivity. The values of dark-V_{oc} and dark-J_{sc} are sensitive to the polarity of electrodes and to number of sweeps taken, i.e., to the history of the sample. These parameters tend to decrease with multiple repetitions of measurements. Note, that corrosion of the bottom contact (ITO) cannot be completely ruled out [9, 10, 18].

Additional experiments were done with PcVO films having different morphology. As known, sublimation of PcVO at very high rate on non-heated substrates results in formation of films with nearly amorphous structure (a-PcVO) (see, e.g., [14] and references therein). Despite the fact that chemical nature of interacting materials remain the same (e.g., redox potentials) and energy level diagram of the cell would not change, morphology of phthalocyanine layer is still an important factor, as can be seen from Figs. 2, 3 and Table 1. While dark-V_{oc} is approximately similar for the cells with PcVO/Al interface, dark-J_{sc} is different. This can be explained by different mobility of ions in quazi-amorphous and fully crystalline phases of PcVO.

Although the catalytic activity of metallocomplexes of phthalocyanine is well-known, it appears to have nothing to do with the above effects. They have already been observed in various cells based on porphyrins and other organic compounds including those without catalytic properties [2–6, 18].

The photovoltaic effect in the samples tested in $NH_3 + H_2O$ or H_2O vapor under illumination is somewhat weaker than in the case of other (dry) atmospheres (see, example in Table 1). Furthermore, it has to be compared to already existing output power in the dark. So, the value of J_{light}/J_{dark} measured for ITO/PcVO/Al cells in $NH_3 + H_2O$ vapor is 2.8 under forward and 23 under reverse bias (see supplementary data).

Discussion

Obviously, the described effects are due to the ionic component of the dark conductivity, which is stimulated by incoming gaseous admixtures and maintained by internal electrical field in asymmetrical sandwich cells. The ionic species are, most likely, formed in the vicinity of the PcVO/metal interface due to free uptake and travel of gas molecules in PcVO layer, thus contributing to redox reactions at the metallic electrode. This electrochemical component seems to be inevitable in such disordered layers composed of low molecular weight compounds [9, 10] but is usually suppressed by thorough keeping high vacuum or fully inert conditions, or by packaging of devices. Nonetheless, it merits additional investigation, since parallel mass transfer processes like this are believed to be responsible for degradation (including parasitic resistances, electrical shorts, and corrosion of electrodes). The question also arises whether this component in itself can be utilized with benefit. For example, switching of rectification by vapors shown in Figs. 2, 3 may be useful.

Conclusion

It is shown that both the dark- and light-assisted currents in the Schottky type cells with photoactive PcVO layer are modified by surrounding gaseous atmosphere. In particular, exposure of samples to the moisture causes appearance of significant dark-J_{sc} and dark-V_{oc}, so that electrochemical power up to 0.2 nW is generated from device area less than 3 mm^2. Meanwhile, photovoltaic parameters, including η, are less affected.

First, this observation implies a very rapid diffusion of absorbed small molecules inside of the phthalocyanine layer. Ionic component of conductivity and/or electrode reactions may contribute substantially to the output characteristics of the phthalocyanine-based devices, also from viewpoint of reversibility and stability. More accurate information can be obtained using time(frequency)-resolved methods, such as impedance spectroscopy (in progress).

Second, great care should be taken of control over actual humidity when carrying out measurements on such type of cells in laboratory conditions. Taking into account that transition metal phthalocyanines selectively interact with ammonia molecules, the prospects for self-contained chemical sensing can be outlined [8].

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