

Electrical properties of hybrid planar diode based on palladium phthalocyanine and titanium dioxide*

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This work presents experimental studies of a planar diode made of the layers of indium tin oxide, titanium dioxide, palladium phthalocyanine and gold. The current rectification ratio was 10^5 at 1.5 V. The analysis of the electrical properties of the system was based on small signal complex capacitance spectra measured in the frequency range of 25 Hz – 1 MHz at different values of bias. No depletion region at the TiO_2/PdPc interface was observed. Forward bias specifically affected both parts of the complex capacitance and the observed effect probably resulted from the rearrangement of charge carriers injected into the organic layer.

Keywords: *organic diode; palladium phthalocyanine; titanium dioxide*

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1. Introduction

This work deals with the experimental studies of the electrical properties of a planar device with an organic-inorganic heterojunction. The system was composed of palladium phthalocyanine (PdPc), applied as an organic material, and titanium dioxide (TiO_2) applied as an inorganic one. We classified it as a hybrid planar diode since it exhibited significant ability to rectify current. The value of rectification ratio as high as 10^5 at 1.5 V is larger than typical values obtained in the other systems with organic layers [1–3]. Therefore, the electrical properties of this system seem to be worth considering. In this study, we attempt to find whether or not the electrical properties of this system are similar to those of semiconductor p-n heterojunctions.

The electrical properties of the systems with planar PdPc/ TiO_2 junctions are also worth studying since the systems containing phthalocyanine and titanium dioxide are promising for photovoltaic applications [4–10]. Devices with a planar hybrid heterojunction may not convert the energy as effectively as the bulk ones, however, they play a significant role

in research. By virtue of their one-dimensional description, planar systems are suitable for the experimental studies of the processes occurring in hybrid heterojunctions.

The subject of this work is a planar system made of thin layers of indium tin oxide, titanium dioxide, palladium phthalocyanine and gold ($\text{ITO}/\text{TiO}_2/\text{PdPc}/\text{Au}$). Our analysis of the electrical properties of the system was based on the spectra of small signal complex capacitance (SSCC). To the best of our knowledge, this experimental method has not yet been applied to planar bilayer systems made of TiO_2 and metallophthalocyanine. However, the methods based on SSCC are commonly used in the studies of inorganic diodes since this approach is particularly useful in the case of semiconductor systems with a region depleted of free charge carriers [11]. Obviously, the similarities in the direct current-voltage characteristics between organic and inorganic systems do not imply similarities in the nature of the processes determining the electrical properties of these systems [12, 13]. Therefore, our aim was to reach general conclusions concerning the charge-carrier transport through the $\text{ITO}/\text{TiO}_2/\text{PdPc}/\text{Au}$ system, without assuming the presence of a depletion region at the TiO_2/PdPc interface. Our analysis focuses on the small signal complex capacitance spectra obtained in the frequency range of 25 Hz – 1 MHz at different values

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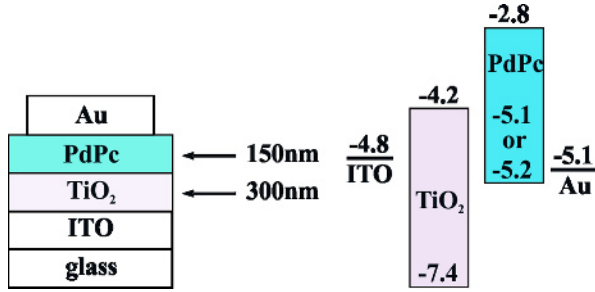


Fig. 1. Structure of the device (left) and the energy-level diagram of the materials used (right). The values of Fermi levels of the electrodes and hole-transport and electron-transport levels are given with respect to the vacuum level.

of bias. The relationship between the SSCC spectra and the direct current (dc) curve is discussed.

2. Experimental details

Fig. 1 shows the structure of the device. Sol-gel-derived TiO_2 films were deposited on an indium tin oxide substrate (ITO: thickness 35 nm, $100 \Omega/\text{square}$) by spin coating at a rate of 100 rps. The starting solution for coating was prepared by mixing titanium (IV) butoxide (97 %) with ethanol (EtOH) at the molar ratio of 1:5, and with acetylacetone (AcAc) as a complexing agent. The resulting gel layers were dried for 24 h at room temperature and then heated at 500°C for 1 h in order to obtain smooth homogeneous TiO_2 films. The thickness of the TiO_2 films, measured with a profilometer, was about 300 nm.

The system of glass/ITO/ TiO_2 was subsequently placed under vacuum of 3×10^{-4} Pa (Auto 306Turbo, Edwards), where the layers of PdPc (150 nm thick) and Au, as the top electrode, were thermally evaporated at a deposition rate of $0.5 \text{ \AA}/\text{s}$. The active area of the electrodes in the devices was $4\text{--}6 \text{ mm}^2$.

SSCC spectra were measured in the frequency range of 25 Hz–1 MHz with a Hewlett Packard 4284A LCR meter. The amplitude of the alternating voltage was constant with a root mean square value of 10 mV. For direct current measurements a Keithley 6517 electrometer was used.

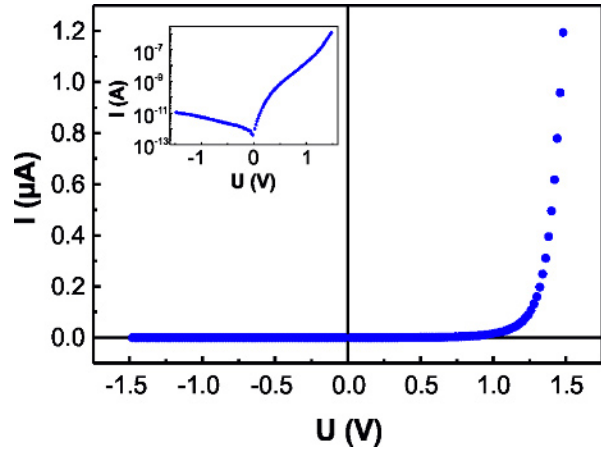


Fig. 2. Direct current-voltage curve on a linear plot. The inset shows the results on a semi-log scale.

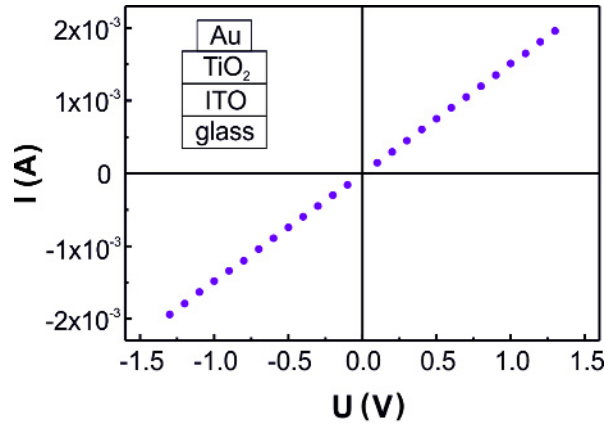


Fig. 3. Current versus voltage obtained for the ITO/ TiO_2 /Au system.

3. Experimental results

Representative experimental results obtained for one of the ITO/ TiO_2 /PdPc/Au samples are presented in Figs. 2 and 4. The direct current-voltage curve of the sample is shown in Fig. 2. Positive values of the voltage indicate higher potential on Au. Fig. 3 shows the direct current versus voltage curve obtained for the system without a PdPc layer, *i.e.* glass/ITO/ TiO_2 /Au.

SSCC spectra are shown in Fig. 4. Open symbols denote the real part (C'), whereas solid symbols denote the imaginary part (C''). The sign of the bias in the SSCC and dc measurements was denoted in the same manner.

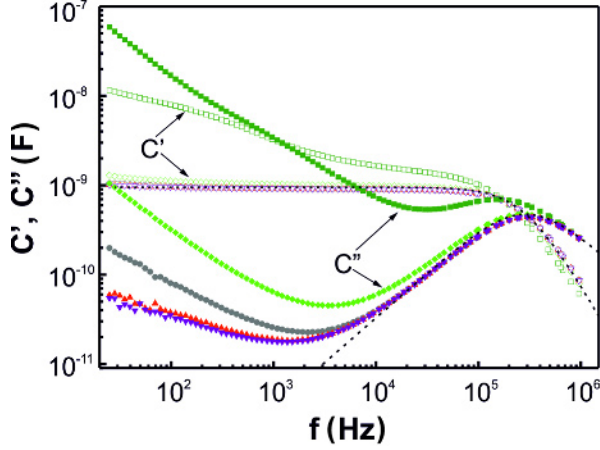


Fig. 4. Real (open symbols) and imaginary (solid symbols) parts of the small signal capacitance versus frequency. The curves were obtained at the following values of the applied voltage: -1.4 V (purple ∇ , ∇), -0.8 V (red $\blacktriangle$, $\triangle$), 0 V (grey $\bullet$, $\circ$), $+0.8$ V (green $\blacklozenge$, $\lozenge$), $+1.4$ V (olive $\blacksquare$, $\square$). The $\triangle$ and $\circ$ symbols coincide with the ∇ symbols. Dashed lines denote the response of $C_g = 0.95$ nF and $R_s = 0.58$ k Ω connected in series.

4. Discussion

Direct current was strongly rectified by the ITO/TiO₂/PdPc/Au system (Fig. 2). The ratio of the forward current to the reverse current was 10^5 at 1.5 V. Forward polarization was observed when Au was at a higher potential. Taking into account the electrical properties of PdPc and TiO₂, as well as the energy levels of the four materials of which the device was made (Fig. 1), we can just predict the forward polarization to be +Au/-ITO. The p-type properties of PdPc layers were confirmed experimentally [10, 14] and the depth of the hole-transport level (HTL) for the PdPc layer was the same as for the copper phthalocyanine layer [15, 16]. The TiO₂ layers are highly capable of transporting electrons [4, 5, 17]. The difference between the edge of the conduction band (CB) for TiO₂ and the Fermi level of ITO, as well as the difference between the Fermi level of Au and the HTL for PdPc are lower than the difference between the edge of CB for TiO₂ and the HTL for PdPc (see the diagram in Fig. 1). Therefore, we expect the PdPc/TiO₂ interface to play a significant role in determining the electrical proper-

ties of the device. In case of forward bias, the holes injected by Au into the PdPc can recombine at this interface with the electrons injected by ITO into the TiO₂. In the case of opposite polarization, since we can rather exclude the injection of electrons by Au into PdPc and of holes by ITO into TiO₂, we can assume that the reverse current is determined by the generation of charge carriers at the PdPc/TiO₂ interface. The question is whether we can find any similarities between the PdPc/TiO₂ heterojunction and a semiconductor p-n junction. In other words, is there any experimental evidence for the presence of a depletion region and band bending at the interface? Starting with the direct current, we can verify whether the forward current can be described by the general formula [11]:

$$j = j_0 \left(\exp \left(\frac{qU}{nkT} \right) - 1 \right), \quad (1)$$

where q is the electron charge, k is the Boltzmann constant, T is temperature, and U is the applied voltage. The parameter n is termed the ideality factor and it can take values in the interval $1 \leq n \leq 2$. This means that such values satisfy the criteria of semiconductor model of p-n junction [11, 18]. However, in the case of our device, the curve of forward current versus applied voltage is not a straight line on a semi-log scale (inset in Fig. 2). Here, the ideality factor is a function of the applied voltage. For higher values of the applied voltage, we can easily estimate the value of n , since the -1 term on the right side of Eq. (1) is then negligible. For the ITO/TiO₂/PdPc/Au system, for forward bias, the value of $n > 2$ was obtained for $U > 0.1$ V. Thus, considering the dc curve, it is highly unlikely that a depletion region resulting in band bending occurs at the PdPc/TiO₂ interface.

Investigation of depletion region in semiconductor devices is most often based on the measurements of small signal capacitance. This method is complementary to the dc method since it allows one to observe the effect of bias on the width of the depletion region and to estimate the diffusion potential, the density of doping and the distribution of this density in the vicinity of the junction [11, 19].

The capacitance of the depletion region was measured using the small signal technique for dif-

ferent values of the reverse bias. The real and imaginary parts of SSCC spectra obtained for the ITO/TiO₂/PdPc/Au system for selected values of bias are presented in Fig. 4. At a reverse bias, both parts of the complex capacitance are mainly determined by two ideal elements, namely by a capacitor of 0.95 nF and a resistor of 0.58 kΩ. The value of 0.58 kΩ was obtained from the real part of the impedance in the higher frequency range, according to the procedure presented in [20], whereas the value of 0.95 nF is the real part of the capacitance at a reverse bias in the lower range of frequency. In Fig. 4, dashed lines show the response of the capacitance of 0.95 nF and the resistance of 0.58 kΩ connected in series. The value of 0.95 nF is the geometric capacitance of the PdPc layer:

$$C_g = \epsilon_o \epsilon_r S / d, \quad (2)$$

where ϵ_o is the vacuum permittivity; ϵ_r is the relative permittivity of PdPc; d is the thickness of the PdPc layer; and S is the active area of the electrodes. Our previous investigations of a single layer of PdPc with planar electrodes confirmed that the dielectric constant of PdPc is independent of frequency in the range of 25 Hz – 1 MHz, and that its value does not deviate from those typical of metalophthalocyanines [21]. The resistance of 0.58 kΩ can be interpreted as a sum of the electrode resistance and the resistance of the TiO₂ layer. Our research shows that a single layer of TiO₂ with ITO and Au electrodes exhibits ohmic characteristics without any current rectification (Fig. 3). From the results in Fig. 3, we can obtain the resistance of the ITO/PdPc/Au system, here equal to 0.667 kΩ. This value can be compared to the value of 0.58 kΩ. The difference between these two values results merely from the difference in the active area of the electrodes.

Fig. 4 shows that the real part of the capacitance was not affected by the reverse bias (compare C' at $U = -0.8$ V and at $U = -1.4$ V). These curves were determined only by C_g for frequencies below 10⁵ Hz and by C_g and $R_s = 0.58$ kΩ for higher frequencies. Therefore, it can be said that no effect corresponding to a depletion region at the PdPc/TiO₂ interface was noticeable in the SSCC spectra at the reverse bias.

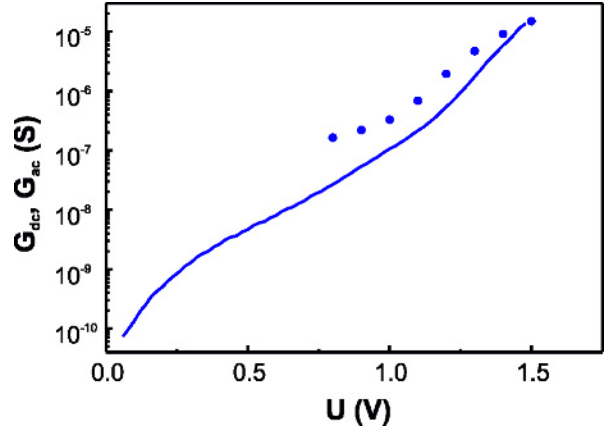


Fig. 5. Differential direct current conductance (lines) and the small signal conductance (points) versus forward bias. The values of G_{dc} were extracted from the results presented in Fig. 2, whereas the values of G_{ac} were calculated from the values of C'' at 25 Hz.

However, the forward bias explicitly affected the SSCC spectra. It resulted in an increase in the values of both components of the complex capacitance, with the effect increasing for lower values of the frequency. Since this effect was enhanced by the forward polarization, we presume that it resulted from the rearrangement of charge carriers injected into the PdPc layer. At $U = +1.4$ V, the curves were qualitatively similar to the response of a p-n junction at a forward bias since they resembled the response of diffusion transport of minority carriers. However, the slopes of C' and C'' versus frequency did not agree with the model corresponding to a semiconductor p-n junction and, therefore, interpreting of the observed charge rearrangement according to the semiconductor model would be dubious. We can check here whether the imaginary part of the small signal capacitance (C'') is directly related to the direct current. At $U = +1.4$ V, the imaginary part of the capacitance significantly exceeded the real part for lower values of the frequency. We can compare $2\pi f C''$ at $f = 25$ Hz with dI/dU estimated from the direct current curve. Fig. 5 presents both the small signal conductance ($G_{ac} = 2\pi f C''$), denoted with points, and the differential direct current conductance ($G_{dc} = dI/dU$), denoted with a line. G_{ac} exhibited the same tendency as G_{dc} , however, it

had higher values than G_{dc} for a bias below 1.5 V. Therefore, we conclude that G_{ac} and G_{dc} are expected to be equal for frequencies below those used here, since even at $f = 25$ Hz, the rearrangement of the injected charge carriers was noticeable.

5. Conclusions

Our investigations allowed us to conclude that:

- direct current was strongly rectified by the ITO/TiO₂/PdPc/Au system, with a rectification ratio of 10^5 at 1.5 V,
- at a reverse bias, the real part of the small signal capacitance was determined by the geometric capacitance and no depletion region at the TiO₂/PdPc interface was noticeable,
- forward bias affected both the real and imaginary part of the small signal capacitance and the observed effect probably resulted from the rearrangement of charge carriers injected into the PdPc layer.

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