Smart actuators based on electromechanically active conjugated polymer diodes

Gilles Dennler[1*], Reinhard Schwödiauer[2], Christoph Lungenschmied[1], Siegfried Bauer[2], Niyazi Serdar Sariciftci[1], and Howard Reiss[3]

[1]Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, [2]Institute of Experimental Physics, Department of Soft-Matter Physics, Johannes Kepler University, Altenbergerstrasse 69, A-4040, Linz, Austria, and [3]University of California, Department of Chemistry and Biochemistry, 607 Charles E. Young Drive East, Los Angeles, CA 90095.

**To whom correspondence should be addressed. E-mail : gilles.dennler@jku.at*

ABSTRACT

Conjugated polymers are nowadays used in two different types of device. On the one hand, they act as electronically active semiconducting/conducting materials in organic electronic devices. On the other hand, one exploits them as electromechanically active materials since it has been observed that they can experience huge macroscopic strains upon electrochemical doping. We investigated the combination of these two effects by measuring the electromechanical behavior of typical polymeric electronic devices like rectifying (and/or light emitting) diodes. In the case of a poly(*para*-phenylene-vinylene) (MDMO-PPV) based diodes, we observed two types of electromechanical actuation. In the forward direction, a significant current (up to several mA/cm^2) is flowing. Joule heating induces a thermo-electrostrictive bending of the device substrate. In the reverse direction, the diode behaves like a capacitor. Therefore the strains are induced by Maxwell forces. For poly(3-hexyl-thiophene) (P3HT) based diodes, displacement versus voltage in the reverse direction revealed a power law with an exponent of 1.5. This surprising result can be modeled by Coulombic attraction of the doped impurities present in the depletion zone and the charges present in the metal at the interface.

Keywords: conjugated polymers; organic electronics; diodes; electrostriction; joule heating; Schottky; PPV; P3HT.

1. INTRODUCTION

The discovery of the conducting and semiconducting properties [1] of conjugated polymers [2] resulted in the development of application possibilities of this material class in opto-electronic devices. Today, semiconducting, conjugated polymers are widely investigated and technologically implemented as electroluminescent light emitters [3] in organic light emitting diodes (OLED) [4], and as active semiconductors in organic, polymeric transistors [5, 6], high-rectification ratio diodes [7, 8], non-volatile memories [9], photodiodes [10] and solar cells [11,12]. The outstanding characteristic of conjugated polymers are also exploited in transducers. Numerous examples of mechanical motion in macroscopic devices induced by redox [13,14,15] reactions or based on Joule heating [16] have been reported and used for actuators [17]. However, to the best of our knowledge, the electronic and electromechanical properties of organic electronic materials have not yet been exploited in one and the same device, which could then be qualified as "monolithic". In the work presented hereafter, we investigate the electromechanical properties of typical conjugated polymer rectifying and/or light emitting diodes. We study both the forward bias case, where a current flows through the device and the reverse direction, where the diode operates in the blocking regime. Besides, we use two different active materials, one being intrinsic with a very low concentration of free carriers (PPV), and a second one, which is modified by impurities (P3HT).

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2. EXPERIMENTAL

The diodes are fabricated on 1 mm thick glass or 0.2 mm thick polyethyleneterephtalate (PET) substrates coated with indium tin oxide (ITO). Two different conjugated polymers are used as active materials, namely poly(3-hexyl-thiophene) (P3HT from American Dye Inc.) and poly-[2-(3,7-dimethyloctyloxy)-5-methyloxy]-para-phenylene-vinylene (MDMO-PPV from COVION GmbH). In the former case, a 5% weight solution in chloroform is doctor bladed onto the substrate giving a film of about 1 µm in thickness. In the latter case, a 0.5% solution in chorobenzene is spin coated onto a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, Baytron from Bayer GmbH) previously deposited on the substrate. The MDMO-PPV thickness varies between 100 and 300 nm depending on the spinning speed. In both cases, the active material is covered with an 100 nm thick evaporated aluminum cathode resulting in a simple sandwich type device (Figure 1a)

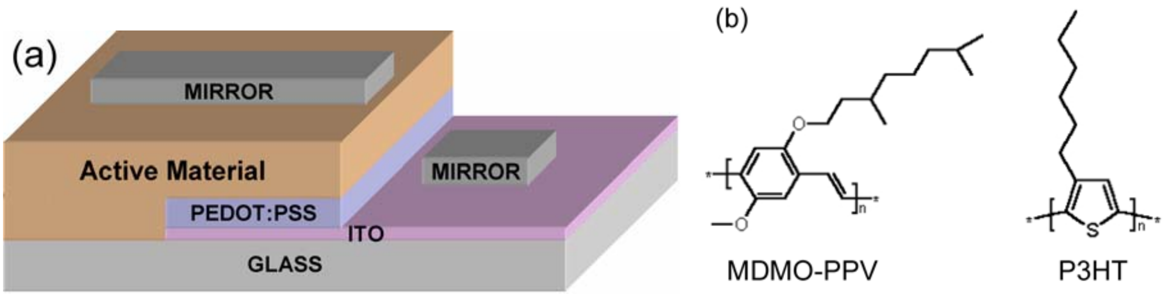

Figure 1: (a) Structure of the conjugated polymer based diode; (b) Chemical structure of the two active materials exploited, namely (poly-[2-(3,7-dimethyloctyloxy)-5-methyloxy]-para-phenylene-vinylene) (MDMO-PPV) and poly(3-hexyl-thiophene) (P3HT).

The electrical behavior of the device is first characterized by measuring current versus voltage (I-V) curves with a Keithley 286 source measurement unit. In addition, the complex impedance is determined with a HP 4284A LCR bridge allowing to scan a frequency range going from 100 to 10^6 Hz with the possibility of applying a bias from -20 to + 20V. The amplitude of the a.c signal applied is always kept below 200 mV.

The electromechanical behavior of the diode is studied with a Nomarsky optical interferometer [18]. This set-up is capable of detecting periodic subpicometer displacements over a wide range of frequencies between 0.1 Hz and more than 10 kHz. As shown in Fig. 1a, the top electrodes contacting the active material and the ITO are designed to act as mirrors for the interferometer.

3. INTRINSICALLY ACTIVE MATERIAL : MDMO-PPV

3.1. Results

3.1.1. Electrical characterization

MDMO-PPV based diodes are usually considered to be Metal-Insulator-Metal (MIM) devices [19]. As sketched in Figure 2a, the very low concentration of free charge carriers in the conjugated polymer may hinder the alignment of the Fermi levels of the different layers. Therefore, the vacuum levels of the stacked materials shall align themselves accordingly to the Schottky-Mott model. Figure 2b shows the I-V curve of such a diode with a surface area of 0.1 cm^2. The rectification ratio can be estimated to be about five orders of magnitude at 15 V. The diode strongly injects in the forward direction for voltages above 1 V: The current follows a V^3 dependence, which is indicating a non ideal space charge limited current [20]. Despite the quite high rectification ratio, the current in the reverse direction in not negligible and attributed to leakage effects.

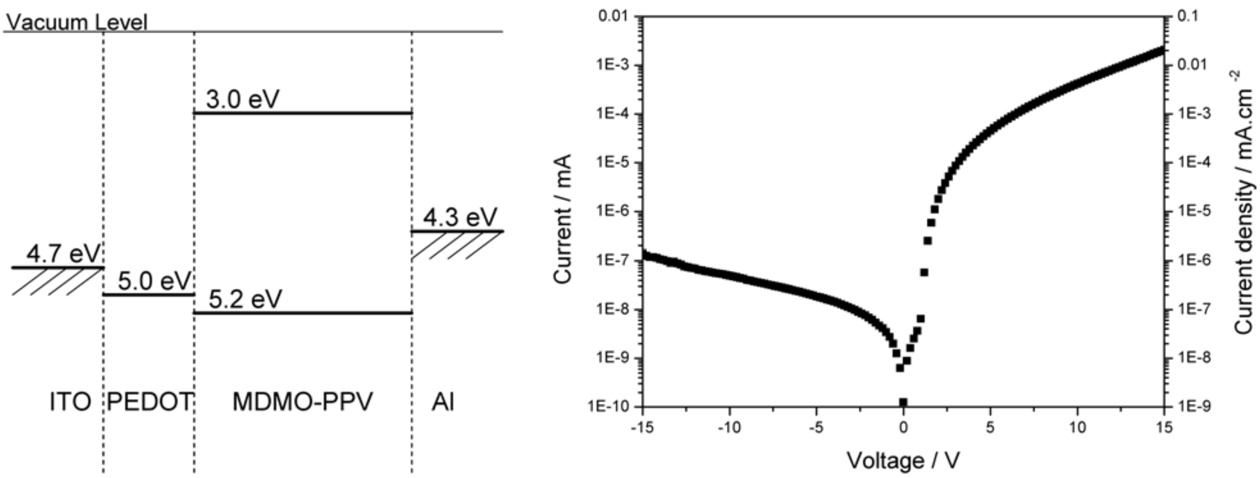

Figure 2 : (a) Energetic level diagram of the MDMO-PPV based diodes according to the MIM picture; (b) Current versus voltage graph of a MDMO-PPV diode (active surface area of 0.1 cm^2).

Figure 3a shows the Cole-Cole diagram of a 150 nm thick diode with a surface area of 0.2 cm^2. When the diode is forward biased a simple model of a capacitance in parallel with a resistance (C_pR_p) can be applied. The fit in the case of a 2 V bias is shown in Figure 3a (full line) and was obtained with a resistance R_p = 77 kΩ and a capacitance C_p=4.9 nF. The latter value is close to the capacitance calculated from the thickness and surface area and in accordance with the capacitance displayed in Figure 3b. When the diode is closed (bias ≤1V), the Cole-Cole diagram does not show circles anymore due to a too high R_p (in the 10^6 Ω range) rendering the fitting procedure quite difficult and inaccurate. Figure 3b illustrates the measured capacitance versus frequency for different d.c. bias voltages applied. The capacitance is constant above 5000 Hz and independent of the bias voltage, showing a value close to the capacitance as determined from the sample geometry. However, at high voltages and low frequencies, a negative capacitance effect is observable [21]. Although very interesting, this inductive contribution will not be discussed here.

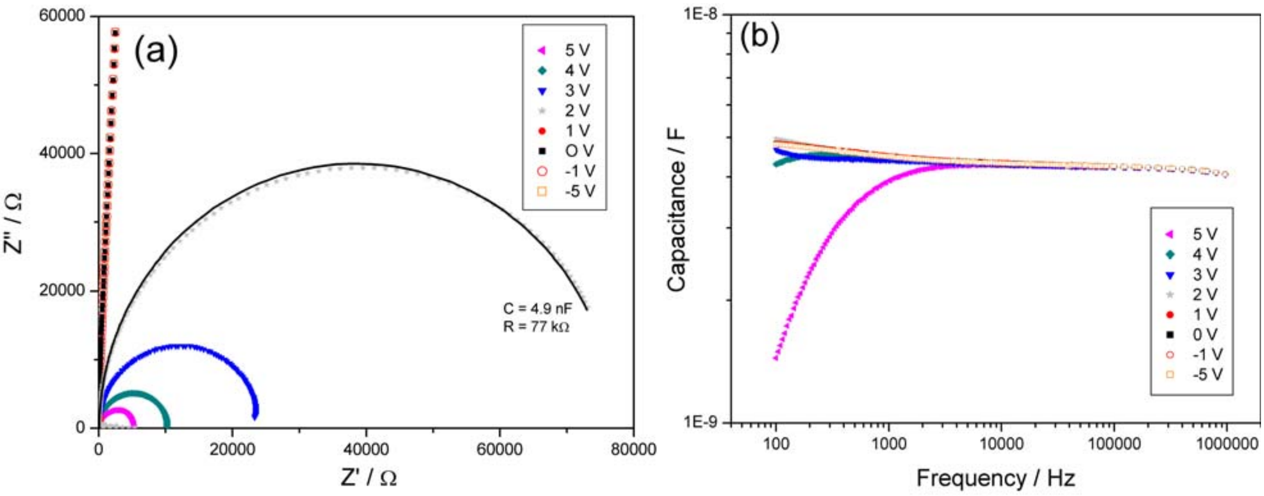

Figure 3 : (a) Cole-Cole diagram and (b) capacitance versus frequency of a MDMO-PPV diode (thickness:150 nm; surface area: 0.2 cm^2) under different applied voltages.

3.1.2. Electromechanical characterization.

Figure 4 shows the displacement (absolute values) of the mirror electrode on the diode versus the frequency (f) of the applied sinusoidal voltage $V=V_0(1+\sin 2\pi ft)$, for three forward and two reverse bias voltages respectively. Under reverse bias, the electromechanical displacement is nearly frequency independent within the frequency range of our set-up, that is from a few 100 mHz to 10 kHz. However, below 10 Hz, a slight increase appears. In forward direction, the displacement saturates at low frequencies, while at higher frequencies a 1/f decrease is observed.

The amplitude of the electromechanical strain versus the amplitude of the applied voltage was found to obey a power law under both forward and reverse bias conditions. In the first case, the exponent is $\alpha \cong 4.4$, whereas in the latter case the measurements performed at three different frequencies revealed a power law exponent α decreasing slightly with increasing frequency from 2 (for 33.3 Hz) to 1.8 (for 10 kHz).

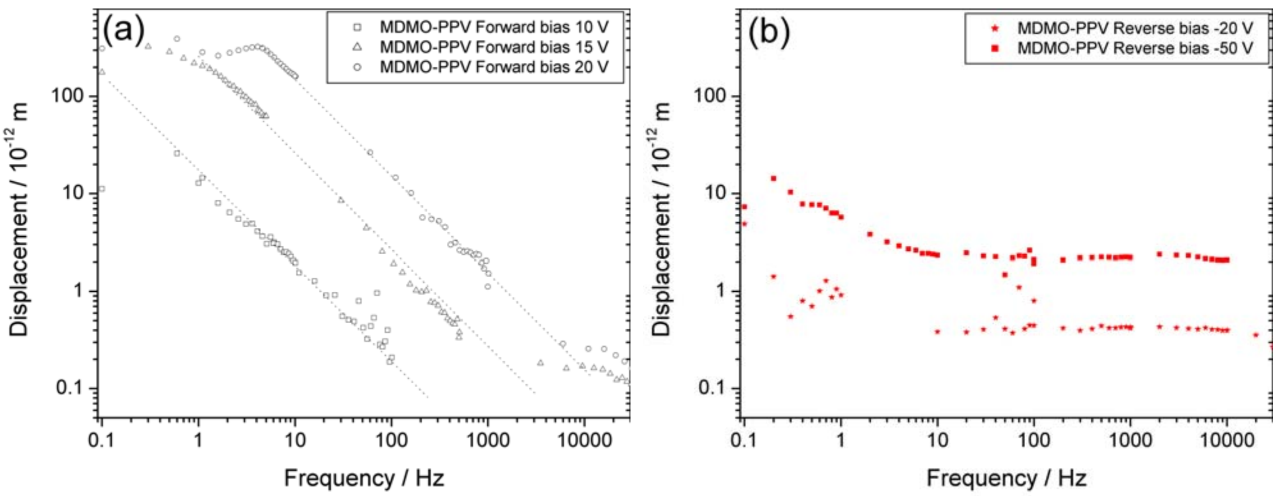

Figure 4 : Electromechanical strain recorded at the surface of a MDMO-PPV diode under (a) forward and (b) reverse polarization.

The displacement recorded by the Nomarsky interferometer being close to the nanometer range, we have also investigated the movement of the surface with a stylus profilometer in a regime close to steady state conditions (about 0.1 Hz). As sketched in Figure 5a, the sample was fixed on one side letting the rest free to move and deform. The voltage output of the profilometer was recorded and converted into a length scale (Figure 5b). It can be seen that the 1 mm thick 1.5 cm x1.5 cm glass substrate "cantilever" experienced a bending strain. For an applied voltage of 35 V (corresponding to a current of about 5 mA and a dissipated power of 170 mW) the free edge of the sample moved with an amplitude of more than 170 nm. Changing the substrate from glass (Young's modulus : Y≈ 65 GPa) to PET (Young's modulus : Y≈ 4 GPa), the displacement attains several micrometers for voltages as low as 5 V.

3.2. Discussion

The complex impedance characterization of the MDMO-PPV diode reveals that the device can be modeled as a capacitance and a resistance in series. Though the resistance depends on the applied bias when the diode is opened, neither the capacitance nor the resistance vary for reverse bias (at constant frequency). These observations tend to confirm that the MIM picture can be used to describe the diode. Therefore, when a reverse bias is applied, the field within the active material is homogeneous and the conjugated polymer can be considered as being a pure dielectric.

Thus, the strains observed for reverse polarization are believed to result from electrostatic forces (Maxwell stress) [22]. The effective compressive stress *p*, is expressed by :

$$p = \varepsilon\varepsilon_0 E^2 \quad (1),$$

where ε is the relative dielectric constant of the material, ε_0 the vacuum permittivity and *E* the constant electric field in the material. For small stress the strain *s* is simply given by :

$$s = p/Y = \varepsilon\varepsilon_0 E^2/Y \quad (2),$$

where Y is the Young's modulus of the active material. Considering $\varepsilon \approx 4$, $E \approx 10^8$ V/m and Y on the order of a few GPa, a quick estimate gives indeed a strain in the picometer range. The strain should follow a square law versus voltage which is indeed observed in our measurements at low frequencies. However, the power law exponent slightly decreases with increasing frequency presumably due to the development of a non-uniform electric field in the polymer at high frequencies.

In the forward direction, a totally different type of actuation is observed. We presume that the 1/f dependence of the strain indicates a thermo-electrostrictive effect [23, 24]. As shown in Fig. 5b this actuation bends the whole substrate. We propose that this electrothermal actuation in forward bias of the device originates in the associated high current density in the diode. The power dissipated in the resistance of the device induces Joule heating of the surface of the substrate. This local heating creates an "*in situ* bimorph" in the temperature gradient through the cross section of the substrate. This bimorph structure may be the cause of the deflection and bending extending up to several hundreds of nanometers. This interpretation was substantiated by gluing on a bare substrate a surface mounted device (SMD) of roughly the same resistivity as the organic diode (≈10 kΩ) and demonstrating similar electro-thermo-mechanical effects. Furthermore, choosing a low coefficient of thermal expansion (CTE) material like quartz as the substrate, the electro-thermo-mechanical effects was drastically reduced. Besides, this explanation also clarifies the small increase of the displacement recorded in the reverse direction at low frequencies. Indeed as mentioned above, the diodes leak slightly. Therefore, at high reverse bias, a small Joule effect might be expected at low frequencies. Finally, it has to be mentioned that even under forward bias, Maxwell forces should act. Even though the transport appears to be space charge limited, the field may not be totally screened. Simply, electrostatic striction might be much smaller than thermoactuation and hence will be hidden. However when the Joule heating effect vanishes at high frequency, a remaining frequency independent strain is observed in Figure 4a which may arise from this Maxwell contribution in the forward bias.

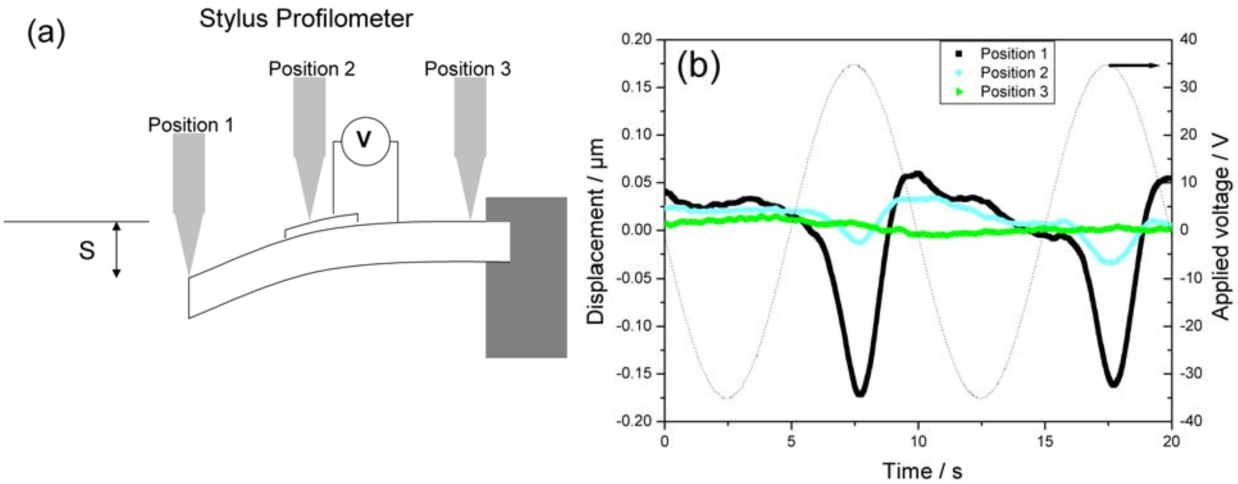

Figure 5 : Displacement measured at (a) different points of the glass substrate (b) versus applied voltage.

4. DOPED ACTIVE MATERIAL : P3HT

4.1. Results

4.1.1. Electrical characterization

P3HT is a conjugated polymer well known to be doped by ambient air [25]. Although the exact mechanism is still not fully understood, it is commonly accepted that oxygen having diffused in the polymer might act as an electron acceptor. Therefore P3HT exposed to air does not behave like an intrinsic semiconductor. Figure 6a illustrates this statement. As mentioned above, the capacitance of a MDMO-PPV diode does not change with applied voltage. However, in the case of P3HT exposed to air, the situation appears to be totally different. Indeed, in the reverse direction the capacitance is reduced by one order of magnitude when the voltage is swept between 1.5 V and -10 V. The decreasing capacity with increasing voltage is a clear sign for the presence of a depletion region within the device with a variable width depending on the applied voltage. When the device obeys the simple model of an abrupt p-n+ junction (Schottky contact), the capacitance should follow equation [26]:

$$\frac{1}{C^2}=\frac{2(V_{bi}-V)}{A^2 q.\varepsilon.\varepsilon_0.N_A} \tag{3}$$

where q is the elementary charge, ε is the relative dielectric constant of the material, ε_0 is the vacuum permittivity, A the surface area of the diode and N_A the concentration of impurities. As shown in Figure 6b, $1/C^2$ linearly scales with the voltage in the reverse direction, proving the existence of a Schottky like contact between the P3HT and the aluminum electrode. Thus N_A is determined from the slope of the fit line: It is estimated to be about 2.10^{17} cm^{-3}. Moreover, the intercept of the fit line with the X axis gives access to V_{bi}, which is found to be close to 1.5 V. Finally, the width W of the depletion zone is calculated according to [26]:

$$W=\sqrt{\frac{2.\varepsilon.\varepsilon_0.(V_{bi}-V)}{q.N_A}} \tag{4}$$

At 0 V the depletion zone is estimated to be 70 nm wide. In the case of a -30 V bias, this width reaches about 300 nm, still far below the total thickness of the film (1µm). It has to be mentioned that diffusion of impurities in the active material is time and temperature dependant. Therefore the Schottky like contact described here is only observed after a long period of time, long enough to let the impurities modify the electronic behavior of the conjugated polymer [27].

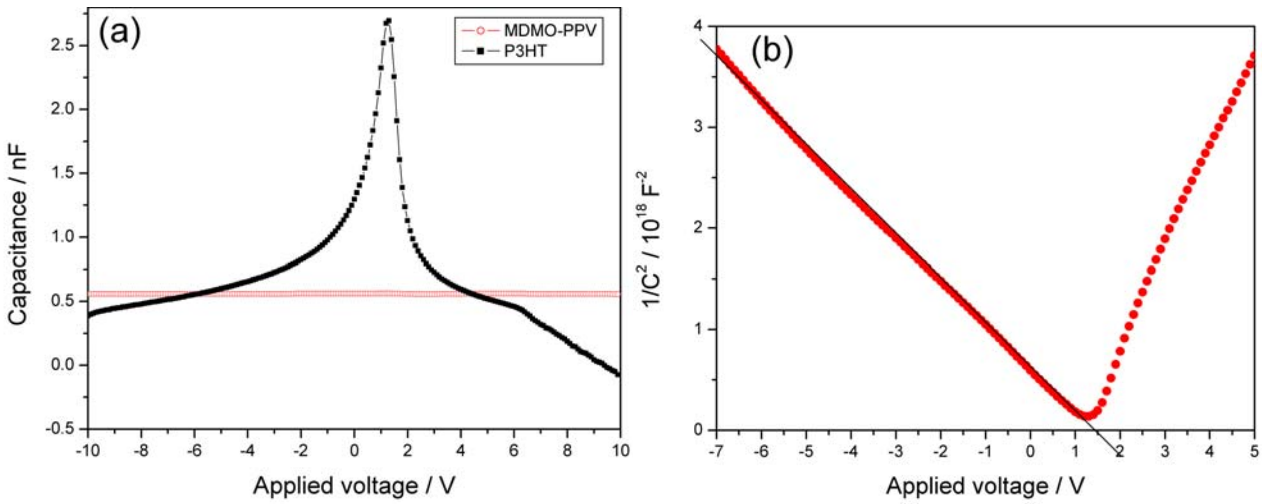

Figure 6 : (a) Capacitance versus voltage performed at 1 kHz on MDMO-PPV and P3HT diodes ; (b) $1/C^2$ plotted versus voltage for the P3HT case.

4.1.2. Electromechanical characterization

As in the case of the MDMO-PPV diode, we investigated the electromechanical behavior of the P3HT device with a Nomarsky interferometer. In the forward bias, we observed the same trend: A displacement scaling with 1/f.

In the reverse direction, the displacement was found to be constant over the entire range of frequencies scanned. While the same voltage dependence of the strain is observed as for MDMO-PPV in the forward direction, in the reverse direction a quite different tendency was found: The strain does not any more scale with the square of the applied voltage, but follows a power law with an exponent close to 1.5. This value may slightly change depending on the time exposure to air, thus presumably on the concentration and profile of impurities incorporated in the active material. For freshly prepared samples only shortly exposed to air, the exponent is about 1.8 (very slight doping). It reaches 1.5 when the Schottky type contact is built-up (intermediate doping) and finally decreases below 1.5 for long exposure times to air.

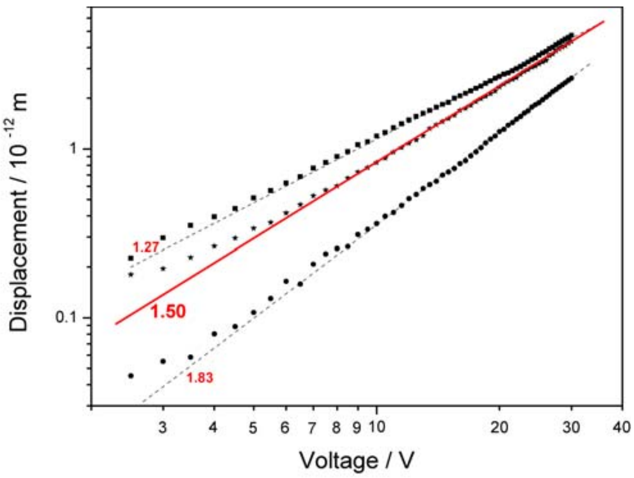

Figure 7 : Displacement versus voltage applied for a doped P3HT diode.

4.2. Discussion

Although the actuation in the forward direction is believed to be due to Joule heating, the reverse direction case deserves to be discussed more intensively. A Schottky contact can be sketched as shown in Figure 8. In the depletion zone W, the impurities are reduced. A net negative charge appears due to the lack of holes. The total applied voltage drops in the depletion zone, whereas the electric field is screened in the rest of the semiconductor. As mentioned before, the depletion zone width W never exceeds the thickness of the film in the range of voltages used in this study. The displacement of the mirror electrode observed is therefore caused by the Coulomb attraction force between the charged impurities and the charges accumulated in the metal at the interface with the semiconductor. A model developed by Howard Reiss and described in detail elsewhere [27] shows for the displacement in a Schottky contact the following power law behavior:

$$\Delta d = -\frac{1}{Y}\left(\frac{2.q.N_A.\varepsilon.\varepsilon_0}{9}\right)^{1/2}.(V_{bi}-V)^{3/2} \quad (5)$$

Considering $Y \approx 5$ GPa and $N_A \approx 10^{17}$ cm^3 one obtains a displacement of about 2.5 pm at 10 volts. Thus, we believe that the model describes quite accurately the electromechanical effects in our organic Schottky like contact.

It is important to mention that if the semiconductor and the electrode have different Young's modulus (which is quite likely), the model does predict a piezoelectric effect in the contact [27]. Besides, this model might hold as well for inorganic materials despite the displacement might be extremely small due to the quite high elastic modulus Y. Finally we want to point out that Schottky contacts can be considered in a first approximation as an abrupt one sided p-n junction. Therefore we presume qualitatively the same type of electromechanical behavior response in all types of p-n and Schottky junctions.

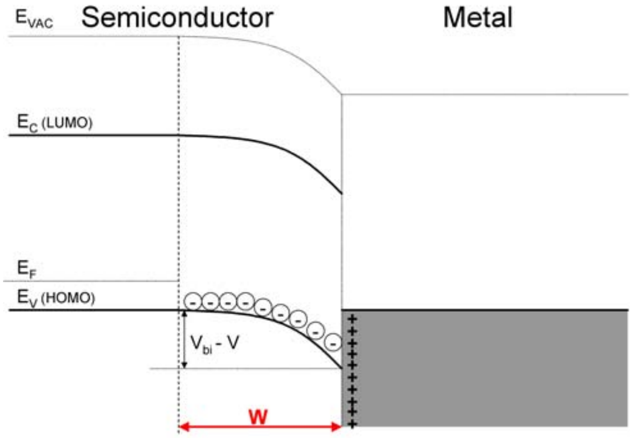

Figure 8 : Energy diagram of a Schottky contact.

5. Conclusion

We have observed that conjugated polymer diodes possess two distinguished electromechanical actuation properties. In the forward direction, Joule heating due to current flow induces a bending of the device which can easily reach several microns in the case of a plastic substrate. In the reverse direction, for intrinsic materials, electrostriction due to Maxwell forces appears since the electric field within the diode is homogeneous. However, in the case of doped conjugated polymers, a Schottky contact was shown to appear. The electromechanical behavior of such a diode has been modeled by Howard Reiss, calculating Coulomb attraction forces between the charged impurities present in the depletion zone and the charges accumulated in the metal. The model predicts a power law type voltage dependence of the displacement with an exponent of 1.5, in between piezoelectricity and electrostriction. Although the displacements are relatively small so far, several strategies can be applied to enhance the electromechanical response of these devices: foaming the active polymer film or mixing it with elastomers like polyurethane. Merging different fields of physics, namely soft matter transducers and organic electronics, such devices might open a route for monolithically "smart actuators" based on organic diodes or transistors.

ACKNOWLEDGMENTS

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