Electromechanical strain in conjugated polymer diodes under forward and reverse bias

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Organic polymeric semiconductor diodes based on poly(paraphenylene vinylene) exhibit electromechanical strain under reverse and forward bias operation. Under reverse bias, the strain in the organic diode is created by Maxwell forces ("electrostrictive" actuation). Under forward bias, the large electrical current results in Joule heating and thus in a thermally induced electromechanical strain. These electromechanical effects might be used for transducer applications of organic electronic materials. © 2005 American Institute of Physics. [DOI: 10.1063/1.1925779]

Conjugated polymers are at the heart of organic electronics, due to their conducting and semiconducting properties.¹ They are widely investigated and technologically implemented as electroluminescent light emitters² in organic lightemitting diodes (OLED), and as active semiconductors in organic, polymeric transistors,³ nonvolatile memories,⁴ photodiodes,⁵ and solar cells.⁶ Besides their use in organic optoelectronics and integrated circuits, conjugated polymers are also envisaged for transducers.⁷ Examples of mechanical motion in macroscopic devices induced by redox⁸⁻¹⁰ reactions or Joule effect¹¹ have been reported and used for actuators.¹² We aim in this study to investigate the electromechanical properties of typical conjugated polymer OLED operated under forward and reverse bias.

The diodes are fabricated on an indium tin oxide (ITO) coated glass substrate with 90 nm of spin-coated poly(3,4ethylenedioxythiophene) poly(styrenesulfonate) (Baytron, BAYER AG) as anode. As conjugated polymer thin film a 300 nm thick layer of poly[2-(3', 7'dimethyloctyloxy)-5-methyloxy paraphenylene vinylene] (from COVION Gmbh) is spin cast from solution and covered with an evaporated aluminum cathode resulting in a metal-insulator-metal $(MIM)^{13}$ sandwich [Fig. 1(a)]. The top aluminum electrode has an area of $1.5 \times 1.5 \text{ mm}^2$ in the middle of the 15 $\times 15 \text{ mm}^2$ substrate. In addition, a second aluminum layer is evaporated directly onto the ITO glass to serve as a reference mirror for the interferometric determination of the electromechanically induced strain in the diodes (see below). This standard architecture gives rise to a diode behavior.¹⁴ In the complex impedance of the diode, as measured with a HP 4284A LCR bridge at 1 kHz, the semiconducting polymer behaves like an insulator with a purely capacitive response (phase $\varphi \approx -\pi/2$) when the diode is polarized with a reverse bias [Fig. 1(b)]. However, above the turn-on voltage in the forward direction (≥ 1.2 V), the conductive behavior evolves $(\varphi \approx 0)$ with a rapidly decreasing impedance with increasing forward bias voltage. The typical "rectification ratio" of our diodes is around 10^4 at 5 V.

The electromechanical properties of the diodes are investigated with a two-beam Nomarski interferometer,¹⁵ schematically depicted in Fig. 2. Nomarski interferometers are capable to detect mirror displacements from several tenths of nanometers down to subpicometers over a wide frequency range (0.1 up to several tens of kHz). Light from a HeNe laser (wavelength λ =633 nm) passes through an aperture, an attenuator, and a polarizer. The beam is linearly polarized at 45° relative to the *s* and *p* states. The sensing and reference beam have equal intensities on the sample mirrors. The relative phase $\Delta \varphi$ between the polarization states is adjusted by



FIG. 1. (a) Cross section of the conjugated polymer diode. (b) Impedance of the diode structure at a frequency of 1 kHz, revealing the insulating and conductive behavior of the device under reverse and forward bias, respectively.

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FIG. 2. Scheme of the Nomarsky interferometer for investigating electromechanical properties of conjugated polymer devices.

a Soleil-Babinet compensator. The sensing and reference beams are separated by 4 mm with a birefringent prism. Both beams are reflected back by the electrodes of the device and pass through a Wollaston prism with an optical axis rotated 45° relative to that of the birefringent beam separator. Thereby, the sensing and reference beam are superimposed and split into two light beams with s' and p' polarization states, respectively. The phase-difference $\Delta \varphi$ between sensing and reference beam determines the intensity of each beam I_A and I_B :

$$\begin{split} &I_A \propto I_s + I_p - 2\sqrt{I_s I_p} \cos(\Delta \varphi) \\ &I_B \propto I_s + I_p + 2\sqrt{I_s I_p} \cos(\Delta \varphi), \end{split} \tag{1}$$

where I_s and I_p are the intensities of the sensing and the reference beam, respectively. The intensity related signals Aand B are detected by a two-quadrant photodiode connected to a preamplifier. These two signals are converted by an analog circuit to the measured signal (A-B)/(A+B) $=4\pi V\Delta x/\lambda$, with the wavelength of the laser beam λ and the relative displacement between the electrically driven mirror and the reference mirror Δx . The visibility calculates to V $=2(I_s I_p)^{1/2}/(I_s+I_p)$; it depends on the quality of the mirrors and needs to be determined in a separate experiment. The signal (A-B)/(A+B) is measured with a lock-in amplifier and recorded with a computer which also controls both the lock-in amplifier and the signal generator.

Figure 3(a) shows the displacement (absolute value) 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 two reverse and three forward bias voltages. Under reverse bias, the electromechanical displacement is nearly frequency independent within the frequency range of our setup. In the forward direction, the displacement saturates at low frequencies, while at higher frequencies a 1/f decrease is observed. The amplitude of the electromechanical strain shows a power-law dependence versus the amplitude of the applied voltage under both forward and reverse bias conditions $\lceil \propto V^{\alpha} \rceil$



FIG. 3. (a) Electromechanically induced displacement of the mirror electrodes on the diodes versus frequency of the sinusoidal voltage. The voltage was oscillating between 0 V and +10 V (\Box), +15 V (\triangle), +20 V (\bigcirc), -20 V (\bigstar) and -50 V (\blacksquare). The slashed lines are guides for the eye representing a 1/*f* decrease. (b) Electromechanical displacement of the mirror electrodes versus the amplitude of the sinusoidal voltage at a frequency of 33.3 Hz in forward (\Box) and reverse direction (\blacktriangle). Each curve is fitted by a power law: The exponents found are 4.4 (\Box) and 2 (\bigstar). Right axis: Current through the diode (\bigstar) in forward direction.

see Fig. 3(b)]: Under reverse bias, the exponent is $\alpha \approx 2.0$, whereas under forward bias it reaches 4.4, both values being measured at 33.3 Hz.

Using a stylus profilometer (Fig. 4 inset), the near steady state (0.1 Hz) strain has been investigated by fixing the sub-



FIG. 4. Thermally driven displacement of the substrate measured at three different locations. Deflection is observed only in the case of forward bias. Downloaded 06 Oct 2005 to 140.78.119.3. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

strate on one side and letting the rest free to move and deform. The movement of the surface was followed by recording the output voltage of the stylus profilometer and converting it into a length scale. It is clearly observable that the 1 mm thick 15×15 mm² large glass substrate "cantilever" experiences a bending strain when the diode is polarized in the forward direction. For an applied voltage of 35 V (about 5 mA), the free edge of the glass substrate moved with an amplitude of more than 170 nm. When the voltage is reduced after a maximum, a relaxation like motion takes place: The bending occurs in the opposite direction, decreases, and finally disappears.

The experimental results presented herein indicate the existence of two different types of electromechanically induced strain in organic polymeric diodes. Under reverse bias, that is in the capacitance mode of the organic diode, the conjugated polymer can be considered to be an insulator sandwiched between two electrodes. Hence, the strains are believed to be induced by Maxwell forces. When a voltage is applied to the diode structure, the opposite charges on the electrodes attract each other, leading to a compressive stress and a corresponding compressive strain on the material between the electrodes. The effective compressive stress p, is expressed by $p = \varepsilon \varepsilon_0 E^2$, where ε is the relative dielectric constant of the material, ε_0 is the vacuum permittivity, and E is the constant electric field in the material. For small stress, the strain s_z is simply given by $s_z = -p/Y = \varepsilon \varepsilon_0 E^2/Y$, where Y is the Young's modulus of the conjugated polymer. Considering $\varepsilon \approx 4$, $E \approx 10^8 \text{ V/m}$, and Y on the order of a few GPa, a quick estimate gives a strain of several tens of picometer. The discrepancy between the forecasted and the measured displacements may originate from the geometry of the device. The movement of the organic film is restricted by the rigid substrate to which it is attached. Therefore, the Poisson coefficient tends to substantially increase the effective Young's modulus.¹⁶ Nevertheless, the strain should follow a square-law behavior versus voltage as observed in our measurements [Fig. 3(b)]. Presently, the electromechanically induced strains observed are too small to be used in applications: A field-induced piezoelectric coefficient of 0.1 pm/V is estimated for our diode structure. However, there is great room for improvement by different ways as discussed below.

Under forward bias, the saturation at low frequencies and the 1/f dependence of the strain observed in Fig. 3 seems to be representative of a thermoelectrostrictive effect. We believe that the strain in forward bias originates from the high current density in the diode. The power dissipated (V^2/R) in the diode resistance induces Joule heating of the conjugated polymer layer (and hence also of the substrate). However, the full mechanism of the thermally induced electromechanical strain in our diodes is not yet fully understood, since the power law for the strain is 4.4 while the current-voltage curve shows an exponent of 3. The thermal actuation mechanism was confirmed by gluing a surface mounted device resistor with roughly the same resistivity on a ITO substrate and demonstrating similar electrothermomechanical effects. Furthermore, choosing a low coefficient of thermal expansion (CTE) material, such as quartz as the substrate, the electrothermomechanical effects were drastically reduced. On the other hand, on substrates with a low Young's modulus and a large CTE, such as poly(ethylene terephthalate) ($Y \approx 4$ GPa and CTE $\approx 120 \times 10^{-6}$ K⁻¹ in comparison to glass: $Y \approx 65$ GPa and CTE $\approx 9 \times 10^{-6}$ K⁻¹) used in flexible displays, this thermoelectromechanical effect can be strongly enhanced.

The two mechanisms described above are generally employed separately in actuators. But these two distinctly different effects have not yet been observed in the same device. In order to be used in practical transducing applications, they must be enhanced by increasing the dielectric constant, and decreasing Young's modulus of the conjugated polymer and the substrate. These schemes are feasible, for example, by incorporating polar groups into the conducting polymer, investigating polymer composites of semiconducting and soft polymers, physically foaming the polymer and using flexible substrates with a large CTE.

In summary, we have observed that conjugated polymer diodes show electrostrictive and electrothermomechanical strain under reverse and forward bias, respectively. These nonconventional effects observed in the same organic electronic device may pave the way toward organic transducer chips.

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