Unusual electromechanical effects in organic semiconductor Schottky contacts: Between piezoelectricity and electrostriction

Gilles Dennler,[a] Christoph Lungenschmied, and Niyazi Serdar Sariciftci
Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University, Linz, Austria

Reinhard Schwödiauer and Siegfried Bauer
Soft-Matter Physics, Johannes Kepler University, Linz, Austria

Howard Reiss
Department of Chemistry and Biochemistry, University of California, Los Angeles, California

The converse electromechanical response in an organic Schottky contact follows a power law dependence $S \propto V^\alpha$ of the mechanical strain S versus the applied voltage V, with an exponent $\alpha = 1.5$, in between linear piezoelectricity and quadratic electrostriction. The experimental result is discussed within the frame of a model, where the Coulomb attraction between charged impurities present in the depletion zone of the Schottky contact and the charges accumulated in the metal at the interface with the semiconductor is considered. Electromechanical responses of such devices appear to be of fundamental interest for the investigation of nonuniform electric field distributions and for potential practical applications as electromechanical transducers. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2103406]

Both piezoelectricity and electrostriction are at the heart of numerous applications in electromechanical transducers.[1,2] Experimentally, the converse piezoelectric and electrostrictive responses are usually observed in samples, where the electric stimulus is provided by an applied voltage V, leading to an electric field $E = V/l$ within the material, where l is the sample dimension. In organic materials these strains are expressed with the experimentally controlled, and therefore easily accessible applied voltage V, leading to a linear and quadratic relationship between the electromechanically induced strain and the applied voltage for the piezoelectric and electrostrictive response, respectively.[3] However, expressing the electric field E versus the applied voltage V via $E = V/l$ is only permitted when the electric field within the material is uniform. In materials, where the electric field is strongly nonuniform across the thickness, one might expect different laws governing the electromechanical response versus the applied voltage stimulus. Here we have chosen organic semiconductor Schottky contacts for the experimental investigation of such unusual electromechanical effects for two reasons: (i) Schottky contacts display a strongly nonuniform spatial electric field distribution across the sample[4] (Fig. 1) and (ii) in comparison to their inorganic counterparts, organic semiconductors provide easily accessible converse electromechanical effects due to their softness.[5]

Poly(3-hexylthiophene) (P3HT) is a conjugated polymer p-doped by exposure to oxygen[6] and/or moisture.[7] While intrinsic conjugated polymers usually follow the metal-insulator-metal scheme under reverse bias voltage,[8] P3HT based devices behave differently due to this doping effect. The 1.5×3 mm^2 active surface area devices were prepared in air by doctor blading a 5% solution of P3HT in chloroform onto an indium tin oxide (ITO) coated glass substrate. The substrates were cleaned in de-ionized water, acetone, toluene, and isopropanol in an ultrasonic bath. The top electrode was formed by evaporating Al onto the resulting 1-μm-thick (measured with a stylus profilometer) conjugated polymer film. It has been reported that ITO forms an ohmic contact to the highest occupied molecular orbital (HOMO) of P3HT,[9] especially when the ITO is cleaned the same way we did.[10] The Fermi level of Al is located almost in the middle of the polymer band gap about 1 eV above its HOMO level.[10] Therefore, this contact is expected to be Schottky like when the diode is exposed to air.[11] We measured a diode behavior with a rectification ratio of several orders of mag-
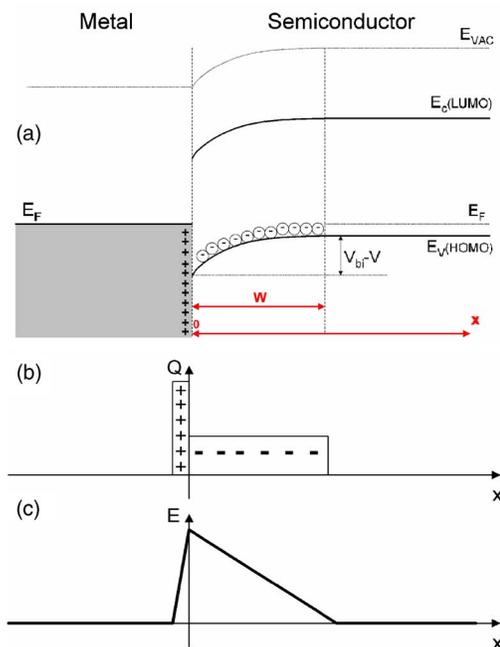

FIG. 1. (a) Schematic representation of an ideal Schottky contact between a p-doped semiconductor and a metallic electrode (in the represented case, $V=0$), (b) spatial charges, and (c) field distribution in such a Schottky contact.

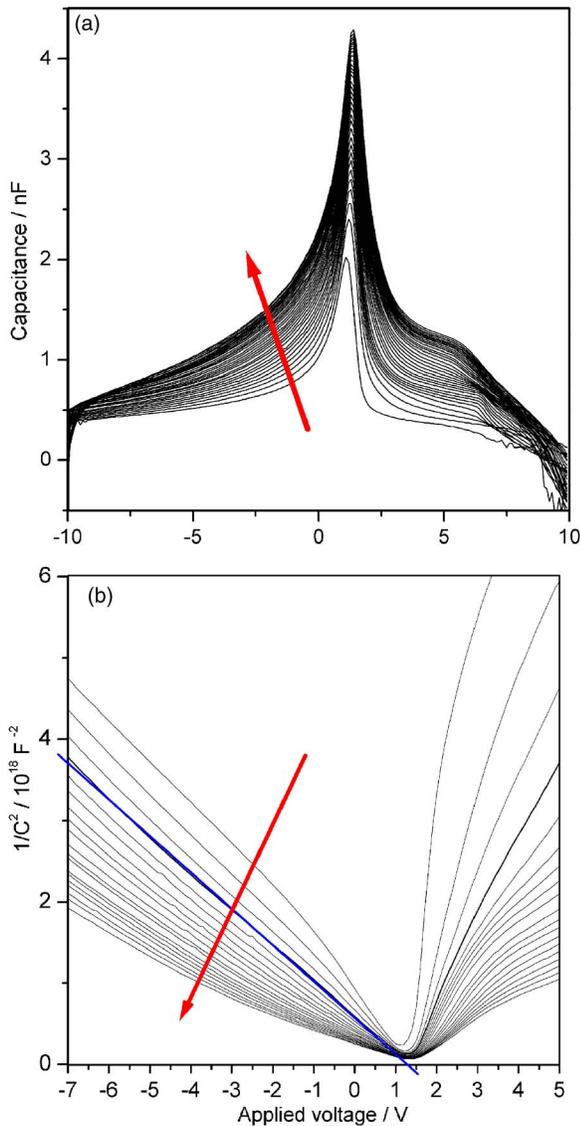[a]Author to whom correspondence should be addressed; electronic mail: gilles.dennler@jku.at

FIG. 2. (a) Capacitance C and (b) $1/C^2$ of an ITO/P3HT/Al diode recorded at 1 kHz every 2 min in air versus the applied voltage V. The arrows indicate increasing time. The solid line in (b) is a linear fit of one intermediate curve.

nitude at ± 10 V[9,12] with currents of several hundreds of microamperes at -30 V probably due to Fowler-Nordheim injection.[10]

Figure 2(a) displays capacitance versus voltage curves measured with a HP 4284A LCR bridge at 1 kHz in air. The curves have been recorded successively every 2 min, just after having taken the sample out of the evaporation chamber: The arrow indicates the increasing time direction. For each measurement, the capacitance changes with the applied voltage, indicating the modulation of a space charge region width.[13] The capacitance increases with time, suggesting a ongoing doping procedure. In the case of a Schottky contact, $1/C^2$ evolves linearly with the voltage, according to[13,14,11]

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

where V_{bi} is the built-in potential, V is the applied voltage, A is the active surface area of the device, q is the charge of the impurities, ε is the relative dielectric constant of the semiconductor, ε_0 is the permittivity of vacuum, and N_A is the

concentration of acceptor impurities. Figure 2(b) shows linear intermediate scans characteristic for Schottky contacts. The concentration of impurities can be evaluated according to Eq. (1): Taking $\varepsilon = 3$ for P3HT,[15] $V_{bi} = 1.2$ V (voltage extrapolated for $1/C^2 = 0$), and $A = 1.5 \times 3$ mm^2, N_A is determined to evolve from about 5×10^{16} to 1×10^{17} cm^{-3} with increasing time, in accordance with previously published values.[16] However, only intermediate scans can be fitted by a line in Fig. 2(b) indicating a non-homogeneous doping profile in the depletion zone. The first scans show two slightly different slopes while the last ones evolves sublinearily. This can be interpreted in terms of a basic uniform doping induced during the doctor-blading step performed in air. This doping might be slightly reduced close to the surface of the sample during the evaporation step (second slope for early scans) and overwhelmed by further doping during the measurement (sublinear behavior for late scans), though slowed down by the presence of the protective aluminum electrode. Therefore the doping concentration range calculated above should be seen as a first approximation. Exposure to oxygen and moisture might change the electronic structure at organic/metal interfaces.[17] However, we think that this effect may induce a shift of the V_{bi}[16] as visible in Fig. 2(b), but might not influence the doping concentration.

The electromechanical strain of the diodes was investigated with a two-beam Nomarski interferometer,[18] as described in more detail earlier.[19] Figure 3 shows the displacement of the top electrode versus the applied reverse bias voltage. The curve can be fitted by a power law with an exponent of 1.5. The error bars represent the statistical deviation calculated from more than 20 measurements performed on five different samples.

The unusual converse electromechanical response of Schottky diodes can be modeled by the Coulomb attraction between the charged impurities in the depletion zone and the mirror charges in the electrode. In the following, an ideal Schottky contact between a p-doped semiconductor and a metal [Fig. 1(a)], is considered. The semiconductor is supposed to contain only acceptor impurities with a constant concentration N_A [Fig. 1(b)]: The depletion zone hosts ionized impurities not compensated by holes. The following convention is adopted in the further discussion: For forward bias (positive bias) the metal is connected to the ground and the semiconductor to a source with a positive potential. When an external voltage V is applied to the Schottky contact, the total electrostatic potential variation across the junction is given by $V_{bi} - V$. For $0 < x < W$, the electric field $E(x)$ and the width W of the depletion zone are given by[14]

$$E(x) = \frac{qN_A}{\varepsilon \varepsilon_0}(x - W),$$

$$W = \sqrt{\frac{2\varepsilon \varepsilon_0 (V_{bi} - V)}{qN_A}}.$$ (2)

The elastic response of the Schottky contact arrangement is determined by the attraction between the negative charges in the depleted zone of the p-doped semiconductor and the positive charges present in the metal at the interface with the semiconductor. The ions responsible for this charge will be assumed to be firmly bound to the semiconductor, so that the induced strain is compressive. No strain components in the y
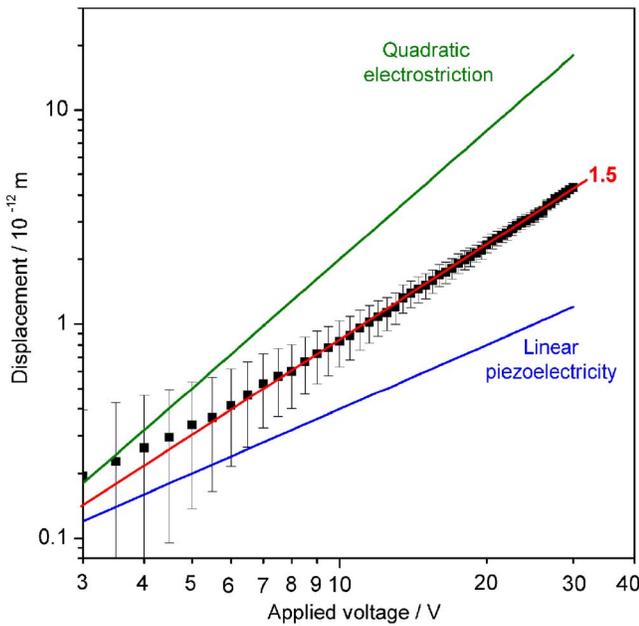
FIG. 3. Displacements recorded with a Nomarski interferometer on a Schottky ITO/P3HT/Al diode for reverse applied voltages.

and z directions, and only a compressive strain in the x direction are assumed.

Consider a slab of semiconductor of unit area and thickness dx lying perpendicular to the x direction. The total negative charge in the slab is $dQ = qN_A dx$ and the electrical force $df(x)$ on this slab is in the negative x direction

$$df(x) = E(x)dQ(x) = \frac{qN_A}{\varepsilon\varepsilon_0}(x - W)qN_A dx. \quad (3)$$

Since the semiconductor is in mechanical equilibrium, df must be balanced by the local pressure gradient in the x direction $dP(x) = df(x)$. Since $P(x)$ vanishes at $x = W$, we obtain

$$P(x) = \frac{q^2 N_A^2}{2\varepsilon\varepsilon_0}(x - W)^2. \quad (4)$$

In linear elasticity theory, the strain is related to the pressure by $dS/dx = P(x)/Y$, where Y is the effective Young modulus of the organic semiconductor on the rigid substrate. Thus, the total strain S that appears in the depletion zone is given by

$$S = \int_0^W \frac{P(x)}{Y} dx$$

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

In Eq. (5) the strain scales with $V^{3/2}$, when the external voltage exceeds V_{bi}, in full agreement with the experiments (Fig. 3). This $V^{3/2}$ dependence is located exactly in between pure dielectric elastomer effects (Maxwell stress)[19] and pure piezoelectricity,[2] that scale quadratically and linearly with the applied voltage, respectively. Considering $Y \approx 5$ GPa[20] and $N_A \approx 10^{17}$ cm^{-3}, a depletion width of about 200 nm is calculated (well below the overall thickness of the device) and a sample displacement of about 2.5 pm at 10 V is esti-

mated, fitting quite well the measurements. Thus, the model describes the electromechanical response of our organic Schottky contacts. The same unusual strain should be observed in all kind of *p-n* junctions, too. However, the strains in inorganic devices are expected to be much smaller due to the large Young modulus of inorganic materials. It should be noted that for a spatially nonuniform Young modulus, the electrostrictive effect described herein turns into a highly nonlinear piezoelectric effect. Finally, deviations from the 1.5 power law exponent in Fig. 3 may indicate spatially nonuniform doping profiles in the Schottky contact. Therefore, the electromechanically induced strain may also be interesting for the investigation of spatially inhomogeneous acceptor concentration profiles $N_A(x)$.

In conclusion, we have presented a model predicting the Coulomb attraction between ionized impurities present in the depletion zone of a Schottky contact and the image charges present in the metal electrode. According to the model, the induced strain scales with the applied voltage in the reverse direction of the diode according to a power law with an exponent of 1.5, in between linear piezoelectricity and electrostriction. Experimental observations performed on organic Schottky contacts are presented to fulfill the predictions of the model.

[1]M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Oxford Classic Texts (Oxford University Press, Oxford, 2001).
[2]C. Rosen, B. V. Hiremath, and R. Newnham, *Piezoelectricity* (American Institute of Physics, New York, 1997).
[3]F. I. Mopsik and M. G. Broadhurst, J. Appl. Phys. **46**, 4204 (1975).
[4]J. Bardeen, Phys. Rev. **71**, 717 (1947).
[5]G. Gustafsson, Y. Gao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, Nature (London) **357**, 477 (1992).
[6]M. S. A. Abdou, F. P. Orfino, Y. Son, and S. Holdcroft, J. Am. Chem. Soc. **119**, 4518 (1997).
[7]S. Hoshino, M. Yoshida, S. Uemura, T. Kodzasa, N. Takada, T. Kamata, and K. Yase, J. Appl. Phys. **95**, 5088 (2004).
[8]I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).
[9]H. Tomozawa, D. Braun, S. D. Phillips, R. Worland, A. J. Heeger, and H. Kroemer, Synth. Met. **28**, 687 (1989).
[10]Z. Chiguvare, J. Parisi, and V. Dyakonov, J. Appl. Phys. **94**, 2440 (2003).
[11]A. Assadi, C. Svensson, M. Willander, and O. Inganäs, J. Appl. Phys. **72**, 2900 (1992).
[12]F. Garten, J. Vrijmoeth, A. R. Schlatmann, R. E. Gill, T. M. Klapwijk, and G. Hadziioannou, Synth. Met. **76**, 85 (1996).
[13]M. Meier, S. Karg, and W. Riess, J. Appl. Phys. **82**, 1961 (1997).
[14]H. K. Henisch, *Rectifying Semiconductor Contacts* (Clarendon, Oxford, 1957).
[15]G. Juška, K. Genevičius, R. Österbacka, K. Arlauskas, T. Kreouzis, D. D. C. Bradley, and H. Stubb, Phys. Rev. B **67**, 081201 (2003).
[16]E. I. Meijer, A. V. G. Mangnus, B.-H. Huisman, G. W. 't Hooft, D. M. De Leeuw, and T. M. Klapwijk, Synth. Met. **142**, 53 (2004).
[17]K. Seki and H. Ishii, J. Electron Spectrosc. Relat. Phenom. **88**, 821 (1998).
[18]C. Schönenberger and S. F. Alvarado, Rev. Sci. Instrum. **60**, 3131 (1989).
[19]G. Dennler, R. Schwödiauer, S. Bauer, N. S. Sariciftci, and H. Reiss, Appl. Phys. Lett. **86**, 193507 (2005).
[20]X.-S. Wang and X.-Q. Feng, J. Mater. Sci. Lett. **21**, 715 (2002).