Anomalous charge transport behavior of Fullerene based diodes

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We observed an anomalous voltage–current ($V-I$) characteristics of fullerene based diodes in the low temperature regime. The diodes exhibit a negative differential resistance and voltage hysteresis for opposite current sweep directions. This behavior is directly observable at temperatures below 95 K and indicates the formation of highly conductive filaments in the fullerene thin films. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1651642]

Organic diodes, transistors, light emitting diodes, as well as photodetectors and solar cells are attracting increasing attention in the academic and industrial research and development community.[1–4] The organic optoelectronic devices combine the electronic and optical properties of semiconductors with the cheap processing advantages of dyes such as printing, coating, and processing on large areas. The variation possibilities of organic semiconductor materials using organic synthesis provide unique opportunities to tailor the physical properties such as tuning the band gap, electron affinity, ionization potential, etc. For fullerenes and derivatives of fullerenes the electrical conductivity can be adjusted over a large range[5] upon doping with alkaline metals fullerene thin films with metallic conductivities have been prepared.[6] In such doped films electron mobilities up to 6000 $cm^2/V\,s$ have been observed for fullerene layers grown by hot-wall epitaxy using Ba as a dopant.[7] Fullerene films doped with alkali metals showed superconductivity up to temperatures as high as 32 K.[8] Interesting device architectures such as ''bulk heterojunction'' devices have been realized using this class of materials.[9–11]

For a pristine spin-cast fullerene film charge carrier mobilities typically around 2×10^{-3} $cm^2/V\,s$[12] are observed at room temperature. At this temperature the transport is dominated by thermally activated hopping processes. Since for this type of transport lowering the temperature results in a strong decrease of the mobility one would expect a strong decrease of conductivity with decreasing temperatures in these devices.[13,14] However, in this letter we report an anomalous voltage–current ($V-I$) characteristics of fullerene based diodes indicating extremely *high* conductivity in the low temperature regime: Around 120 K a vanishing differential resistance of the device is observed. Further lowering of the temperature leads to a $V-I$ characteristics with negative differential resistance regions which develop into a hysteresis behavior for opposite directions of the current sweep at temperatures below 61 K.

The fullerene based diodes were prepared as follows: The indium-tin-oxide (ITO) covered surface of a glass substrate was cleaned in three steps with toluene, acetone, and methanol in an ultrasonic bath. An approximately 70-nm-thick film of poly (3,4-ethylenedioxythiophene/poly(styrene sulfonate) (PEDOT:PSS) (Bayer AG) as hole conductor was spin coated on the ITO layer under ambient conditions. A methanofullerene [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) chlorobenzene solution (3% wt) was then spin coated on top of the PEDOT:PPS film resulting in a PCBM film of approximately 150 nm thickness. The top contacts were evaporated on the PCBM film under vacuum ($\approx 7\times10^{-6}$ mbar) through a shadow mask and consist of a stack of lithium–fluoride (LiF) (0.7 nm), Al (70 nm), and Au (100 nm). The thicknesses of the PCBM and PEDOT films were determined with a Digital Instruments 3100 atomic force microscope. $V-I$ curves at various temperatures were measured in a He continuous flow cryostat (Cryo Industries) using a Lakeshore 331 as a temperature controller. For the steady state $V-I$ measurements, a Keithley 236 was used. In the $V-I$ measurements the current through the device was controlled and the voltage monitored as opposed to standard $I-V$ experiments where the voltage is controlled and current is monitored. Time resolved voltage–current measurements were performed using a Tektronix TDS 3032B digitizing oscilloscope and a voltage-controlled current source with $R_i > 10^9\ \Omega$ internal resistance triggered by a Wavetek 20 MHz function generator (model 90).

From the device structure and band diagram given in Fig. 1, a built-in voltage V_{bi} of $\approx$1 V is estimated from the energy difference between the lowest unoccupied molecular orbital (LUMO) of PCBM at 4.2 eV[15] and the Fermi level of PEDOT:PSS at 5.2 eV. In agreement with recent experiments[16] an alignment of the Fermi energy in the LiF/Al contact with the LUMO level of PCBM is assumed. The low energy of the highest occupied molecular level (HOMO) of PCBM (6.1 eV)[15] results in a large energy bar-

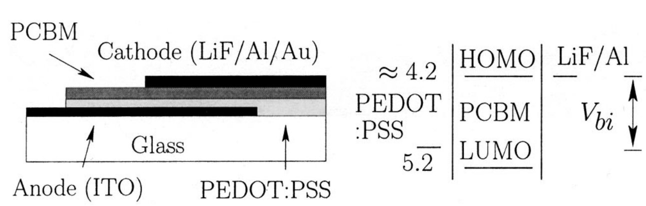

FIG. 1. Geometric structure and band diagram under flatband conditions for the PCBM based diodes.

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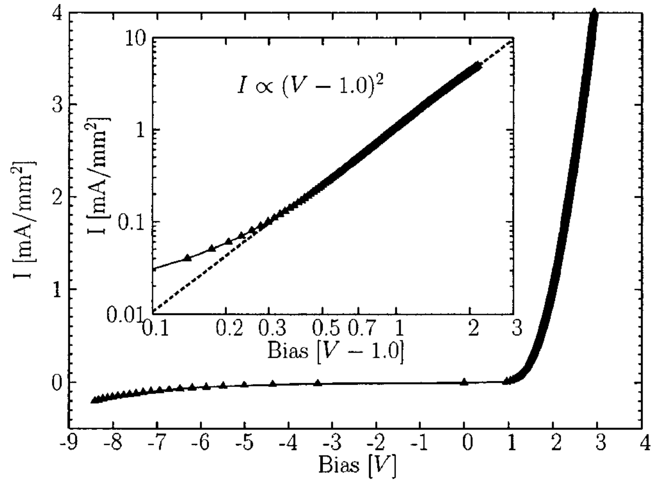

FIG. 2. Room temperature $V-I$ characteristic of ITO/PEDOT:PSS/PCBM device with LiF/Al/Au (0.7/70/100 nm) top contact. Above 1 V, effective charge injection takes place. The injected electron current is SCLC as evidenced by the quadratic dependency vs the effective measured bias $V-V_{bi}$ shown in the inset.

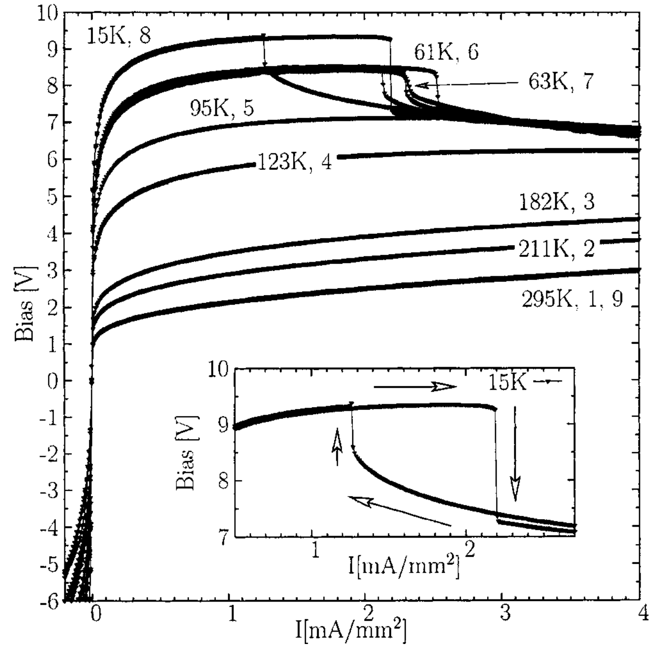

FIG. 3. $V-I$ characteristic at various temperatures T from 295 to 15 K. The curves are labeled by the respective temperature together with the order of the measurement. The room-temperature $V-I$ (No. 9) measured after the 15 K (No. 8) curve, shows no significant difference to the initial room-temperature (No. 1) measurement. This indicates that no nonregenerative effects took place in the sample. For $T \leqslant 95$ K and a current–density above 3.1 mA/mm^2 a NDR is observed. Below 61 K the voltage at the sample is instable and a voltage step to smaller voltages followed by a NDR regime is observed. Subsequently decreasing the current density, the voltage snaps back to the bijective part of the $V-I$ characteristic featuring a hysteresis (see inset). At lower temperature the hysteresis becomes more pronounced.

rier of 0.9 eV between the Fermi energy in the PEDOT:PSS contact and the HOMO of PCBM. This energy barrier effectively suppresses hole injection from PEDOT:PSS into the PCBM. Therefore, for biasing the diode in forward direction (i.e., biasing the PEDOT/ITO contact positive with respect to the LiF/Al/Au contact) only an electron current is injected from the LiF/Al/Au contact into the LUMO of PCBM and no hole current has been considered for this device.

Steady state and time-resolved $V-I$ spectroscopy via applying a certain current density and measuring the resulting voltage drop on the sample has been performed from room temperature down to 15 K. Above 123 K no difference between $I-V$ and $V-I$ spectroscopy could be detected. At room temperature, a quadratic dependency of the current versus the $V-V_{bi}$ is observed, where V denotes the externally measured voltage (see inset in Fig. 2). Such behavior is characteristic for space charge limited current (SCLC) and is described by the Mott–Gurney[17] law

$$I=\frac{9}{8}\epsilon\epsilon_0\mu\frac{V^2}{L^3}, \tag{1}$$

where $\epsilon\epsilon_0$ is the dielectric constant, μ is the mobility, L is its thickness and $V-V_{bi}$ is the effective measured bias. Using $\epsilon=3.9$, $L=150$ nm with a mobility of 1.2×10^{-3} cm^2/V s is evaluated. This value is in agreement with Ref. 12. By lowering the temperature, the high current injection regime is shifted to higher voltages. Also a decrease of the differential resistance at high current densities is observed. Below 95 K all $V-I$ characteristics above 3.1 mA/mm^2 become virtually identical featuring a regime of negative differential resistance (NDR). At 61 K the sample clearly shows a bistable $V-I$ behavior as evidenced by the hysteresis loops shown in Fig. 3. The hysteresis loops become more pronounced at lower temperatures and extend over larger area in the $V-I$ diagram (see Fig. 3).

We interpret these observations as being due to the formation of highly conducting current filaments between the diode contacts. It is well known that a semiconductor exhibiting NDR is inherently unstable because a random fluctuation of the carrier density at any point in the semiconductor produces a momentary change in the equilibrium carrier concentration which will grow exponentially in the time.[18] As a general classification of NDR, it appears that current controlled (S-shaped $I-V$) characteristics can result from filament formation which is regenerative; creation of a single conduction filament leads to conditions in the medium which bring a rapid radial growth or conductivity rise of the filament (for example, by a phase change). On the other hand, voltage-controlled (N-shaped $I-V$) characteristics can result from nonregenerative filament formation[19] and generally result in irreversible changes in the $V-I$ characteristics of the sample.

To estimate the time scale on that the filament formation occurs, pulsed current measurement at 15 K were performed (see Fig. 4). For current pulses of a current density below and in the hysteresis region at 1 and 1.6 mA/mm^2, respectively, the time-resolved voltage response of the sample shows a stable plateau at a voltage consistent with the value observed in the steady-state $V-I$ characteristic. In contrast, applying higher current densities of 3 and 4 mA/mm^2 (i.e., current densities that correspond to the NDR regime), the instability of the voltage response is clearly observable as a voltage drop from ≈ 10 to ≈ 6.5 V at a time scale of 5–10 ms in Fig. 4.

The inset in Fig. 4 displays a magnified part of the voltage response around $t=0.1$ s. This time corresponds to the end of the current pulse. For $t>0.11$ s the voltage is exponentially decreasing with the same time constant for all cur-

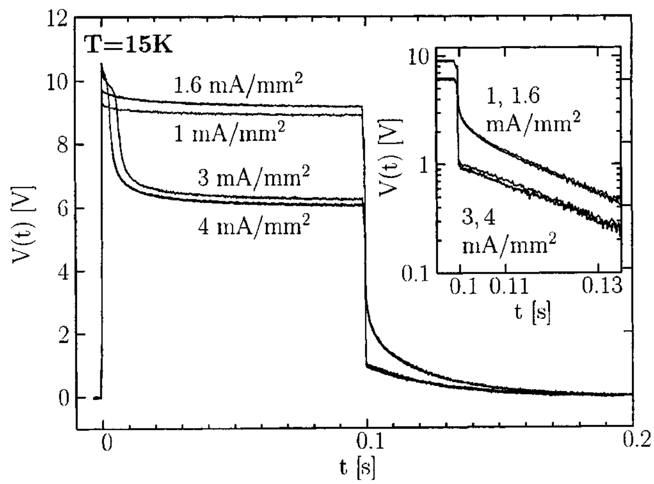

FIG. 4. Low temperature ($T=15$ K), time-resolved voltage response $V(t)$ for a 100 ms current pulse with various injected current densities. At $t=0$, the current density is set to 1, 1.6, 3, and 4 mA/mm^2, respectively, and at $t=0.1$ s it is set back to zero. The inset displays a magnified part of the voltage response on a logarithmic voltage scale around the end of the current pulse at $t=0.1$ s.

rent pulses independent of the magnitude of the injected current (note that the inset of Fig. 4 has a logarithmic voltage scale). In the interval $0.1<t<0.11$ s the voltage decay for the current pulses with 1 and 1.6 mA/mm^2 magnitude differs significantly from the decay observed for the 3 and 4 mA/mm^2 current pulses: For the former pulses a well-resolved and smooth transient is observed in this time window, whereas for the latter pulses (with magnitude in the NDR regime), the voltage drops to ≈ 1 V (i.e., to the flatband voltage) within in the time resolution of the setup. Such fast discharging is an evidence for a low parallel resistance of the device and is consistent with the proposed highly conducting phase of the current filaments in the diode.

In summary, we have observed an anomalous current voltage characteristics of a fullerene based organic diode at low temperatures. The results indicate the formation of highly conductive current filaments in the bulk of the fullerene thin film. The filamented state appears to be metastable and causes hysteresis loops in the $V-I$ characteristics at low temperatures. Up to now, we cannot determine the electronic structure of the highly conducting PCBM within the filaments but a metallic or superconducting state of the PCBM in these filaments cannot be ruled out.

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