Switching effect in poly(p-phenylenevinylene)

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Abstract

A switching effect was investigated in poly(p-phenylenevinylene) (PPV). N-shaped current–voltage (I–V) characteristics of thick ITO–PPV–Al structures were observed, which correspond to switching at a threshold voltage typically in the range 2–5 V from a conducting to a resistive state. The behaviour was independent of the polarity of the applied voltage and the sweep direction. At the threshold voltage, the current changes by approximately one and a half orders of magnitude of its previous value. Pulsed measurements show that the transition time from one to the other conductive state is less than 1 μs. The switching effect can be associated with strongly localized current pathways.

Keywords: Poly(p-phenylenevinylene); Threshold voltage; ITO–PPV–Al structures

1. Introduction

A switching effect, i.e., a rapid and reversible transition between different conducting states initiated by electric field or current, was observed in various types of disordered inorganic materials, particularly in chalcogenade glass semiconductors [1,2]. In recent years, there has been growing interest in switching effects in organic polymers [3–5]. There is both practical and physical interest in studying the switching effect in organic devices, e.g., light-emitting diodes (LEDs), based on the conjugated polymer poly(p-phenylenevinylene) (PPV). On one hand, the ability of a polymer layer to have different conduction states can be used for information storage applications. On the other hand, the switching effect has, at the same time, been observed in organic devices as a spontaneous phenomenon causing their instability. In this connection, elucidating the origin of this phenomenon is important for improving LED life.

2. Experimental

We studied the switching effect in PPV films prepared on indium-tin-oxide (ITO)-coated glass substrates by thermal conversion of a soluble precursor polymer as described in Ref. [6]. To avoid enrichment of leaving groups in the film and thus to reduce their reaction with the ITO, we successively casted and converted several PPV layers of about 100–200 nm in thickness each. The total thickness of all PPV layers was 400–1000 nm. Al electrodes with areas of 0.1 cm^2 were evaporated in vacuum onto the PPV layers.

The direct current and transient current–voltage (I–V) characteristics were measured on ITO–PPV–Al sandwich structures with a conventional experimental setup. Voltage pulses of duration in the range between 0.001 and 10 ms were used for pulse measurements. Direct current I–V characteristics were measured with a Keithley Source Measure Unit SMU 237. A 400-MHz digitizing oscilloscope was used in the pulse measurements.

3. Results and discussion

Fig. 1 shows I–V characteristics obtained using dc and pulsed voltage with a duration of 1 ms. The I–V curves have a pronounced N-shape irrespective of the polarity of the applied voltage (curves 1 and 3). The characteristics also demonstrate the independence from the direction in which the voltage amplitude is changed (curves 1 and 2). The N-shaped I–V characteristics correspond to switching at some threshold current or voltage from a conducting to a resistive state. The threshold current and voltage ranged from 10^{-3} to 10^{-2} A, and from 2 to 5 V, respectively. At

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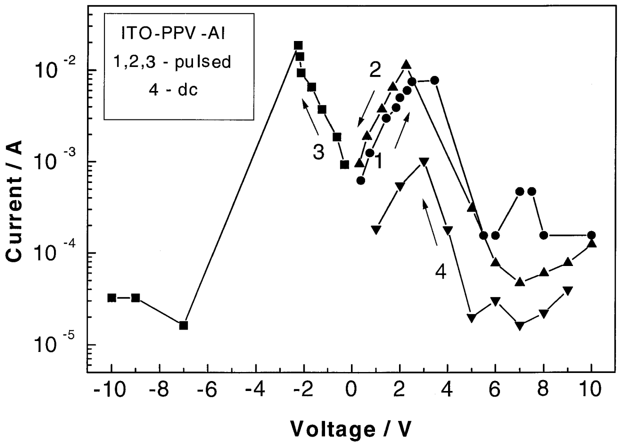

Fig. 1. Direct current and pulsed current–voltage characteristics of an ITO–PPV–Al structure with a PPV layer thickness of 420 nm. The pulse duration was 1 ms.

the threshold voltage, the current changes by approximately one and a half orders of magnitude as compared to its previous value. Usually, after several sweeps, the N-shaped DC I–V characteristics transform into curves with smooth shape and the threshold current decreases with increasing sweep number.

Our investigation revealed that well-reversible switching in PPV can be achieved using pulsed applied voltage. We observed more than 10^3 cycles of switching without any changes in the main parameters at a pulse duration of 1 ms. The good reversibility shows that the nature of switching in PPV is not associated with a simple destruction of localised current pathways.

Also, the characteristics describing the evolution of the switching process with time are very important. Fig. 2 demonstrates the current pulses obtained on a load resistor of 200 Ω upon applying short rectangular voltage pulses of various amplitudes. The current pulses consist of two components. The first of these represents the transient current spike controlled by circuit parameters. This current charges the sample capacity. The second component is the flat part of the current pulse, associated with the injection current seen under the threshold amplitudes of the applied voltage pulses. One can see that the current decreases when the amplitude of the applied pulses overcomes the threshold value of about 4 V. The decay time of the first component limited the possibility of determining the transition time from one to the other conductive state in switching, but it can be estimated to be less than 1 μs.

A specific feature of the switching effect in PPV is the transition from a conducting to a resistive state with increasing electric field. This type of the transition was predicted in the case of the small polaron transport [7], which may take place in PPV [8]. The dependence of the current I on the electric field F obtained in Ref. [7] obeys

$$I \approx \sinh(eFa/2kT)\exp\{-(eFa)^2/16E_a kT\},$$

where a and E_a are the distance and the activation energy of carriers jumps, e, the elementary charge, k, Boltzmann's constant, and T, the absolute temperature. As is evident from the field dependence the departure from Ohm's law begins at a field of $F_0 = 2kT/ea$. At a field $F_1 = 16E_a/ea$, when a carrier will gain an energy eF_1a upon jumping higher than E_a, the differential resistance becomes negative. Assuming $E_a = 0.15$ eV and $a = 10^{-7}$ cm, one can obtain $F_1 = 2.5 \times 10^7$ V/cm, which exceeds the switching threshold voltage by two orders of magnitude. This type of switching was observed in an organic polymer composite system (polyethylene/carbon) [3] and attributed to a sharp decrease of conductivity with temperature increasing to 403 K.

The mechanism of a temperature induced transition is realized if the applied voltage is capable of raising the sample temperature. It is possible to estimate roughly the sample temperature at the threshold voltage. Assuming that heating for 0.5 μs before switching in pulsed case is an adiabatic process, the temperature rise is determined by the relation $\Delta T = IUt/cAd\rho$, where d is the layer thickness, ρ, the density, c, the heat capacity, and A, the area of the device. For a homogenous current flow over the entire device area it is only possible to obtain $\Delta T = 0.005$–0.01 K at the above-given threshold parameters and $c = 5 \times 10^2$–10^3 W s/kg K. Thus, the switching mechanism under consideration can be realized only in the case of a strong inhomogeneity of the current flow. If localized current flow through spots with a total cross-section of 10^{-3}–10^{-4} of the electrode area is assumed, the current density in the filaments can be estimated as 10^2–10^3 A/cm^2, which gives a temperature rise in these spots of about $\Delta T = 10$–100 K.

In conclusion, we present observations of N-shaped I–V characteristics and transient currents in PPV. Our findings indicate that a strongly inhomogeneous current flow is involved in this phenomenon, however, several

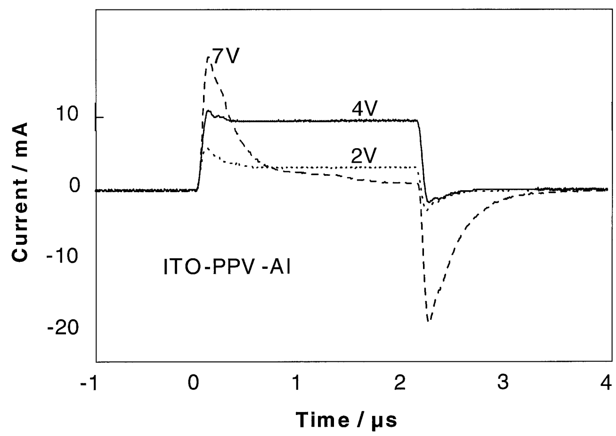

Fig. 2. Transient currents in an ITO–PPV–Al structure for different pulse amplitudes. The device current was measured as the voltage drop at a 200-Ω resistor in series to the sample.

questions concerning the microscopic nature of this effect and the involved mechanisms remain to be answered, which will require further investigations.

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