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Temperature and Frequency Dependence of the Electrical Properties of Thin Organic Films

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We performed an experimental investigation of the low temperature electrical behavior of thin films of conducting polymers. Using the self-assembly technique, thin samples with a total thickness in the range of 5-60 bilayers were prepared by the alternate deposition of polypyrrole (PPY) and polythiophene acetic acid (PTAA) layers on a glass substrate. The intrinsic anisotropy of the samples was manifested in their electrical characteristics, since the temperature dependence observed for the conductivity along the surface was different from that measured in the direction perpendicular to the substrate. While the longitudinal component of the resistivity tensor changes with temperature as in a typical semiconductor, a 'metallic-like' profile is identified for the transversal component, confirming that different transport mechanisms must dominate the charge transfer along these two directions. A preliminary investigation of the dielectric characteristics of those samples has allowed us a better understanding of the charge storage processes in these samples.

Keywords: polypyrrole and derivatives; self-assembly; conductivity; organic/inorganic interfaces.

INTRODUCTION

The low temperature behavior of the resistivity tensor of conducting polymer samples has been subject to a long standing interest due to the possibility of identifying independent mechanisms for the intra- and

inter-chain charge transfer. For this reason, it becomes important to examine the electrical characteristics of better organized samples of these materials, such as those prepared by Langmuir-Blodgett and self-assembly (SA) techniques[1,2], where the preferential deposition of the material on a planar substrate must contribute to improved microscopic organization. Unfortunately, the large physical anisotropy of these samples (with characteristic longitudinal dimensions of the order of mm but transversal thickness in the nm range) poses severe technical problems for the simultaneous measurements of the longitudinal and transversal components of the corresponding electrical resistivity tensor. These difficulties have so far precluded more extensive investigations of the characteristics of these individual components. To our knowledge, in this work we present the first set of results in the 4-300 K temperature range for the anisotropy of the electrical resistivity tensor of thin organic films prepared by the self-assembly technique.

EXPERIMENTAL

Sample Preparation

Gold recovered common glass slides of 25 x 25 mm size had the dual purpose of serving as substrates for the SA deposition and as bottom electrodes for the conductivity measurements. A 400 Angstroms chromium layer was initially deposited on each substrate and, subsequently, it was recovered by a 600 Angstroms layer of evaporated gold. A protecting mask was used to establish a 1 mm gap between two disconnected regions of the evaporated metal that could to be later used as independent electrodes for the electrical measurements in the longitudinal direction.

Once clean, the substrates were used for the deposition of the polymeric layers accordingly to the SA method. Each substrate was immersed for 15 min in the polycation (PPY) solution, and then removed and dipped for 3 min in a water recipient. Afterwards, a nitrogen flow was used to dry the substrate before an immersion for 15 min in the polyanion (PTAA) solution and the repetition of the cleaning and drying steps. After this first bi-layer has been deposited, the entire procedure is repeated for the number of times desired to form the sample of a given thickness. (The samples used in this study had thickness in the range of 5-60 bilayers).

The polymeric layers were deposited over the entire immersed surface of the substrate and hence they bridged the gap between the two

previously deposited electrodes, a fact that was confirmed by measuring the longitudinal conductivity of the sample at room temperature. Using the same mask, a second evaporation of gold on top of the polymeric layers (Figure 1) produced a final electrode arrangement which permitted not only an independent measurement of the longitudinal component but also to determine the transversal conductivity, i.e. the charge transport across the deposited bi-layers. Epoxy silver paint CW2400 (Chemtronics, USA) was used for establishing the required external electrical contacts.

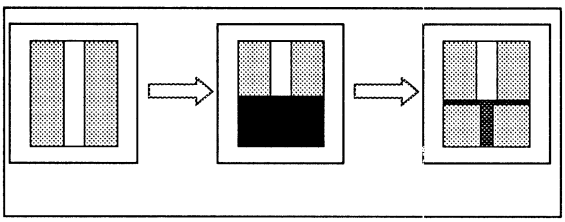

FIGURE 1: Consecutive steps adopted for the preparation of the samples: deposition of the bottom electrodes (left), of the polymeric bi-layers (center) and of the top electrodes (right).

Experimental Setup

A Supervarimag cryogenic system (Janis, EUA) was used for the low temperature investigation of the electrical properties of the samples, and we monitored the level of helium by a 241 Lakeshore (USA) controller. The experimental setup for the electrical measurements consisted of an ITC 503 (Oxford, UK) temperature controller with a GaAs sensor, a voltage/current source model 237 and a model 195A multimeter (Keithley, USA) for the measurement of the resistance along the longitudinal and transversal directions of the sample, respectively. All equipments were controlled using a computer under the GPIB protocol.

The Labview 4.1 software (National, USA) was used for controlling the experiment and registering the data points for the longitudinal and transversal components of the resistivity tensor, the temperature and the interval of time required to stabilize the temperature gradient of the sample to less than 0.2K/min. Consecutive data points were collected within a time interval of 5 s.

RESULTS

We have first examined the experimental conditions for obtaining an Ohmic behavior in the electrical response of the samples, since the range of linear I-V behavior becomes smaller for the lower temperatures (Figure 2).

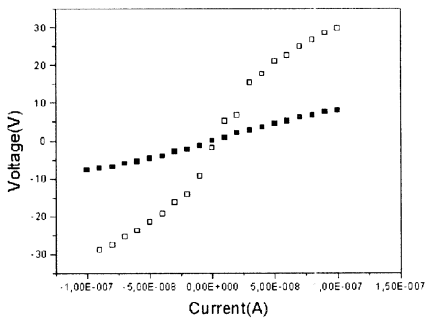

FIGURE 2: I-V characteristics for measurement of the resistance of a PPY/PTAA 25-bilayers sample along the longitudinal direction at 17K(■) and 11K (□).

When obtaining the value of the resistance along the surface and in the transversal direction, special care was taken to limit measurements to the linear regime for each temperature considered.

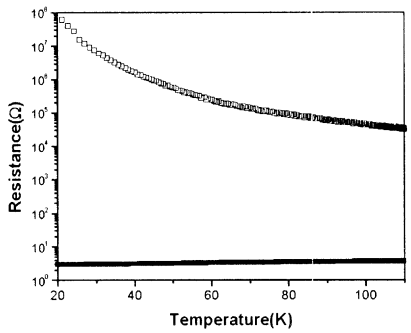

FIGURE 3: Resistance in the longitudinal (□) and transversal (■) directions of 25-bilayers PPY/PTAA sample as a function of temperature.

In a typical experiment lasting 24 hours, more than 17,000 individual measurements were performed in the entire temperature range. In general terms the electrical behavior of the resistance of all samples examined is that presented in Figure 3, where one can see that the longitudinal component increases as the temperature approaches the lower limit. Since the ratio R_{long}/R_{transv} also increases markedly (from $\sim 10^3$ at room temperature to $\sim 10^9$ at 4.2K), it seems reasonable to assume that the charge transport along the longitudinal plane of the samples is more affected by the decrease in temperature than that along the transversal direction[3]. A detailed analysis of the individual components reveals a complex pattern for the temperature dependence, as discussed below.

Longitudinal Resistivity

For a better analysis of the electrical behavior of the samples we can convert the measured resistance in resistivity data by assuming an average thickness of 20Å for each deposited bilayer[1]. In Figure 4 we present the results for the longitudinal resistivity of samples prepared under slight different conditions, varying number of deposited layers and distinct aging history.

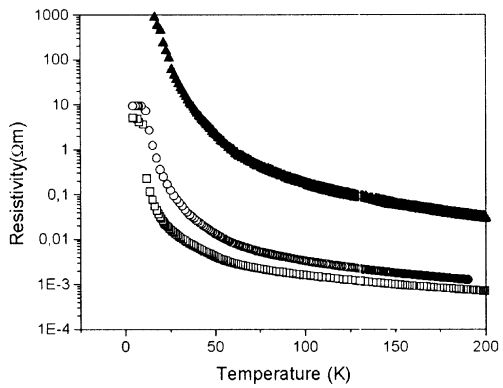

FIGURE 4: Longitudinal resistivity of PPY/PTAA 15- (○), 20- (□) and 25- (▲) bilayers samples.

In spite of the differences between the samples considered, in the above curves one can observe a similar profile for the variation of the longitudinal component of the resistivity tensor with the temperature

change. Two different conduction regimes can be identified: a high temperature (50<T<300K) region, where the resistivity has a moderate rate of change with the variation of the temperature, and a low temperature regime (T<50K), where the resistivity increases in a marked way[4]. This is more clear in the data of Figure 5, where we plot the thermal activation energy[5-7]

$$W = -\Delta \log \rho / \Delta \log T$$

of the corresponding charge transfer processes.

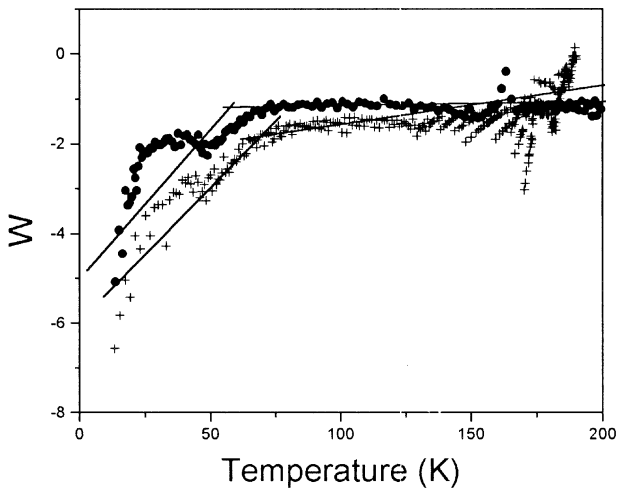

FIGURE 5: Activation energies associated to the longitudinal resistivity of PPY/PTAA 15- (+) and 20- (•) bilayers samples.

Transversal Resistivity

As shown in Figure 6, a less simpler behavior emerges from a detailed analysis of the temperature dependence of the transversal component of the resistivity. While for T > 40 K the resistivity has a 'metallic-like' characteristic and increases with the temperature, a minimum is observed in the 10-20 K region, below which a normal semiconducting behavior is observed. As it can also be seen in the curves of Figure 6, the position of the observed minimum and its shape depend on the total thickness of the sample examined. We should point out that although the existence of minima in the resistivity of thin samples of conducting polymers has been previously observed[2,8], no low-temperature

measurement of the individual components of the resistivity tensor has been made so far.

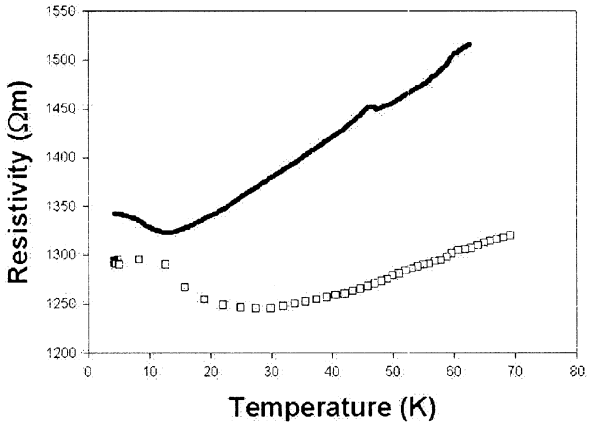

FIGURE 6: Transversal resistivity of PPY/PTAA 10- (□) and 15- (•) bilayers samples.

AC Characterization of the Thin Samples

To better explore the electrical characteristics of the thin organic films, we have used a model 4192A impedance analyzer (Hewlett-Packard, USA) for the investigation of their response to a frequency-dependent applied field in the 10^1-10^7 Hz range.

If we adopt the model of conducting grains usual for the description of conducting ceramics[9-11], we can describe the polymer by a set of conducting islands immersed in an insulating medium. This model not only accounts for the observed dissipative conduction in the static regime but also allows for polarization effects, i.e. energy absorption by internal modes with consequent reorganization of the bound charges. In this manner the conducting polymer sample would be the electrical equivalent of a parallel association of resistors and capacitors. We should point out that in previous work[12], we have been able to describe the thermal behavior of the dielectric relaxation of polypyrrole samples by a network of resistors and capacitors excited by an electrical field of the same frequency as that used in the actual experiment.

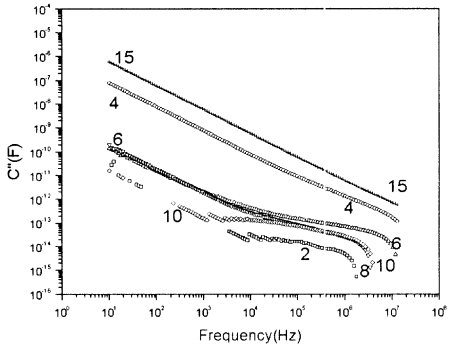

FIGURE 7: Imaginary part of the dielectric constant of PPY/PTAA samples with thickness varying between 2- and 15-bilayers.

In Figure 8 we present a RX diagram of the polarization Rs as a function of the losses Xs[9-11].

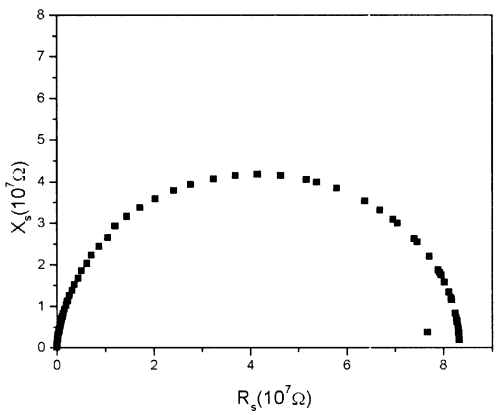

FIGURE 8: RX diagram for a 8-bilayers PPY/PTAA film.

From the above curve, we can obtain directly the value ($8.5x10^7\Omega$) of the resistance of the sample in the quasi-static regime (right side), infer the frequency (1,3KHz) in which the relaxation occurs in the

parallel configuration (central part) and estimate the limiting values (zero) for the real and imaginary parts of the impedance when the frequency tends to infinity (left side).

Due to the success of the conducting grains model in describing the frequency dependent behavior of these thin films, one can think of their nature as composed by small conducting domains. A more detailed investigation of the dielectric properties of thin organic films is being carried in our laboratory and will be reported elsewhere.

CONCLUSIONS

We have shown that very thin films of conducting polymers prepared by the self-assembly technique exhibit an strong anisotropy in their electrical properties. The longitudinal component of the resistivity of PPY/PTAA samples varies inversely with the temperature, while the transversal component shows a 'metallic-like' behavior for $T > 20$ K. A preliminary investigation of the dielectric properties of these samples shows that the charge storage processes can be well described by a model of small conducting domains immersed in an insulating medium.

Acknowledgments

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