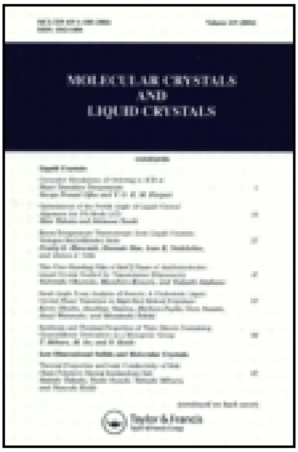

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S. A. Jeglinski [a] , M. E. Hollier [a] , J. Gold [a] , Z. V. Vardeny [a] , Y. Ding [b] & T. Barton [b]

[a] University of Utah, Physics Department, Salt Lake City, UT, 84112

[b] Iowa State University, Chemistry Department, Ames, IA, 50011

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ELECTRICALLY SYMMETRIC POLY(PHENYLENE ACETYLENE) DIODES

S.A. JEGLINSKI, M.E. HOLLIER, J. GOLD, AND Z.V. VARDENY
University of Utah Physics Department Salt Lake City UT 84112

Y. DING AND T. BARTON
Iowa State University Chemistry Department Ames IA 50011

Abstract A diode has been fabricated with poly(phenylene acetylene) [PPA] as the electroluminescent polymer. The device exhibited an unusual symmetric (positive and negative bias) I-V characteristic and electroluminescent output. These experimental results are discussed in terms of tunneling of electrons and holes *via* localized states.

INTRODUCTION

Luminescent conjugated polymers have recently attracted considerable interest because of their use as active materials in light-emitting devices (LEDs).[1] Operation as such depends upon the ability to inject into the polymer electrons and holes, which then recombine to emit light.

EXPERIMENTAL SETUP AND PROCEDURE

A PPA solution was made by mixing powder with $CHCl_3$ (about 50 ml/mg). The solution was thoroughly dissolved by immersion in an ultrasonic agitator. The solution was then filtered into clean glassware with a 0.2 μm Nalge syringe filter. Semitransparent ITO-coated silica plates (≈ 200 Ω/sq, 25 nm thick ITO on 1.5 mm thick silica) were procured and cut with a diamond saw into approximately 12 X 12 mm squares. Approximately one-third of the ITO (a 4 mm strip on one end) was removed with a standard solution of *aqua regia*. The substrates (2/3 ITO-silica, 1/3 silica-only) were then thoroughly cleaned by ultrasonic agitation in a $CHCl_3$ bath several times, with a final wash in distilled deionized water.

Fabrication was accomplished by spin-casting the filtered PPA solution onto the prepared substrates, forming a polymer layer about 1000-1500 Å thick. The spin-casting and handling of the polymer/ITO substrate were performed in a glove-box purged with nitrogen. Part of the polymer was then stripped off with a solvent-dipped cotton swab. Aluminum electrodes were thermally evaporated onto the PPA/ITO substrates in a vacuum chamber with an operating pressure of about 8 X 10^{-6} Torr. Figure 1 shows the final

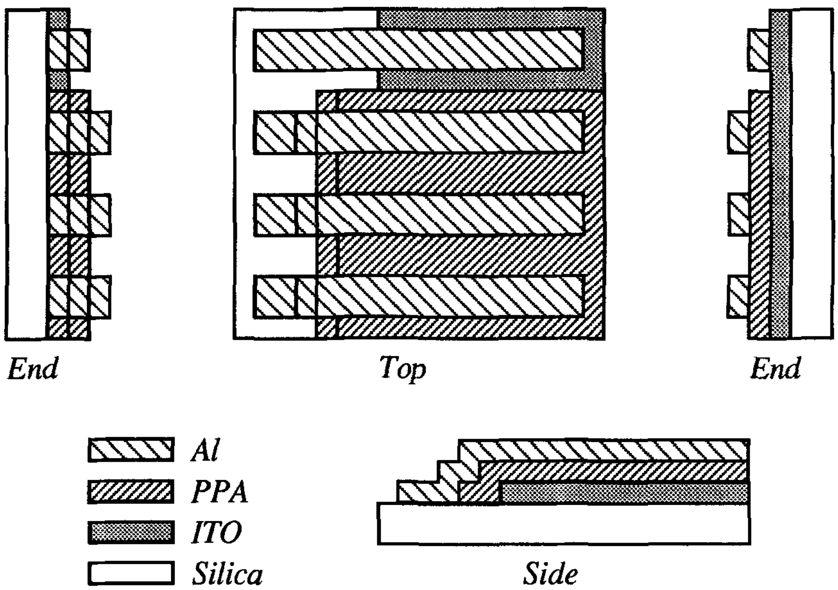

Figure 1. Al/PPA/ITO Device Construction (not to scale)

geometry of the prepared device. The stripping procedures described above helped ensure that there was no inadvertent shorting between the Al and the ITO.

A Keithley 236 source-measure-unit (SMU) was interfaced to a PC and connected to the aluminum electrodes with microclips. The SMU was then used to bias the ITO layer positively and negatively with respect to the Al electrodes. Swept measurements were made in the range from -20 to +20 Volts. All handling and measurements were made either in the nitrogen-purged glove-box or in an evacuated cryostat.

RESULTS

A variety of results were obtained. Many devices never exhibited anything other than resistive behavior. Some devices exhibited a nonlinear I-V characteristic after the device was "burned-in" by applying a constant voltage for a relatively long period of time (several minutes), during which time the electrical properties eventually settled into a repeatable pattern. Some devices exhibited a well-defined nonlinear I-V characteristic immediately, but often would fail rapidly unless operated while immersed in liquid nitrogen, probably due to excess power dissipation in the device. Two of the devices constructed showed a symmetric electrical characteristic, *i.e.*, equal but opposite forward-bias and reverse-bias behavior. This result is shown in Figure 2.

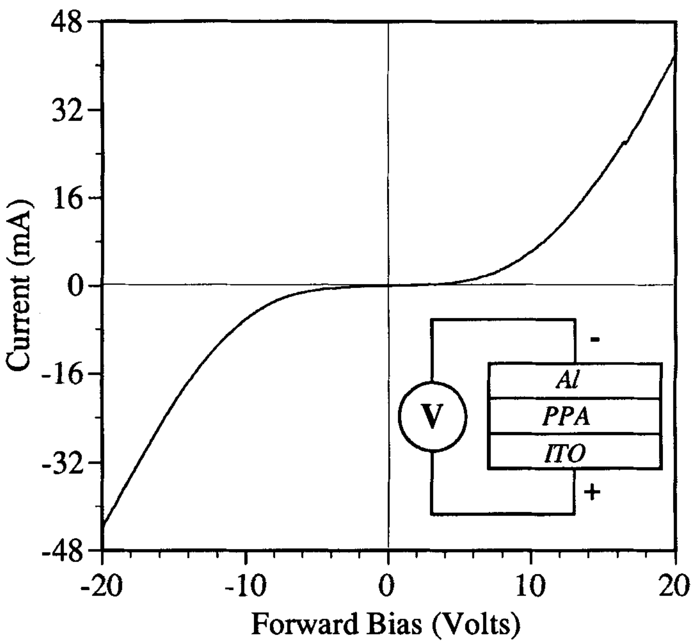

Figure 2. I-V Characteristic of symmetric Al/PPA/ITO Diode

The device represented in Fig. 2 was observed to emit light from an activated electrode in both forward-bias and reverse-bias. The light was easily seen with the naked eye and judged to have equal intensities in both forward- and reverse-bias. The device failed before quantitative measurements of the emitted light could be made.

DISCUSSION

The basic theory of tunneling predicts the relationship[2]

$$I \propto V^2 \exp(-\beta d / V) \tag{1}$$

where d is the polymer thickness. Figure 3 shows $ln(I/V^2)$ plotted versus $1/V$ for the reverse-bias curve (the curve for forward-bias is virtually identical).

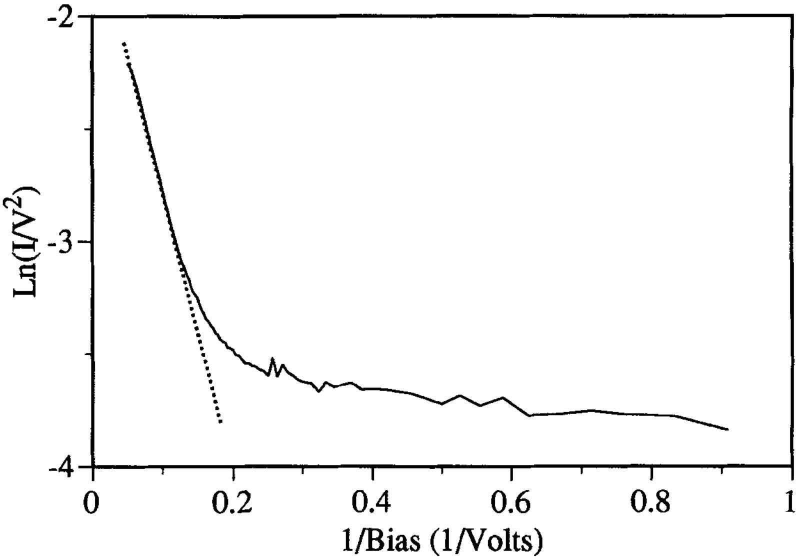

Figure 3. Ln(I/V²) vs. 1/V for the data in Fig. 2.

The plot is linear above a certain voltage range (dotted line), indicating a tunneling mechanism. If we assume a triangular barrier, β is given by[3]

$$\beta = \frac{4\sqrt{2m^*}\varphi^{3/2}}{3e\hbar} \tag{2}$$

where φ is the barrier height and m^* is the carrier effective mass. If we assume that the effective mass equals the free electron mass, data from Fig. 3 results in $\varphi = 0.07$ eV.

The lower voltage range in Fig. 3 cannot be considered a valid range for an alternative linear fit to the excess current because the tunneling length ($L = \varphi/F$) is too large for direct tunneling (L ≈ 60 Å for F = 1 Volt / 1000Å) to occur.

It has been suggested by Raikh[4] that the excess current at low voltages is due to sequential tunneling of electrons via localized states in the gap. This theory predicts the following I-V relationship:

$$I \propto \exp(-\gamma\sqrt{d/V}) \tag{3}$$

where $\gamma = 4\sqrt{\frac{\Gamma}{3}}\left(\frac{2m^*}{\hbar^2}\right)^{1/4}\varphi^{3/4}$ and $\Gamma = \ln\left(\frac{1}{p}\right)$.

p is defined as the probability that an electron finds a localized state with an energy close to the Fermi level. Figure 4 shows *ln(I)* plotted versus $1/\sqrt{V}$ for the reverse-bias data in Fig. 2.

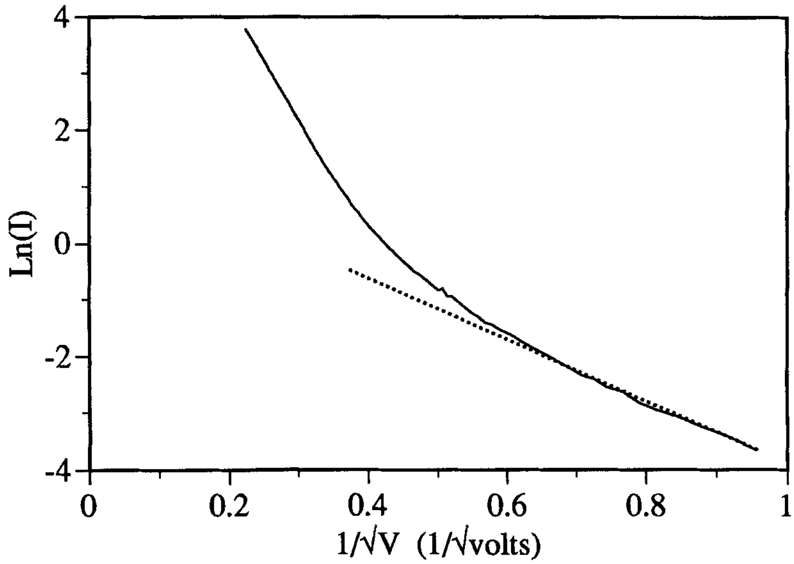

Figure 4. Ln(I) vs. 1/√V for the data in Fig. 2.

The plot is linear below a certain voltage range (dotted line), as predicted by the theory. Since neither p nor φ change with field strength, the higher voltage range in Fig. 4 must still be explained by an alternative mechanism, such as standard tunneling described for Fig. 3.

The electrically symmetric I-V characteristic in Fig. 2 can be explained for low voltages by the localized-state theory (Eq. 3), with defects providing the localized gap states. If the defects are amphoteric (able to accommodate either electrons or holes), it is possible to observe electrically symmetric behavior at low voltages. The symmetric I-V characteristic at higher voltages is more difficult to explain. Barriers to electron and hole injection should in principle be different because the work function of Al (4.0 eV[5]) does not match the electron-injection band as well as the work function of ITO (4.7 eV[6]) matches the hole-injection band. On the other hand, it is well-known that the effective work function of a material strongly depends on surface characteristics. The cleanliness of surfaces and/ or the presence of insulating oxide layers can themselves create barriers and surface states which appear to minimize differences in work functions. In particular, it may be possible for each contact to inject electrons or holes, depending on the bias conditions and the metal/ polymer interface properties.

If both contacts have the ability to inject electrons or holes because of effectively equivalent work functions and the presence of surface states, a symmetric I-V characteristic due to tunneling through relatively small barriers may logically follow. This possibility is difficult to evaluate because of a lack of knowledge of the details of the metal/polymer interface.

SUMMARY

The fabrication and testing of a luminescent polymer diode device has been reported and discussed. The device exhibited symmetric I-V characteristics and luminescence in both forward- and reverse-bias. A theory involving tunneling *via* localized gap states[4] was considered to explain excess current and electrically symmetric behavior at low voltages. Direct tunneling from the contacts into hole- and electron-injection bands is the likely mechanism for the electrical characteristics and luminescence at higher voltages. To explain the electrically symmetric behavior at higher voltages, it is suggested that non-ideal metal/polymer interface properties allow the injection of holes or electrons through similar barriers from either contact. Future work will address this issue.

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