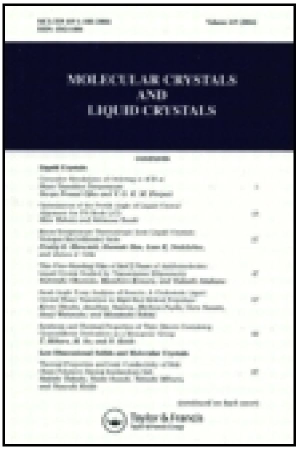

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Semiconductor Devices Using the Plasma-Polymerized Pyrrole

Soo Young Park [a], Ki Poong Lee [a], Dong Hoon Choi [a], Nakjoong Kim [a] & Suk Kyu Song [b]
[a] Polylmer Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, 130-650, Korea
[b] Dept. Textile Eng., Faculty of Engineering, Hanyang Univ., Seoul, 133-791, Korea
Version of record first published: 04 Oct 2006.

Mol. Cryst. Liq. Cryst. 1994, Vol. 247, pp. 321–329
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SEMICONDUCTOR DEVICES USING THE PLASMA-POLYMERIZED PYRROLE

SOO YOUNG PARK, KI POONG LEE, DONG HOON CHOI,
NAKJOONG KIM, AND SUK KYU SONG*
Polylmer Division, Korea Institute of Science and Technology,
P.O.Box 131, Cheongryang, Seoul 130-650, Korea, *Dept. Textile Eng.,
Faculty of Engineering, Hanyang Univ., Seoul 133-791, Korea

Abstract Organic semiconducting thin film of 10^{-6} S/cm conductivity was prepared by the plasma polymerization of pyrrole followed by the thermal treatment in nitrogen. Obtained film (TPP-Py) was uniform, pin-hole free, and optically clear. We investigated the electrical and photoelectrical properties of the semiconductor devices consisting of the TPP-Py sandwiched between the two planar electrodes, such as the Au, Al, ITO, and n-Si. It was found that the TPP-Py formed ohmic contact with either Au or ITO electrode and showed a weak photoconducting behavior. On the other hand, the Schottky contact and heterojunction of TPP-Py with Al and n-Si respectively showed the rectification and photovoltaic properties. The performances of these cells were characterized in detail through the measurement of dark- and photoconductivity, and also of the capacitance-voltage (CV) characteristics.

INTRODUCTION

There is a great research interest in the fabrication of polymer electronic devices with the semiconducting π-electron conjugated polymers. Polymeric Schottky diode,[1,2] light emitting diode,[3] heterojunction device,[1] and the field-effect transistor [4] are under active research in this field. The advantage of polymer electronic devices comes mainly from the simple fabrication method such as the spin coating, casting, and dip coating which are suitable for the large area device fabrication.

Recently, we have developed a more convenient way of device fabrication utilizing the direct plasma-polymerization coating of semiconducting organic films in vacuum.[5] In particular, we have demonstrated the good performance of the polymeric field-effect transistor (FET) using the thermally-treated plasma-polymerized pyrrole (TPP-Py) as an active p-type semiconductor layer.[5]

In the present work, we extend the application of this plasma polymerization method to the fabrication of polymeric Schottky diode and the heterojunction device.

EXPERIMENTAL

Fabrication of TPP-Py film

Pyrrole (Aldrich Chemical) was purified by the vacuum distillation and was degassed repeatedly by the freeze-pump-thaw method just before the plasma polymerization. Plasma polymerization was carried out in a capacitively-coupled bell-jar reactor operating at 13.56 MHz frequency under the discharge power of 5 W, pyrrole flow rate of 14.5 mg/min, and the system pressure of 70 mTorr, where the average deposition rate of the film was 270 Å/min. The thickness of the film was adjusted by the duration of glow discharge. Post-plasma thermal treatment was effected at 300 °C for 1 hr under N_2 atmosphere.

Device structure

FIGURE 1 illustrates the structure of semiconductor devices fabricated in this work. The ohmic and Schottky diode were prepared on the ITO-coated glass substrate as shown in the FIGURE 1(a), where the upper electrode metals, Au and Al respectively, were thermally evaporated under the vacuum of less than 10^{-4} Pa. On the other hand, thoroughly cleaned and oxide-removed n-Si wafer ([100], Lucky Advanced Materials Inc.) was used for the preparation of the heterojunction device shown in FIGURE 1(b). The insulating SiO_2 layer was formed by the CVD method and was patterned by etching out using the buffered HF solution.

Measurements

For the current-voltage measurement, Keithley 617 electrometer and the Hewlett Packard 100 MHz digital oscilloscope were used. The Oriel Xe lamp with IR-cut and neutral filter was used as a light source for the photocurrent measurement. The capacitance-voltage (CV) characteristic was measured using the Hewlett Packard precision LCR meter.

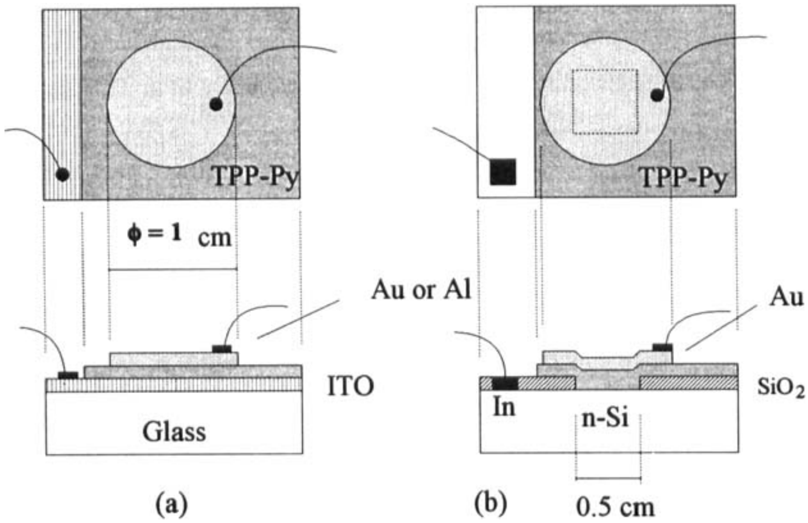

FIGURE 1 Schematic view of (a) the ohmic or Schottky diode, and (b) the p-n heterojunction.

RESULTS AND DISCUSSION

The as-prepared film of plasma polymerized pyrrole (PP-Py) was very uniform, pin-hole free, optically clear, and semiconducting (2×10^{-9} Scm^{-1}). However, the conductivity could be increased further (about three orders of magnitude) by the post-plasma thermal treatment in nitrogen without any adverse effect on the film (TPP-Py) quality.

FIGURE 2 shows the dark- and photocurrent of TPP-Py film sandwiched between ITO and gold electrode (ITO// TPP-Py// Au). The current value is seen to be very linear against the bias voltage and also symmetric, which is perfectly the same as when we measured the Au//TPP-Py//Au ohmic cell. These facts suggest that TPP-Py forms quite good ohmic contact with both the gold and ITO electrode. The bulk conductivity of TPP-Py was calculated as 1.4×10^{-6} S/cm from the slope of the curve, and the photocurrent was estimated to be around 10% of the dark current at the low electric field shown in the FIGURE 2. Comparing the conductivity values, such an enhancement in the dark- and the photoconductivity of TPP-Py from those of PP-Py is likely to result from the enhanced π-electron conjugation by the thermal treatment as was evidenced by the change of IR, and UV-visible spectra in our previous work.[5]

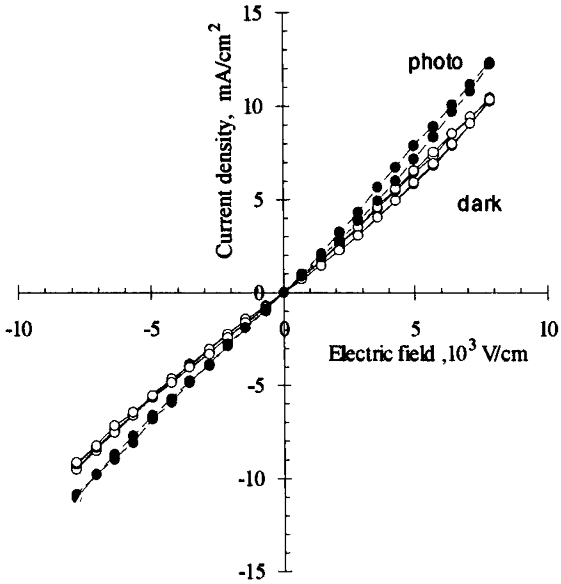

FIGURE 2 Dark- and photocurrent of Au // TPP-Py // ITO cell.

Since the TPP-Py was proven to be a p-type semiconductor[5] and formed an ohmic contact with Au (see FIGURE 2), we expect the TPP-Py to make a Schottky barrier with the low work-function metal such as Al. FIGURE 3 shows the dark- and photocurrent of this Al//TPP-Py//Au Schottky diode as a function of the bias voltage. The performance of this device was not reproducible at the higher bias-voltage region (over 2 V) due to the occasional electrode damages and the erratic switching phenomena. However, the device performance was very reproducible in the bias voltage range shown in the FIGURE 3, where we find that the observed current value (μA order) is much lower than the ohmic value (mA order) of FIGURE 2. It is also seen that the photocurrent sensitivity in the reverse bias region is very high, which is well consistent with the usual polymeric Schottky diodes.[1,2]

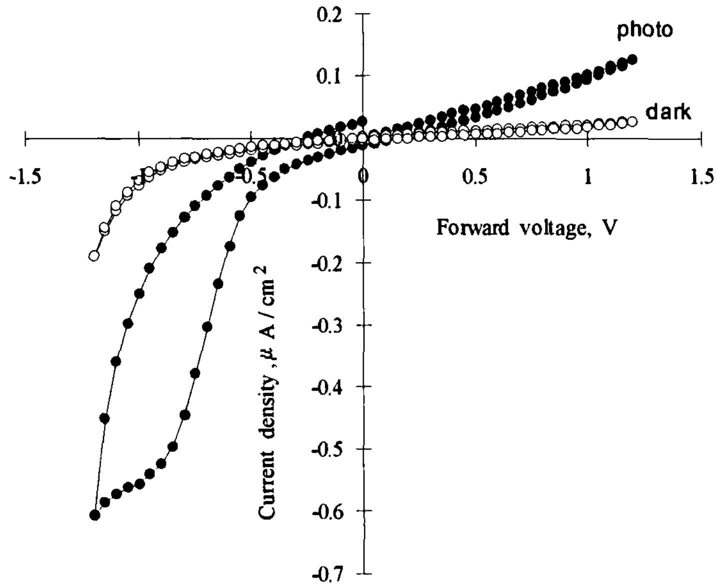

FIGURE 3 Dark- and photocurrent of Al // TPP-Py // Au cell. TPP-Py is 2000 Å thick and the contact area is 0.78 cm^2.

FIGURE 4 shows the dark- and photocurrent of TPP-Py//n-Si hetero-junction structure. The rectification of this polymer device is shown in the inset (a), where the forward bias corresponds to applying negative voltage to n-Si. Although some extent of leakage current is observed in the reverse bias region, it is clear that the forward-biased current follows the standard Eq. (1) of p-n heterojunction

$$\ln(J / J_0) \cong q(V - R_s I) / nkT \qquad (1)$$

where J is the current density, J_o is the saturation current density, V is the forward applied voltage, R_s is the series resistance of TPP-Py, I is the current, and n is the perfection factor. The linear relationship between ln J and V (according to Eq. (1)) is shown in the inset (b) of FIGURE 4, from which J_o is calculated as 2×10^{-10} A/cm^2, and n as 4.3. It is also seen that the photocurrent is very large in the reverse bias region compared to that in the forward bias region. Such behavior is normally observed in the polymer/semiconductor heterojunction and is likely to be explained by the enhanced collection efficiency of photogenerated carrier under reverse bias condition.[1]

When the TPP-Py//n-Si heterojunction device was operated in the photovoltaic mode under the 1.45 mW/cm² white-light illumination from Xe lamp, the short-circuit current was 3.2 μA/cm², the open-circuit voltage was around 0.35 V, and the fill-factor was 0.17. The maximum photovoltaic conversion-efficiency was calculated as 2.8×10^{-2} %.

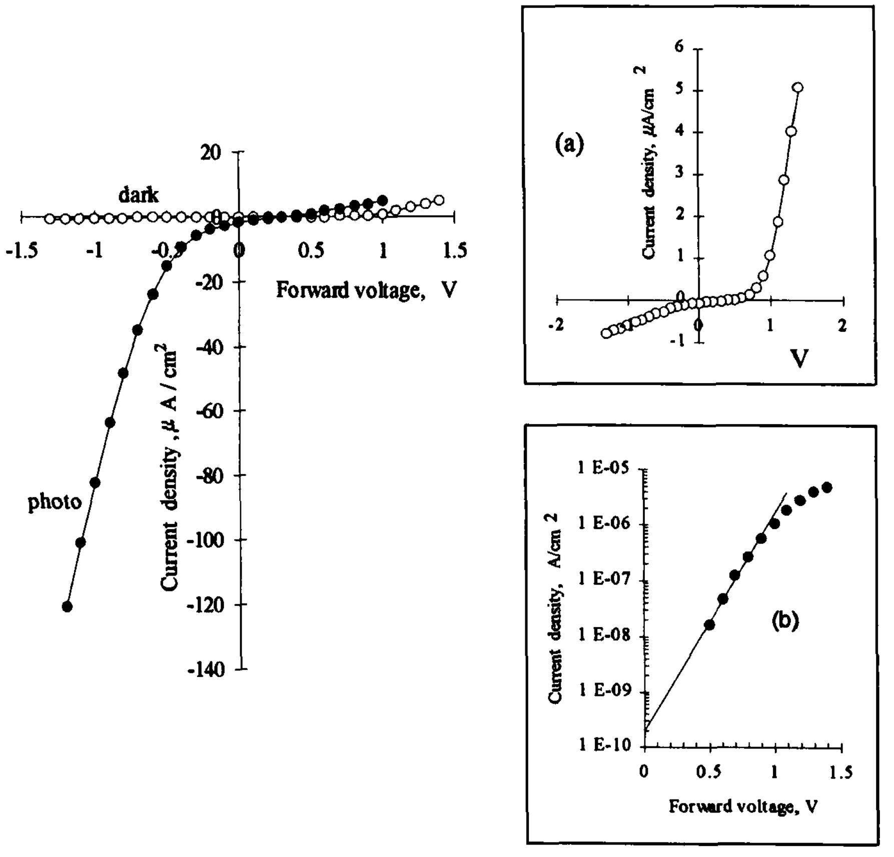

FIGURE 4. Dark- and photocurrent of TPP-Py n-Si heterojunction.

FIGURE 5 shows the time-response of the photocurrent. In the photovoltaic mode (a), it takes around 1 sec both for the switching on and off. In contrast, the switching is much faster in the photocurrent mode (b) under 1 V negative bias. It is seen that the photoresponses are very stable and reproducible.

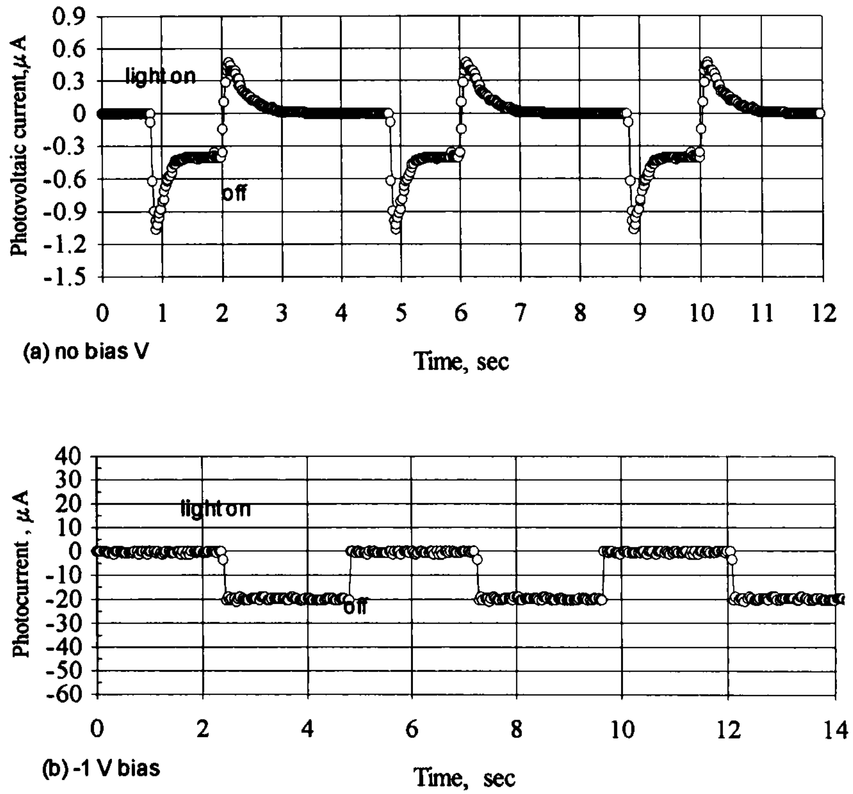

FIGURE 5. Photocurrent response of TPP-Py // n-Si heterojunction.

By measuring the capacitance of a heterojunction as a function of bias voltage, the value of the diffusion voltage V_d can be found according to the Eq. (2)

$$A_c C = \left[\frac{qN_D\varepsilon_{sn}\varepsilon_{sp}}{2(\varepsilon_{sn}N_D + \varepsilon_{sp}N_A)(V_d - V)}\right]^{1/2} \quad (2)$$

where C is the capacitance, A_c is the contact area, N_D and N_A are the number density of donor and acceptor impurity in the n-type and p-type semiconductor, respectively. ε_{sn} and ε_{sp} are the dielectric constants of n- and p-type semiconductor, respectively. We obtain the value of V_d by the extrapolation in the plot of $1/C^2$ versus V for TPP-Py//n-Si heterojunction (see FIGURE 6). The linear relationship of $1/C^2$ versus V according to the Eq. (2) is clearly observed and the value of V_d is estimated as 0.75 V.

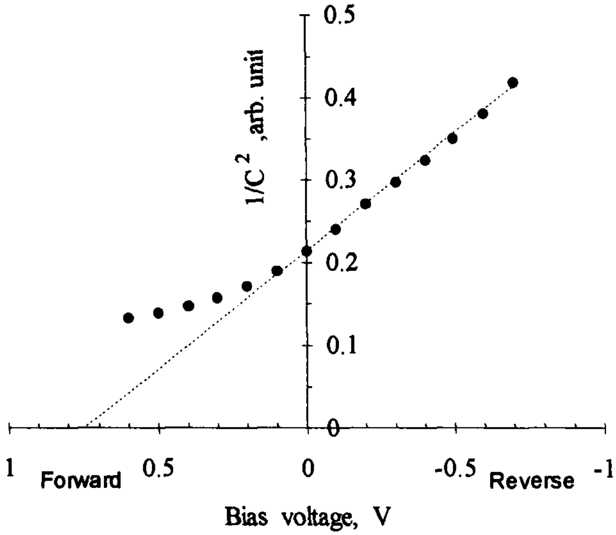

FIGURE 6 Room temperature C^{-2} versus applied voltage for TPP-Py // n-Si heterojunction.

CONCLUSION

The semiconducting organic film of 10^{-6} S/cm conductivity (TPP-Py) was prepared by the plasma polymerization of pyrrole followed by the thermal treatment in nitrogen. The p-type behavior of TPP-Py was demonstrated by the formation of Schottky contact with the low work-function metal (Al), and the p-n heterojunction with n-Si.

REFERENCES

1. J. Kanicki, in Handbook of Conducting Polymers, edited by T. A. Skotheim (Marcel Dekker, New York, 1986), Chap. 17, pp. 543 - 560.
2. V. Y. Merritt, in Electrical Properties of Polymers, edited by D. A. Seanor (Academic Press, New York, 1982), Chap. 4, pp. 127 - 213.
3. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature, 347, 539 (1990).
4. A. Tsumura, H. Koezuka, and T. Ando, Appl. Phys. Lett., 49 (18), 1210 (1986).
5. K. P. Lee, S. Y. Park, N. Kim, and S. K. Song, Mol. Cryst. Liq. Cryst., 224, 53 (1993).