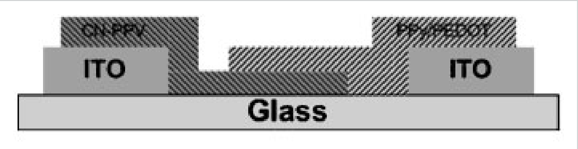
Summary: The fabrication of polymer diodes on a glass substrate by an ink-jet printing technique is reported. Both an n-type semiconductive polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CN-PPV), and a p-type semiconductive polymer, polypyrrole (PPy) or poly(3,4-ethylenedioxythiophene) (PEDOT), were printed through a piezoelectric ink-jet printer. The printed CN-PPV/PPy and CN-PPV/PEDOT diodes showed good rectifying characteristics. These results indicate the potential of the low-cost ink-jet printing technique to produce polymer microelectronic devices and circuits.



Schematic diagram of the printed polymer diode.

Polymer-Based Rectifying Diodes on a Glass Substrate Fabricated by Ink-Jet Printing

Yi Liu,[1] *Tianhong Cui**[1,2]

[1] Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71270, USA
[2] Department of Mechanical Engineering, University of Minnesota, 111 Church Street SE, Minneapolis, MN 55455, USA
Fax: +1-612-625-9395; E-mail: tcui@me.umn.edu

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Introduction

Much interest has been shown in the application of conjugated polymers to microelectronic/optoelectronic devices such as organic thin film transistors,[1,2] organic light emitting diodes,[3,4] light emitting electrochemical cells,[5] Schottky diodes[6] and photovoltaic diodes.[7] Compared to traditional inorganic materials such as silicon and germanium, polymer materials have the advantage of low cost and easy processing. Due to the nature of the materials used, a variety of methods have been used to deposit polymers, including spin coating,[8] screen-printing,[9] ink-jet printing,[10] electropolymerization,[11] vacuum evaporation[12] and soft lithography.[13]

Ink-jet printing (IJP) has been gaining more attention for device fabrication due to the advantages of low temperature processing, compatibility with various substrates, availability of non-contact, no-mask patterning and less material waste. IJP has been used to fabricate all-polymer transistors,[14] polymer light emitted diodes (PLEDs),[15] all-polymer capacitors,[16] RC filter circuits[17] and nanoparticle microelectromechanical systems.[18]

We have fabricated two kinds of polymer diodes, CN-PPV/PPy and CN-PPV/PEDOT. PPy is an air-stable p-type polymer that is regarded as a potential material to be applied to electrical or mechanical devices due to its good electrical conductivity and mechanical strength.[19] PEDOT, doped with poly(styrene sulfonate) (PSS), is also a p-type semiconducting polymer with high stability. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-(1-cyano-vinylene) phenylene] (CN-PPV), a high electro-affinity cyano derivative of PPV, has been applied to the polymeric light-emitting diode[20] and photovoltaic diodes.[7] In our polymer rectifying diode, CN-PPV has been employed as the electron injection and transport material, while PPy or PEDOT/PSS works as the hole injection and transport material.

Polymer rectifying diodes have been fabricated previously using thermal evaporation[21] or spin coating.[22] However, using the ink-jet printing technique to deposit semiconducting polymers for the application of simple polymer diodes has not yet been reported, probably due to the clogging problem when printing out the desired polymer solutions.[23] Our approach to overcome this problem was to print out the water dissolved PPy and PEDOT/PSS solutions and the tetrahydrofuran (THF) dissolved CN-PPV solution with optimized drive parameters (voltage, pulse duration and dispensing frequency) through a customer-designed piezoelectric printer. The printed polymer diodes, CN-PPV/PPy and CN-PPV/PEDOT, showed both rectifying and breakdown behavior. To the best of our knowledge, this is the first report on simple polymer rectifying diodes based on two layers of semiconducting polymers entirely formed by the ink-jet printing technique.

Experimental Part

The ink-jet printer employed in the device fabrication was a customer-designed piezoelectric ink-jet printing system, the Autodrop dispensing system from Microdrop Company in Germany. A precision positioning system controlled the movement of the dispensing head in the XYZ directions with high speed and high accuracy. The dispensing temperatures were also controlled by a heating element on the substrate holder.

When the work function of a metal is lower than that of the p-type semiconductor, a Schottky barrier, or rectifying barrier, may be formed at the interface.[6] In order to avoid a Schottky junction between the contact metal and the semiconductive polymer, indium tin oxide (ITO) was chosen as the contact electrode due to its high work function (4.8 eV), which is close to the work functions of PPy (5.19 eV) and PEDOT (5.0 eV). Thus the junction between ITO and PPy or PEDOT was an ohmic contact, not a rectifying contact. ITO can also form an ohmic contact with CN-PPV. In order to verify that no rectifying behavior existed between the polymer and the ITO contact electrode, we fabricated a monolayer with three configurations (ITO/PPy/ITO, ITO/PEDOT/ITO and ITO/CN-PPV/ITO) using ink-jet printing, for comparison. These monolayer devices exhibited linear I-V characteristics.

A schematic of the all-polymer diode fabricated is shown in Figure 1. Glass coated with ITO of 60 Å thickness was chosen as the substrate. First, the top ITO layer was patterned by lithography to define the ITO contact electrodes, and the glass left between the ITO electrodes exposed outside. Next, the CN-PPV (0.5% dissolved in THF solution) was dispensed onto the glass between the two electrodes, and extended onto one of the two electrodes at a substrate temperature of 70 °C. After dispensing the CN-PPV layer, the glass substrate was heated at 115 °C for two hours to dry the solvent totally. Following that, PPy (10% in water solution) or PEDOT (10% in water solution) was printed onto the CN-PPV between the two electrodes and also extended onto another ITO electrode. The substrate temperature was 40 °C for dispensing PPy and 60 °C for dispensing PEDOT. The active area for the overlapped CN-PPV and PPy/PEDOT was 300 μm × 1 500 μm.

Our experiments showed that the substrate temperature was one of the most important factors in the deposition process. A higher temperature would normally be preferable for quick solidification and reducing the flow of the solution on the substrate. However, lower substrate temperatures avoid the problem of frequent nozzle clogging and form much more stable droplet flow as well as better thin film coverage.[24] The substrate temperature also depends on the material properties. Several temperatures (from 20 °C to 90 °C) were investigated for each function material, and the above temperatures were found to lead to the best coverage and a continuous semiconductor thin film. It can be seen in Figure 2 that the printed PPy thin film was much more uniform than the printed PEDOT thin film, so PPy formed a better junction with CN-PPV than PEDOT.

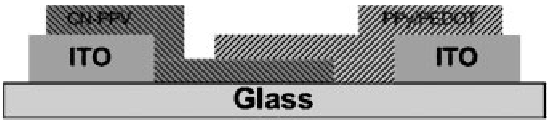

Figure 1. Schematic diagram of the printed polymer diode.

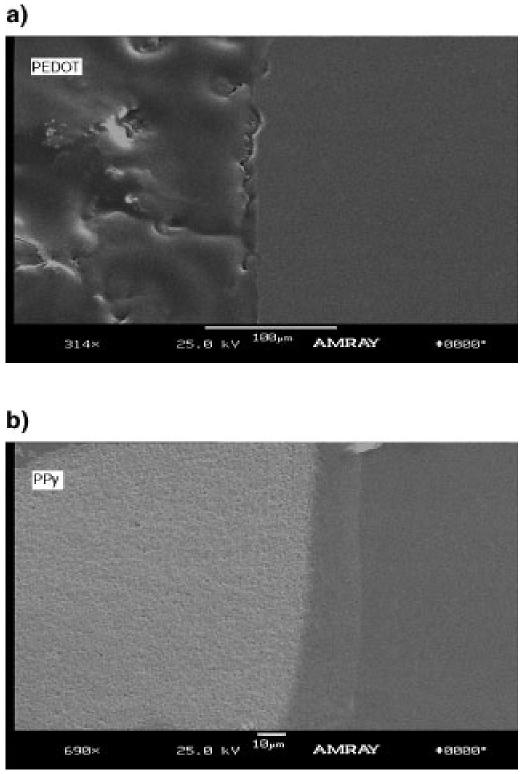

Figure 2. SEM picture of printed (a) PPy thin film and (b) PEDOT thin film.

Results and Discussion

The characteristics of the CN-PPV/PPy diodes (current vs. voltage) were measured with a Keithley 236 source measure unit in the atmosphere at room temperature. The forward bias was applied to the PPy/PEDOT contact electrode. Our preliminary bi-layer devices showed diode-like behavior with remarkable reproducibility. The measured current density vs. voltage characteristics of CN-PPV/PPy and CN-PPV/PEDOT are illustrated in Figure 3 and Figure 4, respectively. From the experimental data, the rectification ratio was calculated to be 117 ± 2 V for the CN-PPV/PPy diode and 26 ± 2.5 V for the CN-PPV/PEDOT diode. The breakdown voltage of the CN-PPV/PPy diode was −6 V, which is 0.6 V higher than the breakdown voltage of the CN-PPV/PEDOT diode (−5.4 V).

The interface properties between the n-type polymer material and the p-type polymer material will greatly affect the diode characteristics. Since the PPy thin film is more uniform than the PEDOT thin film, the junction between PPy and CN-PPV will be smoother than that between PEDOT and CN-PPV. Thus, the charge carrier in CN-PPV/PPy can transport much more easily at forward bias than in CN-PPV/PEDOT and leads to the higher on/off rectifying

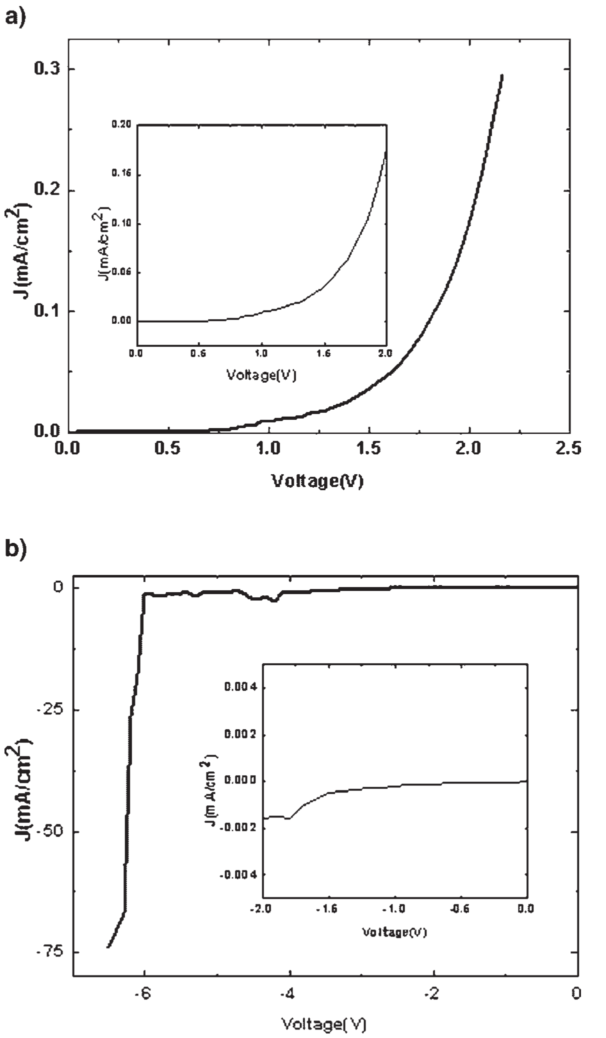

Figure 3. Electrical characteristics of polymer diode with ink-jet printed bilayer of CN-PPV/PPy: (a) the forward electrical characteristic; (b) the reversed electrical characteristic with breakdown behavior.

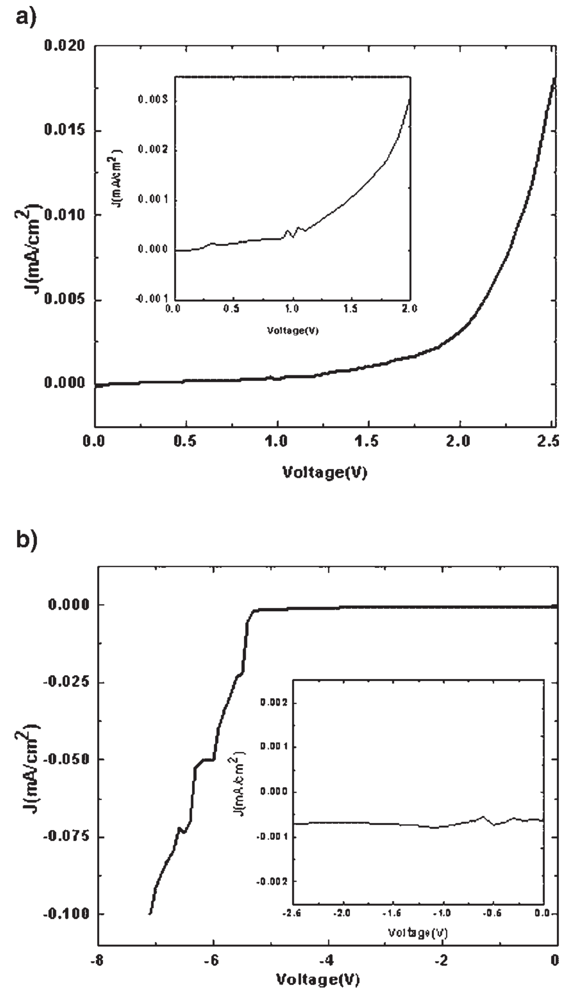

Figure 4. Electrical characteristics of polymer diode with ink-jet printed bilayer of CN-PPV/PEDOT: (a) the forward electrical characteristic; (b) the reversed electrical characteristic with the breakdown behavior.

ratio. Also, the better interface properties between CN-PPV and PPy can stand a lower negative voltage than CN-PPV/PEDOT and result in a higher breakdown voltage.

The band transport theory widely used in inorganic semiconducting devices is not applicable to polymer devices based on disordered organic semiconductors. In organic semiconductors, the carrier transport takes place by hopping between localized states and carriers are scattered at every step.[25] The rectifying behavior of the CN-PPV/PPy diode and the CN-PPV/PEDOT diode can be explained by the relative energies of the highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO) levels.[22] The CN-PPV has high electron affinity cyano groups in the main chain of PPV. Thus its HOMO and LUMO levels are relatively low compared to PPy and PEDOT. Figure 5 shows the energy diagram of ITO/PPy/PEDOT/CN-PPV/ITO under thermal equilibrium. When there is no bias voltage applied onto the two contact electrodes, the charge carrier in the semiconductive polymer will be bound to the polymer chain due to the chain distortion[26] so there is no current flow across the diode under thermal equilibrium. Under the forward bias condition in Figure 3a and 4a, holes will be injected into the PPy/PEDOT layer and electrons will be injected into the CN-PPV layer. The applied voltage can also reduce the potential barrier between the LUMO of PPy/PEDOT and the LUMO of CN-PPV, enhancing the electron hopping

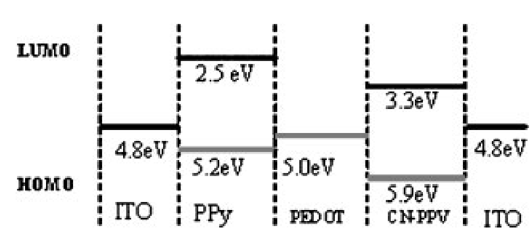

Figure 5. The energy diagram of the polymer diode at thermal equilibrium.

from the CN-PPV side (n-side) to the PPy/PEDOT side (p-side). In other words, electrons are injected into the p-side and holes are injected into the n-side. Under the reversed bias situation in Figure 3b and 4b, a negative voltage is applied to the p-side with respect to the n-side. Then, the potential barrier between the LUMO of CN-PPV and that of PPy/PEDOT is increased, which prevents carrier transport through the junction. Consequently, the current flow through the junction will be extremely small. Further increasing the reversed bias will break the weak π bond in these two conjugated polymers and result in avalanche multiplication of electrons through the junction, which causes the diode to break down.

The resolution of the ink-jet printing will affect the size of the polymer diode. Currently, we are using a printing head with nozzles of 50 µm, which can print out polymer droplets with diameters of about 50$\sim$100 µm depending on the materials used. Therefore, it is possible to print diodes on a sub-100 µm scale. Further miniaturization of ink-jet-printed diodes will need printing heads with a smaller nozzle size.

Conclusion

We have been successful in using an all-ink-jet printing technique to fabricate polymer diodes, consisting of CN-PPV as the n-type semiconductor and PPy or PEDOT as the p-type semiconductor. Both of these diodes have been characterized and show good rectifying behavior. The rectifying ratio of the CN-PPV/PPy diode can be as high as 117, which is higher than the rectifying ratio of the CN-PPV/PEDOT diode. This is due to the more uniform thin film properties of PPy than those of PEDOT. The breakdown voltage of the CN-PPV/PPy diode is -6 V, while the breakdown voltage of the CN-PPV/PEDOT diode is -5.4 V. The rectifying mechanism of the polymer diode, which is different from that of the traditional inorganic diode, was also discussed here in detail. Compared with other thin film techniques used in diode fabrication, such as thermal evaporation and spin coating, ink-jet printing has the advantages of needing no mask, low temperature processing and good compatibility with non-silicon substrates. It also has some disadvantages such as poor thin film uniformity and low throughput. Currently, there are few papers about ink-jet-printed stable n-type semiconducting polymers and no publications on ink-jet-printed n-type polymer field-effect transistors. This work may contribute to the development of ink-jet-printed n-type all-polymer transistors and further lead to ink-jet printing of complementary polymer transistors and circuits.

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