Hybrid Materials-Based Rectifying Diode Fabricated by Printing on a Flexible Substrate

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ABSTRACT

In recent years, printing has received substantial attentions both in research community and industrial sectors for realizing low-cost and flexible electronics. One of the most critical components in printed flexible electronic circuits is the rectifying diode, which is proved to be extremely difficult due to problems in materials choice and printing. In this paper, we report to use hybrid materials based on poly-(3,4-ethylenedioxythiophene) (PEDOT) and copper phthalocyanine (CuPc) as active layer for printing diodes on a flexible substrate, though CuPc has poor solubility in most solvents. The current-voltage characteristics demonstrated that the printed diode has rectification ratio over 1000. These preliminary results are leading to deeper understanding of the hybrid CuPc material and its properties in printed flexible electronic devices.

Keywords: Flexible, Hybrid Materials, Printed electronics, Rectifying Diode, Schottky Barrier

1 INTRODUCTION

Printing as an additive fabrication method has in recent years attracted a great deal of attentions both in research community and industrial sectors, because of its low-cost, and the capability of manufacturing electronic devices on flexible substrates.[1] Examples of flexible electronic devices, which have drawn great interests, include radio frequency identification (RFID) tags [2] and sensors.[3] One of the most critical components in RFID tags or other flexible electronic circuits is the rectifying diode, which serves to transform radio frequency signals into DC driving current and other special waveforms. It is easy to fabricate rectifying diodes by traditional methods including evaporating, sputtering materials, or high temprature treatments. However, printing diodes on flexible substrates is proved to be extremely difficult, due to problems such as inappropriate inks, clogging of printer nozzles, incompatible interface between printed layers, instability of printed materials, etc. [4]

The nonmetallic material for printed rectifying diode, which must be dispersed in the ink and easy to from a film, should also be stable, conductive, and has proper work funtion. As the best-known intrinsic conducting polymers (ICP), poly-(3,4-ethylenedioxythiophene) (PEDOT, shown in Figure 1) plays a dominant role in antistatic, electric and electronic applications mainly because of its excellent electrical conductivity, stability, and electrooptical properties. [5] This insoluble polymer can be dispersed in water doped with poly(styrenesulfonate) (PSS, shown in Figure 1) for spin-coating or printing. And its work function can also be ajusted by changing PEDOT:PSS weight ratio, pH, or alkalic metal content.[6] At present the PEDOT:PSS was mainly used as conductor material, though it can also act as a hole-transport semiconductor.

Copper phthalocyanine (CuPc, shown in Figure 1) is another material which has been widely used for charge transport and switching in vacuum deposited thin-film devices because of its good thermal and chemical stability [7]. It was also reported being used for rectifying diodes [8]. However, CuPc is difficult to print because of its poor solubility in most solvents.

In this paper, we report to use hybrid materials containing CuPc and PEDOT:PSS as the active layer for printing diodes on a flexible substrate. This kind of ink cannot be printed by high-resolution inkjet printer for clogging of printer nozzles, but it can be printed with an aerosol jet printer.

2 EXPERIMENTAL

MATERIALS: Nanoparticle silver ink from Cabot Corporation (CSD-32 Fine Particle Silver Ink) was used for printing silver electrodes. Aqueous solution containing PEDOT and PSS was purchased from H.C.Starck GmbH & Co. KG (CLEVIOS™ P VP AI 4083, with PEDOT:PSS weight ratio of 1:6). CuPc powder was purchased from Alfa Aesar, and used without any further treatments.

The CuPc:PEDOT:PSS colloidal suspensions were prepared by adding CuPc powders (20 mg.ml^{-1}) and glycerol (250 mg.ml^{-1}) into the commercial PEDOT:PSS solution. The colloidal suspensions were diluted by 1 ml deionised water before printing.

DEVICE FABRICATION AND PRINTING: The diode structure and printing process are shown in Figure 2. The bottom electrode was inkjet-printed on a precleaned 100 μm thick flexible polyimide substrate using nanosilver ink, and then sintered at 200 ℃ for 30 min. After that CuPc:PEDOT:PSS colloidal suspension or PEDOT:PSS solution were printed onto the Ag electrode layer by an aerosol jet printer. The devices with active layer printed using PEDOT:PSS solution or colloidal suspensions were respectively were labeled as device A and B. Pieces of aluminum foil were covered on the printed hybrid layers as top electrodes.

MEASUREMENTS: All of the SEM images were obained by a Hitachi's S-4800 Field Emission Scanning Electron Microscope (FE-SEM).

The electrical characterization of devices were carried out using a Keithley 4200 and a probe station. All the electrical measurements were done in ambient conditions at room temperature without any device encapsulation.

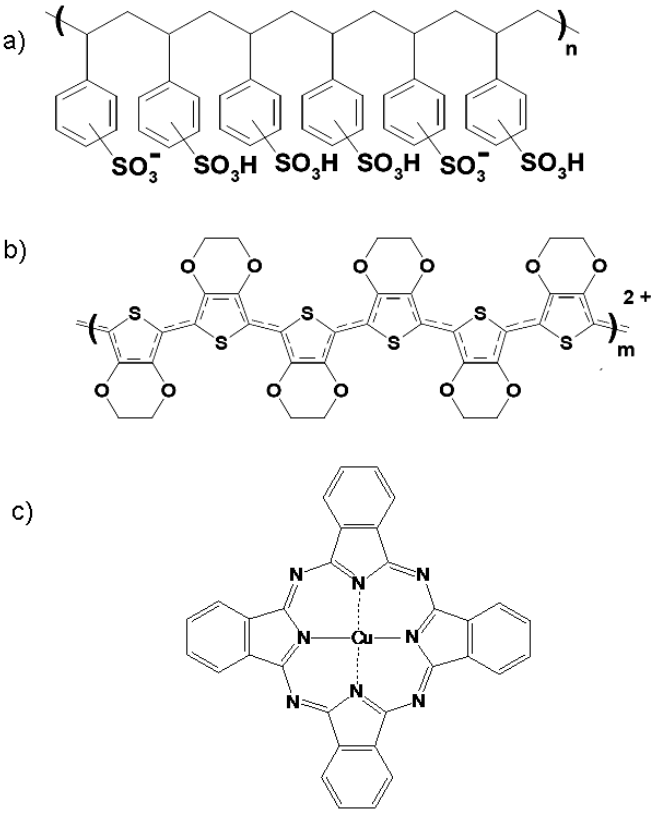

Figure 1: Schematic chemical structures of PEODT (a), PSS (b), and CuPc (c), respectively.

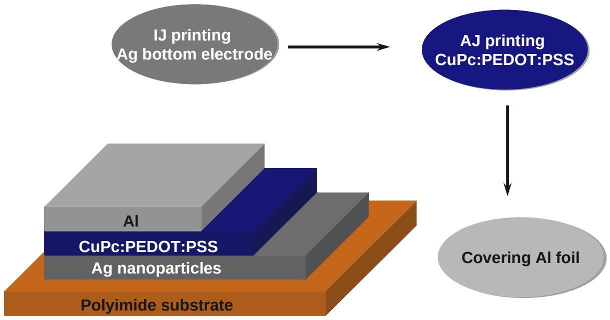

Figure 2: The schematic image of the device structure, and a three-step process flow for the fabrication.

3 RESULTS AND DISCUSSION

The printed diodes were tested with its current-voltage (*I-V*) characteristics shown in Figure 3. It demonstrated that both of the printed diodes show rectifying effect, the currents under Ag electrode positive bias (called as forward current in this paper) are larger than the one when Al foil electrode positive biased (called as reverse current in this paper). On the other hand, Device B have larger rectifier ratio than Device A (1000 and 20 at 10 V respectively), showing that the CuPc:PEDOT:PSS hybrid material has better performance than the commercial PEDOT:PSS solution.

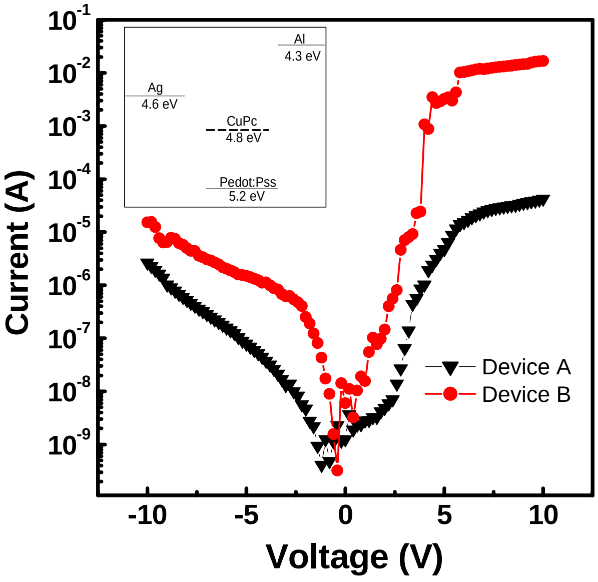

Figure 3: Rectifying *I-V* curves of the devices with different semiconductor layers. Inset shows the energy level diagrams of the electrodes, PEDOT:PSS, and CuPc.

The rectifying diodes in our study were designed based on the theory of schottky energy barrier and charge injection limited current. [9] Work funtion of Ag and Al are 4.6 eV and 4.3 eV, which means that the hole injection barrier between Ag and hybrid active layer was 0.3 eV lower than the Al side. Considering both PEDOT:PSS and CuPc are hole transport materials, the difference of the barriers should be the reason of the rectifying effects. The inset of Figure 3 shows the energy level diagrams of PEDOT:PSS and CuPc electrodes.

However, the work function of PEDOT:PSS is about 5.2 eV, which is much higher than the work function of Ag or Al. To obtain better rectifier ratio, the barrier between Ag and active layer should be reduced significantly. CuPc is an ideal material because it has an ionization potential of 4.8 eV, and has been reported to have a charge transfer between CuPc and PEDOT:PSS occurs. [11] As a result, the schottky energy barrier between Ag and hybrid active layer should be decreased and leads to better rectifier ratio.

Figure 4 shows the reversely biased rectifying *I-V* curves of the devices, which is fitted to linear relationships in log(*I*) vs $V^{1/2}$. This suggests that reverse biased currents were thermionic emission injection limited current.[12] In other words, the results confirm that too high barrier between Al and active layer is the main reason why reverse currents are much smaller than the forward currents.

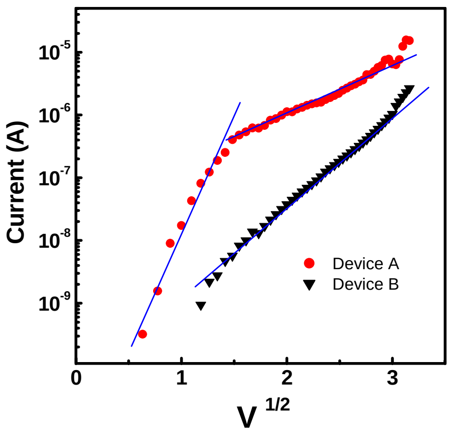

Figure 4: Reverse currents of the devices fitting ln (*I*) vs. $V^{1/2}$.

The forward currents shown in Figrure 5 are suggested to the space charge limited conduction (SCLC) current [13] in the region of 2.4-10 V, which means that injection barriers are not the key limiting factor to the currents. The rapidly increasing region with the linearity larger than 3, which are very similar to the trap filling in the case of SCLC with single discrete shallow traps. [13] The results suggest that adding CuPc introduces more traps in the active layer and the electrode-active interface. However, there were more holes injected into the device B because of the lower injection barrie. These results are similar to the *I–V* characteristics of vacuum deposited CuPc film which were reported before. [14]

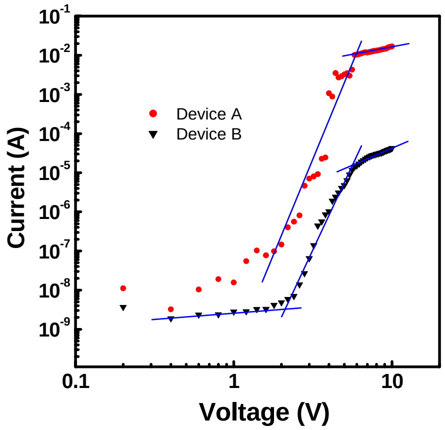

Figure 4: Forward currents of the devices fitting log (*I*) vs. log (*V*).

The surface mophology of printed Ag and CuPc hybrid layer were also observed by SEM, as shown in figure 5. It can be found that both Ag and hybrid films are quite homogeneous, which confirms that the printing methods are suitable for device fabrication.

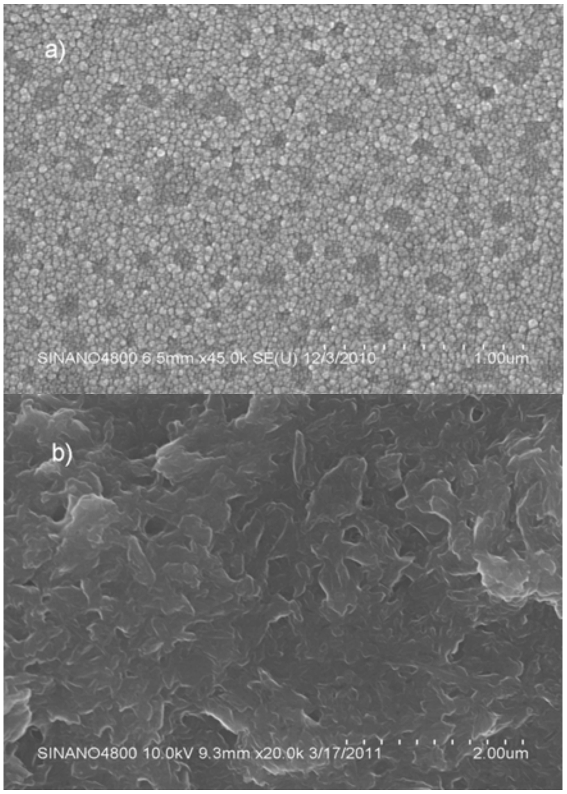

Figure 5: SEM images of the printed Ag (a) and CuPc:PEDOT:PSS hybrid (b) layers.

4 CONCLUSION

In conclusion, we have demonstrated printed rectifying diodes based on hybrid CuPc:PEDOT:PSS materials. The inclusion of CuPc can decrease the schottky energy barrier between Ag bottom electrode and hybrid active layer, and increase the rectification ratio from 20 to 1000. These preliminary results are leading to deeper understanding of the hybrid CuPc material and its properties in printed flexible electronic devices.

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