

Characterization of carbon nanotube doped PEDOT:PSS thin film devices

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ITO/PEDOTOPSS/Al devices containing dispersed Carbon Nanotubes (CNTs) and pure PEDOT:PSS are compared. It was found that the conductivity of each CNT doped PEDOT: PSS film was reduced upon application of 20Hz pulses of -20V at reversed bias. Deformation of the aluminium electrode was found to occur upon application of voltage on the PEDOT: PSS film. However, no aluminium electrode deformation occurs on CNT-doped PEDOT: PSS films. This was verified by Scanning Electron Microscope (SEM). Depth profiling by Auger spectroscopy indicated high level of oxidation at the aluminium PEDOT: PSS interface for device with pure PEDOT: PSS but significantly less with PEDOT doped with CNTs. Resistance is found to vary in periodic high/low values dependent on direction of voltage sweep.

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1. Introduction

PEDOT: PSS is an important conductive polymer for use in a wide range of electronic devices because it has many useful properties. For instance, it has a flexible structural backbone[1-5]. Such flexibility permits low-cost manufacturing of flexible roll-up displays, RFID tags, flexible sensors and large photovoltaic arrays.

The conductive nature of PEDOT: PSS polymer is of great use in opto-electronic devices such as OLEDs (Organic Light Emitting Diodes), photovoltaic cells and photodetectors [6-7]. The highly conductive nature with absorption comparable to ITO makes it a possible replacement for ITO (indium tin oxide) in solar cells and possibly in touch-screens and electronic paper devices. PEDOT is reported to have good electrochemical and thermal stability and high conductivity [8]. Blending PEDOT with PSS [poly (4-styrenesulfonic acid)] produces a mixture that disperses very well in water [6,9]. Thus, the PEDOT: PSS polymer blend is solution process-able and hence allows new technologies such as ink jet printing, stamping, or other relatively cheap processes to produce PEDOT: PSS based electronic circuits.

In this research we characterize the electrical current-voltage (IV) properties of PEDOT: PSS and Carbon Nanotube doped PEDOT: PSS thin film devices.

2. Experiment

ITO-coated glass was used as substrate. PEDOT: PSS was spin-coated on top of the ITO substrate at 2000 rpm for 1 minute. Thermal evaporation was used to deposit aluminium (Al) electrodes on top of the PEDOT: PSS thin film at 2.5×10^{-5} mbar. IV characterization was then performed using cyclic 2V to -3V sweeps in air.

Apart from this, single-walled carbon nanotubes

(SWNTs) with 1-2nm diameter and average length of $30\mu\text{m}$ purchased from Timesnano were added into fresh PEDOT: PSS at a concentration of 0.5%wt. and then ultrasonicated for 1 hour in sonication bath. The procedure is repeated for SWNT – PEDOT: PSS mixture.

The device cross-section is shown on Fig. 1.

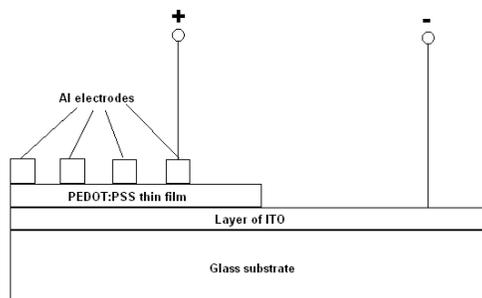


Fig. 1. Cross section of PEDOT:PSS device.

Subsequently, the SWNT – PEDOT: PSS thin film is subjected to a square wave of 0V – -20V pulses at 20Hz for the following duration: 900s, 1200s and 1500s. IV sweeps from 2V to -3V and -10V to 10V are performed for each of the above intervals.

3. Results and discussion

3.1 Influence of square wave pulsing

PEDOT: PSS thin film devices containing SWNTs are found to have their resistances increased upon application +/- 20V pulses at 20Hz. The increase in resistance is proportional to the duration of pulsing administered upon the SWNT – PEDOT: PSS device. The IV curves leading to observations are shown in Fig. 2.

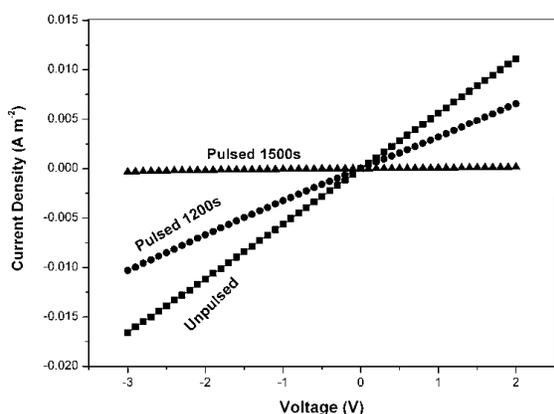


Fig. 2. IV characteristics after applying square pulses.

This may result from the de-activation of metallic SWNTs within the PEDOT: PSS thin film. Metallic SWNTs have lower resistance than semiconducting SWNTs, and hence metallic SWNTs have higher current density flowing through them. Since high current tends to destroy carbon nanotube strands by oxidizing their outer shell [10], it stands to reason that metallic SWNTs suffer greater oxidation due to their higher current density. Hence, the conductivity of SWNT/PEDOT: PSS composite was reduced.

3.2 Deformation of aluminium electrodes

Bubbles were observed to have formed on the aluminium (Al) electrode surface. Observation was performed using SEM as shown in Figure 3(a). We suggest that this phenomenon was caused by the evolution of gas from the electrolysis of water absorbed in the PEDOT: PSS polymer. PEDOT: PSS is known to be hydroscopic [11]. When electrical current is applied upon the device, electrolysis of water moisture present on the PEDOT: PSS thin film occurs. Electrolysis of water produces hydrogen and oxygen.

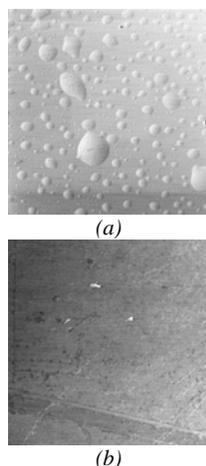
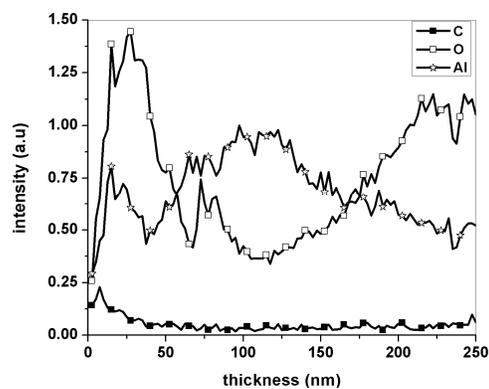


Fig. 3. Aluminium electrode after applying voltage for (a) pure PEDOT:PSS (b) PEDOT:PSS doped with CNT.

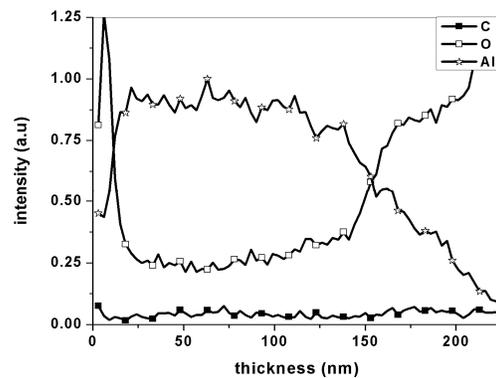
The evolution of hydrogen and oxygen was also observed by Lee *et al* [12] on his organic electroluminescent device which also uses Al electrodes, as well as exposed to moisture from ambient air analysed in-situ using differential electrochemical mass spectrometer.

Nonetheless, no deformation was observed in thin films of SWNT/PEDOT: PSS. Fig. 3 (b) supports this observation. We suggest that this is due to the fact that SWNT is a better conductor than PEDOT: PSS. Thus, the SWNTs conduct away the electrons which were originally involved in the electrolysis of water which was shown to inhibit corrosion in metal [13]. Minimal electrolysis occurs due to the lack of electrons available.

3.3 Auger spectroscopic depth profiling



(a)



(b)

Fig. 4. Auger spectroscopic depth profiling of aluminium electrode after IV measurement for (a) pure PEDOT:PSS (b) PEDOT:PSS doped with SWCNT.

The chemical depth profiling of aluminium electrode is performed. The typical thickness of aluminium is about 250nm. At 0nm as shown in Fig. 4 (a) and (b) represent the aluminium and PEDOT:PSS interface. The graphs are normalized by the peak value of aluminium which is usually located at the middle of the cathode. For device without SWCNT, there is a very high level of oxygen

inside the aluminium at the interface. The oxygen permeates into deeper inside the cathode. Aluminium oxide is formed at the PEDOT:PSS interface for device with PEDOT:PSS only but significantly less with PEDOT:PSS device doped with SWCNT. This might explain the observation in Fig. 3. Aluminium oxide is evidently observed at the aluminium air interface for both devices.

3.4 Current shift at -1V following change in voltage sweep direction

A periodic shift in current level which is taken at -1V out of each -10V to 10V cyclic sweeps is observed. This might be attributed to alternating higher and lower resistance each time the device is subjected to a bias of -10V or 10V for 1 minute prior to each sweep.

PEDOT: PSS thin film consists of p-doped PEDOT chains. Hence, when negative bias (-3V in this case) is applied to the device, electrons are injected into the PEDOT: PSS thin film which recombines with the holes available in the thin film. This reduces the amount of charge carriers available in the thin film which subsequently increases the resistance of the thin film at negative bias [14].

Conversely, each biasing by positive voltage into the device injects holes into the PEDOT: PSS thin films. Hence, the PEDOT: PSS which uses holes as majority charge carriers becomes enriched with even more holes; increasing the amount of charge carriers in the thin film and consequently decreasing the device resistance.

Periodic switching at -1V was observed. The occurrence is illustrated in Fig. 5. The on/off ratio is initially about a factor of 5; it gradually decreases to 2. This could be the result of device degradation bought about by the oxidation of the aluminium electrode at the polymer – aluminium interface due to the presence of water [15].

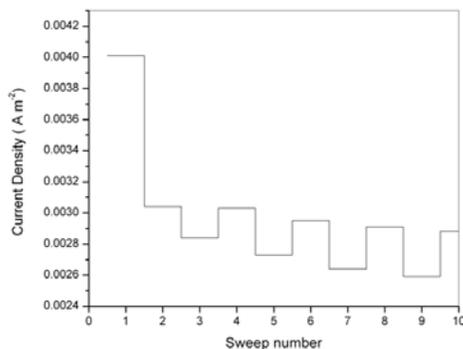


Fig. 5. Graph of resistive switching. 10 cyclic sweeps of -5V to 5V were performed with on/off ratio of a factor of 2. Sample is of PEDOT: PSS thin film.

The presence of SWNTs in PEDOT: PSS thin films are shown to inhibit resistive switching as illustrated in Fig. 6. The ability of SWNTs to suppress resistive switching may prove useful in reducing current error in

Organic Light Emitting Diodes which is also caused by hysteresis [16].

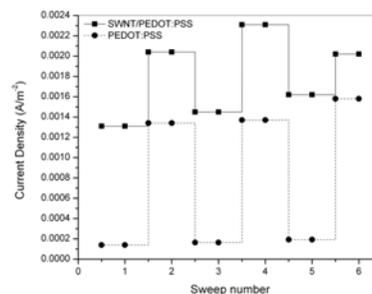


Fig. 6. SWNT is shown to inhibit resistive switching. Sweeping -4 to 3Vs performed 6 times.

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References

- [1] H. T. Ham, Y. S. Choi, M. G. Chee, M. H. Cha, I. J. Chung, *Polym. Eng. Sci.* **4**, 1 (2008).
- [2] X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, C. V. Haesendonck, A. V. Auweraer, W. R. Salaneck, M. Berggren, *Chem. Matter.* **18**, 4354 (2006).
- [3] W. Feng, E. Sun, A. Fujii, H. Wu, K. Niihara, K. Yoshino, *Bull. Chem. Soc. Jpn.* **73**, 2627 (2000).
- [4] Y. Yang, A. J. Heeger, *Appl. Phys. Lett.* **64**, 1245 (1994).
- [5] B. Wessling, *Synthetic Met.* **135**, 265 (2003).
- [6] S. Kirchmeyer, K. Reuter, *J. Mater. Chem.* **15**, 2077 (2005).
- [7] D. Hohnholz, H. Okuzaki, A. G. MacDiarmid, *Adv. Funct. Matter.* **15**, 51 (2005).
- [8] G. Latessaa, F. Brunettia, A. Realea, G. Saggioa, A. Di Carloa, *Sensor Actuat. B-Chem.* **139**, 304 (2009).
- [9] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **12**, 481 (2005).
- [10] P. C. Collins, M. S. Arnold, P. Avouries, *Science* **292**, 706 (2001).
- [11] J. Huang, P. F. Miller, J. C. de Mello, A. J. De Mello, D. D. C. Bradley, *Synthetic Met.* **139**, 569 (2003).
- [12] M. D Lee, O. Mitsuaki, K. Amane, E. M. Han, Y. Noritaka, F. Masamichi, *Thin Solid Films* **273**, 209 (1996).
- [13] X. H. Chen, C. S. Chen, N. H. Xiao, F. Q. Cheng, G. Zhan, G. J. Yi, *Surf. Coat Tech.* **191**, 351 (2005).
- [14] H. Ha, O. Kim, *Appl. Phys. Lett.* **93**, 033309 (2008).
- [15] K. Norrman, C. K. Frederik, *Sol. Energ. Mat. Sol. C* **90**, 213 (2006).
- [16] J. H. Lee, W. J. Nam, K. S. Shin, M. K. Han, *J. Cryst. Solids* **352**, 1719(2006).

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