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Variation of Interfacial Capacitance in PEDOT-PSS Films

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ABSTRACT

This paper presents a simple method to measure the interfacial capacitance of PEDOT-PSS films by measuring the contact resistance at the metal semiconductor junction. Rectifying behavior was identified for tin and copper contacting PEDOT-PSS films and the order of contact resistance was estimated by a diode model. In this work determination of bulk and contact resistances was made using standard four probe measurement methods. It was found that the contact resistance offered by the metal semiconductor junction is nearly 6 to 7 times more than the bulk resistance of the film. Large contact resistances compared to rest of the film can pose problems as a device. In this study we report that there is an existence of large capacitance at the metal semiconductor interfacial which varies with frequency and applied bias. Existence of large capacitance at the metal semiconductor junction of PEDOT-PSS makes it a contender to be used as super capacitors and is a suitable material to be explored as storage devices. This work can be used to model the performance precisely considering interconnect and contacts in parametric analysis of the circuit.

KEY WORDS: CONTACT RESISTANCE, CAPACITANCE MEASUREMENTS, INTERFACIAL CAPACITANCE, PEDOT-PSS, SUPER CAPACITOR.

INTRODUCTION

Conducting polymers have attracted vide spread applications in recent days. Main emphasis has been in development of organic LEDs, solar cells and FETs (Sarita et al., 2019). Off late conducting polymers are explored to be used in biological applications which demand compatibility and large flexibility (Nambiar and Yeow, 2010). Conducting polymers are suitable materials to be used in flexible electronics which possess electrical properties of metals or semi-conductors, with mechanical characteristics of polymers. PEDOT-PSS (poly3, 4 ethylenedioxythiophene– polystyrenesulfonic acid) is one such conducting polymer used in many devices that is commercially available from HC stark Germany.

PEDOT-PSS is a highly conductive semiconductor in its pristine state. By doping PEDOT-PSS with DMSO (Dimethyl sulfoxide) in varying proportions its conductivity can be enhanced by several folds. (Chou et al., 2015; Ouyang et al., 2004). When a metal to PEDOT-PSS interface is formed, there can be two types of contacts, rectifying contact (Schottky junction) or ohmic contact. Formation of rectifying contact or ohmic contact depends on the work function differences between the contact metal and the semiconductor in this case PEDOT-PSS (Bindu and Suresh, 2015; Baca 1997; Bindu et al., 2013). Rectifying contacts offers low resistance for flow of current in the forward direction and substantially high resistance to current flow in the reverse direction.

Ohmic contacts result in a linear symmetric relationship between the junction voltage and current. Whenever metal contacts a semiconductor, Fermi levels of the two

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materials align which cause electrons to flow from higher energy level to lower energy level creating an energy barrier for further flow of electrons. If DC voltage applied to the contacts increase the barrier, the current flow is further hindered and if the direction of external voltage is applied to decrease the energy barrier current flows easily. In this paper we discuss the contact phenomenon existing between copper and tin as the contact metal to PEDOT-PSS. We also present the method of measuring the junction capacitance at the PEDOT-PSS interface.

MATERIAL AND METHODS

Films of PEDOT-PSS procured from M/S Stark, Germany is available as a dispersion of PEDOT to PSS in water with ratio of 1: 6. Four copper contacts are first etched over glass epoxy substrates, where each contact is 0.5mm wide and 5mm apart as shown in [Fig.1]. The substrates are cleaned before use to remove dirt and impurities by first sonicating in acetone and then by distilled water and isopropyl alcohol each for 10 minutes. Known quantity of PEDOT- PSS dispersion is spread (drop casted) on the etched copper contacts to fuse the film having dimension of 20mm in length, 5mm in width and 30 micrometers thick. The thickness of the film is measured using Mitutoyo dial gauge with 1 micrometer resolution. Thickness of the films is achieved by spreading the same amount of suspension over different areas. The film is annealed at 450C for an hour so that water evaporates and stable films with lower resistivity are formed (Bindu et al., 2017).

Experimental Details: Measurement of sheet resistance is made using simple potentiometeric technique. Resistance measurements are made by applying several DC voltages to [Fig. 2a]. By measuring the voltage across the external resistance RL (VO) using the formula shown in equation 1, Contact and bulk resistances of the film can be calculated. Impedance measurements at different frequencies are made by superimposing AC signal over the DC using the circuit shown in [Fig. 3]. Capacitor shown in [Fig. 2b] is used to block the DC components present in the AC. DC voltage measurements are made using Fluke 287 digital multimeter and digital storage oscilloscope, Agilent make is used to make AC measurements. During measurements temperature was maintained within 26 + 30 C.

R = ((Vi/VO) -1)*RL in KΩ....... Eqn. 1

Measurements and Results

RESULTS AND DISCUSSION

For Dc Measurements

When a thin film of conducting polymers, in this case PEDOT-PSS, Contacts with a metal, a metal semiconductor diode is formed due to work function differences between conducting polymers and metals (Park et al., 1996). This diode will have its cathode as metal depending on whether the polymer is a ‘p’ type or ‘n’ type semiconductor. If two metallic contacts are made for electrical connection, one contact acts as a forward biased diode where as the other one acts as reverse biased diodes. DC voltages measurements are made using the potentiometric circuit shown in [Fig. 2a]. A plot of the voltage between terminals 1-2, 2-3 and 3-4 vs. current are shown in [Fig. 3] and the slope of the V-I curve gives the resistance between respective terminals.

Figure 1: Showing copper contacts etched on glass epoxy substrate.

Figure 2a: Resistance and impedance measuring circuit

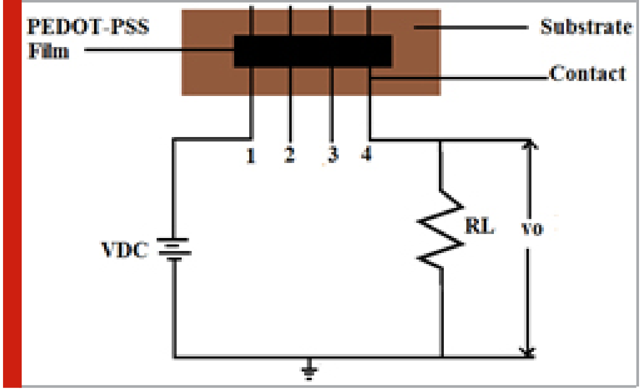
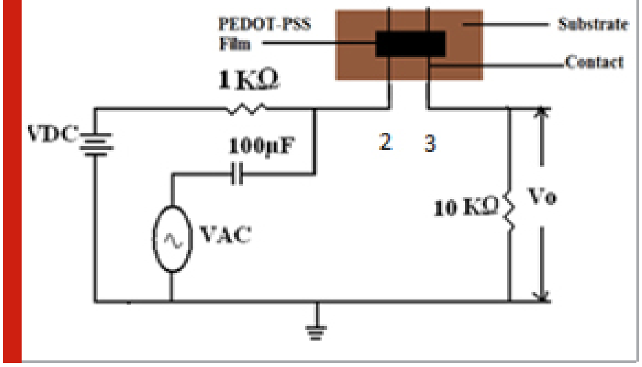


Figure 2b: Circuit diagram used to measure films Resistance and impedance



It may be observed that V-I relationship between contacts 2 and 3 and contacts 3 and 4 are linear but between contacts 1 and 2 it is nonlinear with a much higher slope than that between the other two contacts. From the slopes the resistance between contacts 2 and 3 (R23) is equal to 143 KΩ and that between contacts 3 and 4 (R34) is 156 KΩ. From the average slope the resistance R12 is 809 KΩ, far greater than that between other two contacts. The fact that metal semiconductor interfaces are known to form rectifying contacts, prompts us to consider modeling the interface as diodes as can be understood by referring to the model shown in Fig.4 where R12 includes the reverse biased leakage resistance of D1(PEDOT-PSS being a p-type semiconductor) in addition to the film resistance.

Figure 3: Plot of terminal voltages V12, V23 and V34 vs. current with copper as contact metal to PEDOT-PSS film.

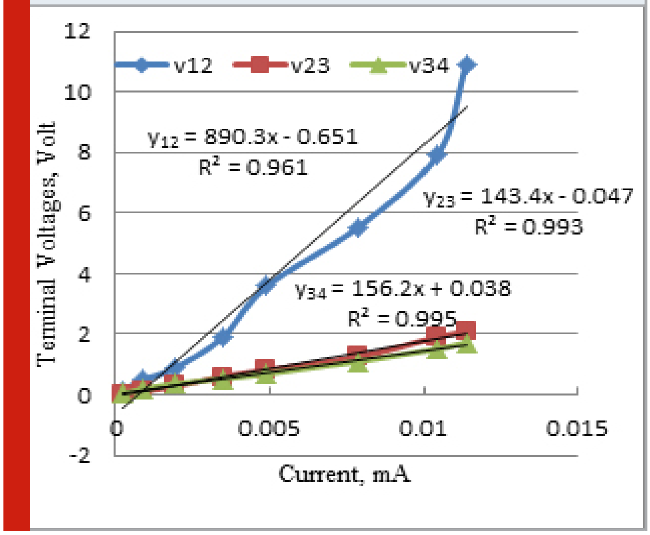
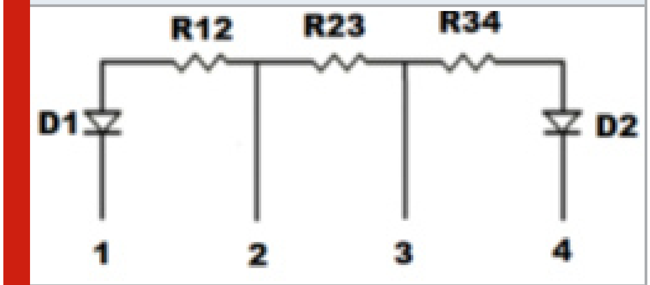


Figure 4: Equivalent Model of PEDOT-PSS film for four metallic roller contacts showing diodes at the current carrying interface.



However, R34 includes only forward biased diode resistance of D2 apart from film resistance and R23 is just the bulk resistance of the film between contacts 2 and 3. It may be observed that the resistance R34 is greater than R23 as it includes the forward resistance of the diode. This proves the existence of rectifying contacts between PEDOT-PSS and copper. There is a mention in literature about existence of rectifying contacts, but not detailed about the order of contact resistances. In our earlier work (Bindu and Suresh, 2010) we have detailed all the aspects of interface between tin and PEDOT-PSS; we have proved the existence of rectifying contacts between tin and PEDOT-PSS.

It may be observed from [Fig 5.] for tin coated copper as contact metal to PEDOT-PSS that the slope voltage V23 vs. current is a straight line with resistance between 2-3 as 30.75 KΩ indicating Ohmic relation between V23 and current(i.e.R23= 30.75 KΩ).

Fig. 6 compares R14 with R23 for varying terminal voltages (VDC). It may be observed that the measured resistance between 1 and 4 is not constant with applied voltage while R23 is nearly constant at 30.75 KΩ and independent of applied voltage. The resistance R14 decreases from750 KΩ and settles at 252 KΩ. The total bulk resistance between terminal1 and 4 should have been equal to three times that between 2 and 3 (92.25 KΩ) as the contacts are equidistant, but is as large as 252 KΩ clearly showing presence of high contact resistance.

Figure 5: Plot showing voltage V23 vs. Current for tin coated copper contacts

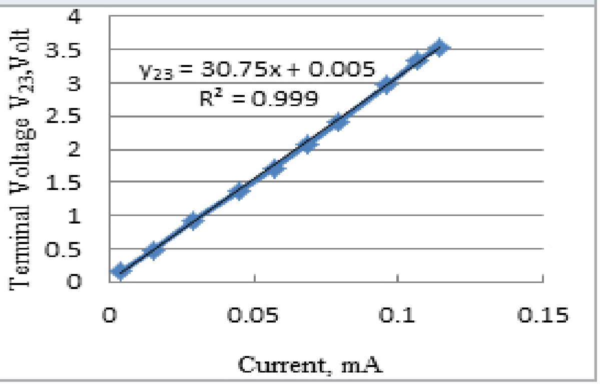


Figure 6: Fig. 7: Plot showing variation of resistance R23 and R14 vs. DC voltage for tin as contact metal

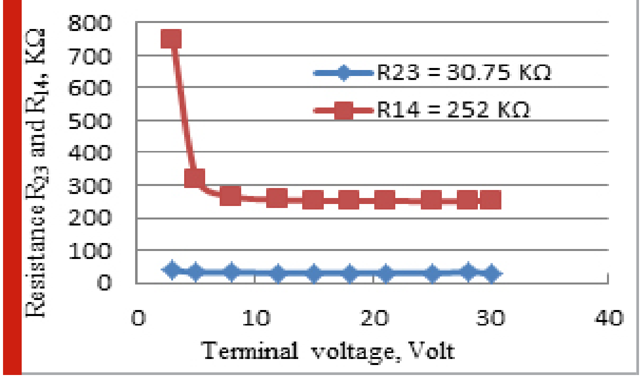
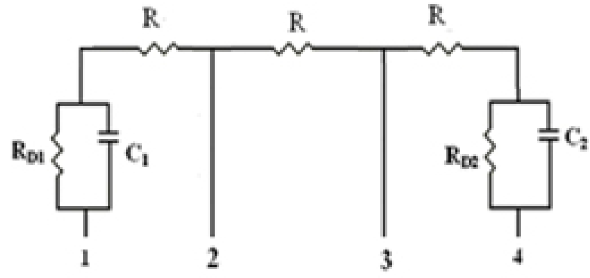


Figure 7: Equivalent diode model for AC excitation applied to terminals1 and 4.



Whenever a diode is formed the junction also creates a charge depletion layer which can be modeled as a capacitor as shown in Fig. 7. A resistance in parallel with the capacitor accounts for the current that flows when DC voltage is applied. In the model shown in Fig. 7 the metal semiconductor contact capacitances are represented by C1 and C2, leakage resistance of diode D1is represented by RD1and the forward resistance of the diode D2 by RD2. RD1 >> RD2 as D1 is reverse biased and D2 is forward biased. The transition capacitance of diode D1is represented by C1 and the diffusion capacitance of D2 is represented by C2 when positive voltage is applied to terminal 1 with respect to terminal 4.

(C1/RD1 and C2 / RD2 are interchanged for reverse polarity). When AC excitation is applied, diodes D1 and D2 are alternately forward and reverse biased. For AC excitation the depletion layer capacitance C1 dominates the overall frequency response as it is smaller of the two capacitances. As the applied signal frequency increases the voltage drop across C1 starts reducing and for all frequencies of f >> 1/ [2π (RD1) C1] the impedance of the capacitors becomes negligibly small when compared to the resistance of the interfacial diode. Thus interfacial diode resistance can be bypassed by the parallel capacitance if AC signal is applied at a frequency f >> 1/(RD1C1). Effect of C2 may be neglected as diffusion capacitance is far higher than the depletion capacitor. All the above arguments and modeling are valid if terminals 2 and 3 are used for passing current with terminals 1 and 4 left open.

Results and Discussion for AC Measurements: The AC signal over the DC is superimposed and is as shown in Fig. 2b. Referring to Fig. 8 it is observed that for frequency varying from 100Hz to 50KHZ, the impedance varies from 66 KHz to 30KHz. The interfacial capacitance C1 can be easily measured by superposing AC signal on different values of DC voltages. At any one frequency the impedances of the circuit are measured and capacitances of the contact can be calculated as shown.

From Fig. 8. It may be observed that at frequency 110 Hz with DC bias, VDC = 0V, impedance Z = 66.79KΩ and film resistance R = 30KΩ.

We know that the impedance Z can be expressed as shown in equation 2

$$Z = \sqrt{R^2 + X^2} \tag{2}$$

Where R is the bulk resistance of the film and X is the reactance.

$$\text{Where } X = \sqrt{Z^2 - R^2} = 59.67\ \text{K}\Omega$$

$$\text{Therefore, } C2 = \frac{1}{2\pi f X} = 24.26\text{nF}.$$

The interfacial capacitance at a frequency of 110 Hz is calculated as 24.26nF. Similar calculations for ranges of DC voltage superimposed give a plot as shown in Fig 9. It may be observed from Fig. 9 that the capacitance increases to about 138nF with applied DC bias up to 1.5 V. and there on reduces. A details analysis of such variations need further study. Also by knowing the interfacial capacitance other performance parameters such as charge carrier concentration and its mobility in the bulk of the film, relative permittivity, which is a measure of polarizability, can be calculated (Sze, 2002; Belmonte 2008).

Interfacial capacitance using impedance analyzer, Agilent 4294 was measured to confirm our measurements. Interfacial capacitance measurements were made and found that they vary from 28nF at low frequencies to 2nF to 3nF for frequencies above 100 KHz. So, this measurement gives the order of magnitude value of capacitance and also shows that capacitance decreases with increase of frequency (see Fig.10).

Figure 8: Plot of Impedance Vs frequency for different DC bias

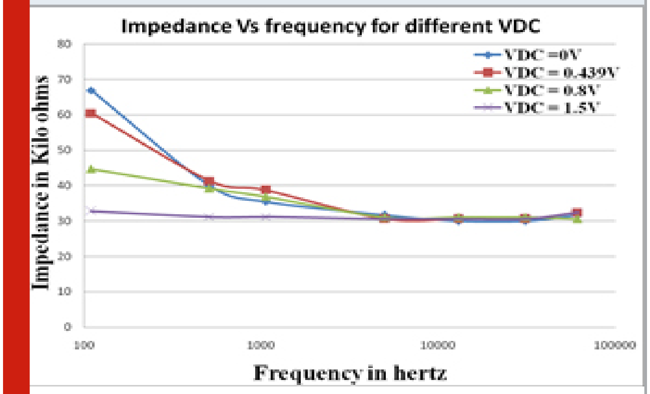


Figure 9: Plot of capacitance Vs Input DC bias

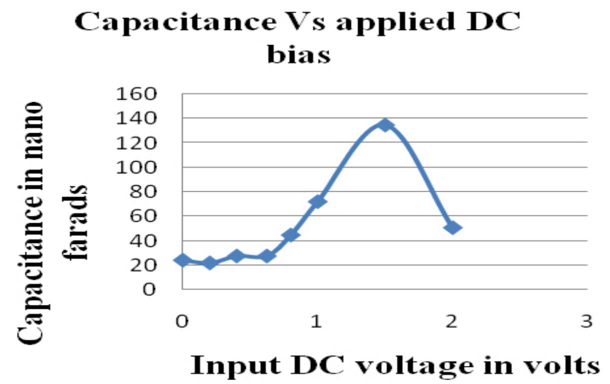
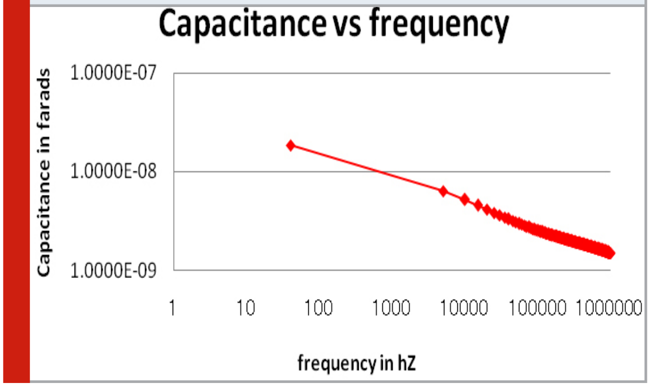


Figure 10: Plot of capacitance Vs frequency



Literature review reports about dependency of junction capacitance on PEDOT: PSS/Cu interface (Aleksandrova, 2016). In this work the authors have reported that surface conditions at the interface contribute to large capacitance. They have also reported that they have used stainless-steel electroconductive yarn as the electrodes in textile-based energy storage device. (Gokceoren et al., 2017) have reported a similar energy storage device using textile which are flexible. Volkov et al., 2017) in their paper have reported that PEDOT-PSS has double layer capacitance and has the potential to be used as super capacitors.

They have also reported on the capacitance – voltage characteristics showing that for increasing voltage bias the capacitance gradually increased except for some small variations up to 1 V. Researchers have also reported that they have used this large capacitance existing due to contact effects in energy storage. Lin et al., (Lin, 2009; Cheng, 2016; Lay et al, 2017 in their paper has reported for having formed a Schottky diode on n-Si using PEDOT-PSS as the contact metal electrode. It is also reported in literature that high-performance super capacitor are being develop based on the needs (Su et al., 2013; Cai et al., 2016).

CONCLUSION

In this work we have reported about the identification of rectifying contacts between tin and copper as a contact metal to PEDOT-PSS and have identifies the order of contact resistances. We have estimated the order of interfacial capacitance and have found that the capacitance increases with DC bias. Literature does not report about the variation of interfacial capacitance with DC bias. In this study all contact related effects are taken into account. A simple method to estimate the order of the capacitance is reported without the need of any sophisticated measurements. This method estimates the order of the capacitance to decide on whether this material is suitable for use in super capacitors or not. This work indicates that PEDOT- has the potential to be used in Super capacitors.

Conflict of Interest: The authors have no conflict of interest.

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