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The Determination of Mega Permittivity in PEDOT-PSS Films

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ABSTRACT

This paper presents measurement of the relative permittivity (εr) of PEDOT-PSS films by measuring the capacitance at metal semiconductor junction. PEDOT-PSS films with and without contact resistances were investigated and it was observed that relative permittivity of the PEDOT-PSS films at low frequencies without contact resistance was large as 5143 and in presence of contact resistances it was 41838 which is 8 times more than the relative permittivity obtained without contact resistance. Such materials with mega permittivity are suitable to build super capacitors.

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

INTRODUCTION

Development of super capacitors is emerging to be a fore runner technology in energy research. Super capacitors use double layer capacitances and sometimes electrochemical capacitance. The most important property that makes super capacitors possible is large relative permittivity (εr) and very thin dielectric layer. Most of the materials have εr in the range 3-100 (Daphne et al., 2014; Donzel et al., 2011; Musil et al., 1975). Of late super capacitors are built using dielectric materials having "Mega permittivity". PEDOT-PSS (poly3, 4 ethylenedioxythiophene– polystyrenesulfonic acid) is a conductive polymer that is being used in many devices and one of the recent applications is in super capacitors (Su et al., 2013; Cai et al., 2016).

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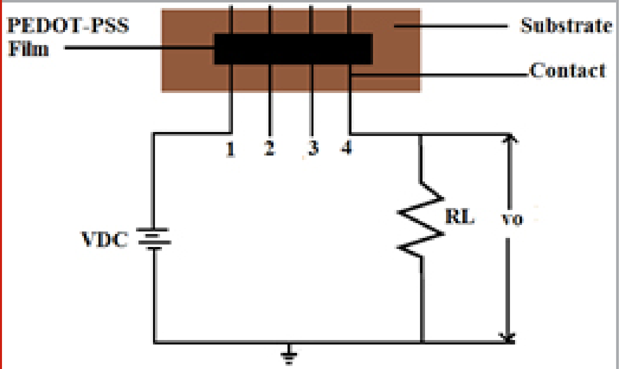
PEDOT-PSS is a semiconductor which has high conductivity in its pristine state. Its conductivity can be increased by several orders by doping it with DMSO (Dimethyl sulfoxide) in varying proportions (Ouyang et al., 2004). When a metal to PEDOT-PSS interface is formed, a rectifying junction is formed due to differences in their work functions (Baca et al., 1997). The thickness of the depletion layer depends upon the number of charge carries available per unit volume and consequently conductivity. Thus, larger conductivity should lead to thinner depletion layer and consequently, larger capacitances. The depletion layer capacitance per unit area is a measure of the value of relative permittivity. In this paper, measurement of εr of PEDOT-PSS is presented by measuring the interfacial capacitance between metal and PEDOT-PSS interface.

Experimental Details: In the present measurement, a PEDOT-PSS film is formed on a Kapton substrate with which a metal contact is made. This results in the formation of a depletion capacitor at the metal-polymer interface whose capacitance is measured to estimate relative permittivity. PEDOT-PSS is dispersion in water procured from H.C. Stark, Germany with a weight ratio of PEDOT to PSS as 1:6. PEDOT-PSS is drop cast (spread evenly) on a 120μm thick Kapton sheet to form a film.

Kapton substrate is made hydrophilic by etching in potassium hydroxide for 10 minutes before making the film and then it is ultrasonicated in acetone, triple distilled water and isopropyl alcohol for 30 minutes each. The drop casted film is annealed for about 24 hours at 50˚C to ensure water evaporates. Tin coated roller pressure contacts of 0.61 mm diameter are used to make electrical connections to the film. Pressure is applied using a C clamp to the roller contacts which holds the PEDOT-PSS film between two rigid Perspex sheets. Fluke 287 digital multimeter and Agilent digital storage oscilloscope are used for measurements.

Figure 1: Circuit used to measure resistance and impedance of films



Theory and Modeling: When a thin film of conducting polymers, in this case PEDOT-PSS, with work function of 5.1 eV (Thomas 2005) come in contact with a metal(tin having work function of 4.32 eV (Park 1996), a metal semiconductor diode(Rectifying contact) is formed owing to work functions differences of conducting polymer and metal (Bindu, 2013 and Bindu and Suresh 2015). Rectifying contacts offers very large contact resistances when compared to the bulk resistance of a film and to eliminated contact resistance conventional four probe resistance measurements are made.

A film of pristine PEDOT-PSS having dimensions 20mm length, 5mm width and 20 micrometer thickness is formed on KAPTON substrate by drop casing (evenly spreading) and four tin coated rollers of 0.61mm diameter are placed 5mm apart (equidistant) on the film(effective length of the film equals to 15mm) and pressed against the film using a C-clamp as contacts. These four rollers form the four terminals 1 to 4. Current is passed between terminals 1 and 4 by applying different DC voltages between these terminals as shown in Fig. 1 and the potential between contacts 1-4 and 2-3 are measured using Fluke 287 high impedance Multimeter (>10Mohm). This is similar to standard four probe measurement used in semiconductor technology.

If the contact 1 and 4 are ohmic (Fig.1), the resistance between terminal 1 and terminal 4, R_{14} will be nearly three times R_{23} (also $R_{12} = R_{23} = R_{34}$) as the contacts are equidistant.

Figure 2: Circuit used to measure resistance and impedance of films

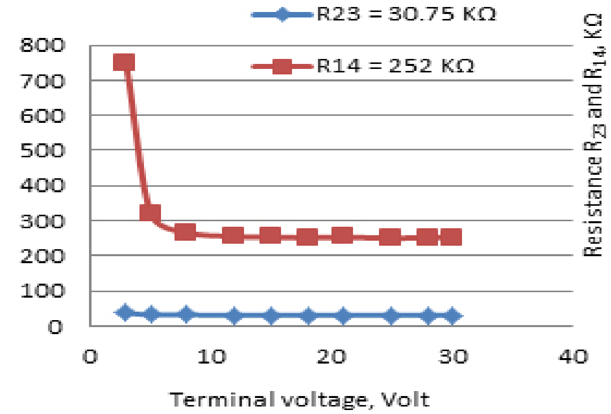
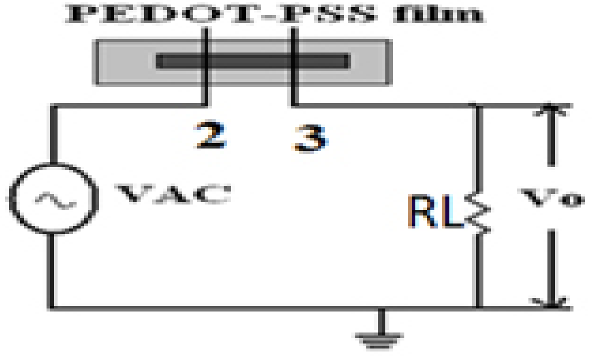


Figure 3: Circuit used to measure the impedance of the film Z_{23}



A plot of the variation of resistance at terminals 1-4(R_{14}) and 2-3(R_{23}) vs. terminal voltage for a pristine PEDOT-PSS film is as shown in Fig.2. The contact resistance when measured between terminal 1 and 4 does not appear to be constant with applied voltage while R_{23} is nearly constant at 30.75 KΩ and it is independent of applied voltage. The resistance R_{14} decreases from 750 KΩ and settles at 252 KΩ. The bulk resistance of film between terminal 1 and terminal 4 should have been equal to three times that between terminal 2 and terminal 3 (30.75 KΩ * 3 = 92.25 KΩ) as the roller contacts are equidistant, but is as large as 252 KΩ clearly showing presence of high contact resistance (252 KΩ - 92.25 KΩ = 160 K Ω).

The surmises made by DC measurements was tested by applying AC voltage to the terminals 2-3 (contacts 2 & 3 were selected as R_{23} was measured earlier with DC excitation) as shown in Fig.3 to measure the impedance Z_{23} and to compare it with DC measured value, R_{23}.

RESULTS AND DISCUSSION

Fig.4 shows the measured impedance Z_{23} of the film for varying frequencies from 100Hz to 50 KHz between terminals 2 and 3. From the observations, it is evident that the impedance of the film reduces from 60 KΩ to

31 KΩ and then settles to 31 KΩ for frequencies above 10 KHz. The impedance measured above 10 KHz is observed to be similar to that measured by four probes DC measurements shown earlier.

Figure 4: Plot showing variation of Impedance Z_{23} vs. frequency for pristine PEDOT-PSS film with tin coated pressure contacts.

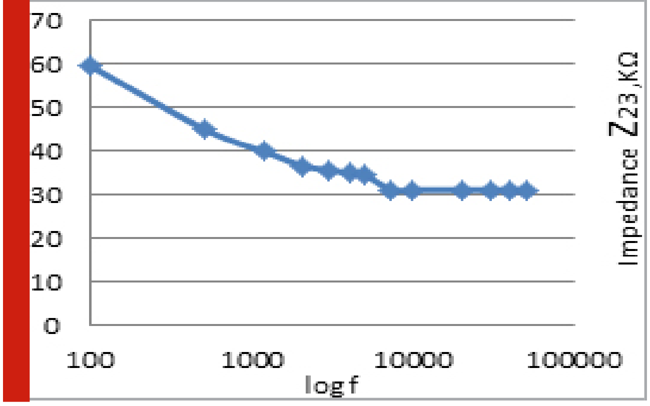
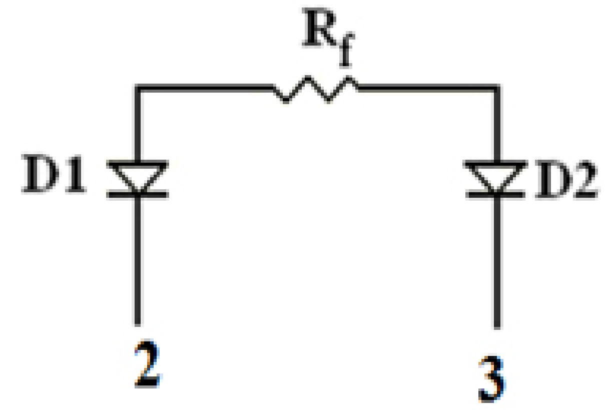


Figure 5: Diode equivalent Model of Fig. 3.



It may be proved that when measured beyond certain frequencies; two probe AC measurements give the bulk resistance of the film between the terminals completely bypassing contact resistance. The authors have reported the detailed work in earlier publications (Bindu and Suresh, 2014). When a diode at the junction is formed it will have its cathode as metal depending on whether the polymer is a 'p' type or 'n' type semiconductor. It is reported in literature that PEDOT-PSS is a P type semiconductor.

The PEDOT-PSS film connected to measure impedance shown in Fig.3 can be replaced by diodes between terminals 2-3 as shown in Fig.5. The diode equivalent model is as shown in Fig.6 where capacitances C_1 and capacitance C_2 represent the metal-semiconductor interface capacitances, RD_1 refers to the reverse leakage resistance of diode D_1, and RD_2 refers to the forward diode resistance of the diode D_2. As the diode D_1 is reverse biased and diode D_2 is forward biased, diode D_1 possesses a larger value of resistance RD_1 compared to RD_2.

Also, C_1 refers to transition capacitance of the diode D_1 which is reverse biased and C_2 refers to the diffusion capacitance of the forward biased metal-semiconductor junction. When the power supply terminal is reversed $C1/RD_1$ and C_2/RD_2 are interchanged. When AC excitation is applied diodes D_1 and D_2 are alternately forward and reverse biased. For AC excitation C_1 (the depletion layer capacitance) is smaller of the two capacitances and dominates the overall frequency response and impedance of the film.

The voltage drop across the diode capacitor (C_1) reduces as the frequency of the signal applied increases and at frequencies for $f >> 1/2\pi\ (RD_1)\ C_1]$ the impedance of the capacitors is negligible compared to the interfacial diode resistance. Thus, the interfacial diode resistance can be bypassed by the parallel capacitance if AC signal is applied at a frequency $f >> 1/(RD_1C_1)$. Effect of C_2 may be neglected as diffusion capacitance is far higher than the depletion capacitor.

Figure 6: Equivalent diode model Circuit used to measure Impedance of the film.

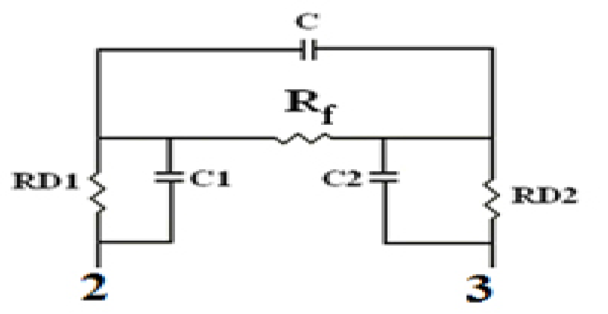
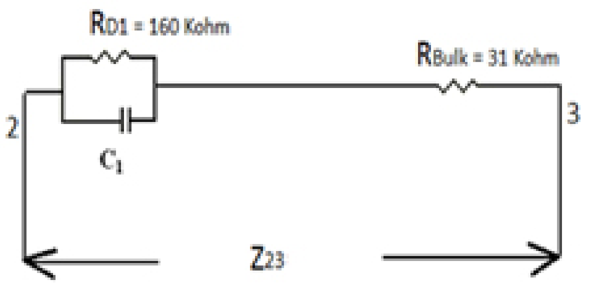


Figure 7: Simplified diode equivalent circuit.



To estimate the interfacial capacitance a simplified diode equivalent circuit may be considered as shown in Fig.5. The effect of diffusion capacitance C_2 has been neglected for calculation purposes as its value is far higher than the depletion capacitance C_1. By knowing the values of contact, bulk resistances and impedances between terminals 2-3, the interfacial capacitance could be calculated.

The contact resistance measured earlier with DC excitation is RD_1 =160 KΩ and bulk resistance R bulk (R_{23}) = 31 KΩ, measured by both AC and DC excitations. Referring to Fig.4 we observe that at 100Hz the measured impedance Z= 60 KΩ, and at 1.2 KHz the impedance is 38.89 KΩ. The interfacial capacitance C_1 was calculated as 35nF at 100 Hz and 30nF at 1.2 kHz from the values of contact, bulk resistance and impedance. So, depletion capacitance for other calculations can be taken as C_1 = 35 nF.

Diode equivalent circuit shown in Fig.7 was simulated (using 5 spice software) for the measured and calculated values of RD_1, R bulk (R_{23}), Z_{23} and C1 = 35 nF. It is observed from Fig.8 that the plot of impedances Vs frequency for measured and simulated is similar. It implies that if the value of the capacitance at the interface is known then the relative permittivity could be calculated.

Calculation of Relativity permittivity for pristine PEDOT-PSS film

Large depletion capacitances show that the molecules are highly polarizable. By knowing the interfacial capacitance, charge carrier concentration and its mobility in the bulk of the film, relative permittivity (a measure of polarizability) could be calculated.

We know that the Depletion layer capacitance per unit area (C_1 from our model) (Simon, 2013) is given by

$$\frac{1}{C_1} = \frac{2(vbi-V)}{q\epsilon_0\epsilon_{rn}} \quad F^{-1}m^2 \qquad (1)$$

Where v_{bi}, built in potential; assumed to be 0.5V

V bias voltage = 0

ε_o, permittivity of free space = 8.854×10^{-12}

q, charge of an electron e =$1.6*10^{-19}$ C.

Assuming that only 10% of the roller contacts the film, the contact capacitance is calculated as

$$10\%\ of\ roller\ area = 0.1\,\pi D\ell = 0.9577 * 10^{-6}\,m^2$$

Where D = Diameter of the roller contact = 0.61mm and

l = Length of the film contacting roller = 5mm

Therefore contact capacitance per square meter is

$$C_1^{'} = \frac{C_1}{10\%\ contact\ area} = \frac{35nF}{0.9577*10^{-6}} = 36.54 * 10^{-3}\,\frac{F}{m^2} \qquad (3)$$

To calculate the carrier concentration, the resistivity of the film and mobility of charge carriers μ, must be known.

Resistivity of the film, ρ can be calculated by knowing bulk resistance and film dimensions.

Pristine PEDOT-PSS film dimensions are as given below

Width (w): 5mm

Thickness (t): 20μm

(Considering only R_{23} from model) Length between roller terminals (L): 5mm

Diameter of the contact roller (D): 0.61mm.

Bulk resistance R: 31 KΩ

$$\rho = \frac{RA}{L} = \frac{31K\Omega*5mm*20\mu m}{5mm} = 0.62\ \Omega m$$

Where A= The cross- sectional area of the film. The mobility of charge carriers in PEDOT-PSS (μ) reported in the literature varies from 0.001cm²/ V-s (Garcia, 2008), 0.6 cm²/ V-s (Needham and James 2002) to10 cm²/V-s (Elschner et al., 2011) which is very wide. However, from this point of view Hall measurements are accurate as contact resistances are not involved and mobility of 0.6 cm² /V-S is considered. Another measurement made using optical method which is also a non contact method, has reported 0.7 cm²/V-S which closely corroborates with Hall measurements (Yamashita et al., 2011).

$$\sigma = ne\mu = \frac{1}{\rho} \qquad (5)$$

Assuming the value of μ = 0.6 cm²/V-S and substituting for resistivity and mobility in equation (5), the charge carrier concentration can be calculated as shown in equation (6).

$$n = \frac{1}{\rho e\mu} = 1.68 * 10^{23}/m^3 \qquad (6)$$

Substituting all the calculated values in equation (1)

$$\varepsilon_r = \frac{C_1^{'} * 2(Vbi-v)}{q\varepsilon_0 n} = 5143 \qquad (7)$$

The value of relative permittivity calculated above is strongly dependant on the mobility of charge carrier assumed. We have shown earlier that the contact resistance can vitiate the measurement of bulk resistance which in some cases could be the reason for varying values of apparent mobility. Assuming a value of 0.6 cm²/V-S for the charge carrier mobility, the relative permittivity of the interface is high as 5143. This is an important finding that shows the polymer molecules are highly polarizable. It may be noted that the relative permittivity calculated without contact resistance (R_{Bulk} = 31KΩ) is 5143 but with contact resistance included the relative permittivity is 41838 which is nearly 8 times more.

Literature does not report about the effect of contact resistance on relative permittivity where as this study proves that. In this study all contact related effects are taken into account. 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.9).

Figure 8: Comparative Plot of impedance Vs frequency for pristine PEDOT-PSS (measured and simulated)

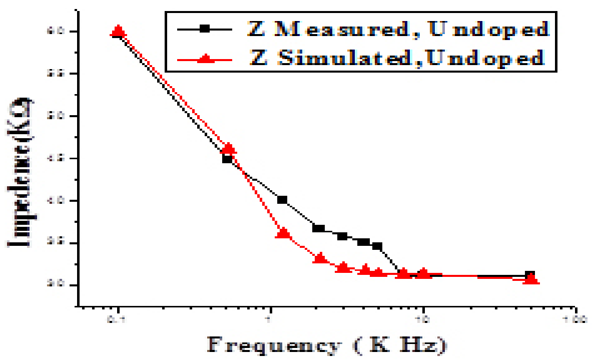
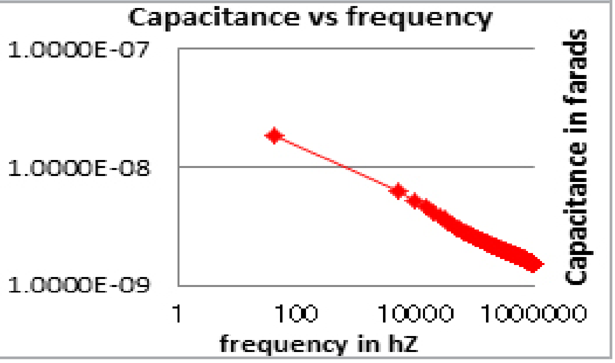


Figure 9: Plot of capacitance vs. frequency for PEDOT-PSS making pressure contact to tin



Similar findings of junction capacitance dependency on the frequency for PEDOT: PSS/Cu interface with UV treated and non-treated polymer layer have also been reported by M.P. Aleksandrova et al 2016). In their work they have reported small variations up to 1 kHz (within the same order of magnitude) and then decreases gradually with the increase in frequency. This trend ascribes low charge carrier mobility in the polymer and the poor ability of the charges to follow the AC signal changes at the same rate. In the low frequency range, the capacitance depended stronger on the surface condition near the electrodes. (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.

CONCLUSION

In this paper we have shown that two probe AC measurements give the bulk resistance of the film between the terminals completely bypassing contact resistance. C_1 is of the order of 35nF at 100 Hz and 30nF at 1.2 kHz. The relative permittivity of the PEDOT-PSS film at the metal semiconductor interface without contact resistances is 5143 and in presence of contact resistances it is 41838, nearly 8 times more than the relative permittivity obtained without contact resistance. Such large value of relative permittivity indicates that the polymer molecules are highly polarizable and has the potential to be used in Super capacitors.

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