Measurement of Bulk Resistance of Conducting Polymer Films in Presence of Rectifying Contacts

Bindu S, M S Suresh

Dept. of Electronics & Communication, B N M Institute of Technology, PB No: 7087, 12th main road, 27th cross, Banashankari 2nd stage, Bangalore, India

Abstract- Measurement of bulk resistance/resistivity of conducting polymers is very common and an important requirement. Conducting polymers are semiconductors and four probe measurements are needed to avoid errors due to contact resistance and spreading resistances. However, in a device it is convenient to make two probe measurements rather than four probe measurement. It has been shown here that the bulk resistance of a thick film can be measured in the presence of rectifying contacts, using two probe method by measuring the impedance of the film beyond a critical frequency. The metal-film contact has been modeled as a diode to explain the behavior.

Index Terms- Critical frequency, Conducting polymer, Four probe measurement, PEDOT-PSS, Strain gauge, Two probe measurement.

I. INTRODUCTION

Semiconducting polymers have emerged as novel electronic materials for use in variety of devices [1]. Use of conducting polymers as strain gauge material to measure force, strain or pressure is a recent application that exploits the piezoresistive property of certain conducting polymers [2-4]. Advantages of using conducting polymers as strain gauge materials are high gauge factor and flexibility [5-6] and also compatibility with biological environment [7]. In strain gauges change in the bulk resistance of the polymer film due to strain has to be measured. Since, conducting polymers are semiconductors, metal-semiconductor contacts form rectifying contacts rather than ohmic contact. In order to measure the change in the bulk resistance of the film it is necessary to use four probe measurements [8] or form ohmic contacts with the film. Thus measurement of bulk resistance of conducting polymer films poses several challenges. However, for strain gauge applications it is convenient to use two probe measurements rather than four probes. This paper proposes a simple two probe method of measuring the bulk resistance of polymer films using AC technique and provides a method for estimation of frequency(critical frequency) at which measurements are to be made. Comparison of two probe AC and four probe DC measurements for PEDOT-PSS (poly 3,4ethylenedioxythiophene – polystyrenesulfonic acid) films pristine and doped with DMSO (Dimethyl sulfoxide) is made to prove the efficacy of the method. A phenomenological model is presented to explain the results. The AC method allows use of any metal contact such as copper or tin rather than expensive gold or ruthenium.

II. EXPERIMENTAL DETAILS

PEDOT-PSS was procured from H.C. Stark, which is dispersion in water, with a weight ratio of 1:6. Film of PEDOT-PSS is drop cast on a kapton sheet of 120µm thickness. Before casting the film on kapton substrate the substrate is ultrasonicated in acetone, triple distilled water and isopropyl alcohol for 30 minutes. The film cast is annealed (at 50-55 deg. C) for about 24 hours [9] so that water evaporates and a thin polymer film of about 20µm thick, 15mm length and 5mm width is formed. Four contacts (1 to 4) on to the film are made by roller pressure contacts, using tinned copper rollers of diameter 0.61 mm with a distance of 5mm between them. Pressure on the contacts is applied using a C clamp which holds the polymer film between two rigid Perspex sheets.

Two sets of measurements are done; one, four probe measurements with DC excitation and another with two probes with AC excitation. These are compared to show that two probe AC method indeed gives the same value as the DC four probe method. For making four probe DC measurements, circuit connections are made as shown in Fig 1 where RL is a standard resistor of known value. The voltage across RL (VO) gives the current through the film. Voltages at contacts1, 2, 3 and 4 are measured to calculate the voltage drop across contacts 1-2, 2-3, 3-4 and consequently resistance between those contacts. Fluke 179 digital multimeter is used for DC voltage measurements. Measurements are made by applying different DC voltages in the range 1 to 30V.

AC measurements was made to determine Impedance between two terminals(2 and 3) by applying AC voltage as shown in Fig.2 and measuring the voltage across RL to get current and the voltage across the film V23 (V2 –V3). Measurements are made by applying a fixed AC voltage of 5V peak and varying

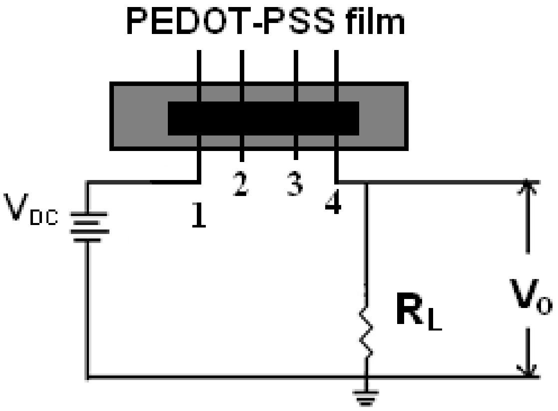

Fig 1: Circuit used to measure film resistance using four probes

frequency from 100Hz to 50KHz. whenever AC measurements are made between contacts 2 - 3, contacts 1 and 4 are left open. For all AC and DC measurements RL was fixed at 10KΩ. Agilent Digital storage oscilloscope was used for all AC measurements.

III. MODELING, RESULTS AND DISCUSSION

The metal conducting polymer contact has been studied by some workers in reference to making devices such as FET, LED where, the contact resistance is very large or comparable to the device resistance [10]. The interface is invariably forward biased and the contact resistance affects the device current/ voltage or the bias characteristics. This forward characteristic is determined by the mechanism of carrier injection such as tunneling or diffusion limited thermionic emission. The mechanism determines the forward characteristic of the schottky diode at the interface. However, they have not studied the frequency dependence of the contact impedance as their focus was on DC bias characteristics. In another study, Akansha Sharma etal, have studied the metal polymer junction in both forward and reverse direction [11]. In that study they have measured the interface capacitance for forward and reverse bias as a function of bias voltage and frequency in order to determine the defect distribution at the interface which in turn affects the carrier injection. Their results show that the interfacial capacitance in reverse bias is nearly constant with frequency in the range 10Hz to 1MHz.

In the present work two metal polymer interfaces are in series with one of them always reverse biased. So, only the reverse biased interface determines the current in the film. Thus the focus is on the reverse biased contact diode which is modeled as a resistance in parallel with the depletion capacitance. In a reverse biased junction diode the AC current is largely due to modulation of depletion layer and not due to carrier injection. In view of this the carrier injection mechanism in the forward bias is unimportant and need not be considered. This allows us to use a phenomenological model for the metal polymer film interface consisting of a capacitance in parallel with a resistance and the results are discussed in the light of this model. An equivalent circuit model for a polymer film with four metallic roller pressure contacts is shown in Fig. 3.

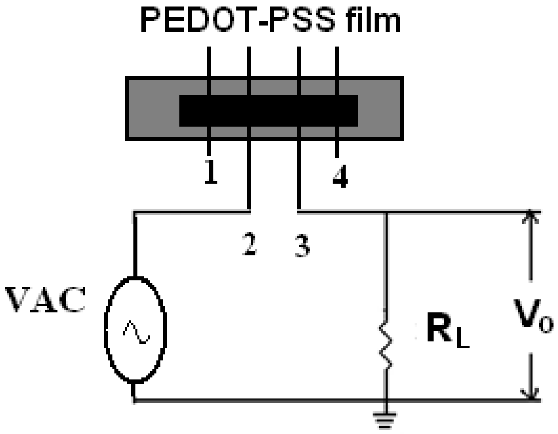

Fig 2: Circuit used to measure impedance of the film using two probes

Roller contacts are shown as 1, 2, 3 & 4 and the film resistances (bulk) between these contacts are shown as R_1, R, and R_2. The resistance R_1 and R_2 also include the spreading resistance at the contact area of the rollers. Diodes D_1 and D_2 represent the metal semiconductor contact as shown in Fig 3.

If a DC voltage is applied to the film between terminals 1 and 4 current determined by the reverse biased diode and film resistance flows between the terminals 1 and 4. Voltages between terminal 4 and the other three terminals (1, 2, 3) along with voltage across R_L (10KΩ) are measured. The voltages across the diodes (V_{12} and V_{34}) and the bulk of the film (V_{23}) may be calculated from the voltages V_1, V_2, V_3 and V_4.The current is calculated as V_4/R_L. Plots of these voltages with respect to current are shown in Fig. 4 to Fig. 6.

It may be observed from Fig. 4 that the diode D_1 is reversed biased as the voltage V_{12} increases more with current. The diode D_2 is forward biased as the voltage drop across it, V_{34}, flattens with increasing current. Fig. 5 shows voltage V_{23} vs. current which is a straight line of slope 30.75kΩ indicating resistive (Ohmic) relation between V_{23} and current(i.e.R_{23}= 30.75 kΩ). However one can calculate the bulk resistance of the film between 1 and 4 as three times that between 2 and 3 equal to 92.25KΩ. This method of making four probe measurements is conventional and is commonly used when contacts are rectifying.

Since there is a reverse biased rectifying junction between terminals 1 and 2 the measured resistance between 1 and 4 is dominated by it as shown in Fig 6.

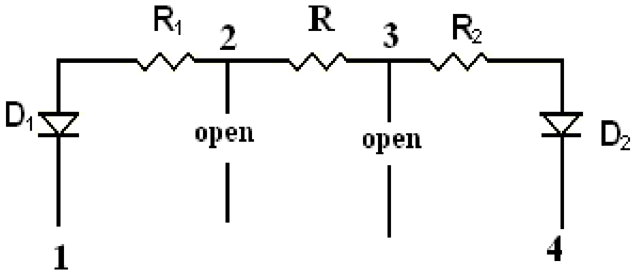

Fig 3: Model of a polymer film with four metallic roller pressure contacts when DC voltage is applied to contacts 1 and 4.

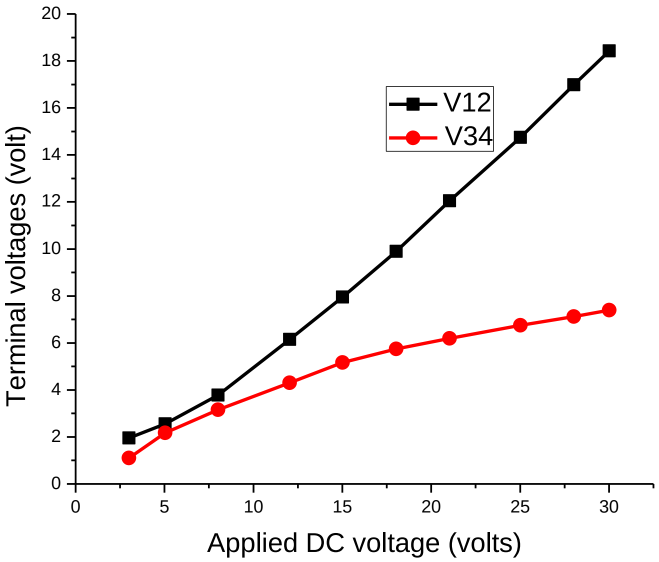

Fig 4: Voltage relationship between terminals 1-2 and 3-4 for undoped PEDOT-PSS.

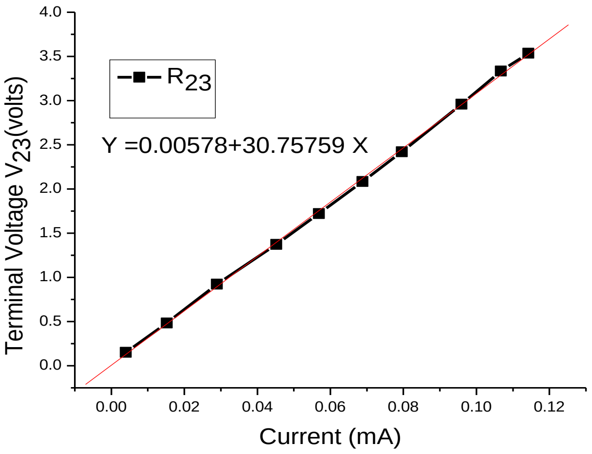

Fig 5: Relationship between voltage V23 and Current for undoped PEDOT-PSS.

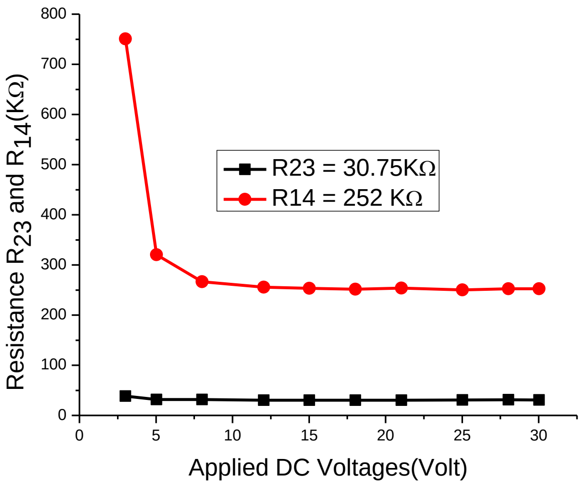

Fig 6: Relationship between resistance R23 and R14 with applied DC voltage for undoped PEDOT-PSS.

The AC equivalent model of diodes is shown in Fig 7. AC voltage is applied to the contacts 2-3 to determine the impedance Z_{23} and to compare it with R_{23} determined from DC measurements. When AC voltage is applied between contacts 2 – 3 at least one of the diodes is reverse biased and the other forward biased. Though there are contact diodes at 1 and 4 they are not shown as they are kept open.The capacitances C_1 and C_2 represent the metal semiconductor contact capacitances. R_{D1} is the reverse leakage resistance of diode D_1 and R_{D2} is the forward static resistance of the diode D_2. R_{D1} is much larger than R_{D2} as diode D_2 is forward biased and diode D_1 is reverse biased. It may also be observed that C_1 represents transition capacitance of the reverse biased diode D_1 and C_2 represents the diffusion capacitance of the forward biased metal semiconductor junction when terminal 2 is positive and terminal 3 is negative. C_1/R_{D1} and C_2 / R_{D2} are

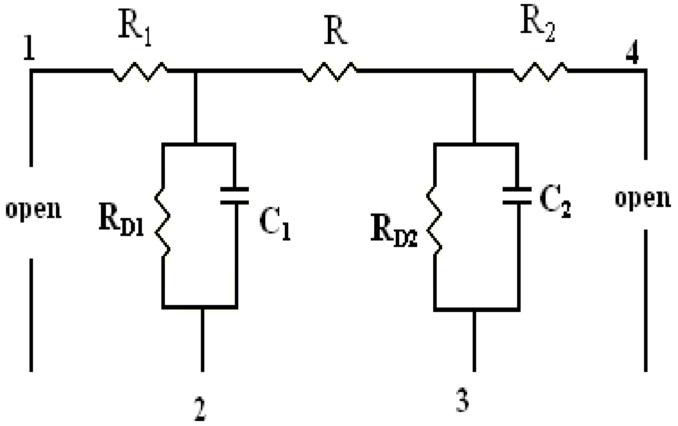

Fig 7: Model of the Diodes and resistors when AC voltage is applied to contacts 2 and 3.

Interchanged when the power supply polarity is reversed. C_1 being the smaller of the two capacitances dominates the overall response. As the frequency of the signal applied increases the voltage drop across the diode capacitor (C_1) reduces and at frequencies f >> $1/[2\pi(R)C_1$ the impedance of the capacitors is negligible compared to the resistance of the film.

To check the above concept impedance of the film between terminals 2 and 3 was measured at different frequencies from 100Hz to 50 KHz which is shown in Fig 8.

It may be observed that the impedance decreases from 60KΩ to 31KΩ and remains at 31KΩ beyond about 10 KHz. The impedance measured beyond 10 KHz is the same as that measured by four probe DC method shown above (Fig 8). This proves that two probe AC measurement of impedance gives the film resistance between the terminals at frequencies greater than the critical frequency.

The modeling of the metal polymer interface was checked by using a 5 spice circuit analysis tool. The interface and the bulk resistance of the film was simulated using the circuit shown in Fig.7 with C1= 12nF and RD1= 30kΩ and R = 31.2KΩ. The fit between the experimental results and the frequency response of the equivalent circuit is very close indicating correctness of the model. The value of C2 and RD2 is neglected as C2 is large compared to C1 and RD2 is very small.

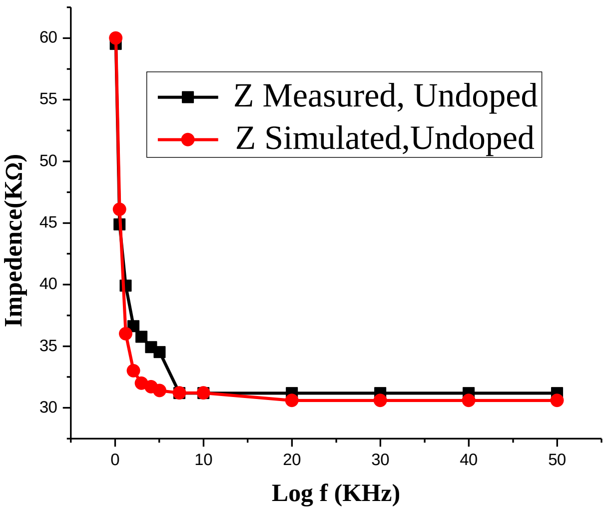

Fig. 8: Impedances of film between terminal 2-3 as a function of frequency for undoped PEDOT-PSS

IV. CALCULATION OF CRITICAL FREQUENCY FOR UNDOPED

Frequency at which resistance of the film is equal to the reactance of C1 can be treated as the critical frequency fc. For frequencies above 2 to 5 times fc the measured impedance is equal to the resistance of the film.

$$f_c = 1/(2\pi C_1 R)$$

The order of magnitude of f_c can be estimated by calculating the value of C_1 which can be estimated if the carrier concentration and its mobility are known. Some simplifying assumptions can be made as the interest is in approximate value of capacitance.

The carrier concentration (n) can be calculated from the resistance of the film which is 31kΩ (Fig.8)

Dimensions of the undoped PEDOT-PSS film are;

Total Length (ℓ_T): 15mm, Width (w): 5mm, and Thickness (t): 20µm, Length between each roller contact (ℓ): 5mm.

Diameter of the contact roller (D): 0.61mm

Resistivity of the film is calculated as shown in equation 1.

$$\boldsymbol{\rho} = \frac{R\,a}{L} = \frac{31K \text{ x}5mm \text{ x}20\mu m}{5mm} = 0.62\Omega m \qquad 1$$

Where ‘a’ is the cross sectional area of the film

$$\sigma = \frac{1}{\boldsymbol{\rho}} = ne\mu \qquad 2$$

The relationship between conductivity and charged carrier mobility is given by equation 2, where Charge carrier mobility µ for undoped PEDOT-PSS is assumed to be 10 $cm^2/$ (V.s) [12][13], and e the charge of an electron is a standard value.

Therefore carrier concentration

$$n = \frac{1}{\boldsymbol{\rho} e\mu} = 1.00806 \text{ x } 10^{22}/m^3 \qquad 3$$

Depletion layer capacitance per unit area [14] is given by equation 4.

$$\frac{1}{C^2} = \frac{2(Vbi - V)}{q\ \varepsilon o\ \varepsilon r\ n} \ \frac{F}{m^2} \qquad 4$$

Where $V_{bi,,}$ built in potential assumed to be 0.5V

V, bias voltage = 0,

$\varepsilon_{o,}$ permittivity of free space = $8.854\text{x}10^{-12}$ and

$\varepsilon_{r,}$ relative permittivity of 3 is assumed for polymer film [15].

Substituting for ‘ n’ obtained from equation 3 into equation 4 the depletion capacitance C_1 = 206.98 µF/ m^2. 5

The contact capacitance is calculated assuming that only15% of the area of the roller makes contact with the film.

$$15\% \text{ Contact Area} = 0.15\pi DL = 1.465 \text{ x } 10\text{-}^{6}\ m^2 \qquad 6$$

Therefore contact capacitance

$$C1 = 1.465 \text{ x } 10\text{-}^{6} \text{ X } 206.98\text{X } 10^{-6} = 297.32pF \qquad 7$$

Substituting for C1 and R, Critical frequency can be calculated as shown in equation 8

$$f_C = 1 / 2\pi RC_1 \approx 17KHz \qquad 8$$

So beyond about 20 KHz (refer Fig. 8) rectifying contact does not affect the measurement of bulk resistance of the film and no difference will be seen between two probe and four probe measurements.

It is well-known that conductivity of pedot-pss can be increased by several folds by adding Dimethyl sulfoxide(DMSO) to pedot-pss [16].Measurements were also done with PEDOT-PSS film doped with 25% DMSO having same dimensions as undoped film. It may be observed from Fig. 9 that as the frequency is varied from100 Hz to 8MHz the impedance of the film decreases from 1.1KΩ to 120Ω and remains at about 120Ω beyond 2MHz. The interface with the doped polymer film is simulated using the same model shown in Figure 7 with C_1= 1μF and R_{D1}= 1.1kΩ and R = 120Ω. The frequency response of the simulated circuit fits well with the experimental results as shown in Figure 9. It may also be observed that the as the bulk resistance of the film has decreased density of charge carriers has increased consequently reducing the depletion layer thickness and increase of interfacial capacitance and decrease of interfacial resistance. Calculations similar to that for undoped films for f_c, assuming the mobility is increased [17], [18] by a factor of 10 due to doping, gives a value of f_c = 2.77 MHz beyond which impedance is constant at 120 Ω.The cutoff frequency f_c calculated gives only an approximate value of frequency at which the measurements are to be made as the value of carrier mobility μ (assumed is 10cm^2/v-s) reported varies by a large value. For accurate calculation of cut-off frequency the values of carrier concentration and mobility μ are to be known individually, while in the calculation above one has to be assumed to calculate the other. One can determine the AC characteristic for applied input voltage and then decide at what frequency the measurements of the film have to be made. The main point to make here is that the AC resistance of a PEDOT-PSS film could be used to measure bulk resistance of polymer film in presence of rectifying contacts. The lowest frequency however, depends on the contact metal, area of the contact, contact type and the resistivity of the polymer film. The area of contact is at the control of designer and the lowest frequency of measurement can be tailored to the needs. This AC method has been developed to measure strain in conducting polymeric gauges.

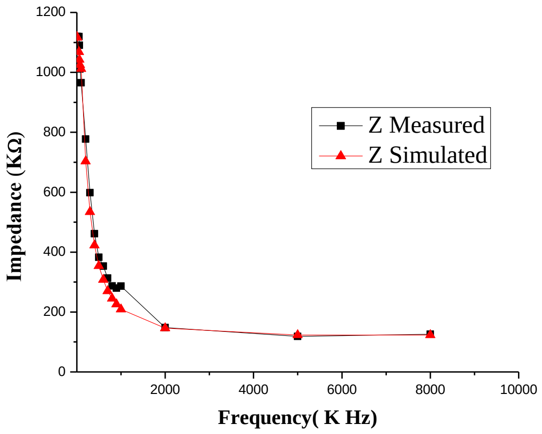

Fig 9: Impedances of film between terminal 2-3 as function of frequency for PEDOT-PSS doped with 25% DMSO.

V. CONCLUSION

Four probe measurements are normally employed to measure bulk resistance of films. This is difficult and cumbersome when film is used as a device as in a polymer strain gauge. The bulk resistance of film can be measured by measuring its impedance beyond a critical frequency as shown above. The frequency above which measurements have to be done depends also on the area of contacts. A simple diode model explains the behaviour.

ACKNOWLEDGMENT

We thank management of B N M Institute of Technology, Bangalore, for permission and support in carrying out the work. We also thank Dr Satish Amrutrao Patil from SSCU, IISc, Bangalore and Dr Praveen C R, Dept of Materials Engineering, IISc, Bangalore, for their help.

REFERENCES

[1] H Fengling Zhang and Olle Inganas. Conducting and Transparent Polymer Electrodes.In Niyazi Serdar Sariciftci and Sam-Shajing Sun, editors. Organic photovoltaics mechanisms, Materials,and Devices. CRC Press 2005.

[2] Blake w. Axelrod, Michael L. Roukes. Polymeric Piezoresistive Sensors. United States Patent no US 2006/0071286 A1, 2006.

[3] Ramona Mateiu, Michael Lillemose, Thomas steen Hansen, Anja Boisen, Oliver Geschke. Reliability of Poly3,4ethylenedioxythiophene strain gauge. Microelectronics engineering 84(2007) 1270-1273.

[4] M. Lillemose, M. Spieser, N.O. Christiansen, A. christensen, A. Biosen, Intrinsically conductive polymer thin film Piezoresistors, Microelectronics engineering 85(2008)969-971

[5] Giuseppe Latessa. A glove-based system equipped with home-made piezoresistive bend sensors. Aug-2010. Available: http://art.torvergata.it/handle/2108/1388

[6] Seiichi Takamatsu, Tomoyuki Takahata, Masato Muraki, Eiji Iwase, Kiyoshi Matsumoto and Isao Shimoyama. Transparent conductive-polymer strain sensors for touch input sheets of flexible displays. J. Micromech. Microeng. 20 (2010) 075017 (6pp). Online at stacks.iop.org/JMM/20/075017

[7] Ching Hsiang Cheng, Chen Chao, Yin-Nee Cheung. Piezoresistive Strain Gauge Using Doped Polymeric Fluid. United States Patent no US7,500,399 B2 , Mar 2009.

[8] Ulrich Lange, Vladimir M. Mirsky, Separated analysis of bulk and contact resistance of conducting polymers: Comparison of simultaneous two- and four-point measurements with impedance measurements, short communication , J. Electro analytical Chemistry, 622 (2008) 246-251.

[9] C.S. Suchand Sangeeth, Manu Jaiswal, Reghu Menon. Correlation of morphology and Charge transport in poly (3,4- ethylenedioxythiophene)–polystyrenesulfonic acid (PEDOT– PSS) films. 2009 J. Phys.: 21 072101

[10] S. Alborghetti and P. Stamenov. Modeling of Electronic Transport through Metal/Polymer Interfaces in Thin Film Transistors, ISRN Electronics, Volume 2013 (2013), Article ID 652587, 6 page, http://dx.doi.org/10.1155/2013/652587

[11] Akanksha Sharma, Sarita Yadav, Pramod Kumar, Sumita Ray Chaudhuri, and Subhasis Ghosh Defect states and their energetic position and distribution in organic molecular semiconductors, Appl. Phys. Lett. 102, 143301 (2013); doi: 10.1063/1.4801636

[12] http://en.wikipedia.org/wiki/Electron_mobility

[13] Andreas Elschner, Stephan Kirchmeyer, Wilfried Lovenich, Udo Merker, Knud Reuter. PEDOT : Principles and Application of an intrinsically conductive polymer. CRC press, Taylor and francis group,p147. 2011.

[14] Simon .M. Sze, Semiconductor Devices Physics and Technology. 2nd edition, John Wiley & sons, New-York, 2002, p. 229

[15] Germà Garcia-Belmonte, Antoni Munar , Eva M. Barea , Juan Bisquert , Irati Ugarte Roberto Pacios . Charge carrier mobility and lifetime of organic bulk heterojunctions analyzed by impedance spectroscopy. Organic Electronics 9 (2008) 847–851.

[16] Jianyong ouyang, Quianfei Xu,Chi-Wei Chu, Yang Yang, Gang Li,Joseph shinar.On the mechanism of conductivity enhancement in Poly(3,4-ethylene dioxythiophene):Poly(styrene Sulfonate film through solvent treatment.polymer 45(2004)8443-8450.

[17] Yow-Jon Lin, Cheng-Lung Tsai, Yu-Chao Su, and Day-Shan Liu. Carrier transport mechanism of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) films by incorporating ZnO nanoparticles . Appl. Phys. Lett. 100, 253302 (2012)

[18] James Needham. Thesis. Investigations in the conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) in a field-effect transistor configuration. University of Memphis. Aug. 22, 2002

AUTHORS

First Author – S Bindu completed her Bachelor’s degree in Electrical and Electronics Engineering from Bangalore University in 1996 and Masters degree in Power Electronics from UVCE, Bangalore in 2002. She is currently pursuing her Doctoral program in the area of Development of Flexible strain gauges from VTU, Belgaum, India.

Major fields of study is in conducting polymer sensors and nano materials. She has about 17 years of teaching experience and has published and presented papers in International Conferences. She is currently Associate Professor, Department of Electronics and Communication, B N M Institute of Technology, Bangalore. , e-mail: bindu.ct@gmail.com

Second Author – M S Suresh received the B.E. degree in Electrical Engineering from Bangalore University, Bangalore, India, in 1971 and the M. Tech. degree in Electrical Engineering and the Ph.D. degree in Impedance of sealed nickel/cadmium cells at low states of charge from the Indian Institute of Science, Bangalore, in 1973 and 1990, respectively.

He was with Bharat Electronics LTD., Bangalore, from 1973 to 1977 designing power electronic equipment. He was with ISRO satellite Centre, Bangalore, from 1978 to 2006 and was involved in the design of satellite power systems. He turned to teaching in 2006 and is presently the principal, B N M Institute of Technology, Bangalore. He has several technical reports and papers to his credit. His areas of interest are solar cell capacitance, Impedance spectroscopy, nano materials and sensors.