Electrical Characterisation of Polypyrrole Thin Film Conducting Polymer

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Abstract. It is known that organic acids doped Polypyrrole (PPy) will conduct electricity, and the electrical characteristics of the polymer is presented in this paper. The PPy is deposited on a glass substrate using a spin coater, resulted in a thin film with of 0.0823 μm thickness. The I/V characteristics of the PPy thin film were measured using two-point and four-point probe at room temperature. The finding shows that the I/V characteristic is nonlinear. Comparison between these two methods is further explored, and statistically it shows that there is no mean difference between the two methods. Hence, it helps in designing future experiment to measure I/V characteristics at elevated temperature.

1. Introduction

The processability of polymers allow flexibility in producing polymers for desired applications. Polymers in general are insulator, however addition of dopants introduce the electrical conductivity into the polymers, becoming a conducting polymer. Polypyrrole (PPy) is a conductive and highly stable polymer, it has been used in wide range of sensor base applications. Conducting polymers are quasi-unidimensional conductors rather unidimensional, however when deposited as a thin film it possesses properties that are predicted for unidimensional electron systems [1].

Electrical characterisation of the PPy thin film is necessary to determine the suitable application and its effective range for the desired application. Several characterisation approach and methods has been reported such as the LCR meter, multi-meter, dielectric probe, Van der Pauw, capacitance meter [2], two-point probe and four-point probe [3-5]. Every method has its own advantages and disadvantages depending on the measured material. For example, a non-ohmic sample material is not suitable be tested using an LCR or a multi-meter but it is preferred using either a two-point or four-point probe. All these methods have its input requirements such as current, voltage or frequency. The four-point probe has advantage over the conventional two-probe method is that it minimises error due to contact resistance [6], hence improve in accuracy. The four-point measurement is known best for the measurement of low electrical resistance material in nΩ ranges [7], thus not suitable for high resistance material. It is claimed that the two-point measurement method is suitable for high resistivity which is greater than 1 M Ω/m2 [7].

Several articles have reported the measurement of electrical properties of the PPy thin film using the four-point probe instead of two-point probe method. This could be to the reason that the four-point measurement is chosen for the irrelevance of the contact resistance in the measurement. In this paper, electrical characterisation of PPy thin film will be discussed, and comparing the measurement from these two methods, two-point and four-point probe accordingly. The overall results will highlight finding from
each method and conforming the most suitable method in the measurement of electrical properties of a PPy thin film. The PPy is chosen as the potential sensing material for thin film based sensor because it is easy to synthesis, stable at room temperature [8] and has higher conductivity values than other organic conducting polymers [9].

2. Experimental

2.1 Sample preparations
A Glass slide of 25.4 mm x 25.4 mm x 1 mm dimension was used as the substrate material. The glass substrate first rinsed with Ethanol and DI water. Later immersed in Ethanol solution for 5 minutes and dried using an air gun. The glass substrates then were vacuumed in a chamber that contain UV light and oxygen gas for 6 minutes. Other material used were Ethanol (95% of purity, molecular weight: 46.07g/mol) and Deionized (DI) water.

A PPy thin film was prepared using a spin coating technique on the pre-cleaned glass substrate. A dispensed PPy liquid on the glass substrate was spun at 500 rpm for 5 seconds with acceleration of 1000 rpm/s for the first stage followed by spinning at 1899 rpm for 20 seconds at acceleration of 1000 rpm/s in the second stage for thickness of 0.0823 μm. The sample is then dried on a hotplate for 2 minutes at 70 °C. Only one layer of deposition is performed. A commercially available PPy solution (Sigma Aldrich, 482552) doped in proprietary Organic Acids was used without further alteration.

2.2 PPy thin film characterisation
The thickness of deposited layer of PPy on a glass substrate was measured using a High Power Microscope (HPM) profiler (DextarTAR) as shown in Figure 1. The electrical characterisations were performed by using two-point and four-point probe method accordingly. The I/V characterization were performed on the same sample. The measurement on PPy thin film sample was conducted at room temperature where the sample was injected with voltage range from 0 to 5 V. Both methods were performed on the same sample and the findings were compared. Later, sheet resistance for both methods were calculated. Two sets of experiments were conducted as follows:

i. The current-voltage (I/V) characterization of the PPy thin film was measured by four-probe method using Keithley 2400 pre-set frequency of 50 Hz manually where the two-point probe measurement were using indigenously developed computer controlled I/V measurement system with probe separation distance of 2 cm.

ii. The current-voltage (I/V) characterization of the PPy thin film was measured by four-probe method using Keithley 2400 pre-set frequency of 50 Hz manually and compared to the measured I/V by using the same device (change sense mode to two-point).

Figure 1. Measurement probe and stage setup (a) the overall setup measurement (b) four- probe position on the sample (c) two-point of 2 cm probe separation
2.3 Sheet resistance measurements

The calculated sheet resistance, $R_s$ for four-point measurement is calculated using Equation (1). The equation is used for this study as the PPy thin film is 40% smaller than the probe separation with a big sample size. Thus, the correction factor of the geometry is not needed [5].

$$ R_s = \frac{\pi \Delta V}{\ln(2) I} $$  \hspace{1cm} (1)

Solving for (1), giving Equation (2) to calculate resistance:

$$ R_s = 4.53236 \frac{\Delta V}{I} $$  \hspace{1cm} (2)

where, $R$ is the resistance in ohms, $R_s$ the sheet resistance in ohms/square. The sheet resistance, $R_s$ for two-point measurement is calculated by using the Equation (4), by rearranging Equation (3) [7].

$$ V = (2 + R_s) I $$  \hspace{1cm} (3)

Solving for (3), giving equation (4) to calculate resistance:

$$ R_s = \frac{\Delta V}{I} - 2 $$  \hspace{1cm} (4)

3. Results and discussions

3.1 The Two-Point Probe versus Four-Point Probe Characterization

This section will discuss the measurement results of PPy deposited from the two-point and four-point method. The findings were compared. Results section is divided into 2 parts: part 1 is the comparison between the different probes, where the two-point current were measured using probe with 2 cm separation distance. The second part is to discuss the results by using the same probe for both methods.

3.1.1 Part 1 (two-point probe with 2 cm separation vs four-point probe)

The I/V characteristics of organic doped PPy doped in organic acids at room temperature measured by four-point probe and two-point probe is shown in Figure 2. The I/V plot demonstrate similar pattern, with a sharp increase of current given voltage from 0 to 1 V and it becomes stable. In addition, the plots reflect a non ohmic behaviour for the given voltage range, thus suggesting a lower current flow. The characteristic curve passes through the origin, implying that the PPy thin film does not primarily store energy. Also, the current output does not really change as the voltage input changes, implying that the PPy thin film from this view operate more like an ideal current source. At low voltage input, the material passes a very small current output measurement. In this study, the negative region was not included as the PPy is not a diode. Due the nonlinearity of the I/V curve, it can be concluded that PPy doped in organic acid at 0.0823 μm is not suitable to be applied as resistor. The nonlinearity is caused by the effect of temperature changes in the material due to the change in voltage. The curent are non-ohmic in nature which when added together gives rise to an overall nonlinear characteristic for the composite at the microscopic level. In order to see a better resolution of the I/V curve, more data point of input must be applied.
Resistance values were then calculated from the measured value, and the plot for resistance for organic acid doped PPy thin film is illustrated in Figure 3. The resistance value increases as the voltage increased. Comparing these two plots, the two-point probe has recorded higher value than the four-point probe, affirming the existence of contact resistance.

Overall, it can be observed on both Figures 2 and 3, the two-point current and resistance curve data are close to the four-point current and resistance curve data when determined under input voltage from 1 to 5 V with increment of 1 V. The only difference is on the prefix which might be due to the bigger separation distance of the two-point probes. Nevertheless, these differences are very small thus can be neglected.

3.1.2 Part 2 (two-point vs four-point mode by the same probe)

The plots in Figure 4 illustrate the I/V characteristics of organic acids doped PPy thin film at room temperature measured using similar probe, but different mode, four-point probe and two-point respectively. Both plots show similar I/V characteristics pattern but bigger value than the I/V curve in Figure 2 for two-point mode due to smaller separation distance.
Figure 4. Comparison of two-point and four-point mode measurement I/V plot.

3.1.3 Comparison between Part 1 and Part 2
The null hypothesis is that there is no difference between the measurement of these two modes. The difference between measurement of the two modes in part 1 and Part 2 are given in table 1, column for Part 1 and Part 2 respectively. Also given the averages, sample standard deviation of the differences, and the standard error of the mean differences for each set. The probability that the measurement of current in organic acids doped PPy thin film are different is very small, 0.6% and 0% for Part 1 and Part 2, respectively. The difference in Part 1 is slightly bigger than in Part 2 due to wider separation between electrodes in two-point probe in Part 1, compared to Part 2.

Table 1. Comparisons on Part 1 and Part 2 measurements

| Voltage Input (V) | Part 1       | Part 2       |
|------------------|--------------|--------------|
| Mean             | 9.5983E-09   | 5.966E-09    |
| Standard Deviation, STD | 1.2592E-08 | 2.9515E-09 |
| Standard Error   | 2.0987E-09   | 4.9192E-10   |
| T- statistics    | 4.57344977   | 12.1279782   |
| P (t|)             | 0.00598306   | 6.7334E-05   |

4. Conclusion
Based on the research result, it can be concluded that organic acids doped PPy deposited on glass substrate at 0.823 μm thickness do not obeys the ohms’ law thus it cannot be used in future as a resistor. Due to the change of resistance with voltage, it is best to test this material with temperature in future. Furthermore, the R/V curve shows that the resistance increases with voltage suggesting a temperature sensitive characteristic.

The overall experiments were aimed to analyse the I/V curve pattern for the organic acids doped PPy thin film using different methods. Hence, in terms of accuracy, more studies need to be performed as this material is tested without any metal contact and not yet fabricated into a whole sensor. This study is an on-going project in determining the materials ability to be used as a thermistor. The two-probe with indigenously developed computer controlled I/V measurement system will be chosen as the best method to be used in future. The two-point probe is much suitable as the two-point probe can be used to be tested with varied temperature feature later. The manual two-point and four-point probe on the other hand, has a fixed stage for thin film sample, thus it is complicated to conduct
test with heat source. Even though, it was reported that the four-point probe technique has more accuracy due to the absent of contact resistance during characterisation, the final sensor can be tested its accuracy by adding another two wire in between the sensor. Hence, two-point method is sufficient at this stage of this study. Furthermore, both methods produced the same non-linear I/V graph patterns and the t-statistics percentage are found to be small, signifies that both measurements output are almost the same. Thus, agree with the null hypothesis of four-point and two-point methods. Also, the two-point I/V measurement method is suitable for high resistivity which is greater than 1 MΩ/m², whereas the four-point-probe method is best suited for measuring low electrical resistance, usually in nΩ ranges [7]. The PPy thin film in this study proven to poses high value of resistance, thus unsuitable for further characterization using the four-point probe. Two-Point Probe Method is the best method to measure the electrical properties of the thin film Polypyrrole material for further characterization with temperature.

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