



Ohmic Contact Formation to PEDOT-PSS Films Using Graphite-Clay

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Authors' contributions

This work was carried out by author SB under the guidance of author MSS. All the design calculations and experimentations were done by author SB along with literature survey. The paper draft was prepared by her and the second author reviewed it for details, accuracy and theoretical aspects. Both authors read and approved the final manuscript and agree to the terms of publication.

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ABSTRACT

Metal-to-semiconductor contacts are present in every semiconductor (conducting polymer) device which can behave either as a Schottky diode (rectifying junction) or as an ohmic contact. Whether a contact is ohmic or rectifying depends not only on the difference in work functions of the contact metal and semiconductor but also on the contact surface defects. Many methods and processes are being developed to make ohmic contacts to organic semiconductors. In this paper, we report simple and inexpensive methods to achieve ohmic contacts to PEDOT-PSS which otherwise makes rectifying contact to copper. It has been shown that by coating the contact metal with graphite-clay using commercially available pencils, ohmic contacts can be produced. It is also demonstrated that by dispersing graphite powder in PEDOT-PSS on copper ohmic contacts can be made.

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1. INTRODUCTION

Conducting polymers, discovered a few decades ago, are novel materials that have properties of a semiconductor with mechanical flexibility. Researchers in materials science, organic chemistry as well as theoretical and experimental physics have contributed significantly for making several devices [1-4]. Conducting polymers have applications in Organic Light Emitting Diodes (OLED) [5], sensors [6-7], solar cells [8] and many more devices which ultimately need a metallic contact at the input-output terminals [9-14]. When conducting polymer (semiconductor) contacts a metal, a rectifying contact rather than ohmic contact is produced. This is due to differences in their work functions as well as large differences in their conductivities leading to formation of a depletion layer in the semiconductor [15]. Rectifying behavior at polymer-metal interface is a well known phenomenon observed and reported by many researchers [16-19]. Such contacts pose several problems as the contact conductivities are far less than that of the bulk. Problems due to metal-conducting polymer contacts have also been reported in the context of fabrication of devices such as Field Effect Transistors (FET) and Light Emitting Diodes (LED) where, the contact resistance is very large or comparable to the device resistance [20]. A simple method of making ohmic contacts is thus essential for making efficient devices.

In our earlier work [17], we studied the contact between tin (Sn) and PEDOT-PSS (poly 3,4-ethylenedioxythiophene-polystyrenesulfonate). We were able to prove the existence of rectifying contact and proposed a method to make ohmic contacts to conducting polymer film using carbon nano-ink. The ink was made by processing carbon nano powder such that it was suitable for printing using inkjet printers. In the present work, we propose simpler inexpensive methods to make ohmic contacts between copper and PEDOT-PSS films at room temperature, by using graphite-clay pencils. We have also studied the effect of doping (dispersing) PEDOT-PSS with graphite on the contact resistance. A four probe resistance measurement technique has been used to show the existence of a rectifying contact between PEDOT-PSS and copper, and to show that ohmic contacts can be formed by methods described here. The major purpose of this work

is to develop inexpensive method for formation of ohmic contacts on PEDOT-PSS films to be used as strain gauges in biological environment.

2. MATERIALS AND METHODS

All films of PEDOT-PSS tested in this work are formed on copper clad epoxy glass substrates. Four copper contacts are first etched over the substrates which are 0.5 mm wide, 5mm apart and 25 mm long which form the four contacts for resistance measurement as shown in Fig. 1. Before using, the substrates were cleaned with acetone, triple distilled water and isopropyl alcohol. PEDOT-PSS films, 30 μm thick, were formed on the substrate overlapping the copper contacts. Known quantity of PEDOT-PSS procured from HC Stark, Germany was evenly spread over the unmasked area and heated to 50°C. The substrate was spun slowly at 200 rpm to ensure proper heating and uniform film formation. The water evaporates slowly in about 15 minutes forming a film of PEDOT-PSS. However, the film is maintained at 50°C for 1.5 hours before use. The dried film was covered (encapsulated) by adhesive coated Mylar tape procured from M/s 3M to prevent exposure to atmosphere. The thickness of the film was measured before encapsulation using Mitutoyo dial gauge with 1 μm resolution at 5 places and its average value was taken. The dimensions of the PEDOT-PSS film are maintained constant at 20 mm long, 5mm wide.

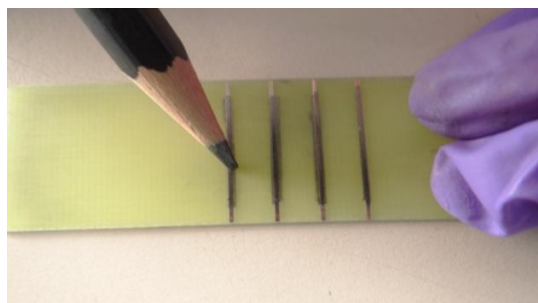


Fig. 1. Image showing copper conductors coated with graphite-clay using pencil

For making ohmic contact the copper contacts (conductors) were abraded with HB grade pencil (Apsara, a local brand pencil freely available in market for writing purposes) forming a film of 5 to 7 μm thick graphite-clay over the copper contacts

(see Figs.1 & 2). The thickness of the graphite-clay coating is measured using Mitutoyo dial gauge as above. Film of pristine PEDOT-PSS was formed over the graphite-clay coated copper contacts as described above.

One more set of films were made using graphite dispersed in PEDOT-PSS. Five milligrams of pure graphite procured from M/s Graphite India, Bangalore, was dispersed in one gram of PEDOT-PSS (0.5% weight of PEDOT-PSS) and films were formed on the substrate overlapping bare copper contacts.

Measurements were done on three types of films at room temperature, one on pristine PEDOT-PSS over bare copper contacts, second on pristine PEDOT-PSS films with graphite-clay coated contacts and third on graphite doped (dispersed) with PEDOT-PSS on bare copper contacts and the results were compared.

3. EXPERIMENTAL DETAILS

When the contact resistance is comparable to the bulk resistance of a film four probe resistance measurements are made to eliminate the effect

of contact resistance (Fig. 3). Contact between semiconducting PEDOT-PSS with copper is rectifying and the measurements were repeated to estimate the nature of contact resistance. When the distances between contacts and contact areas are kept equal the resistance between the contacts 2 and 3 (R_{23}) gives the bulk resistance of the film between contacts 2 and 3 and the resistance between contacts 1 and 2 and contacts 3 and 4 (R_{12} & R_{34}) gives the sum of contact resistance and the film resistance between the contacts 1 and 2 or 3 and 4. If the distances are equal the difference between the resistance R_{23} and R_{12} (or R_{34}) gives the contact resistance.

When the contact is rectifying the V-I characteristic between the terminals will be a diode characteristic. However, if high bulk resistance of the film is included in the measurement, V-I characteristic may look nearly linear as if the contact is not rectifying. But, if the resistances between the contacts 2 and 3 is equal to the resistance between contacts 1 and 2 (R_{12}) and contacts 3 and 4 (R_{34}) one can say the contact is non-rectifying or ohmic.

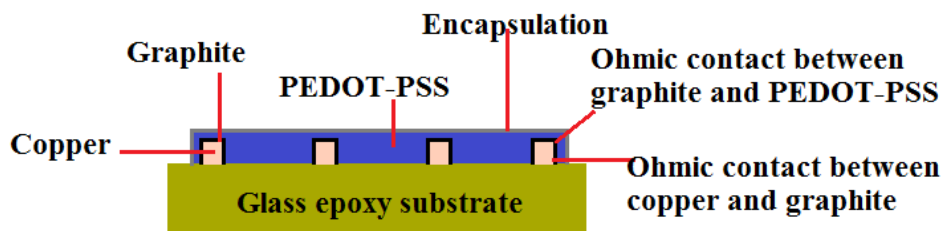


Fig. 2. Schematic showing PEDOT-PSS making contact to graphite-clay coated copper conductors

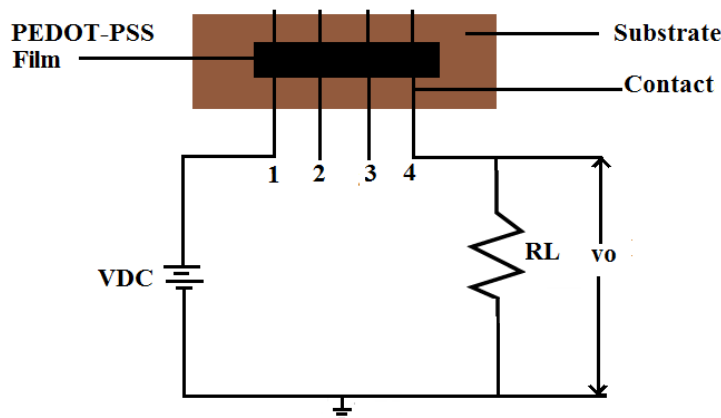


Fig. 3. Circuit used to measure film resistance using four probes

Three experiments using four probe DC measurements were made at room temperature (25°C to 30°C) to explore the nature of the metal – semiconductor contacts.

- First experiment was conducted on pristine PEDOT-PSS film making direct contact with copper conductors to show formation of rectifying contacts.
- Second one was on pristine PEDOT-PSS film making contact to graphite-clay coated over copper to prove formation of Ohmic contacts.
- Third experiment was on PEDOT-PSS dispersed with graphite powder making direct contact with copper to demonstrate formation of ohmic contact.

Measurement of resistance of the film was made by potentiometric technique shown in Fig. 3 using Fluke 287 digital multimeter to measure voltages, where R_L is a known resistance.

Several DC voltages were applied to contact 1 with reference to ground and voltages V_1 (V_{DC}), V_2 , V_3 and V_4 (V_O) were measured. Current i (Fig.4) was calculated by measuring the voltage drop across R_L . The resistances between contacts 1 and 2, 2 and 3, and 3 and 4 were determined as shown below.

$$R_{12} = ((V_1 - V_2) / V_O) * R_L \quad (1)$$

$$R_{23} = ((V_2 - V_3) / V_O) * R_L \quad (2)$$

$$R_{34} = ((V_3 - V_4) / V_O) * R_L \quad (3)$$

The equivalent diode model of the circuit at Fig. 3 is shown in Fig. 4 which consists of the film resistances and contact diodes. When current is passed between contacts 1 and 4, diode D_1 is reverse biased and diode D_2 is forward biased. The resistance between contacts 1 and 2 (R_{12}) includes leakage resistance of the diode D_1 apart from film resistance, while resistance R_{34} is nearly equal to the film resistance as diode D_2 is forward biased. As current is passed through contacts 1 and 4 the voltage drops between contacts 1 and 2 (and contacts 3 and 4 for current in reverse direction) include voltage drops due to contact resistances which are very large if they are rectifying. If the contacts are ohmic the voltage drop due to contact resistance is negligible. The voltage drop between contacts 2 and 3 (V_{23}) does not include drop due to contact resistance as only voltage measurement using high input impedance voltmeter (>10M Ω) is

made, and it gives the bulk resistance between 2 and 3. If the contacts 1 and 4 are ohmic, the resistance R_{14} will be nearly three times R_{23} (also $R_{12} = R_{23} = R_{34}$) as the contacts are equidistant (differences in R could be due to small variations in film thickness). These can be determined by plotting voltage versus current.

4. RESULTS AND DISCUSSION

The V-I relationship between different contacts for pristine PEDOT-PSS making direct contact to bare copper are plotted in Fig. 5. The slopes of these V-I curves give the resistance between respective contacts. It may be observed from Fig. 5 that V-I relationship between contacts 2 and 3 and contacts 3 and 4 are linear but that between contacts 1 and 2 is nonlinear with a much higher slope than that between the other two contacts. From the slopes the resistance between contacts 2 and 3 (R_{23}) is equal to 200 k Ω and that between contacts 3 and 4 (R_{34}) is 157 k Ω . From the average slope the resistance R_{12} is 809 k Ω , far greater than that between other two contacts. This variation can be understood by referring to the model shown in Fig.4 where R_{12} includes the leakage resistance of the reverse biased contact diode D_1 in addition to the film resistance. However, R_{34} includes only forward biased diode resistance of D_2 apart from film resistance and R_{23} is just the bulk resistance of the film between contacts 2 and 3. While one would expect R_{23} to be equal to R_{34} , resistance R_{34} is less than R_{23} possibly due to non-uniform thickness of the film. This proves the existence of rectifying contacts between PEDOT-PSS and bare copper.

A similar V-I characteristic is shown for PEDOT-PSS film on graphite-clay coated copper Contacts in Fig. 6. It may be observed that the V-I plots of contacts 1 and 2, contacts 2 and 3 and contacts 3 and 4 are all linear and their slopes give the resistance between respective contacts. The resistance between contacts 1 and 2 is 310 k Ω and that between 2 and 3 (bulk resistance) is 308.3 k Ω while that between 3 and 4 is 245 k Ω (the differences in the three resistances are due to slight non uniformity in the film thickness). The fact that the contact resistance is negligible (310 k Ω -308 k Ω = 2 k Ω) compared to film resistance (R_{23}) proves that the contact between graphite-clay and PEDOT-PSS is ohmic. The procedure was repeated several times to ensure that ohmic contacts of negligible contact resistance are formed every time.

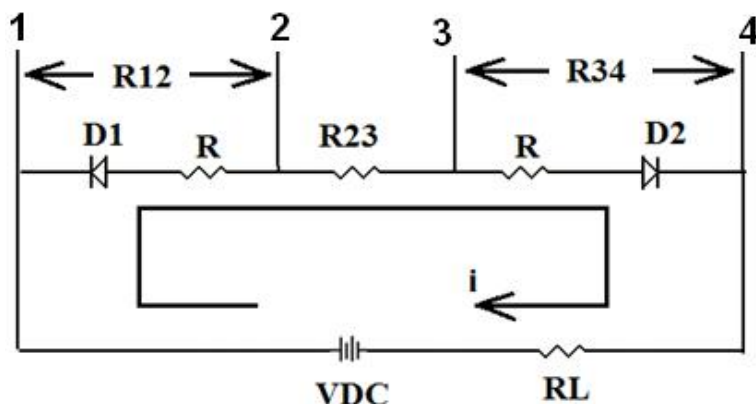


Fig. 4. Model of a polymer film with four contacts when DC voltage is applied between contacts 1 and 4

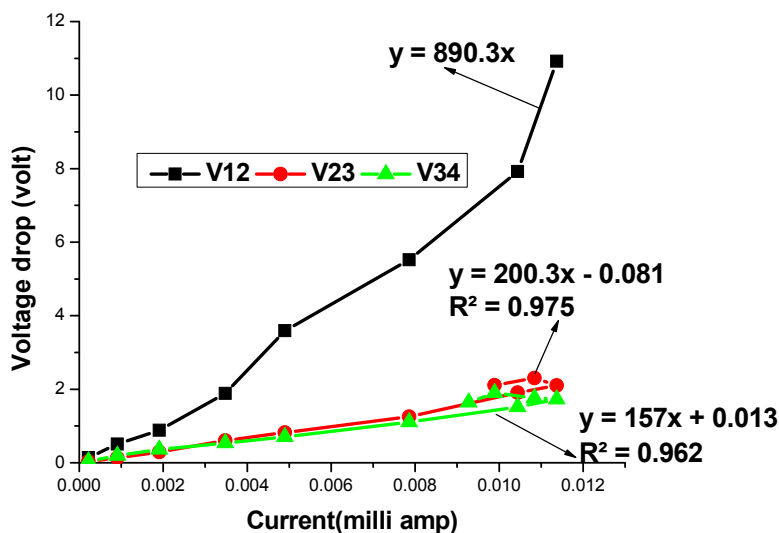


Fig. 5. V-I Plots showing voltage drops across V_{12} , V_{23} and V_{34} vs. I for pristine PEDOT-PSS making contacts to copper electrodes

S. Alborghetti et al. [21] have shown that even though the V-I characteristic is linear at room temperature it may still be rectifying at lower temperatures as the thermal energy of charge carriers are reduced. Leonard J et al. [22] have shown and discussed the causes for conductivity enhancements at the metal-polymer interface and established that it is due to strong increase of defects at the metal-polymer surface promoting tunneling. These could be the reasons for formation of ohmic contacts. Since our interests are to build biological devices measurements are made at room temperatures and low temperature behaviour is not being explored. The enhancement of conductivity due to graphite layer between copper and PEDOT-

PSS could also be modeled as a percolation bond layer [23]. The critical probability for graphite to conduct charge carriers across the layer is 0.5 (co-ordination number being 3 and $P_c = 1/(z-1)$). This perhaps makes the thickness of graphite film irrelevant in converting the PEDOT-PSS / graphite/ copper interface ohmic.

It is well known that a semiconductor can form ohmic contact when heavily doped due to thin depletion region resulting in tunneling of charge carriers. So doping (dispersing) PEDOT-PSS with graphite powder was considered. Pure graphite powder procured from M/s Graphite India was dispersed in PEDOT-PSS (0.5 percent by weight) and a film is made the same way as

before and its V-I characteristics were measured. The current voltage relation between contacts is shown in Fig. 7.

The resistance of film between contacts 1 and 2 is 145Ω and that between contacts 2 and 3 is 137Ω while that between 3 and 4 is 167Ω . This clearly indicates that contact resistances are negligible compared to the bulk resistance of the film and the contacts are ohmic. It may also be

observed that the film bulk resistance has reduced from $308\text{ k}\Omega$ to 137.5Ω between contacts 2-3. As shown in reference [24,25] a small amount of filler/dopant can produce large changes in conductivity due to formation of percolation bond layer. A similar possibility exists in graphite powder doped PEDOT-PSS and the critical doping concentration is less than 0.5%. More measurements at different doping levels are necessary to ascertain critical concentration

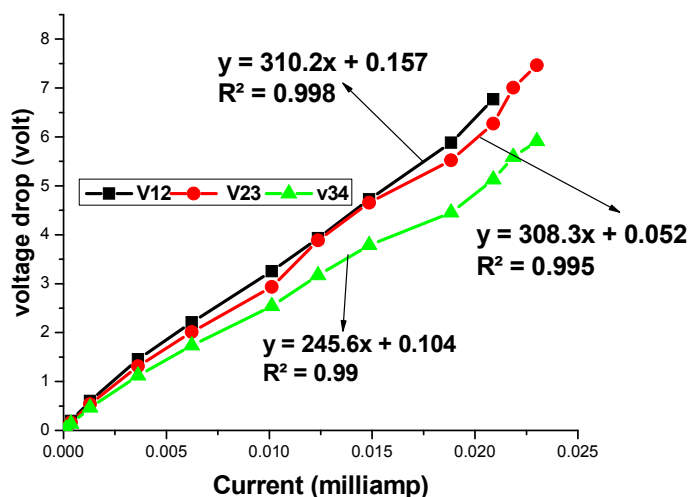


Fig. 6. V-I Plots showing voltage drops across V_{12} , V_{23} and V_{34} vs. I for pristine PEDOT-PSS making contact to graphite-clay coated copper electrodes

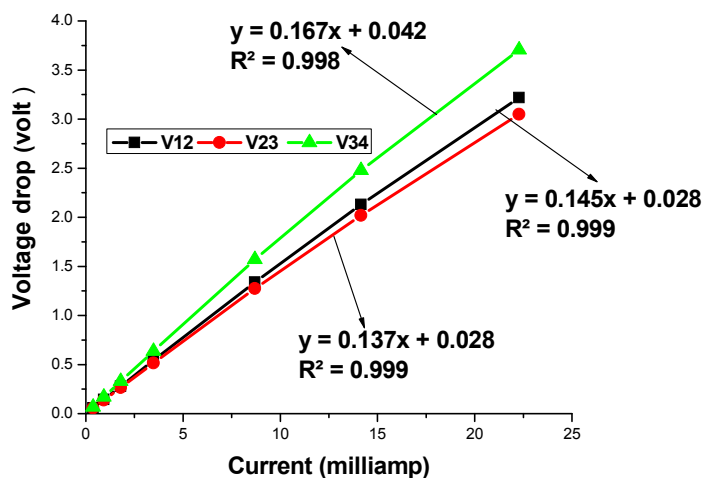


Fig. 7. V-I plots showing voltage drops across V_{12} , V_{23} and V_{34} vs. I for PEDOT-PSS dispersed with graphite powder making contact to copper electrodes

4. CONCLUSION

It has been shown that PEDOT-PSS forms rectifying contact with copper producing large contact resistance and the contacts can be made ohmic with low contact resistance by introducing a thin film of graphite-clay. The procedure is very simple and cheap involving no special process technology. It has also been proved that dispersing PEDOT-PSS with pure graphite also produces ohmic contact but changes the resistance of the film. These methods of making ohmic contacts are very useful in building devices such as strain gauges, FET and other devices.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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