



Electric Field Induced Resistance Change in PEDOT-PSS Films

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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

Resistance of PEDOT-PSS films changes considerably with time after application of DC voltage. Since, variation of resistance over time can lead to serious errors when used as a strain gauge or gas sensors or any device, a detailed study of the variation of film resistance with time has been made. It has been observed that AC resistance is stable with time (constant) compared to DC resistance which has been explained in terms of contact diode model. It has also been found that doping with graphite leads to lower variation (better stabilization) in the resistance over time. The results indicate that the variation of resistance is an interfacial phenomenon at the contacts and either an ohmic contact or AC measurement removes this behavior. The change of resistance is attributable to high electric field in the interfacial region of the PEDOT-PSS/metal contact.

Keywords: Conducting polymers; PEDOT-PSS; rectifying contacts; ohmic contacts; depletion region; electric field.

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1. INTRODUCTION

The resistance of conductive films is normally constant on application of DC voltage or electric field. A small change is expected due to joule heating of the film due to power dissipation and consequent increase in local temperature [1]. The change in resistance depends on the temperature co-efficient of resistance which is normally negative and the resistance of film reduces. When we applied DC voltage to PEDOT-PSS films to measure its resistance we found that the film resistance increased with time, contrary to expectations. The resistance measurements were made as part of building high gauge factor strain gauges using PEDOT-PSS films and the constancy of resistance for changes other than strain is an important parameter to build strain gauges. Many have reported about strain gauges built from PEDOT-PSS films [2-3] but none have reported instability of film resistance on application of DC voltage or the effect of electrical contact material over PEDOT-PSS. It should be recognized here that PEDOT-PSS is a p type semiconductor and the interface between the metal contact and the film may not be ohmic. This paper presents the measurement of resistance of PEDOT-PSS films over time with copper contacts and proposes a model that explains the observations. The study includes measurements on pristine and graphite doped PEDOT-PSS films.

2. EXPERIMENTAL DETAILS

PEDOT-PSS films (Pristine and doped) are cast on epoxy glass substrates of dimension 75 mm * 25 mm and thickness 0.8 mm. Two copper contacts 10 μ m thick, 0.5 mm wide, spaced 1 mm apart are pre-etched on the substrate to serve as electrical contacts. PEDOT-PSS films 5 mm X 5 mm are formed overlapping the copper contacts by evenly spreading (drop casting) a known quantity (20 μ L) of aqueous suspension of PEDOT-PSS (VP AL 4083) procured from H C Stark Germany as shown in Fig. 1. The film is baked in a temperature controlled box for one hour at 45°C \pm 0.1°C and the films thus formed had a thickness of 10 μ m, measured using a mitotoyo dial gauge of 1 μ m resolution. The films formed are encapsulated using flexible transfer adhesive tape to prevent exposure to atmosphere. As will be explained later, the copper contacts on some samples are treated appropriately to make PEDOT-PSS metal contacts ohmic. As the contacts are spaced

1 mm apart the effective film area is 5mm². Measurements are also made on films with contact width of 1 mm to study the effect of interfacial area on the resistance. The film resistance is measured by applying voltage, DC or AC, to a potential divider network with the film forming one resistor and another fixed resistor is connected in series to measure the current. Voltages of 1V, 3V, 6V, 12V and 24V are connected and the resistances of the films are measured over time up to 45 minutes to see the variation of resistance with time after application of voltage.

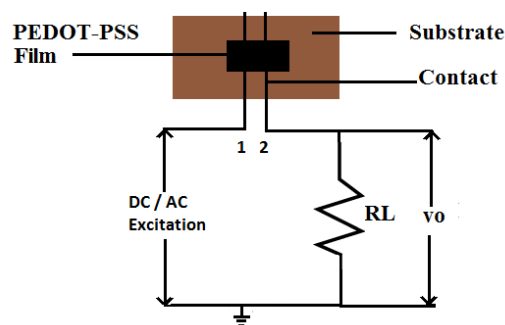


Fig. 1. Circuit used to measure film resistance/impedance

3. RESULTS AND DISCUSSION

3.1 Variation of Resistance of Pristine PEDOT-PSS Films with Time

Variation of film resistance with time for pristine PEDOT-PSS film for applied DC voltages 1V, 3V, 6V, 12V and 24V is shown in Fig. 2. The voltages shown on the figure are the total applied voltage and the actual voltage across the film is 0.7V, 2.4V, 5.2V, 9.8 and 19.4V respectively. It may be observed that the film resistance at 1V is nearly constant with time, slightly reducing with time in fact, while at higher voltages the film resistance increases with time by about 1.3 to 1.6 times the initial value in 45 minutes; higher the voltage higher the variation. At 24V change in resistance with time suddenly decreases and is about the same as that at 3V. At 12 V there is a small fall in resistance after initial increase.

Fig. 3 shows the initial resistance and resistance after 45 minutes for different voltages. It may be seen that initial resistance is nearly same for all applied voltages while the resistance after 45 minutes peaks around 8V.

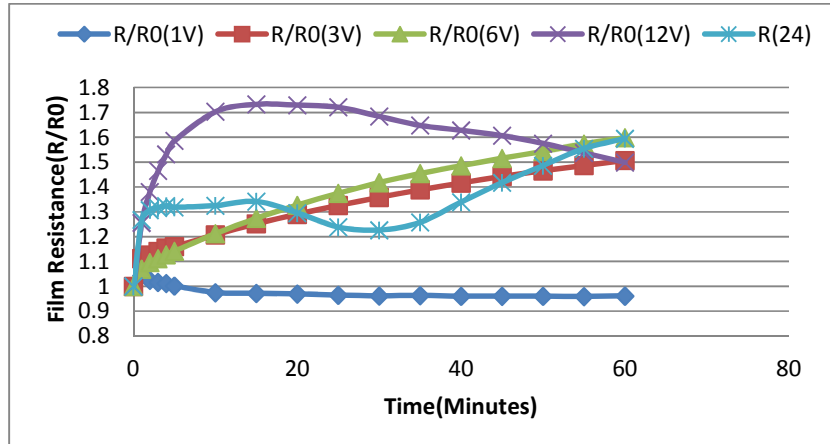


Fig. 2. Variation of film resistance vs. time for pristine PEDOT-PSS film making contact to 0.5mm wide copper contact

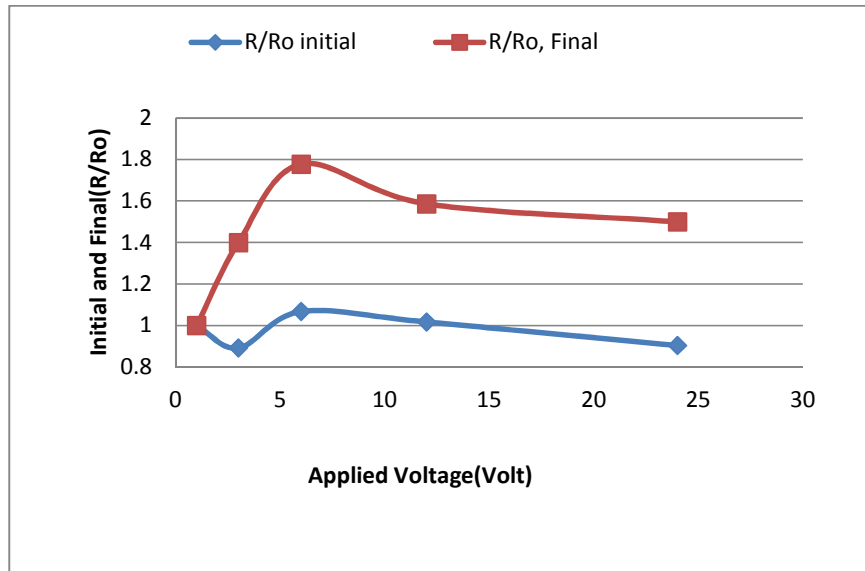


Fig. 3. Variation of initial and final resistances of pristine PEDOT-PSS film for different applied voltages for a period of 45 minutes

It is reported in the literature that PEDOT-PSS resistance has a negative co-efficient of temperature [4] and is given by;

$$\alpha_t = -3.5 \times 10^{-3} \text{ K}^{-1} \quad (1)$$

The Joule heating should have reduced the resistance instead of increasing as temperature co-efficient is negative. This clearly indicates that the cause for the observed behavior of film resistance is not joule heating.

A metal semiconductor interface will form either a rectifying junction or an ohmic junction

depending on the work functions of the semiconductor film and the contact metal [5-8]. When the interface is rectifying, the total resistance consists of two parts, the leakage resistance of a reverse biased diode and the bulk resistance of the film. An equivalent circuit of such a situation is given by Fig. 4 which presents a reverse biased diode in either direction of current flow together with bulk resistance. Resistance of forward biased diode can be neglected and hence, the total resistance is dominated by the interfacial resistance due to reverse biased metal semiconductor film diode. The presence of diode has been shown in an

earlier work and the leakage resistance of the diode could be about 5 times or more than the bulk resistance [9].

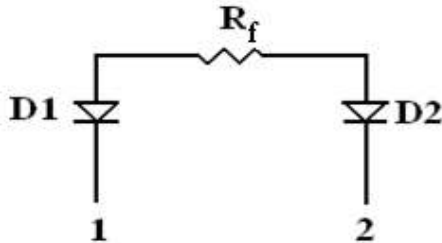


Fig. 4. Model of a polymer film with two metallic contacts

To study the effect of interfacial resistance of PEDOT-PSS film with copper contacts another film is cast with double the copper contact area; i.e the width of copper contact is increased from 0.5 mm to 1 mm, with the distance between contacts held constant at 1 mm. All other process parameters are held constant.

The variation of PEDOT-PSS film resistance with time for 1 mm wide copper contacts is shown in Fig. 5. It may be seen that the film resistance increases over a period of 45 minutes by about 4.2 to 4.6 times the initial value compared to about 1.3 to 1.6 times for 0.5 mm wide copper contacts.

3.2 Impedance (Resistance) of Pristine PEDOT-PSS Film with AC Excitation

Invoking the diode model explained earlier, the reverse biased contact diode can be modeled as

leakage resistance in parallel with depletion capacitance as shown in Fig. 6. The reverse leakage resistance is bypassed by low impedance of depletion capacitor at sufficiently high frequency. Hence, the measured resistance is that of the bulk of the film if the applied voltage is AC of sufficiently high frequency.

The variation of resistance of pristine PEDOT-PSS film measured by applying AC voltage at a fixed frequency of 10 KHz is shown in Fig. 7. It may be observed that the film resistance for an applied AC voltage of 3V (rms) and 6V (rms) is nearly constant with time.

The above observations prove that the Variation of film resistance with time on application of DC voltage is largely confined to the depletion or the interfacial region and not the bulk.

3.3 Effect of Graphite Doping on PEDOT-PSS Film Resistance

A pristine PEDOT-PSS film produces high resistance films and it is common practice to dope PEDOT-PSS to produce films of lower resistance. So, a set of measurements are made on graphite dispersed PEDOT-PSS films with varying graphite concentrations in weight percentages of 0.1%, 0.25%, 0.5%, 0.75% and 1%. All dimensions of substrate and film are maintained same as earlier.

Fig. 8 shows the variation of film resistance with different concentration of graphite. The resistance is nearly constant at about 1 MΩ up to 0.5% and suddenly reduces to 650Ω.

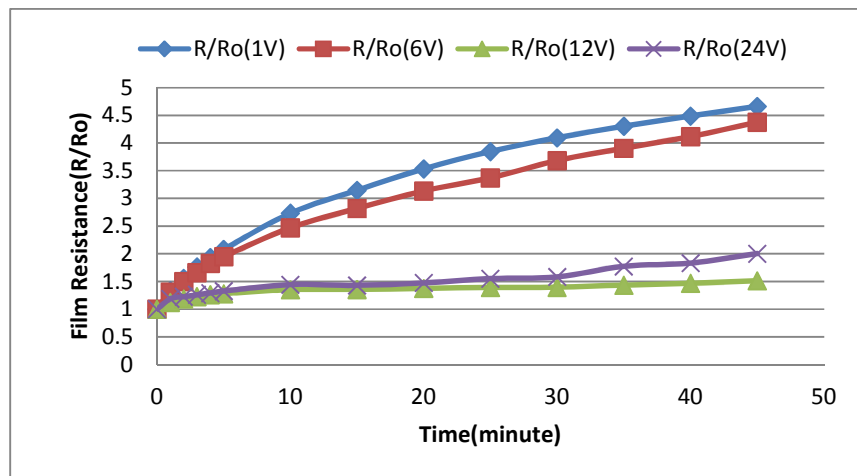


Fig. 5. Variation of film resistance vs. time for pristine PEDOT-PSS film making contact to 1mm wide copper contacts

This behavior is in conformity with the predictions by percolation theory. The general proposition of the percolation theory comes from the fact that the conductivity of a composite dramatically increases at a certain concentration called the percolation threshold of the (filler) material [10-11]. At doping/dispersing concentrations above the critical level, the conductivity reaches a plateau and does not rise significantly with further addition of filler. At low graphite loading, the particles are homogeneously distributed without contact between adjacent filler particles and the conductivity of this composite is comparable to that of the pristine material. With increasing graphite concentration, however, clusters of filler particles begin to form and in these clusters the filler particles are in contact with each other. At a certain critical graphite concentration, the growing clusters reach a size which enables a contact between them; a continuous network structure of the conducting filler is formed. This network formation can be detected by a drastic decrease in the electrical resistivity of the composite. Increase in number of parallel paths does not significantly change the conductivity.

3.4 DC Measurements on PEDOT-PSS Films Dispersed with Graphite Powder

Fig. 9 shows the variation of film resistance with time for different concentrations of graphite powder dispersed in PEDOT-PSS for an applied DC voltage of 3V. Since the resistance of film changes considerably with concentration of dispersed graphite, the resistance values are normalized to their initial values and plotted to get better comparison between films.

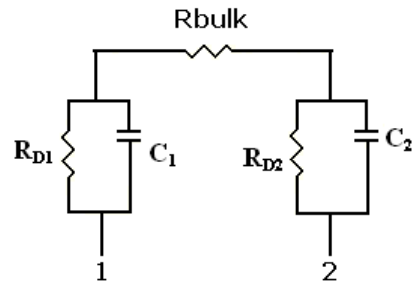


Fig. 6. AC equivalent circuit of contact diode at metal-polymer interface

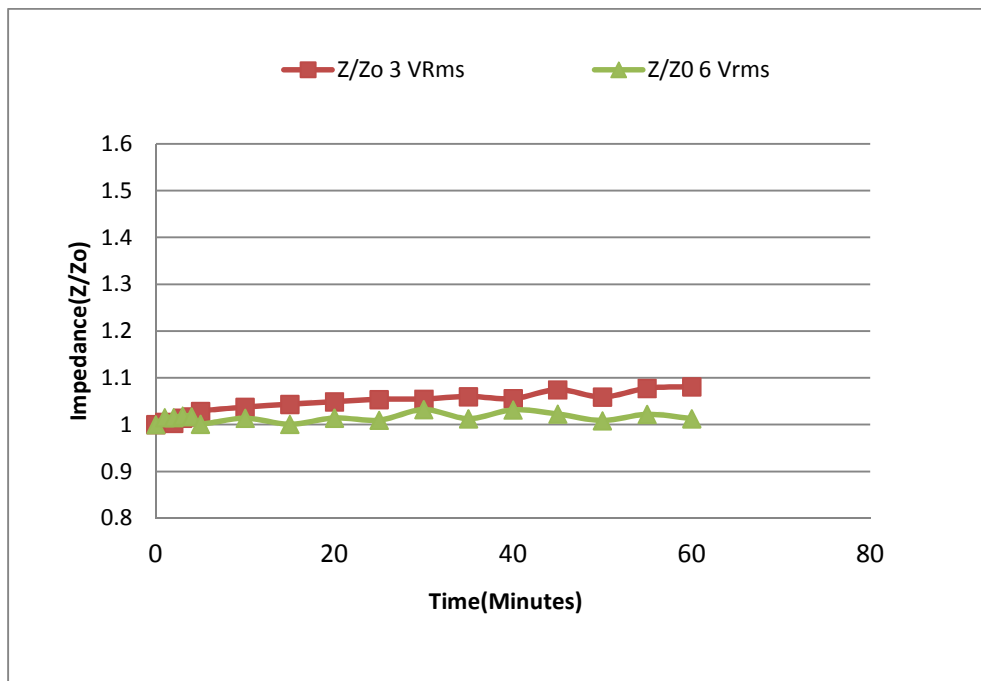


Fig. 7. Plot of Impedance vs. time for pristine PEDOT-PSS film making contact to 0.5 mm wide copper contact for shown rms voltages at 10KHz

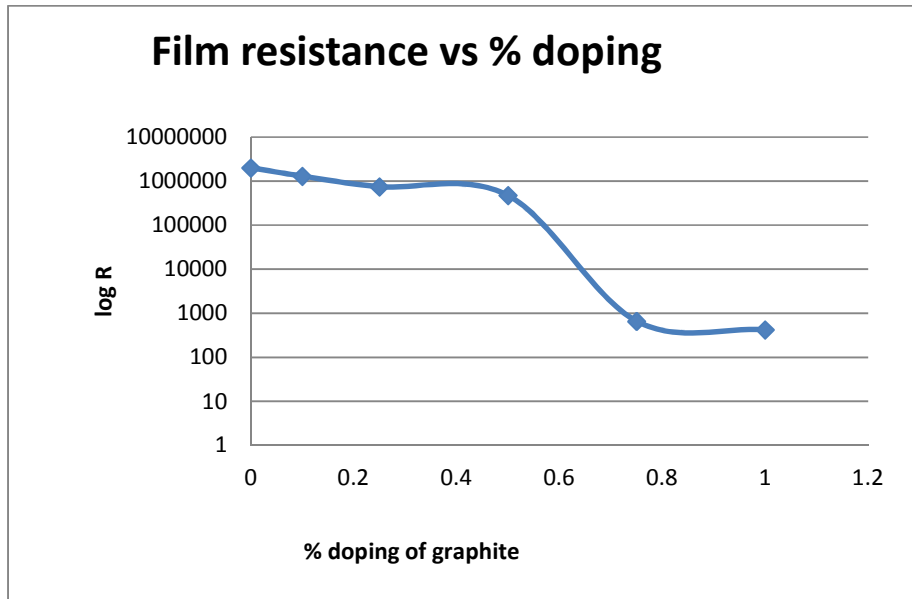


Fig. 8. Variation of film resistance with concentration of graphite into PEDOT-PSS

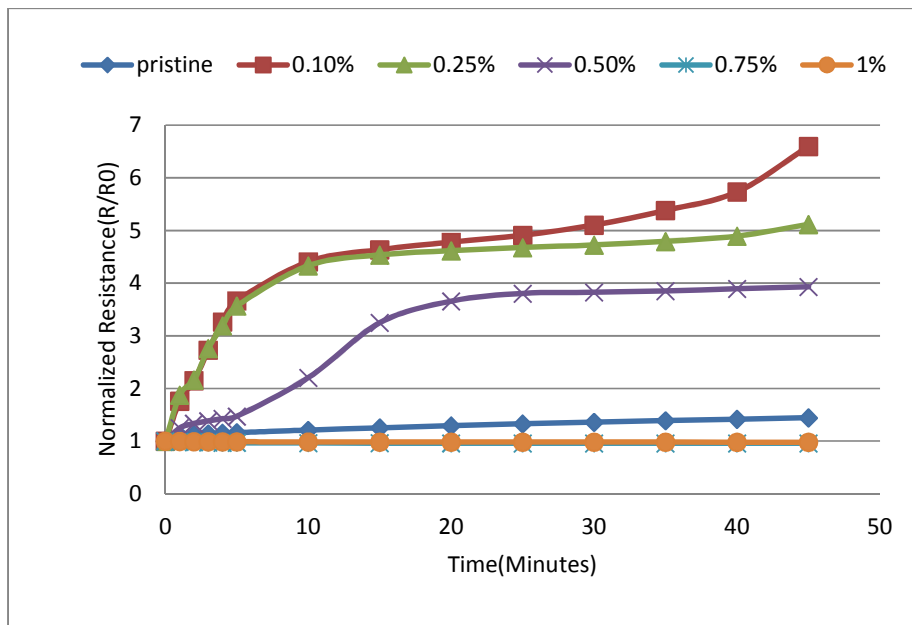


Fig. 9. Normalized resistance vs. time for PEDOT-PSS films dispersed with different concentrations of graphite powder

It may be observed that the extent of variation of film resistance with time is 1 to 7, a remarkable increase, depending on the percentage of graphite dispersed. It may also be observed from Fig. 9 that the variation of resistances with time is 1.5 times for pristine PEDOT-PSS which increases suddenly to 7 times for 0.1% graphite powder dispersed film and then reduces as the

dispersing concentration is increased and at 1% the resistance is nearly constant with time. Increased dispersion of graphite powder in PEDOT-PSS films nearly eliminates increase of resistance and stabilizes resistance; there is a sudden increase in the rate of resistance increase on low dispersion (0.1%) which decreases on higher doping. The above

observations can be explained by the invoking the interfacial diode where one diode is forward biased and another diode reverse biased.

3.5 Impedance (Resistance) of PEDOT-PSS Film Dispersed with Graphite Powder with AC Excitation

As discussed earlier AC excitation practically removes the effect of interfaces that lead to large change in the overall resistivity. So AC measurements are made on graphite dispersed films. The variation of normalized AC impedance with time for films dispersed with different concentrations of graphite is shown in Fig. 10. It may be observed that with AC excitation the variation of film resistance (impedance) with time is very minimal and variation of resistance is very low compared to DC excitation.

3.6 Discussion on the Cause of Resistance Increase after Application of DC Voltage

First we can summarize the observations made till now:

1. Resistance of pristine PEDOT-PSS film increases with time on application of DC voltage.
2. The resistance measured consists of bulk resistance and the leakage resistance of an interfacial diode.

3. The interfacial diode dominates the increase in resistance as proved by AC resistance.
4. AC excitation of the film bypasses the interfacial resistance.
5. Doping PEDOT-PSS with graphite reduces film resistance.
6. At 0.1% graphite doping resistance of doped films increases by a factor of 7 (see Fig. 9) compared to 1.8 times for pristine films. However, at concentrations above 0.75% graphite the resistance variation is negligible.

Based on the above observations one can conclude that the variation of resistance is concentrated at the metal film interface.

Mrunal S. Mahajan et al. [12] have reported in their paper that the PEDOT-PSS film subjected to intense electric field of the order 2 -5 KV/cm at 120°C for long time showed decrease of electrical conductivity over time in the plane of the electric field. If this is the possible reason for increase in resistance of PEDOT-PSS films how such high electric field is generated? If we look at the diode model at the metal PEDOT-PSS interface we observe a large voltage is dropped at the interfacial diode as the leakage resistance is 4 -6 times larger than the bulk resistance. The voltage drop in a reverse biased diode occurs in a very small width of its depletion region and hence the electric field in this region is intense compared to any other region of the film. An interfacial capacitance of 35nF was

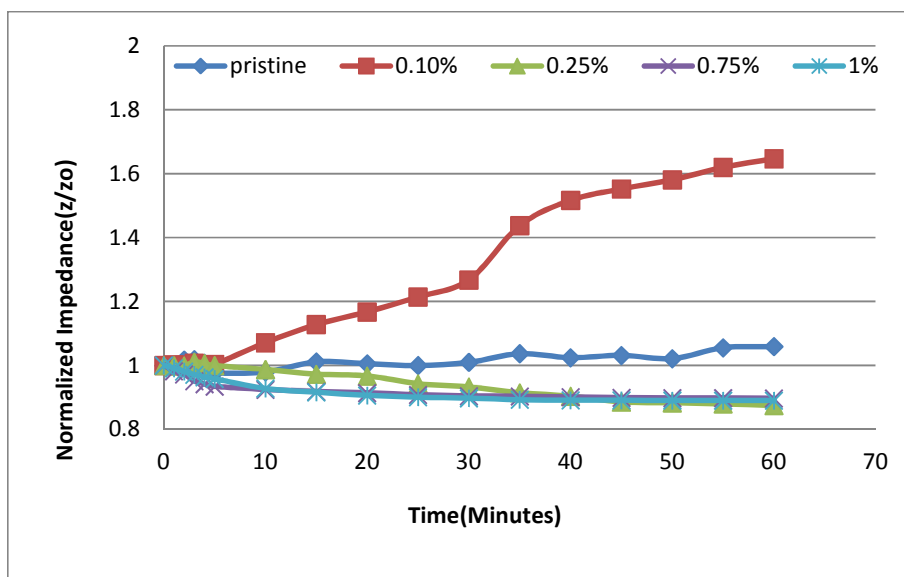


Fig. 10. Normalized impedance plot vs. time for different percentages of graphite doping

measured using precision impedance analyzer, Agilent 4294 and found that the interfacial capacitance varies from about 17nF at low frequency to about 2 to 3nF for frequency above 100 KHz. For example if 3V is dropped at a depletion width of 1 μm the resulting electric field is 3×10^6 V/m which is large. This conclusion together with the observation that resistance increase is largely at the interface leads us to conclude that the variation of resistance is due to high electric field generated at the depletion region. When PEDOT-PSS is lightly dispersed with graphite the depletion layer thickness at the contact reduces as more current carriers are available. So, the electric field at the contact is higher consequently increasing the rate at which resistance increases. It may also be observed that with 0.1% doping of graphite the relative rise of resistance increases to 7 which decreases as the concentration of dopant is increased. So, when the film is doped the depletion layer thickness decreases producing higher electric field at the interface before the interface turns ohmic due to high tunneling which is evident at 1% doping. The reduction of variation of resistance between 0.1% doping to 1% doping is a region of complex nature where several competing phenomenon contribute to changing behavior of interface from rectifying to ohmic.

The above discussion explains two observations; increase in resistance with time and increase of rate of increase of resistance on low level dispersing, very low change of resistance with time at higher concentration of 1% graphite. This is consistent with the observations reported by Mrunal S. Mahajan et al. [5] that the conductivity of PEDOT-PSS film reduces on application of high electric field.

3.7 Comparison of Resistance with DC and AC Excitation in Pristine PEDOT-PSS Films

It is interesting to compare the effect of DC and AC excitation on the same scale. Variation of film resistance with DC (3V) and AC (3Vrms) excitation is compared on the same scale and the resistances are normalized to their initial values as shown in Fig. 11.

It may be observed that $R_{AC}(Z)$ is constant with time which indicates that the interface resistance is bypassed by AC input which measures the true bulk resistance of the film which is fairly constant with time due to low electric field.

The variation of resistance with time is an important information needed for making good strain measurements. The above discussion shows that the resistance of PEDOT-PSS films varies with time due to increase in electrical resistivity caused by high electric field at the reverse biased contact diode. Interfacial capacitive reactance bypasses the contact resistance at a suitable high frequency and allows more accurate time measurement of film bulk resistance when made by AC excitation. It is also observed that making the interface ohmic by dispersing 1% graphite will reverse the time variation of DC resistance. It may also be observed that the variation of pristine film resistance is negative for 1V when the electric field at the interface is low. However at 3V and above the electric field at the interface is large enough to cause increase in resistance. With these observations one can conclude that a large part of the variation of resistance in PEDOT-PSS films with time comes from the interface.

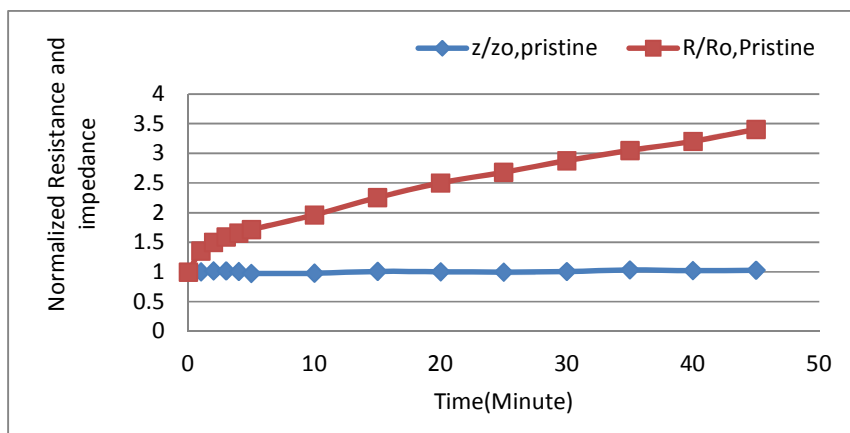


Fig. 11. Normalized resistance and Impedance plot for 6V DC and 6Vrms

There is another aspect to be considered apart from high field at the interface is the concentration of heating at the interface. Fig. 12 shows the photograph of a PEDOT-PSS film formed by the method described earlier except the terminals are connected to a 5V power supply during baking process.

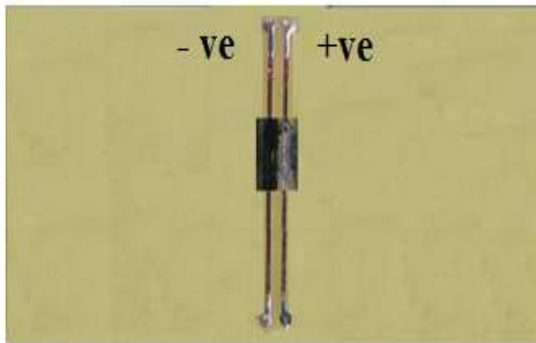


Fig. 12. Image of PEDOT-PSS film taken after film formation (DC potential was applied when the film is getting formed)

It is evident that the film is burnt near the +ve terminal while a good adherent film is formed at the -ve terminals. This observation is indeed a graphic proof of formation of diodes at the interface and concentration of heat at the +ve terminal. The burning has occurred at the reverse biased diode where most of the dissipation occurs and locally the temperature is high. This causes the water to evaporate faster causing blisters locally. This is a good proof that heating is intense at the interface and locally the temperature is high.

4. CONCLUSION

The study shows that the resistance of PEDOT-PSS films increases with time between two metal contacts (contrary to negative temperature coefficient reported). The increase is attributable to high electric field in the interfacial region of the PEDOT-PSS/metal contact with consequent slow reduction in the interfacial conductivity. AC excitation bypasses the interfacial resistance and gives bulk resistance.

It has conclusively been shown that increase in resistance is largely an interfacial phenomenon. The variation of resistance with time is important information needed for making good strain measurements.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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