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Degradation process in organic thin film devices fabricated using P3HT

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Abstract. The stability of regioregular poly(3-hexylthiophene 2,5-diyl) (P3HT) thin films sandwiched between indium tin oxide (ITO) and aluminium (Al) electrodes have been investigated under normal environmental conditions (25°C and RH∼45–50%). Electrical and optical properties of ITO/P3HT/Al devices have been studied over a period of 30 days. Mobility μ of the order of 10^{-4} cm^2/V-s has been obtained from the V^2 law in the as-deposited P3HT films. Scanning electron microscopy (SEM) investigations show blistering of Al contacts in devices with a poly(3,4-ethylenedioxythiophene) (PEDOT) interlayer on application of voltage whereas no blistering is seen in devices without PEDOT. The results have been explained in terms of trap generation and propagation and the moisture-absorbing nature of PEDOT.

Keywords. Poly(3-hexylthiophene); organic semiconductors; conducting polymers; degradation.

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1. Introduction

In recent years, there has been growing interest in the use of organic materials for applications as microelectronic devices. Polymer diodes, transistors, solar cells and gas sensors are typical examples of applications of these materials ([1–4] and references therein). In microelectronic applications, among many conjugated polymers, the potential of poly(3-hexylthiophene) (P3HT) to perform as an efficient organic semiconductor in organic thin film transistors and solar cells has been demonstrated in the last few years [5–8]. Organic light emitting diodes have reached the market, solar cells have reached 2.9% efficiency and transistors have shown performance comparable to the amorphous silicon transistors. However, it is well-known that the devices based on these organic materials degrade very fast under normal environmental conditions. Many aspects of degradation behavior of organic devices have been studied and reported in literature [9–12]. Influence of moisture on P3HT

thin film transistor (TFT) characteristics is also studied in particular [13]. However, the process that leads to inefficiency and instability in these devices under ambient conditions is still not very well-understood.

In this article we present a comprehensive study, which includes the electrical, optical and scanning electron microscopic investigations of P3HT/Al devices fabricated on an indium tin oxide (ITO) coated glass substrate. We report the results obtained on device fabricated on substrates treated in two different ways and propose a suitable explanation for the degradation behavior of these devices.

2. Experimental details

The P3HT/Al devices were prepared by spin coating P3HT on ITO-coated glass substrates, prepared by different treatments. The ITO was patterned and the substrates were thoroughly cleaned by using the wet cleaning procedure. The studies were carried out on devices fabricated on (a) substrates treated with oxygen plasma (10 min, 600 sccm flow rate at 100 W) and subsequently coated with a thin film of PEDOT (3000 rpm, 60 s and baked at 120°C for 10 min) and (b) substrates subjected to wet cleaning process only. The P3HT used for coating was obtained from Sigma Aldrich and used as such without any further purification. A 3-wt% solution of P3HT in distilled and filtered chlorobenzene was used for spin coating both the substrates at 2000 rpm for 60 s. The films were then baked for 5 min at 100°C on a hot plate to evaporate the remaining solvent. This gives an approximately 250 nm thick film. To form the metal contacts, aluminium was evaporated over the film through a shadow mask in an evaporation chamber at a base pressure better than 2×10^{-6} mbar. A 400 nm thick Al film was deposited at the rate of $\sim$1 nm/s, resulting in diodes of active area 0.04–0.045 cm^2.

The I–V measurements were carried out using a Keithley 2410 Source Meter, SEM investigations were carried out on a JEOL-840 SEM and optical measurements were done on a Bio-Rad FTIR and a CARY-5E UV-Vis-NIR spectrophotometer. The measurements were done on samples immediately after deposition. The samples were stored under normal class 10,000 clean room environmental conditions (25°C and RH$\sim$45–50%) and all the measurements were repeated on the stored samples after 15 days and then again after another 15 days.

3. Results

3.1 *Optical transmittance* (*absorbance*)

Figure 1 shows the absorbance spectrum of P3HT film on a plain glass substrate in the visible region. An optical bandgap of $\sim$1.9 eV was determined that matches well with the reported values [14,15]. Also shown in the same figure is the spectrum of the same sample after 15 days. It can be seen that though there is a very small change in the absorption characteristics of the sample, there is no change in the peak positions even after keeping it for 15 days under normal environmental conditions. Since the absorption in this region of the spectrum gives information about

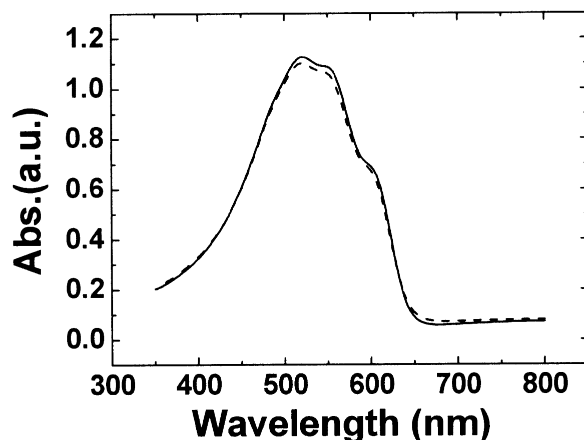

Figure 1. Absorbance spectrum of P3HT film on a glass substrate. The solid line represents the measurements done on fresh sample and the dashed line is for the measurements done after 15 days.

the electronic transitions, nothing can be said about the structural modifications with time, which can be studied by the absorption in the mid-IR region. For this purpose a thick freestanding film of the same solution was prepared by drop casting technique. The IR absorption spectrum of the freestanding film is shown in figure 2. The two spectra were taken on the same sample at an interval of 15 days. During this period the sample was kept under similar environmental conditions as the spin coated P3HT films. It can be seen that the two curves almost match each other.

3.2 *Electrical characteristics*

The I–V characteristics were measured on two samples, viz. sample A with an interlayer of PEDOT on oxygen plasma treated substrate and sample B without the PEDOT interlayer. As stated earlier, both the samples were prepared under similar conditions and also stored in similar environment. The I–V characteristics of sample A are shown in figure 3a and that of sample B are shown in figure 3b. Also shown in the figures are the I–V characteristics measured after 15 days and after one month on the same samples. It can be seen from figure 3a that the I–V characteristics of the freshly prepared samples show a very stable current and excellent rectification behavior (rectification ratio $>10^4$ at 2 V). The current does not show any linear dependence with voltage in the low voltage region (within the resolution of the measurement) indicating that there are very small amount of background impurities in the sample. The current rises superlinearly with voltage and subsequently goes through a transition region towards a V^2 dependence at high voltages. The current flow in trap-free conducting organic materials with field-independent mobility μ is described by the Mott and Gurney model of space charge limited current (SCLC) which gives the well-known V^2 law for current density J given by [16–19]

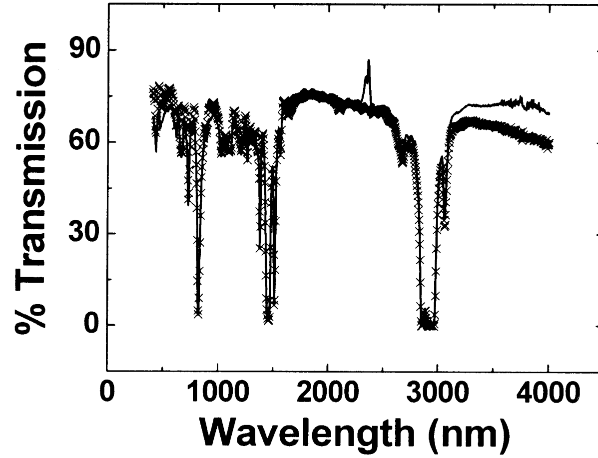

Figure 2. The IR spectrum of freestanding film of P3HT taken initially (solid line) and after 15 days (crossed symbols).

$$J = \frac{9}{8}\varepsilon_s\varepsilon_o\mu\frac{V^2}{d^3}, \quad (1)$$

where ε_o is the permittivity of vacuum, ε_s is the dielectric constant of the material, V is the applied voltage and d is the film thickness. The existence of this behavior and the absence of ohmic region do not mean that the material is trap-free but it indicates that the trap density is too small and/or that traps are completely filled. The hole mobility was calculated by eq. (1) in the V^2 region of the I–V characteristics and also from the SCLC region using exponential distribution of traps. The thickness of the film was taken to be 250 nm and dielectric constant $\varepsilon_s = 2.7$ to obtain hole mobility of 7.5×10^{-4} cm^2/V-s, which is typical of these materials.

The I–V characteristics measured after 15 days and one month show great deterioration in the forward characteristics. The reverse current did not change much except that there was a sudden increase in the current at 4 V indicating the breakdown, which was not observed in the measurements taken on freshly prepared samples, even above 8 V. However, the forward current shows several changes: (a) the overall current values have decreased by two orders of magnitude causing a reduction in the rectification ratio. A linear region is also seen at low voltages indicating an ohmic current. This implies that the background impurity concentration has increased causing the extension of the ohmic region to higher voltages [20]. (b) The variation of current in the mid-voltage region is rather slow as compared to the initial measurements. The slope of the curve is 4 in this region. This indicates a space-charge limited current with traps having some distribution in the energy gap. The influence of traps energetically distributed exponentially, Gaussianly, uniformly or in discrete single and multiple levels, on the current–voltage characteristics has been examined extensively in literature [17,18]. Detailed theoretical expressions [21,22] for $J(V)$ for any arbitrary trap distribution function have been reported. It was observed that in these devices, the exponential distribution of traps gives the

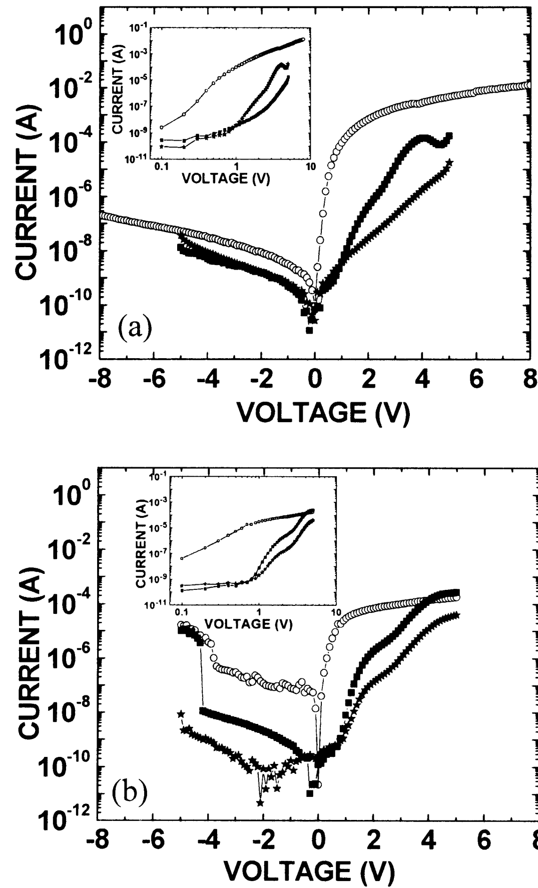

Figure 3. (**a**) The comparison of I–V characteristics of ITO/PEDOT/P3HT/Al device measured initially (open circles), after 15 days (dark squares) and after 1 month (dark stars). Reverse voltage implies hole injection through aluminium contact (+ on Al) and forward voltage implies hole injection through ITO contact (+ at ITO). Log-log plot is shown in inset. (**b**) Log-linear plot of I–V characteristics of ITO/P3HT/Al device measured initially (open circles), after 15 days (dark squares) and after one month (dark stars). Log–log plot is shown in the inset.

best fitting of the characteristics. (c) The current does not approach the trap-filled limit even for the highest voltage measured, and this could be due to very high trap concentration whereas it is clear from the figure that in the case of freshly prepared samples the trap-filled limit is reached at 1.5 V only.

As stated earlier, the hole mobility has been obtained from (i) J–V characteristics in the SCLC region and also (ii) from the square law region. As a consequence of the degradation of the device neither the SCLC nor the square law region was observed. Therefore, only a comment can be made that the hole mobility has deteriorated

considerably as compared to fresh samples. This is evident from the lower current observed in the two cases as compared to the current observed in the fresh sample for the corresponding voltages.

The I–V characteristics for devices without the PEDOT layer are shown in figure 3b. It is clear that the characteristics are noisy and also the rectification ratio is smaller compared to the devices with PEDOT layer. However the change in current after 15 days and one month is relatively less as compared to the films with PEDOT. Also the I–V characteristics taken after 15 days still show a transition towards trap-filled behavior. This indicates that the change in trap density is relatively lower in these devices. The capacitance–voltage (C–V) measurements (not shown) of the ITO/PEDOT/P3HT/Al device show a hysteresis that indicates the presence of bulk and interface traps. The detailed C–V analysis is being carried out and will be reported later.

3.3 *Scanning electron microscopy*

SEM images of the aluminium contact over the active area of the device were taken. Some blisters were seen on the Al contact over the active area of the diode when I–V measurements were done after a period of time as can be seen from figure 4. The blisters were formed only after the application of voltage. The blisters increased in numbers and reduced in size when the voltage was applied for longer duration (figure 5). The blistering of metal contacts was observed only in devices with a thin layer of PEDOT coated over oxygen-plasma-treated ITO substrates, prior to spin coating of P3HT. The device in which PEDOT was not coated does not show any blisters even after applying high voltage and repeated measurements over a period of 30 days (figure 6). The blistering of contacts has been reported

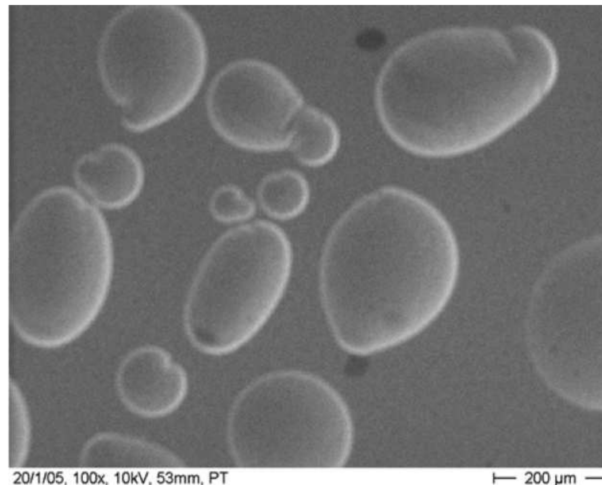

Figure 4. SEM image of bubbles/blisters formed on aluminium contact of 15 days old ITO/PEDOT/P3HT/Al device on application of voltage.

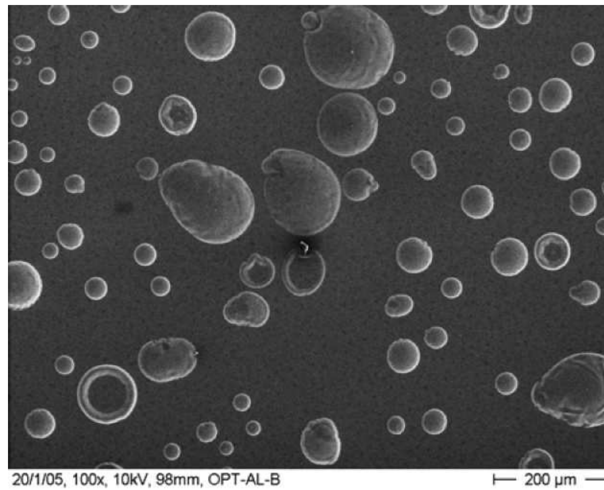

Figure 5. The SEM image of the same device as in figure 4 after the voltage was applied for longer duration.

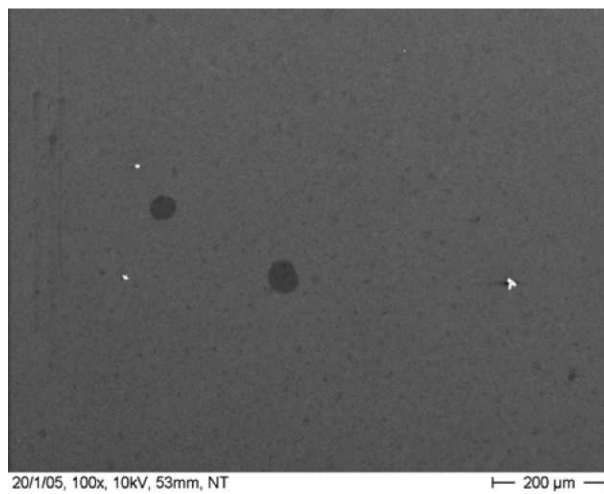

Figure 6. SEM image of aluminium contact of the 15 days old ITO/P3HT/Al device showing no blisters on the metal surface upon application of high voltage.

earlier also [10,23,24]. However till date no comparative study exists to the best of our knowledge.

4. Discussions

Various factors affect the performance of a device. The degradation in device characteristics is caused by two major factors. The first factor is the development

of traps at the polymer/electrode interface or in the bulk of the polymer, and the second one is structural changes in the polymer itself. Introduction of traps at the interface or in the bulk might be due to various environmental factors such as doping due to oxygen present in the atmosphere, absorption of moisture from the humidity present in the surroundings and impurities etc. Similar factors may also induce structural changes in the semiconducting polymer itself and alter its conducting properties, thereby causing degradation of the device.

The comparison of I–V characteristics of the devices with and without PEDOT as an interlayer also gives an idea on the degradation mechanisms occurring in them. Though PEDOT plays a very important role as far as efficiency in current [25] is concerned, it is observed that it increases the rate of device degradation when stored in normal environmental conditions. This is evident from the fact that the relative degradation in I–V characteristics is more in the case of the device with a PEDOT layer.

The study of I–V characteristics done at different intervals clearly indicates that the degradation in the devices proceed mainly through the traps developed at the metal/polymer interface and also in the bulk of the polymer. As stated earlier, the occurrence of linear region after a period of time shows the increase in background impurity concentration. The absence of trap-filled limit in later measurements is also an indication of huge increase in trap concentration in the polymer. Jain *et al* [20] have shown that transition to trap-filled limit shifts to higher voltages as the trap concentration increases. The most probable explanation of the degradation behavior can be given by the mechanism of oxygen or moisture being trapped by the PEDOT layer, which initially increases the trap density in the bulk of the polymer. This is evident from the I–V characteristics taken after 15 days, which is typical for the SCLC behavior in material containing traps. The increase in defect states is also observed from the C–V characteristics, in which the hysteresis starts appearing in measurements done after 15 days.

The results obtained in this paper can be compared to the degradation studies in characteristics of organic thin film transistors reported by different groups [12,13]. The investigations reveal that major factor causing degradation is moisture and encapsulation of the devices results in remarkable improvement in characteristics.

It may be argued that the trapped moisture is responsible for the origin of bubble-like structures in the Al contact. The moisture gets electrolyzed as the bias is applied and the gases are released causing formation of bubbles on the metal surface [10,23,24]. Thus the defects in the bulk increase and in addition to that the metal contact also gets delaminated and deteriorated. This whole process proceeds at a much slower rate in devices fabricated without a PEDOT interlayer. The fact that blisters are seen only in device in which a PEDOT layer was coated prior to spinning of P3HT, makes us to believe that the hygroscopic nature of PEDOT is responsible for the observed behavior.

The optical bandgap calculated from absorbance spectra shows no change even after storing the film in normal conditions, which indicates that the P3HT does not deteriorate. Similarly, the FTIR results also show that there is no major difference in structure of the polymer in the interval in which the measurements are done. This suggests that the degradation in the device proceeds through the introduction of traps in the bulk and the interface and the deterioration of contacts, whereas the

structural change in the polymer might become one of the factors causing degradation at later stages. Thus, one tends to believe that the rate of degradation is more due to defects and traps in the polymer and polymer/electrode interface and is less due to the structural changes in the polymer itself. The PEDOT might increase the rate of degradation further as it is hygroscopic in nature thereby enhancing the moisture trapping process. The increased rate of degradation might also result from an additional interface existing due to PEDOT.

5. Summary

Stability of the organic thin film devices has been one of the most important criteria required for commercial use. The degradation behavior of P3HT/Al devices fabricated on ITO-coated glass substrates have been reported. Results show a relatively higher degradation rate in devices with PEDOT interlayer. A possible explanation in terms of trap generation and propagation has been given. Observations are supported by optical measurements and SEM investigations.

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