Characterization of depletion layer using photoluminescence technique

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Abstract

The depletion layer formed at the interface of Aluminum (Al) with Poly (3-hexylthiophene-2, 5-diyl) (P3HT) has been studied using the bias dependent Photoluminescence (PL) spectra in ITO(Indium Tin Oxide)/P3HT/Al sandwiched cells. A quenching in the PL intensity has been observed under the reverse bias conditions, which has been attributed to the increase in the depletion layer width. A direct relationship between the depletion layer width and the PL quenching has been derived and explained.

The depletion layer formed at the interface of Al/P3HT junction, also behaves as a Schottky junction[1-3] has been utilized to give various functionalities viz. polymeric solar cells (PSCs)[5-6], polymeric light emitting diodes (PLEDs)[7-8] and the polymer based photo induced memory devices (PIMDs)[4,9]. In the light of these applications the dependence of depletion layer width on the applied bias voltages assumes critical significance. In uniformly doped crystalline semiconductors the depletion width given by the Eq. (1)[10]. However, this is strictly not true for conjugated polymer based semiconductors, owing to the non uniform charge carrier density in these materials. Thus a bias dependence study of depletion width would be helpful in the development of more accurate model for various organic devices based on Schottky junctions.

$$w = \sqrt{2\varepsilon_s (V_{bi} - V)/qN_A} \qquad (1)$$

Photoluminescence (PL) emission spectrum can be utilized to study the interface and other related phenomena. It can also be used to estimate the degree of π-conjugation in the conjugated polymeric semiconductors. Magnitude of PL intensity gives a direct indication of the number of excitons undergoing radiative decay[11-13].

In this letter we report the relation between PL quenching (Q_{PL})[12-13] and the depletion layer width (w), and thus obtain the bias dependence of depletion width using bias dependent PL. Formation of depletion layer leads to observed PL quenching due to the increase in the Non radiative decay of excitons[4]. Also, it is known that the depletion layer width increases with increasing reverse bias voltage[10,12]. An increase in depletion width results in a decrease in the bulk active region leading to PL quenching, with increasing reverse bias. This bias dependent quenching was then utilized to obtain the bias dependence of the depletion width. Further the depletion width at zero bias was estimated by varying the Film thickness of the P3HT film. The depletion width at zero bias was found to be 17nm.

Two type of cells were fabricated, one with an active cell area of 36 mm^2 in sandwiched geometry (ITO/P3HT/Al) and the other having an area of 3 cm^2 with (P3HT/Al) configuration, half coated with Al on P3HT film on a glass substrate as shown in the inset of Fig. 1 and 2 respectively. After obtaining a good quality film by spin coating a chloroform solution of P3HT (as obtained from Merck Lisicon SP001), Al (30 nm thick) was coated on to the top of these films in both the cases. The thickness of P3HT films was varied from 20 nm-850 nm in the latter case. Thicknesses of the films were measured using Dektak 6M surface profiler.

PL measurements were done under ambient conditions using photonic multi channel analyzer, (Hamamatsu PMA-11), kept at a distance of 70 cm from the sample. A He-Cd laser having a beam area 20 mm^2 (300 mW, CW, 442 nm, Kimmon IK4121R) was used as a light source. The intensity of light incident on the sample was later calculated to be 0.15 W/cm^2, at an inclination of about 30^o to the normal. In-situ electrical bias was applied on the cells using Keithley 6517 A electrometer. Care was also taken to avoid the over exposure of samples to the laser beam.

The bias dependent PL Quenching Q_{PL}, defined as[12-13)]

$$Q_{PL} = \left(I_{PL}(0) - I_{PL}(V)\right) / I_{PL}(0) \qquad (2)$$

Where $I_{PL}(0)$ and $I_{PL}(V)$ denotes the PL emission intensity at zero bias and at applied bias voltage V, respectively. Figure 1 shows the plot of PL quenching against applied electrical bias. Increase in PL quenching was observed with increasing reverse bias voltage. These observed values of Q_{PL} were then used to calculate the change in depletion width using Eq. (6) (derived later), and plotted against the voltage as in Fig. 1. The plot of depletion width calculated theoretically using the Eq. (1) is also shown in Fig. 1. The parameters V_{bi} and N_A of Eq. (1) were determined from the Mott-Schottky plot of the cell. It must be noted that experimentally determined depletion width deviates from theoretically calculated values using Eq. (1), which is derived assuming constant charge carrier density. However, the presence of localized charge carriers and traps near the Al/P3HT interface lead to non-uniform distribution of charge carriers which in turn results in the observed deviation. Similar observations were made by Takshi et. al.[10) However, their method of measuring the depletion layer was based on electrical measurement. It is important to note that the voltage dependence of the depletion width calculated here is purely based on optical measurement. Also it must be noted that the difference in the built in voltage for the theoretical and the experimental curves was not substantial, although the depletion width at zero bias for experimental curve is significantly less than the depletion width at zero bias for theoretical curve.

The intensity of PL emission (I_{PL}) in general is given by $I_{PL} = I_{abs}\eta_{PL}\eta_C$. Where I_{abs} , η_{PL} and η_C denotes the intensity of absorbed laser light, the radiative PL efficiency and the photon capturing efficiency of the detector respectively. The PL efficiency η_{PL} is in general given by Eq. (3)[11)].

$$\eta_{PL} = K_R / (K_R + K_{NR} + K_Q) \tag{3}$$

Where K_R , K_{NR} and K_Q denote the rates of radiative, non radiative and electric field induced quenching decay respectively. It must be noted that in the present study $K_Q << K_R + K_{NR}$. Under these conditions the PL intensity I_{PL} is directly proportional to the absorbed light intensity I_{abs} .

It was found that double excitation of the films occurred when they were coated with Al top layers having a reflection coefficient R . Thus the intensity of absorbed light by the P3HT bulk is the difference of the incident light intensity and the sum total of the transmitted and the reflected light intensity from the cell as is clear from inset of Fig. 2. The absorbed light intensity I_{abs} is given by

$$I_{abs} = I_0 \chi \left(1 - (1 - R)e^{-\alpha x} - \mathrm{Re}^{-2\alpha x}\right) \tag{4}$$

Where I_0 is the incident laser intensity, R denotes the reflection coefficient of Al top layer, χ is the scaling factor, which arises probably due to the interaction of laser light with the depletion layer, although the exact nature of such an interaction needs further investigation. It has been observed that χ =1.5 yields a good agreement between the observed and simulated results for Al coated films, as shown later in Fig. 2. Since the origin of χ is due to the interaction of laser light with depletion layer, therefore for pristine films χ =1, due to the absence of depletion layer in these films and α is the absorption coefficient of the P3HT film (at $\lambda = 442nm$), while x denotes the penetration distance of the laser beam as measured from ITO electrode/glass in the direction of the thickness of the film as shown in inset of Fig. 2. From Eq. (4) it is clear that the change in the value of I_{abs} is due to changing values of x . At zero bias x is given by $x = t - w_0$, while at any applied bias V , $x = t - w(V)$ (Where t is the thickness of the P3HT film) and w_0 and $w(V)$ represent the depletion width at zero bias and at any bias V respectively.

Thus, $w(V) = w_0 + \Delta w(V)$, where $\Delta w(V)$ denotes the bias dependent change in the depletion layer width. Upon combining Eq. (2 & 4) we get

$$Q_{PL} = A\left(e^{\alpha \Delta w(V)} - 1\right) + B\left(e^{2\alpha \Delta w(V)} - 1\right) \tag{5}$$

Where A and B are constants. Solving for $\Delta w(V)$ gives,

$$\Delta w(V) = \frac{1}{\alpha} \ln \left| \frac{-A + \sqrt{(A+2B)^2 + 4BQ_{PL}}}{2B} \right| \tag{6}$$

The values of A and B were 0.07, 0.46 respectively and α was determined experimentally using UV-VIS spectra to be 32000 cm^{-1}.

It must be noted that Eq. (6) describes the voltage dependent change in the depletion width. However, in order to determine the value of depletion width at zero bias the film thickness was varied from 20 nm-850 nm. The observed results are as shown in Fig. 2. The PL counts in the pristine films were to be proportional to the intensity of light absorbed by the sample, which could be obtained by substituting $R = 0$ and $\chi = 1$ in the Eq. (4). However, the PL counts of Al coated identical samples were found to increase rather than decreasing as observed before[4)]. This observed effect was due to the strong reflection occurring from the top Al coating. Although the reflection by Al coating depends on the thickness of Al and the smoothness of film formed. Thus very thin Al coating on to the top resulted in PL quenching[4)], however as thickness of Al increases its reflection coefficient is found to increase, resulting in double excitation of P3HT films by the incident laser beam. The value of the reflection coefficient R was found to be 0.92, for a 30nm thick Al top layer.

However, it must be noted that the PL counts of 20nm thick P3HT film coated with Al were less than the PL counts of the pristine film. This is mainly because for such a small film thickness most of the bulk is captured by the depletion layer width which does not contribute to PL emission, resulting in the observed PL quenching. The simulated curves for the thickness dependent PL, as shown in Fig. 2 was done using Eq. (4). The simulated curves were found to be in good agreement with the experimental results. From these simulated curves the value of depletion width at zero bias was estimated to be about 17nm. Adding this value to the values obtained from Eq. (6) at different bias voltages leads to the overall bias dependent depletion width variation as shown in Fig. 1.

We conclude that under the reverse bias condition the depletion width is mainly responsible for the observed PL quenching. A direct relationship between PL quenching and depletion layer width was thus derived. Also it was concluded that the depletion width dependence of a schottky junction formed due to metal polymer junction is different from the depletion width dependence of schottky junction formed by using metal crystalline semiconductor junction. This may be due to the absence of localized charges in the crystalline semiconductors which are present in the polymeric semiconductors viz. P3HT. A film thickness dependence of PL intensity yielded the value of depletion width to be around 17nm for a Al/P3HT type schottky contact.

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Figure Captions

Fig. 1. Plot of depletion width (left axis) and PL quenching Q_{PL} (right axis) against the applied bias. Inset shows the schematic diagram of the cell.

Fig. 2. P3HT thickness dependence of PL counts for pristine and Al coated films. Inset shows the schematic diagram of cell, also the reflection due to Al top layer is shown.

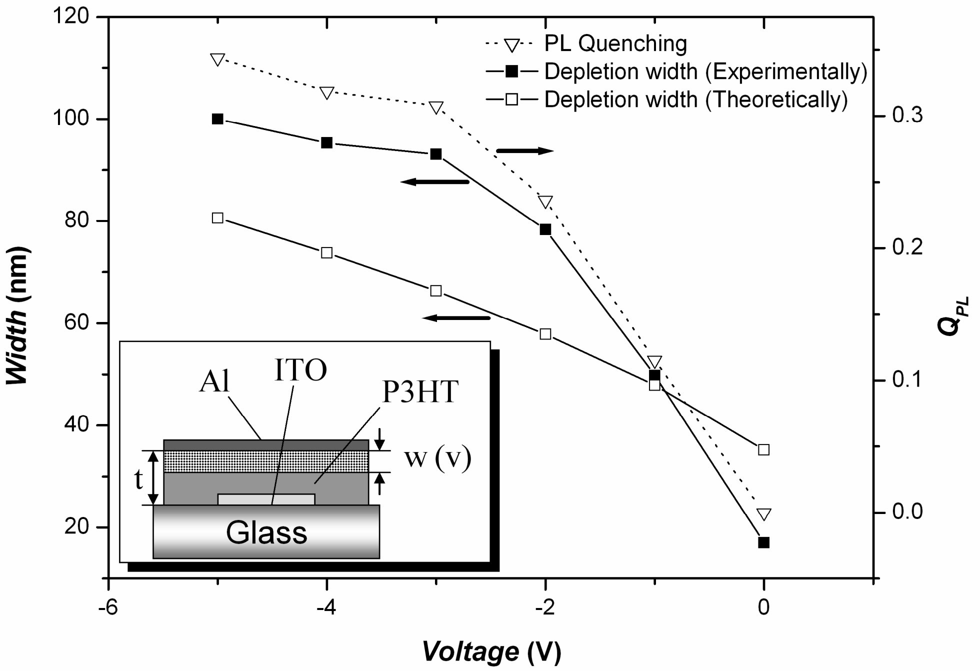
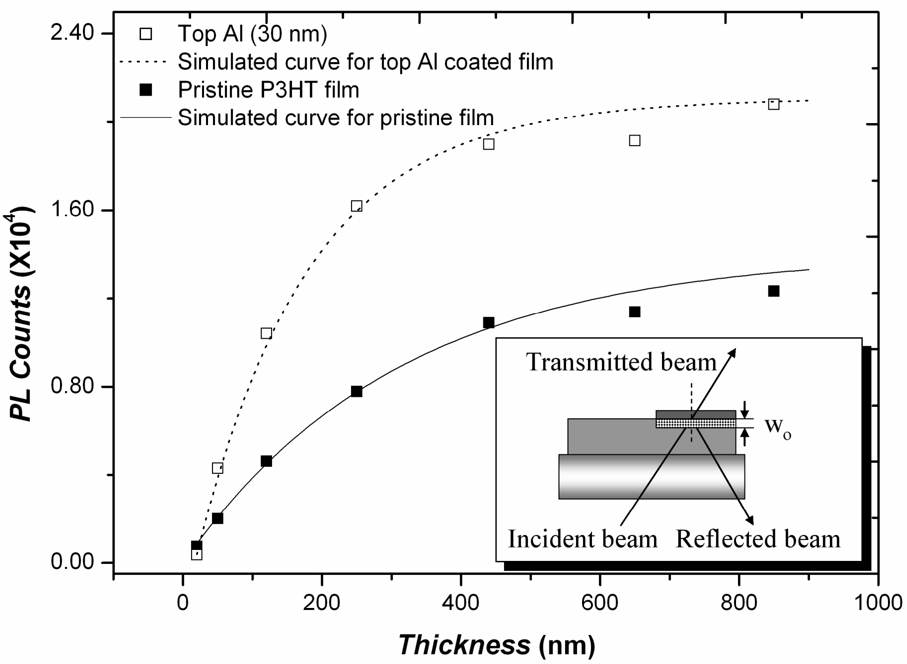

PL Quenching
Depletion width (Experimentally)
Depletion width (Theoretically)
Width (nm)
Voltage (V)
Q_{PL}
Al
ITO
P3HT
w (v)
t
Glass

Fig. 1



Top Al (30 nm)
Simulated curve for top Al coated film
Pristine P3HT film
Simulated curve for pristine film
2.40
1.60
0.80
0.00
PL Counts (X10^4)
0
200
400
600
800
1000
Thickness (nm)
Transmitted beam
w_o
Incident beam
Reflected beam

Fig. 2