In this chapter, we are going to discuss a thin film heterojunction device of conducting polymers with concentration of 10 mg/ml. I-V characteristics of the device demonstrate the negative differential resistance (NDR) behaviour. NDR is a key feature for applications such as novel memories, multi-valued logic, inductor free oscillators and feedback circuits. NDR devices have strong potential for low power applications such as memory and logic. A flexible low power memory would advance the smartcard technology for banking and medical information [1].

The NDR was first observed in tunnel diode also known as Esaki diode which is a special kind of p-n junction diode where p-type and n-type semiconductors are heavily doped so that Fermi levels are located in conduction band and valance band respectively for n-type and p-type materials respectively [2]. As they are highly doped, the depletion region is very narrow due to high carrier concentration. Here filled and empty states are separated by narrow potential barrier at the junction between p and n semiconductors. These devices works on the principle of quantum mechanical tunneling effect, which states that electrons are able to cross the thin barriers even though they have the energies below the potential barrier. Tunneling phenomenon causes its N-shaped I-V characteristics i. e. negative differential resistance (NDR) behavior in their I-V characteristics. [3].
5.1 Quantum Mechanical Tunneling

It is a direct consequence of Quantum mechanics that matter (electron) has both a wave and particle aspect. The probability of finding an electron in a certain region of space can be predicted by wave function ($\psi$). The Schrodinger equation is a fundamental equation which describes the probability distribution and energy of an electron in a system with certain boundary conditions [4]. An electron contained in a one dimensional potential well with infinite potential barriers is a system called the particle in a box. The infinite potential energy at the barriers means that the electron can’t escape the well. The wave function of the electron at barriers has zero value. Solution of Schrodinger equation (with boundary conditions) reveals the acceptable wave function and energies of the electron in the well. Each wave function is quantized and corresponds to specific energy states [4].

![Figure 5.1: The wave function for the electron incident on a potential energy barrier ($V_o$).](image)

However, the situation is different for potential well having potential barrier of finite energy ($E_0$). The wave function of the electron is nonzero at a finite potential barrier showing the probability of electron to occupy the space outside the well. The wave function decays exponentially with distance $x$ inside the barrier of width $a$. therefore the wave function inside the barrier,

$$\psi(x) = A_1 e^{kx} + A_2 e^{-kx}$$  \hspace{1cm} (6.1)
Where, \( k = \sqrt{\frac{8m(V_0 - E)}{h^2}} \)

Where \( A \) and \( B \) are the constants, \( k \) is a positive number, \( h \) is Planck constant, \( m \) is mass and \( E \) is the energy of the particle. \( A_1 e^{kx} \) and \( A_2 e^{-kx} \) represent the exponentially rise and decay function respectively.

A particle can have different wave functions on both sides of the barrier i.e. incident and transmitted waves. This means that electron has the probability to exist in region I and III, even though classically, the electron doesn’t have the needed energy to overcome the barrier. This quantum mechanical phenomenon is known as tunneling. The relative probability of an electron to tunnel through the barrier is called the transmission coefficient (\( T \)) and can be presented as.

\[
T = T_0 e^{-2ks}
\]

Where,

\[
T_0 = \frac{16E(V_0 - E)}{V_0^2}
\]

The tunneling probability of an electron to cross through the barrier depends on energy and the barrier width. If the width of the barrier is wide the tunneling probability is small. Tunneling continue with constant energy means it needs empty and filled electron energy states at the same energy level on both side of the barrier.

### 5.2 Negative Differential Resistance

It has been established that NDR in tunnel diodes, appears on applying a voltage above a certain (peak) value in I-V characteristics. For a specific voltage range, current is a decreasing function of voltage i.e. current have its peak value at low voltage while valley at higher voltage. A typical I-V characteristic of an Esaki diode is shown in figure 5.2. There are three basic parameters used to characterize the TDs characteristics

i) Peak
ii) Valley

iii) Peak to Valley current ratio (PVCR)

$V_p$ and $V_v$ are referred as peak and valley voltage respectively. PVCR is known as figure of merit for tunnel diodes [5].

$$PVCR = \frac{I_p}{I_v}$$  \hspace{1cm} (6.3)

Where $I_p$ and $I_v$ are peak and voltage current in tunnel diodes.

![Figure 5.2: Typical I-V characteristics of tunnel diode.](image)

It can be seen from the figure 5.2 that the tunneling current starts to decrease after exceeding the voltage $V_p$. when the voltage passes this limit the number of aligned empty and filled energy states starts to decrease across the barrier. This is the reason of NDR behavior, where an increase in voltage causes a decrease in current. When the voltage has increased enough, current due to tunneling becomes negligible and a valley region has been achieved. In the valley region small current leakage occurs and device act like conventional diode. Further increasing the current, some different charge transport processes dominate on tunneling transport and current increases again. It is mentioned that the NDR is not possible only due to tunneling.
5.3 Organic Tunnel Diodes

The Esaki diode is an inorganic semiconductor device. These are used in high speed electric circuits and at high frequency operations. Nevertheless they couldn’t attain widespread applications. In 2005, Yoon et al constructed the first hybrid tunnel diode showing NDR at room temperature [1]. This diode comprised of ITO as an electrode, TiO₂ thin film, MEH-PPV film and top electrode Al. In this device, NDR occurred in reverse bias and the high PVCR was obtained as 53. They achieved NDR in this diode with TiO₂ layer of thickness of 4 nm. Other recent computational works discuss NDR in a 2D sheet of atoms [6, 7]. We have observed NDR behavior in a polymeric system (P3HT: PCBM) alone for the first time.

5.3.1 Experimentation

We have synthesized a polymer BHJ device having the structure of ITO/PEDOT: PSS/P3HT: PCBM/ PCBM/ Al following the methodology discussed earlier in chapter 4. To prepare this device, we have made the polymer solutions of concentration 10 mg/ml following the procedure for solution preparation in previous chapter. The device has been prepared in Argon environment. The structure of the prepared device is shown in figure 5.3.
5.3.1.1 Results and Discussion

In the next stage, we have measured the $I$-$V$ characteristics using Keithley sourcemeter (2612 A). The specimen has been mounted on a specially designed holder which ensured stable and better contacts at all time during the measurement. $I$-$V$ characteristics have been measured at room temperature ($27 \, ^{0}\mathrm{C}$). Thereafter we have annealed the sample successively at $40, 60 \, \& \, 80 \, ^{0}\mathrm{C}$ for 2 hours at each temperature in an oven. It has been ensured that the temperature of the oven was stabilized at set value before inserting the sample. Mounting and removing of the samples in the holder would inevitably cause damage to the deposited Al electrode. Therefore the sample has been annealed along with the holder and it is removed only after final annealing at $80 \, ^{0}\mathrm{C}$. After each annealing, $I$-$V$ characteristics have been measured and sample has been placed in oven for next higher temperature of annealing. We have performed three measurements after each stage of annealing to verify repeatability.

![I-V Characteristics](image)

Figure 5.4: Forward bias I-V characteristics of the as prepared device (a); after annealing at $40 \, ^{0}\mathrm{C}$ (b); after annealing at $60 \, ^{0}\mathrm{C}$ (c); and after annealing at $80 \, ^{0}\mathrm{C}$ (d) for 2 hours each at each annealing temperature. Three different curves in each panel correspond to 3 repeated measurement of the sample in a sequence (1, 2 & 3).
In figure 5.4 (a) we have observed peak in the $I$-$V$ characteristics of the as prepared device ($27^\circ$C). Beyond the peak voltage, increase in the applied voltage results in reduction of the current. In other words, it shows the region of negative resistance. As the slope is also changing as we increase the voltage, the negative resistance region can be differentiated to obtain negative differential resistance. The three curves seen in the figures are $I$-$V$ curves of the same device observed one after the other in a sequence as illustrated in the figure 5.4. A single peak Gaussian (solid line) is fitted with each measurement as shown in the figure. There are two main issues related to this repeated measurement – the peak shifts to higher voltage region and the value of the peak current increases in consecutive measurements. Though NDR phenomenon is visible in all three measurements but the measurements cannot be called repeatable because there is about 55% variation in peak-to-peak current and 26.47% deviation in the centre of the peaks. However the variation in FWHM of the peaks of all three curves remains within 5.7%. These changes are significant and suggest that there is a current induced by annealing in the specimen as the passage of the current could produce local heating resulting in opening more channels for current transport. After annealing the sample at $40^\circ$C for 2 hours results in stabilization of $I$-$V$ characteristics to a significant extent. As it is obvious from the shape of the curves, the single peak Gaussian can not be fitted with the measurements. Even double peak Gaussian is not fitted properly. We have measured peak and centre position by putting the cursor on the experimental data in this case. Now the peak-to-peak current variation is 8.7 % and variation in the centre position is 4.2%. This behavior is close to be called repeatable if not perfectly repeatable. The characteristics could be made truly repeatable if we further explore and standardize the annealing and growth parameters such as duration of annealing and exploring real temperature of annealing near $40^\circ$C implying that further detailed systematic studies are needed to resolve the issues. However, the stabilization of $I$-$V$ curves come at the cost of broadening of the peak. From the shape of the peak it can be inferred that it is regions of overlap of two or more peaks. On further annealing at $60^\circ$C, the peak is diminished to a great extent and after annealing at $80^\circ$C, NDR phenomenon have become completely extinct. There is also a reduction in the overall current value on annealing at higher temperature.
Here it is important to compare the polymeric heterojunctions with \( p-n \) junctions for the explanation of the NDR in our devices. P3HT and PCBM are known to as donor and acceptor materials just like \( p \)-type and \( n \)-type materials for inorganic systems. The electronic structure of molecule is referred to as HOMO and LUMO which reflect the correspondence between valance band and conduction band for inorganic semiconductors. However the widths of the bands are quite narrow as compared to inorganic bulk semiconductors [8]. When molecules or polymer chains come together to form an organic solid, the energy of the HOMO and LUMO readjust as result of interaction [8]. In figure 5.5, the electronic band structure of P3HT and PCBM are shown. In forward bias, it is obvious the electron transfer from PCBM to P3HT and hole transfer from P3HT to PCBM both encounters a potential barrier. On increasing the forward bias, the alignment of energy levels takes place as shown in the figure 5.5. The alignment of energy levels provides for unhindered charge transport across the junction leading to a strong current which results in peak as observed in figure 5.4. On further increasing the bias, the alignment of the energy levels will be gradually lost leading to reduction in current with increasing applied voltage (NDR behavior).

Figure 5.5: Schematic of energy band diagram of P3HT and PCBM without any electric field. Solid lines represent the HOMO-LUMO of amorphous phase and dotted line shows the crystalline phase. Right: Alignment of energy levels by applying bias to the system.
The alignment and misalignment of energy levels appears to be the reason for NDR phenomenon in polymers unlike quantum tunnelling across the barrier [5, 8]. Yoon et al also explains the NDR phenomenon as result of tunnelling through localized defects within the TiO$_2$ layers [1].

The thickness of this sample is less than 321 nm since it has been prepared with 10 mg/ml [9], the electric filed across the electrodes at 4V will be greater than $1.25 \times 10^7$ V/m which is quite high. Since the electric fields are very strong in these devices, the delocalized electrons in $\pi$-orbital become available for conduction. On further increasing the voltage beyond peak and valley, current again begins to increase due to the availability of delocalized electrons from hybridized $\pi$-orbital ($SP^2P_z$) in P3HT and PCBM.

In figure 5.6, a schematic model of 3-phase morphology is compared with scanning electron microscope (TESCAN MIRA 3 LMU) image where crystals can be seen dispersed in amorphous phase.

![Diagram of 3-phase morphology](image)

**Figure 5.6:** Left Panel: Schematic model of 3-phase morphology, Right Panel: SEM image of P3HT/PCBM composite.

In our previous work we have also verified with XRD to identify crystalline P3HT and PCBM phases [9]. In P3HT/PCBM composite several type of donor-acceptor can form due to the presence of three-phase morphology [10]. For example, in amorphous phase a P3HT and PCBM molecules form one kind donor-acceptor junction; crystalline P3HT and crystalline PCBM form another kind of junction and one crystalline phase with another amorphous phase will form slightly different kind of junction. In figure 5.5, solid line represent energy levels of amorphous phase and
dotted line represent pure crystalline phase. The complexity of the three phase structure will obviously be reflected in the electronic structure of the composite phase. The availability of slightly shifted HOMO-LUMO levels due to several mixed phases will result in broadening of the peak in measured $I$-$V$ characteristics which is evident in figure 5.4 (b). The inevitable size distribution of crystalline phases also contributes to this broadening.

In figure 5.7 (a) & (b), we have chosen region of negative resistance from the figure 5.4 (a) & (b) respectively. These curves are then fitted with 6-degree polynomial fit. These polynomial fits are then differentiated to obtain $dI/dV$ curves in figure 5.7 (a’) & (b’).

Figure 5.7: Negative differential resistance of as prepared device (a) and after annealing at 40 °C (b) in three different measurements in a sequence of 1, 2 & 3. Lower panels (a’ & b’) are the respective derivatives of the above plots. The scattered points represent experimental data and solid lines are fits to the data. 5-degree polynomial was fitted in $I$-$V$ curves, whereas single peak (a’) and double peak (b’) Gaussian function has been fitted to $dI/dV$ versus $V$ curves.
FWHM of the inverted peaks in dI/dV curves is a crucial parameter of the device where smaller value is advantageous [11]. The values of the room temperature FWHM obtained in this work are shown in figure 5.8 and these are comparable with that of previous devices [12-21]. After annealing at 40 °C, the peaks are broader. The broadening of the peak can arise due to the overlapping of at least two or more energy levels due to presence of several phases in the composite medium of P3HT and PCBM. This study is indirect evidence of different phases of internal morphology of P3HT/PCBM composite medium which serve as an active medium in photovoltaic devices and in other words the I-V characteristics are consistent with the most recent models of the internal morphology of P3HT/PCBM composite system [10].

![Figure 5.8: Comparison of room temperature FWHM of dI/dV curves with other published works.](image)

**5.4 Conclusion**

To conclude this chapter, we have synthesized P3HT: PCBM polymer bulk heterojunction device having structure ITO/PEDOT: PSS/P3HT: PCBM/PCBM/Al. For the first time, I-V characteristics of this purely organic device have shown the NDR behavior. We have also studied the I-V characteristics of annealed device. The I-V characteristics of the as prepared and annealed device have been measured three times one after the other. Quantitative features of I-V curves for the as prepared
device are not repeatable. On annealing at 40 °C, the I-V curves are repeatable with in maximum 8.7% peak to peak deviations.
References


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