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Impedance spectroscopic studies of organic light emitting diodes with dimethyl sulphoxide doped hole injecting and lithium fluoride electron injecting layers

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Organic light emitting diodes(OLEDs) have become one of the potential candidates in display technology. Additional hole injecting and electron injecting layers are shown to be greatly improving the performance and life of OLEDs. In this study, the effects of the thickness of LiF buffer layer with aluminium cathode on the electrical behavior of OLEDs are discussed. Further an effort has been made to investigate the doping effect of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)(PEDOT:PSS) with Dimethyl Sulphoxide (DMSO). It has been found that both the modifications in a device greatly contribute to the electrical characteristics.

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1. Introduction

Organic Light Emitting Diodes (OLED) form the devices for tomorrow's display technology [1] due to many advantages. The problems associated with improvement of efficiency and shelf life [2] are the major impediments to its wider acceptance and commercialization The injection of carriers at electrode-polymer interface and transport through different layers have vital role in determining the performance of the device. The current flow is mainly governed by charge carriers injected from anode and cathode and hence it is imperative that the interfacial layer resistance is a major parameter in the electrical behavior of the device. When this resistance is high, the current is injection limited and if an ohmic resistance at the interface is possible, the bulk properties of the organic layer will govern [3] the current. Use of low work function metals as cathode has been suggested [4] to reduce barrier height and improve injection even though low work function metals are often [5] susceptible to degradation. Research and development of material science in an incredibly faster pace has lead to the synthesis of newer emissive layers [6] and point to the scope of using natural rubber [7] in Polymer Light Emitting Diodes[PLED]. Aluminium, having a higher work function offers better performance and the use of metal cap of 1nm thickness [8] for improvement was reported earlier. Here an attempt has been made to study the effect of modification of the hole injecting layer and the addition of a thick LiF buffer layer on organic an organic LED. Instead of pristine PEDOT-PSS, a dimethyl sulfoxide (DMSO) [9] doped PEDOT-PSS has been used while a buffer layer of LiF with enhanced thickness is employed to catalyse the electron injection. Impedance spectroscopy is used to study and derive the equivalent circuits of the prepared devices since the evaluation of resistance and capacitance values can be optimally used for modeling OLEDs with circuit simulation tools like SPICE [10] (Simulation Program for Integrated Circuit Emphasis).

2. Experimental

The OLEDs were fabricated on ITO coated glass from Sigma Aldrich [40ohms/ square]. ITO coated glass was sonicated in deionized water for 20 minutes followed by cleaning in acetone and isopropyl alcohol in ultrasonic bath. Then the samples were baked in vacuum oven for 2 hours at 100^{o} C. The PEDOT-PSS from Bayers was spun cast from its aqueous solution with 2000RPM for 2 minutes. 5 wt% DMSO was doped in PEDOT and stirred by using magnetic stirrer for 6 hours and a set of ten devices were coated with this solution, keeping the same conditions of spin cast. The samples were baked overnight at 100^{0}C in vacuum oven. Tris(8-hydroxyquinolinato)aluminium(Alq3) was vacuum evaporated at 2×10^{-6} torr for a thickness of 70nm.The cathode area was capped by a lithium fluoride (LiF) layer of 7nm thickness by vacuum evaporation. Then the third stage of evaporation was made for aluminium to a thickness of 110nm. The devices fabricated are Device A: ITO/PEDOT-PSS/Alq3/Al, DeviceB: ITO/PEDOT-PSS/Alq3/LiF/Al; Device C: ITO/DMSO doped PEDOT/Alq3/LiF/Al.

The I-V characteristics were plotted by using Keithley 2400 Source meter interfaced to PC through LabVIEW.

Impedance spectroscopy is a powerful tool [11] to study carrier dynamics and also to observe the impedance responses under different bias conditions. Here Electrochemical workstation IM6 ex from Zahner, Germany was used to obtain impedance spectra and Cole-Cole plots of the devices. Sopra make spectroscopic ellipsometer was used to measure the thickness of the evaporated and spun cast layers.

3. Results and discussions

The turn on voltage and operating voltage are the important parameters which govern the performance of the device. The lowest voltage at which tunneling and emission of light take place is considered as turn on voltage. But it is understood from experiments that the tunneling starts to occur at flat band condition where the device is conductive, but need not be emissive. At higher forward bias voltage, tunneling becomes more intensive and current starts increasing more rapidly. This is normally described as the operating voltage of the device [12] at which emissive behavior of the device is observed.

The I-V characteristics of devices A, B and C are shown in Fig. 1. The operating voltages of the group of devices are 10V, 5.5V and 4V respectively for devices A, B and C, though the flat band condition occurs much earlier. It is to be highlighted that the device with a 7 nm LiF buffer layer (device B) exhibits better electrical behavior than the one without the cap. Enhanced tunneling causes rise in charge carrier density and removal of exciton quenching gap states at cathode/organic layer interface [13]. These contribute to the improvement in electrical and luminance outputs.. With the introduction of LiF metal cap, a small energy barrier against hole injection is introduced as its work function is higher than that of the ITO. Consequently, a smaller bias voltage will be sufficient to produce a given current. It can be seen that the characteristics of device C is more ohmic than A&B. This behavior can be traced to an enhanced conductivity of PEDOT-PSS layer due to the doping effect of DMSO, resulting in the interfacial layer between the ITO and PEDOT becomes more ohmic. Also it exhibits better operating voltage than the device B.

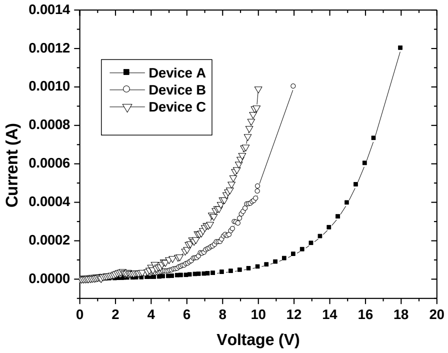


Fig. 1. I-V Characteristics of the three organic LEDs.

Fig. 2 shows the impedance spectra of the devices for a range of frequencies from 10Hz to 1MHz with a sine wave of 1V peak to peak and no superimposing DC voltage. The device B is having impedance less than that of A in the entire spectral range. But in device C, low spectral amplitude remains constant approximately upto 1KHz and between 1 and 10 KHz the impedance values are slightly greater than A and B and in high frequency region it falls more rapidly than that of An and B.

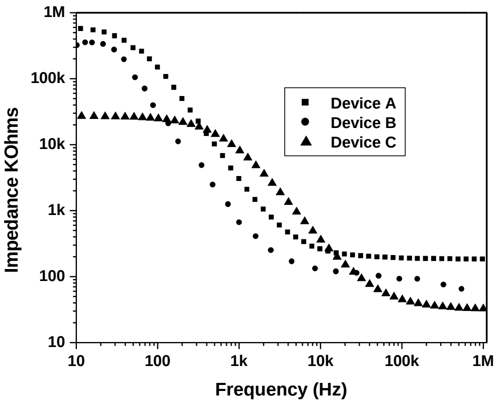


Fig. 2. Impedance Spectra of devices A, B and C.

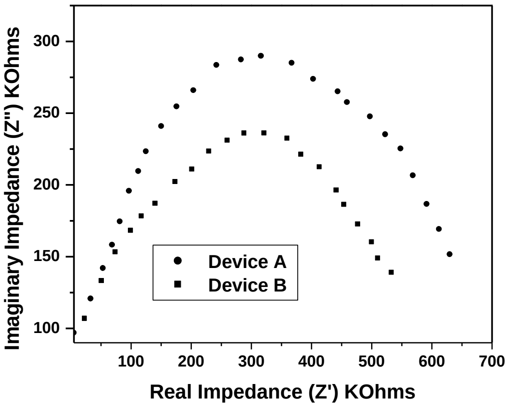


Fig. 3. Cole-Cole plot of Device A and B.

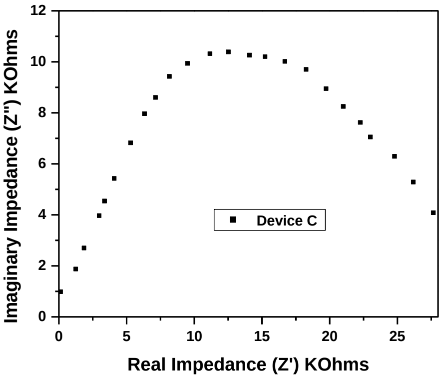


Fig. 4 . Cole-Cole Plot of Device C.

The Cole-Cole plots of the devices are shown in Fig. 3 and 4. The shape of the plot resembles that of a single layer device. However the devices studied here were bilayer. The semi circle plot leads to the equivalent circuit [14] as shown in Fig. 5. The values of the resistance and capacitance in the circuit are computed from the cole-cole plots (Table 1) which is a clear indication of the reactance offered by the device.

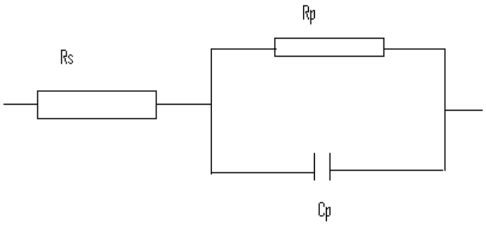


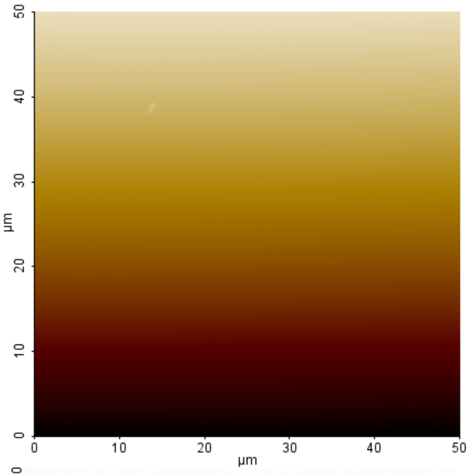
Fig. 5. Equivalent circuit.

Table 1. Values of R and C of the equivalent circuit.

Device	**Value of Rs**	**Value of Rp**	**Value of Cp**
A	10K	680K	4.57nF
B	8 KOhm	592 KOhms	12.3nF
C	2.5 KOhm	27.5K Ohms	8.6nF

The reduction in turn on and operating voltage of the device C can be attributed [15] to the reduction in the values of Rp and Cp for C and hence a substantial reduction in time constants. This verifies suggestion of reduction in barrier height the probable reason for the reduction observed in turn - on and operating voltages due to the modification of PEDOT with DMSO.

Figs. 6 and 7 show the AFM image showing the topographies of PEDOT : PSS films baked overnight which is a major factor determining the film morphology of the device. PEDOT: PSS films doped with DMSO gives a better morphology along with an enhancement in conductivity. It may be an indication of the better performances of the devices with DMSO doped PEDOT.



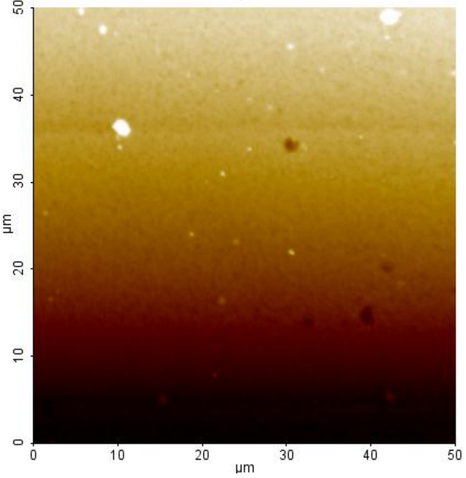


Fig. 6. AFM Image of PEDOT doped with DMSO Fig. 7 : AFM Image of PEDOT without DMSO.

4. Conclusion

Three sets of devices organic LEDs, namely ITO/PEDOT/Alq3/Al,ITO/PEDOT/Alq3/LiF(7nm)/Al and ITO/(PEDOT+DMSO)/Alq3/LiF(7nm)/Al are fabricated and characterized for current and impedance spectra. The current-voltage characteristics of the three sets of devices indicates the improvement in turn on voltage of the device with LiF cap when compared to the one without cap. Further, the device having DMSO doped PEDOT as hole injection layer is still better than the device with no doping in PEDOT. The device with LiF buffer layer is better in terms of impedance behavior compared to its counterpart with no buffer layer. Also the one with the blend of DMSO and PEDOT is having a better conductance and enhanced performance among the three devices fabricated. The impedance spectroscopic studies of the devices lead to Cole-Cole plot which helps to derive the equivalent circuits of the device.

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