Optical And Electrical Properties Of TiOPc Doped Alq$_3$ Thin Films

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Abstract. The Titanyl phthalocyanine (TiOPc) was doped in Tris (8-hydroxyquinolinato) aluminum (Alq$_3$) with different concentration. The thin film of optimized doping concentration was studied extensively for optical and electrical properties. The optical properties, studied using ellipsometry, absorption and photoluminescence. The absorption peak of Alq$_3$ and TiOPc was observed at 387 nm and 707 nm and the photo-luminescence intensity (PL) peak of doped thin film was observed at 517 nm. The DC and AC electrical properties of the thin film were studied by current density-voltage (*J-V*) characteristics and impedance over a frequency range of 100 Hz - 1 MHz. The electron mobility calculated from trap-free space-charge limited region (SCLC) is 0.17×10^{-5} cm^2/Vs. The Cole-Cole plots shows that the TiOPc doped Alq$_3$ thin film can be represented by a single parallel resistance R_P and capacitance C_P network with a series resistance R_S (10 Ω). The value of R_P and C_P at zero bias was 1587 Ω and 2.568 nF respectively. The resistance R_P decreases with applied bias whereas the capacitance C_P remains almost constant.

Keywords: Thin film, Impedance, Electron mobility, Doped.
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INTRODUCTION

Recently, organic semiconductors have become very attractive materials capable of replacing inorganic semiconductors in the development of low-cost, large area and light weight optoelectronic devices, such as organic light emitting diodes (OLEDs), organic solar cells (OSCs) and organic thin film transistors (OTFTs) [1-4]. The doping in organic semiconductor plays a vital role in tuning the optical and electrical properties [5]. The interface between organic semiconductors and metals are also dependent on the doping concentration. The carrier injection in the device is influenced by suitable dopant in the organic semiconductor that leads to the enhancement of device life time [6]. Now a days, there is a new trend in doping of organic semiconductor for reducing the contact resistance with metal and lowering the energy barrier at the interface due to band bending [7]. Since Alq$_3$ is the widely used electron transport material as well as green emissive material, therefore it is important to study the optical and electrical properties of doped Alq$_3$.

In this work we have discussed about the optical and electrical properties of TiOPc doped Alq$_3$ thin films using current density-voltage (*J-V*) characteristics and impedance spectroscopy in the broad frequency range 100 Hz - 1 MHz.

EXPERIMENTAL METHODS

The electron only devices (EOD) were fabricated on glass substrates. In the structure of Al/organic/Al, EOD composed of a 100 nm thick of Titanyl phthalocyanine (TiOPc) doped Tris(8-hydroxyquinolinato) aluminum (Alq$_3$), Aluminium (Al) (100 nm) were used for the anode and cathode both, respectively. The optimized doping concentration of TiOPc was 2% by weight.

Current density-voltage (*J-V*) characteristics of EOD were measured with a programmable Keithley 2400 power source. Impedance spectroscopy (IS) measurement was performed using Impedance/Gain-Phase Analyzer (Solartron, model SI 1260) System. A 100 mV amplitude AC signal superimposed on a DC bias was used to measure the device Impedance as a function of AC frequency and DC bias.

RESULTS AND DISCUSSION

The surface morphology of TiOPc doped Alq$_3$ thin

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film was studied by atomic force microscopy (AFM). Figure .1 shows AFM image of TiOPc doped Alq_3 thin film. The root mean square (RMS) value of roughness for the thin film was found 0.5742 nm. Due to doping of TiOPc the spikes appeared in crystalline form on the thin film. That spikes dominates in charge transport mechanism.

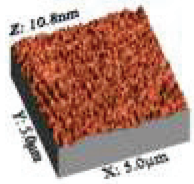

FIGURE 1. AFM image of TiOPc doped Alq_3 thin film.

The optical properties of the thin film were studied by absorption, photoluminescence (PL) and ellipsometry spectroscopy. Figure 2 (a) shows the absorption and PL spectrum in the wavelength range of 200 - 1000 nm. The maximum absorption was observed at a wavelength of 387 nm and 707 nm which corresponds to Alq_3 and TiOPc, respectively. The photo-luminescence intensity (PL) peak was observed at 517 nm. The absorption and PL both show the broad spectrum in the vicinity of the above mentioned peak. The ellipsometric response of the thin film was measured in the 200 - 1000 nm spectral range at an incident angle of 50°. The refractive index (n) and extinction coefficient (k) spectra are shown in figure 2 (b).

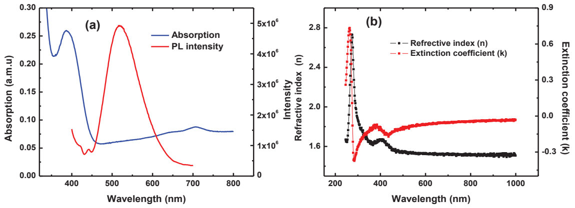

FIGURE 2. (a) Absorption and Photoluminescence (PL) Intensity spectra of TiOPc doped Alq_3 thin film and (b) Refractive index (n) and Extinction coefficient (k) as a function of wavelength

The index of refraction are found between 1.5 - 2.7 whole wavelength range. These n values are higher than the typical organic semiconductor used as electron transport layer. The extinction coefficient (k) is 0.72 at wavelengths of 265 nm which corresponds to an absorption coefficient $\alpha \sim 3.8 \times 10^2$ cm^{-1}.

The *J-V* characteristics of the electron only device are shown in figure 3. Two regions are clearly seen in figure. The slope of double logarithmic *J-V* plot in low voltage region is 1, corresponding to an Ohmic conduction mechanism and the slope of higher voltage region is ~ 2, which is a sign of space-charge-limited current (SCLC) with exponential trap distributions. This indeed indicates the significant Ohmic injection of electrons in the fabricated electron only device. To calculate the electron mobility in the trap-free SCLC region, we use the Mott-Gurney equation for trap-free SCLC [8].

$$J = \frac{9}{8} \mu \varepsilon \varepsilon_0 \frac{v^2}{d^3} \qquad (1)$$

Where ε is the dielectric constant, ε_0 is the permittivity of free space, μ is the carrier mobility, v is the applied voltage, d is the active layer thickness and J is the current density. At high applied bias voltage, current density was found to follow Eq. (1), which could be ascribed as the field and charge carrier density dependence of the mobility. The results show that the electron mobility in the TiOPc doped Alq_3 is $\sim 0.17 \times 10^{-5}$ cm^2/Vs. The electron mobility of TiOPc doped Alq_3 device is of four order compare to Alq_3 (mobility ~ $0.9 \text{ X } 10^{-9}$ cm^2/Vs) device.

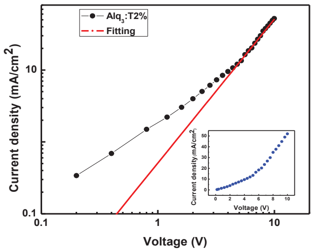

FIGURE 3. Log - log plot of current density - voltage (*J-V*) characteristics of electron-only device. Inset figure shows the normal *J-V* characteristics.

Figure 4. Show the frequency dependence of the real (Re Z) and imaginary (Im Z) parts of impedance at different bias voltages. The complex impedance *Z (f)*, can be represented as a function of frequency as,

$$Z(f) = Z'(f) + Z''(f) \qquad (2)$$

Where Z' and Z" are the real and imaginary parts of impedance. It is observed that the magnitude of Re Z are constant with frequency up to 10 kHz and it decreases with frequency between 10 kHz to 1 MHz. The magnitude of Re Z decreases with applied bias voltages but for all voltage the value of Re Z merges in the higher frequency region at above 50 kHz. The curves also display single relaxation process and indicate an increase in ac conductivity with frequency. The Im Z reaches a maximum peak Im $(Z)_{max}$ for all bias voltage at different frequency. The value of Im $(Z)_{max}$ shifts to higher frequency with applied bias voltage. The frequency corresponding to Im $(Z)_{max}$ called relaxation frequency shifts to higher values with increase of applied bias voltage. This is an indication of increasing loss in the materials with increase of applied bias voltage.

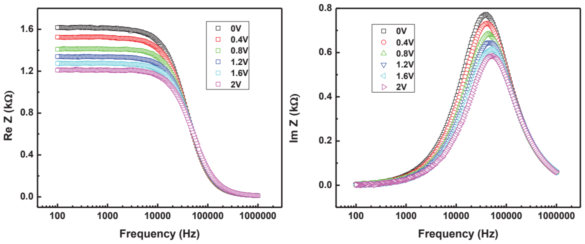

FIGURE 4. Real and imaginary part of impedance as a function of frequency at various applied bias voltages.

The Cole-Cole plots of the Re Z and Im Z at 100 Hz to 1 MHz for different dc bias voltages at room temperature for the electron only device are shown in figure 5.

The plot shows a single semicircle at bias voltages 0 V to 2 V and the size of the semicircle decreases rapidly as the dc bias voltage increases. Therefore, the TiOPc doped Alq_3 device can be modeled as an RC equivalent electrical circuit of which a contact series resistance R_S with a single parallel resistance (R_P) and the capacitance (C_P) network. The impedance of the RC equivalent electrical circuit can be giving by [9]

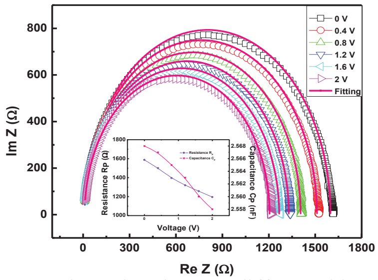

FIGURE 5. Cole-Cole plots at different bias voltages at room temperature. Inset figure shows the variation of bulk resistance R_P and capacitance C_P with different applied bias voltages.

$$Z = Re\, Z + i\, Im\, Z = \left[R_S + \frac{R_P}{1+\omega^2 R_P^2 C_P^2}\right] - i\left[\frac{\omega R_P^2 C_P}{1+\omega^2 R_P^2 C_P^2}\right] \tag{3}$$

By eliminating the angular frequency, the semicircle of the Cole-Cole plot can be written as

$$\left[Re\, Z - \left(R_S + \frac{R_P}{2}\right)\right]^2 + (-Im\, Z)^2 = \left(\frac{R_P}{2}\right)^2 \tag{4}$$

This relation defines a circle centered at ($R_S + R_P/2$, 0) with radius of $R_P/2$. The minimum Re Z value represents the value of R_S with the capacitance and it is about 10 Ω and almost same with the different applied bias voltage. The R_S can be considered as originating from the electrode contact. The maximum Re Z value corresponds to the summation of R_S and R_P to the capacitance. In figure 5 the symbols are the experimental values and the solid lines are the theoretical results obtained from Eq. (4). There is perfect agreement between the experimental and theoretical impedance results.

The fitting data based on Eq. (4) are shown in inset figure 5. It can be seen that the C_P is almost independent on the bias voltage, but the R_P decreases as the applied bias voltage increases. Generally, C_P is directly related to the intrinsic property of used materials, the independent C_P on the bias voltage indicates that the device should be acted as a simple parallel plate capacitor.

The decrease of R_P with bias voltage is then due to a large number of injected electrons increase as the bias voltage increases. This also indicates that the effective conductivity of the organic material will increase with the bias voltage.

CONCLUSIONS

The thin film shows RMS roughness of 0.57 nm with crystalline spikes as integrated morphology. The absorption peaks are found for both Alq_3 and TioPc where as the photoluminescence peak was observed only for Alq_3 in our studied range of wavelength. The PL peak of TioPc might be beyond 800 nm. The electron mobility of doped Alq_3 is 0.17×10^{-5} cm^2/Vs in SCLC region which is four times higher than the pristine Alq_3. The electron only device of doped Alq_3 can be modeled as an equivalent parallel RC network as observed by Cole-Cole plot. The R_P is highly dependent on voltage where as the C_P is independent of applied bias.

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