Effect of Thickness in Electroluminescence spectra on (2-5 dialoxy-PPV) films

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Abstract- The optical properties and electroluminescence of ROPPV (2-5 – dialoxy-PPV) films of various thickness have been studied. The thickness of ROPPV layer on glass slide was measured by Fizeau fringes interferometric technique which varied from 200 to 400nm. The absorption spectra show that the absorption occurred only in ultraviolet region. Thick films show only one peak at 310 nm, whereas by decreasing the thickness, the peaks are obtained at lower wavelength also. Photoluminescence excited by violet light shows three peaks at 380,450 and 510nm and intensity is found to increase with thickness. Electroluminescence from ROPPV films was studied by applying different ac voltage at various frequencies. The light emission starts at certain threshold voltage and then increases with voltage. It is observed that higher threshold voltage is required for thicker films but at higher voltages these give brighter EL. The threshold voltage is found to increase with frequency. The EL spectrum shows two main peaks, one at 510 and the other at 450nm.

Keywords- Electroluminescence, Photoluminescence, ROPPV (2-5 – dialoxy-Poly- Phenelene-Vinayl), Light emitting diode, Electrocromic,

I. INTRODUCTION

In 1990, electroluminescence from a light emitting diode based on the luminescent polymer PPV was demonstrated[1]**.** One year later, a polymer light-emitting diode, was fabricated by spin–casting a polymer film from the soluble PPV derivative ROPPV (2-5- dialoxy-p-phenelene- vinyls). Several application of polymer are based on their luminescence properties, hence, the studies of luminescence of polymer are attracting the attention of large number of workers. Since 1990, considerable progress has been made in the field of semiconducting polymers to understand their electronic and optical properties. There have been several studies on the effect of solvent and annealing condition on the polymer film morphology. Few systematic studies have been made on understanding the changes in the optical properties[2]. Optical and electronic processes in organic molecules and polymers govern the behavior of practical organic optoelectronic devices. Electronic structure of a single organic molecule is used as a guide to the electronic behavior of organic aggregate structures. Emphasis is placed on the use of organic thin films in active organic devices including organic LEDs, solar cells, photodetectors, transistors, chemical sensors, memory cells, electrochromic devices, as well as xerography and organic non-linear optics [3].

The study of EL in thin films is of vital interest both for fundamental and technological reasons. Usually, the thickness of the light-emitting layer lies between 50nm up to 10μm (Robert 1979)**.** Thicker sample up to 5mm have also been fabricated using deposition of organic materials from a hot saturated solution and solidification of a melt[4]**.** Commercial doped and undoped multilayer films of thickness between 4 and 20nm were employed as emitting layer (EML) in some EL experiment [5]. A soluble polymer-dye composite of poly (2, 5-dialkoxy-p-phenylene vinylene) and N, N'-diphenyl glyoxaline -3, 4, 9, 10-perylene tetracarboxylic acid diacidamide (ROPPV-PV) is a new class of organic semiconducting material that would be available for photovoltaic cells [6]. Polymer exhibits a number of attractive characteristics required for opto-electronic devices. Some polymers have been found to exhibit high fluorescence yield [7]. Typical materials include small molecules such as dyes, pentacene, and fused aromatics [8], conjugated polymers [9], and transition metal-containing polymers [10]. The applications of EL devices are EC display, optical switching, and other optoelectronic devices that are operated at the 250-800nm wavelengths and constructed with organic materials.

II. EXPERIMENTAL

Thin Films are made by solution casting method, and their thickness of was measured by Fizeau fringe interferometric techniques. For recording the absorption spectra of ROPPV films, UV/VIS Perkin Elmer Lambda-12 spectrometer is used.

The photoluminescence (PL) studies of polymer films were carried out using mercury lamp with violet filter for excitation. The PL spectrum was obtained by constant deviation spectrometer (CDS). A photomultiplier tube (PMT) RCA-931was used to monitor the light output at the exit slit of CDS. By rotating the position of the drum of CDS, the PL

intensity was measured at different wavelength and subsequently the PL spectra were obtained.

EL cells were prepared by sandwiching the polymer layer between a SnO_2 coated conducting glass plate and Aluminium foil which acted as electrodes. AC voltage of various frequencies was applied at the electrodes and the emitted light was measured with the help of PMT. The EL emission spectra were recorded by using a grating monocromator.

III. RESULTS AND DISCUSSION

The absorption spectra of the ROPPV films are shown in Fig.2. The ROPPV films are found to be transparent in visible region. Results of absorption spectra show that the peaks are observed only in the ultraviolet region. Thick films show only one peak at 310 nm indicating the HOMO level, whereas thinner films shows absorption and peaks also at lower wavelengths.

The changes in absorption may be related to the process involved in the formation of thin films. The ROPPV emissions are found to behave almost similar to that of other polymer like PPV, MEH-PPV, and MEH-CN-PPV.
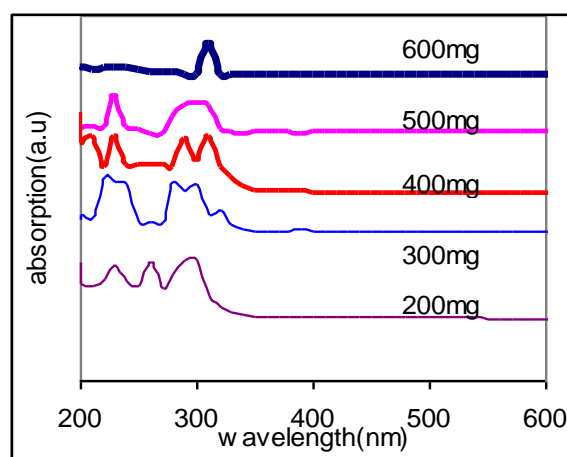

Fig.2. absorption spectrum for different thickness of polymer films

The absorption peaks in different films may be attributed to various possible transitions between bonding, non-bonding and anti-bonding levels. In case of 600mg film there is only one peak at 310nm which may correspond to transition from non-bonding to piantibonding (n ⟶ л*) levels. The films of 500 and 400mg show two peaks due to (n ⟶ л*) (310nm) and (л ⟶ л *) (280nm) transition and the films of 300 and 200 mg exit three peaks corresponding to n ⟶ л*, л ⟶ л *and n ⟶ σ* transitions.

The PL spectra of ROPPV films of various thickness are shown in Fig.4. Three main peaks are observed at 380, 450 and 510nm for all the samples. The emission intensity is found to increase with thickness. Other short peaks may be related to combination of defect states. The maximum photoluminescence (PL) appeared at 510 nm. In case of thinner film less number of

molecules is available for excitation and re-emission of light and therefore PL intensity is low. For thicker film, PL intensity increases since more number of ROPPV molecules can be excited and then make radiation transition increasing the brightness.
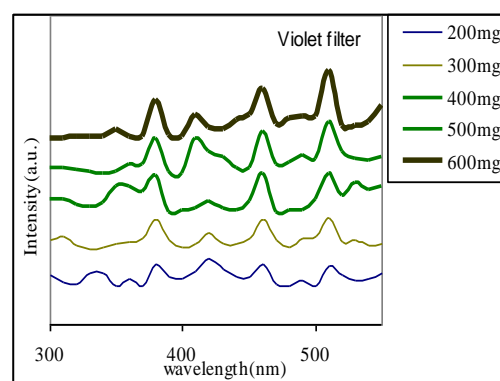

Fig.4. Photoluminescence spectrum for different thickness of polymer films

The EL emission starts at a threshold voltage and it increases rapidly with voltage as seen from the voltage-brightness curve for different frequency shown in Fig.5. Thornton, by considering that the recombination rate to be determined by field-controlled release of electrons from traps, has reported the following relation between EL brightness and frequency

$$B=N_0f [1-exp (-A/f)] \qquad (1)$$

where, N_0 represents constant number of the excited centers for each half cycle, A is a factor which increases with increase in voltage and f is the frequency of applied field. This formula quite satisfactorily explains the starting and the saturation parts of frequency dependence [11]
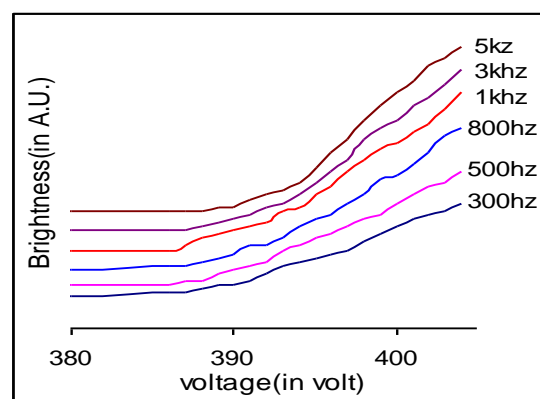

Fig.5. voltage and brightness graph for different frequency at thickness 340nm of polymer film

The EL brightness increases with increasing frequency of the applied electric field and it attains saturation at higher frequencies. At very high frequency, near to 3-5 kHz, the brightness increases slowly and attains maximum value and then falls down due to dielectric heating of samples. When the frequency increases continuously, at very high frequency the available time

for the exhaustion of the trapped electron is decreased, requiring higher voltage or frequency to make the traps empty. The increase in EL brightness with frequency can also be understood on the basis that emptying and refilling of EL center take place more rapidly, with the increase in frequency but when time period of applied AC cycle becomes comparable with lifetime of the excited electrons, the electron does not have enough time to emerge out from trap. Therefore, the brightness will not increase linearly with the frequency. In ROPPV sample, it is found that EL brightness decreases at very high frequency. This is probably due to emission from defect states and impurities. The thickness dependent behavior at fixed frequency and voltage shows that the intensity of emission normally increases with the increase of thickness for both transitions

For different concentration of ROPPV in DMF (200-600mg /10ml), voltage-brightness and EL spectrum are shown in Fig.7.and Fig.8. The EL brightness is found to increase with increasing thickness of the emissive layer seen from Fig.7. It is observed that higher threshold voltage is required for thicker films. The thicker line indicate V-B curve for thick films and vice-versa. The threshold voltages obtain between the ranges 250 - 350 volts.
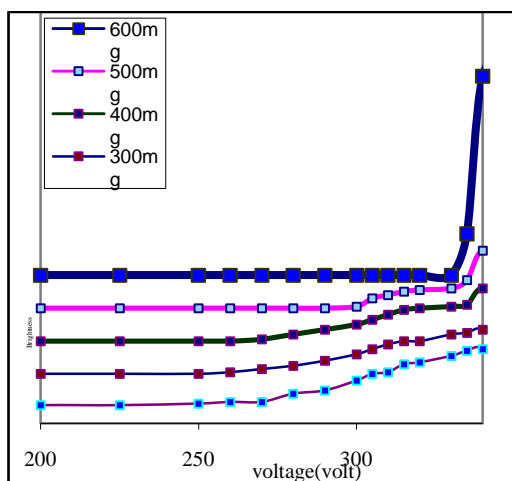

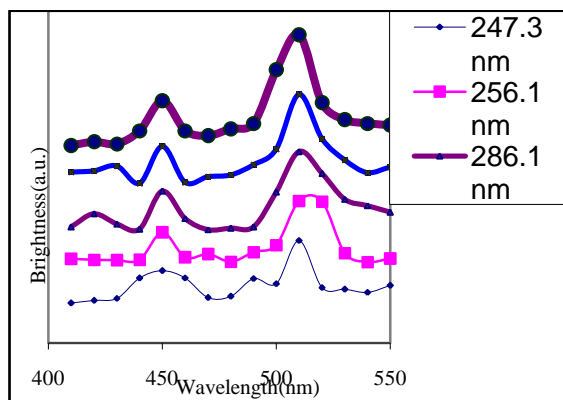**Fig.7**.Voltage-Brightness plot for ROPPV films

Fig.8. EL spectrum of ROPPV films

In the EL spectrum 450nm and 510nm peaks are observed at constant voltage (380Volt) and frequency (1 kHz) for different thickness as shown in Fig.8. When, the thickness of film increases, the intensity of both peaks at 510nm and 450nm increases. It seems that the 510nm emission corresponds to the direct excitation of luminescence center at higher voltage. The 510nm peak is intense which is attributed to radiative exciton decay. The other peak is weaker. This is probably due to recombination of injected charge carriers. It has been found that the EL brightness increases with increasing thickness of the emissive layer. Above a particular threshold voltage the brightness (B) increases rapidly with increasing voltage (V) and the dependence of B on V follows the following relation

$$B=B_0 \exp (-b/V^{1/2}) \qquad \text{------- (2)}$$

where, B_0 and b are parameters, which depend on the temperature, frequency of alternating voltage and also on the material and other details of constructing EL cell. In fact, equation (2) is based on the acceleration-collision mechanism of EL excitation [12].

When, the high electric field is applied in cell, light emission appears as a result of impact ionization and excitation by injected carriers (electron) accelerated in the strong interfacial electric field. They move to the other end of the layer. The opposite sign carriers (holes) remain trapped. At field reversal, the mobile carriers return and recombine with those trapped at the luminescent centers and give rise to the secondary peak. Thus, the EL process comprises the generations of electron and holes and their subsequent separation from each other during one half cycle of the applied alternating field. The return flow and radiative recombination takes place in the next half cycle. .

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