Photoluminescence and Absorption Spectra of ROPPV Films

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Abstract

The study of EL in thin films is of vital interest both for fundamental and technological reasons. Research in case of organic polymers as the active semiconductors in light-emission has advanced rapidly, and prototype devices now meet realistic specifications for applications. The ROPPV films were prepared by the solution casting technology. The thickness of polymer layer was measured by Fizeau fringes technique. The ROPPV films thicknesses were varied between 200 to 400nm. Absorption spectra were taken by Perkin – Elmer – Lambda -12 spectrometer. Result of absorption spectra shows that the peaks are obtained only in the ultraviolet region. Thick films show only one peak at 310 nm, whereas decreasing the thickness it is divided in two or three peaks. The PL spectrum of ROPPV films was excited through violet filter. It has been observed that peaks are obtained at wavelength 380nm, 450nm, and 510nm by violet filter. For lower thickness the PL intensity is less. Here we report the first investigation of defect evaluation in thin films of ROPPV polymer by atomic force microscopy and scanning electron microscope in which we have nondestructively imaged large sets of individual defect between repeated annealing cycles.

Keywords: Electroluminescence (EL), Photoluminescence (PL), Absorption, ROPPV, radiative, nonradiative, conduction band, valance band.

Introduction

Research for the use of organic polymer as the active semiconductor in light emitting devices has advanced rapidly and prototype device now need to realize specification

for application. These achievements have provided insight into many aspect of the background science from design and synthesis of materials through materials fabrication issue to the semiconductor physics of these polymers.

The organic polymers as the active semiconductor in light emitting device now meet diode based polymeric cell. EL cell have become a subject of both scientific and industrial importance in past two decades. The objective of the present investigation is to prepare polymer film useful for EL devices and study their different optical characteristics. Conjugated polymers EL as other material groups of organic EL, is a rapidly expanding field of interest because the development of soluble precursors permits convenient processing and fabrication of EL and photovoltaic devices. The discoveries of efficient emission and stimulated emission from some diode have greatly extended interest in EL leading to the initial developments in semiconductors up to electronic device physics that occurs in the early 1960s. The photo conductance of saturated polymers depends on the type of polymer, impurities, pretreatment by electron irradiation, the electrode materials and other factors. ROPPV are good polymeric photoconductor. The PL emission and absorption spectra lie in the same spectral range (Fujii 2006) [4]. The PL emission and absorption spectra lie in the same spectral range AFM and SEM studies also discussed in this paper.

Experimental

For absorption measurement films are made by solution casting technique. The absorption spectra for the various thicknesses(200nm to 400nm) materials studied The optical processes of absorption discussed in this section are of primary importance in that they essentially define the optical properties of given material. Measuring the absorption spectra of a material is a fairly straightforward experimental process. The absorption spectra of the specific materials used in this work are shown in this paper. For recording the absorption spectra of ROPPV films, UV/VIS Perkin Elimer Lambda-12 spectrometer is used.

For measurement of the absorption of the samples, several pieces of approximately the same size were cut from the grown polymer film. The polymer films were placed at the sample position and reference position was left as it is, taking air as reference. The absorption spectra of all the ROPPV films of different thickness were recorded.

The schematic diagram of the experimental set up used for the study of PL is shown in Fig.1. The main units are Picoammeter, constant deviation spectrometer (CDS), colour filters, light source, PMT and power supply (750 V). PL was excited by monochromatic light of using a mercury lamp and optical filters. The spectrum of emitted light was obtained by a constant deviation spectrograph. Photomultiplier tube was used to measure the intensity of light whose output is connected to a pico-ammeter.

The emission spectrum was obtained with the help of CDS. By rotating the drum of CDS, the wavelength at the exit slit has been varied from 300nm to 800nm. The photoluminescence (PL) studies of polymer films were carried out using mercury lamp with different excitation wavelength violet filter. A photomultiplier tube (PMT)

RCA-931was used to monitor the light output at the exit slit of CDS. A high voltage power supply was connected to the PMT to operate it, and the output of the PMT was fed to a digital pico-ammeter. By rotating the position of the drum of CDS, the PL intensity at different wavelengths was measured in terms of the current in picoammeter and subsequently the PL spectra were obtained. In polymer has previously been investigated by varity of techniques including optical birefringence, neutron scattering and small angle x-ray scattering. Such scattering probes look at spatially averaged behavior and consequently, cannot provide information about individual defects transmission electron microscopy and scanning electron microscopy can image individual defect but typically have been applied to microtome slices of sample.

Result 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. Result of absorption spectra shows that the peaks are observed only in the ultraviolet region. Thick films show only one peak at 310 nm indicating the HOMO level, whereas decreasing the thickness, other higher energy orbital is also revealed.

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. According to energy levels diagram Fig.3, it is shown clearly the possible transitions in 600mg film are n-л* (310nm) and 400,500mg films shows two possible transition n-л*(310nm), π-π*(280nm), 300,200mg films shows three possible transitions n-л*(310nm), π-π*(280nm), n-σ*(260nm) and other small peaks are not identified. It may be due to some defect or impurities. ROPPV can therefore absorb light of those different wavelengths: the pi bonding to pi anti-bonding absorption peaks at 280 nm; the non - bonding to sigma anti-bonding absorption peaks at 260 nm; the non-bonding to pi anti-bonding absorption peaks at 310 nm.

Photoluminescence spectroscopy is a nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy to the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties as shown in Fig.5. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may (a radiative process) or may not (a nonradiative process) include the emission of light. The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. The latter will vanish if the applied energy is higher than the localization energy (Zhuang 2008) [1].

Consequently, the PL emission originates from the recombination of the localized electrons (LE) and delocalized holes (DH) in valence band. When the applied energy increases, the LE tends to be delocalized and excited to the higher energy localized states, which leads to an increase in recombination energy. Due to the strong localization, it is generally difficult to observe the emission corresponding to the delocalized carrier's transition between band–band (BB), instead only one emission involving localized states is visible. Similar behavior was reported on ROPPV layers (Veal 2005, Fan 2000) [2].

In the photoluminescence spectrum shown in Fig.5, the emission peak of films observed at 380nm, 450nm, 510nm may be associated with acceptor levels. However, in the ROPPV films band gap decreases due to thickness of film increases and hence the emission energy is also affected correspondingly. At higher concentration of polymer in DMF shows higher emission. Since the observed result shows a broader peak, the emission cannot be related directly to transitions. It may be related to combination of defect and also generated by more traps. Thus, both of these may correspond to transition in the energy levels. Additional peaks in the red region are observed. It should be noted that films show excess surface defects. The maximum photoluminescence (PL) appeared at 510 nm. These values are similar to those of poly (2, 5-dialoxy-p-pnenylenevinylene) (ROPPV) as observed by Kalinowaski (Kalinowaski 1998) [5]. Photoluminescence due to radiative recombination of singlet excitons is observed at energies just below the onset of the σ*-π* absorption band at 2.25 eV. Photoinduced absorption shows bands peaking at {3.26, 2.69, and 2.25 eV}. The features at 3.26 and 2.25 eV are associated with the same excited state, which we propose is a doubly charged bipolaron, while the third at 2.69 eV is unrelated. We assign this 2.69-eV absorption to a triplet-triplet transition of a triplet exciton.

Fig 6(a) (b) show representative large scale views of the domain structure in the films . The other panels of fig show enlarged details of the Fig 7 images. We observed over sufficiently large areas (2 X 2 micrometer or larger), The average defect density did not vary with the size of the chosen area. However we found that the defect density decreases by 20% during the second anneal.

In conclusion we have performed the first direct tracking experiments of how individual defects evolve in films between repeated cycles of annealing. This was accomplished using atomic force microscopy to image the surface corrugation of ultrathin asymmetric PD-b- PMMA films, films which contained a single layer of PMMA cylinders oriented parallel to the film plane. [6]

Conclusions

1. The absorption spectra and PL of ROPPV films of various thicknesses have been studied and following conclusions have been drawn:
2. The films are transparent in the visible region.
3. The absorption spectra are practically similar for all the samples; the number of peaks is changed for different thickness films.
4. The absorption spectra show that the peaks are observed only in ultraviolet range.

5. Thick films (600mg) show only one peak at 310 nm for due to non-bonding to pi anti-bonding transitions. Increasing the film thickness reduces absorption.
6. Excitation by violet light gives three peaks at 380nm, 450nm and 510nm for all the samples.
7. The thickness of the films does not significantly influence the PL spectra.
8. Peak 510nm is sharp peak for all wavelengths, 380 nm is smallest peak as compared to 450nm.
9. The low energy peak may be because of defect or triplet excitons, whose radiative de-excitation probabilities are very low. The highest peak disappears for lower thickness film.

Our results give direct evidence for defect evolution based on mechanisms such as relinking, joining, clustering and annihilation of defects evolution as a function of annealing conditions.

Fig 6. Defects evolution by relinking and joining bright domain are PMMA ,dark domain are PS (a) 2um by 1.5 um AFM images of microdomain annealed for 2h(left hand side) and 3h(right hand side) at 523 k(b) Defect evolution via relinking and joining . Bright domains are PMMA dark domains are PS 1.5um by 1.5 um AFM images of microdimains annealed for 2h(left hand side) and 3h(right hand side) at 523 k.
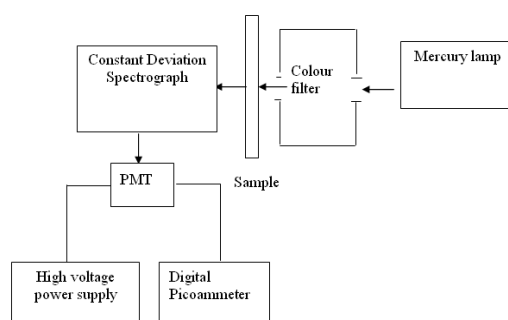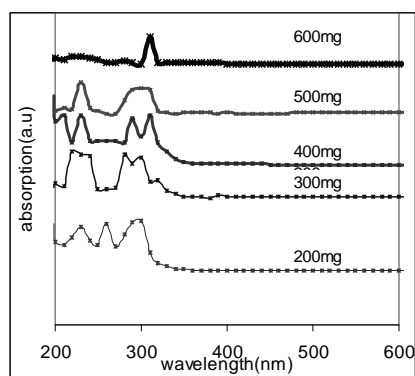

Fig.1. Block diagram of PL set-up

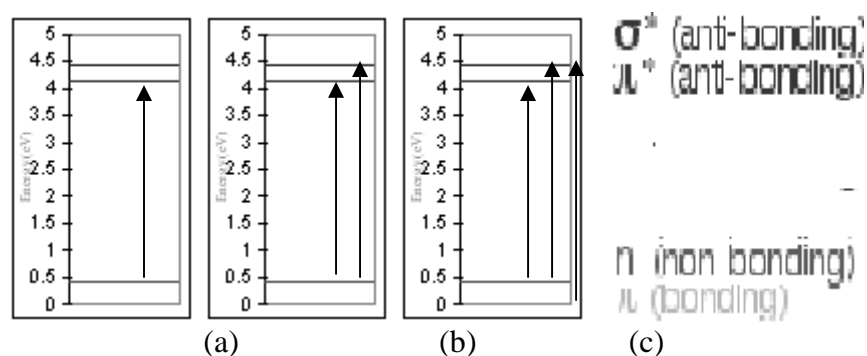**Fig.2.** Absorption spectrum for different thickness of polymer films

Fig.3. (a) Energy levels for 600mg (b) Energy levels for 500mg, 400mg (b) Energy levels for 300mg, 200mg of ROPPV films
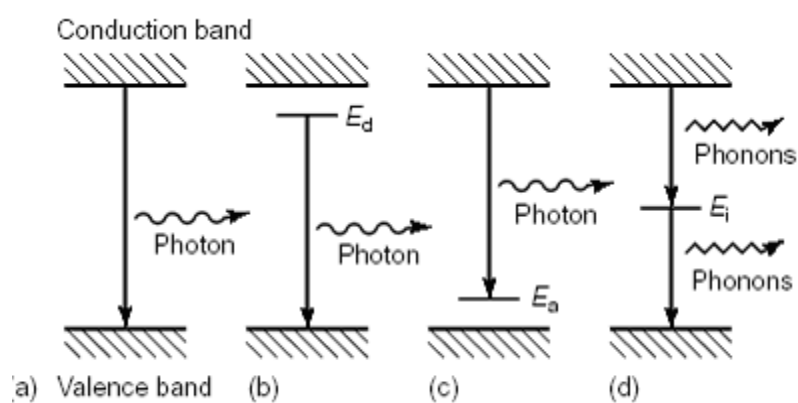

Fig.4. (a-c) radiative recombination paths: (a) band-to- band; (b) donor to valance band; (c) Conduction band to acceptor   (d) Non-radiative recombination via an intermediate state
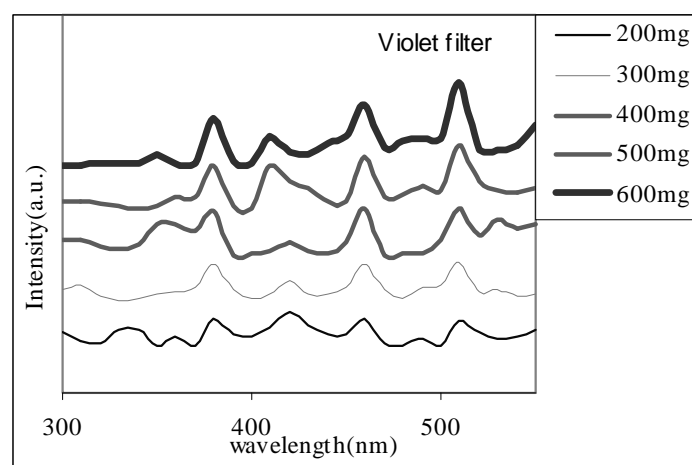

Fig.5. Photoluminescence spectrum for different thickness of polymer films
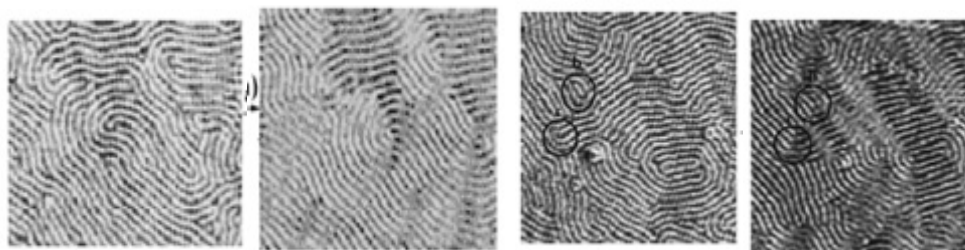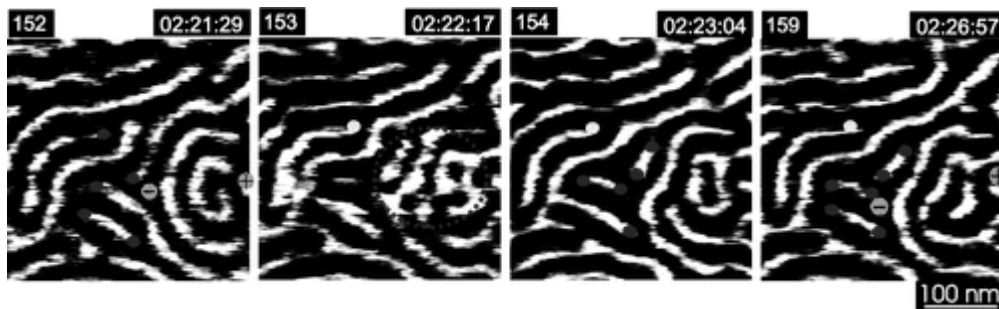
Fig 6(a)   Fig 6(b)

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