

Characterization of Polymer Light Emitting Diodes Fabricated by Ionically Self-Assembled Monolayer Technique

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ABSTRACT

Ionically self-assembled monolayer (ISAM) films are a recently developed class of materials that allows detailed structural and thickness control at the sub-nanometer level combined with ease of manufacturing and low cost. The ISAM fabrication method simply involves the dipping of a charged substrate alternately into polycationic and polyanionic aqueous solutions at room temperatures. Importantly, the ISAM technique yields exceptionally homogeneous, large area films with excellent control of total film thickness. We describe detailed studies of ISAM light emitting diodes incorporating poly(para-phenylene vinylene) (PPV) as the light emitting polymer. The individual thickness of each monolayer and the interpenetration of adjacent layers can be precisely controlled through the parameters of the electrolyte solutions. The effects of the pH and ionic strength of the immersion solutions, the total film thickness, and the PPV thermal conversion parameters on the photoluminescence and electroluminescence yields have been systematically studied. The ISAM process also allows the advantage of depositing well-defined thicknesses of separate polymers at the indium tin oxide and the aluminum electrode interfaces.

INTRODUCTION

Since the first demonstration of a light emitting diode fabricated from a conjugated polymer [1], there has been a continued interest in developing new materials and improving the efficiency of the devices. Conjugated polymers are characterized by a delocalized π -electron system along the polymer backbone, which gives them the semiconducting properties. The advantages of using polymers for the fabrication of optoelectronic devices consist in their ease of fabrication, processability, and the possibility of designing new materials with various bandgaps and electron affinities. For display applications, the most heavily studied polymer has been poly(para-phenylene vinylene) (PPV) [2,3] along with its derivatives [4,5]. The typical process of forming thin films of these materials is the spin coating technique. Our approach is to fabricate homogeneous thin films through the ionically self-assembled monolayer (ISAM) technique, recently developed by Decher and coworkers [6,7] and demonstrated for LED

applications by Rubner and coworkers [8,9]. The technique allows for detailed structural control of materials at the molecular level combined with ease of fabrication and low cost. The ISAM method involves the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping in an aqueous solution of an anion at room temperature. Since the adsorption is based on the electrostatic attraction of interlayer charges, each layer is self-limiting in thickness and uniform at the molecular level. This occurs because the film molecules are free to adjust their positions to improve the overall packing since they are not covalently bound to the substrate. Sequential layers are rapidly fixed by drying at room temperature and pressure. Multilayer films several microns in thickness are easily fabricated by repeating the dipping process with no limit to the number of layers that can be deposited. The resulting pliable films are mechanically very robust and are only removed by vigorous scraping. The advantages afforded by molecular control on the subnanometer level provide opportunities for dramatically enhanced photonic [10], electronic, and optoelectronic [11] devices.

EXPERIMENTAL DETAILS

The materials used for the fabrication of the ISAM films were cationic precursor poly(para-phenylene vinylene) (PPVpc), prepared by the classic route [8, 12] and poly(methacrylic acid) (PMA) purchased from Polysciences. The pH and the ionic strength were adjusted accordingly for the different studies as described below. The films were prepared at room temperature and atmosphere. After the deposition of the films on glass slides and indium tin oxide (ITO) coated glass slides, the films were thermally treated under dynamic vacuum at 300 °C for approximately 8 hours. Absorption spectra were taken with a Jasco spectrophotometer and fluorescence spectra were taken with a Perkin Elmer fluorescence spectrometer. For the electroluminescence spectra we used an Ocean Optics spectrometer. The I-V curves were obtained using a Keithley unit source, and the luminance values were read with a Minolta luminance meter. All measurements were carried in room pressure and temperature. Evaporated aluminum was used as the top electrode of the devices.

DISCUSSION

The initial study was to optimize the parameters of the dipping solutions for the absorbance of the films. Two basic variables have been studied that control the amount of PPV precursor adsorbed into each monolayer: the presence of salt in the PPVpc solutions, and the pH of the PPVpc solution. The polyanion PMA dipping solution was adjusted to 10 mM concentration, pH=3.5 and salt concentration of 0.05 M. For the first series the precursor PPV was 1 mM, 0.05 M salt, and the pH values were 3.5, 6.5, and 8.0. The films were deposited on glass and we recorded the absorption spectra of the films for the three values of the pH, after the thermal conversion of the PPV. The best thermal conversion to the conjugated form of the PPV occurs for pH=3.5. The high pH values of the PPVpc solution decreased the amount of PPVpc that adsorbed to the slides. In order to examine the light emission of the films we also performed fluorescence measurements on the same films. The excitation wavelength was 360 nm. The trends of the fluorescence spectra follow those of the absorption. The slide with the highest fluorescence intensity had the pH of 3.5, having the photoluminescence peak around 485 nm.

The next study examined the adsorption of the (PPV/PMA) films on glass as a function of the ionic strength of the PPVpc dipping solution. All solutions had pH adjusted to 3.5, and the salt content for the PPV varied as shown in **Figure 1** where the absorption spectra were taken after the thermal conversion of the PPVpc. The absorbance of the films increases with increased ionic strength of the solution, up to 0.5 M, after which the absorbance decreases with increased ionic strength. However, the salt concentration does not seem to affect the position of the peak, as all are at approximately 365 nm. The fluorescence measurements (**Figure 2**) for this series also follow the trend observed in the absorption. The excitation wavelength was 360 nm. The spectra show increasing luminescence up to 0.5 M and decreasing luminescence beyond that point, similar with the absorbance results.

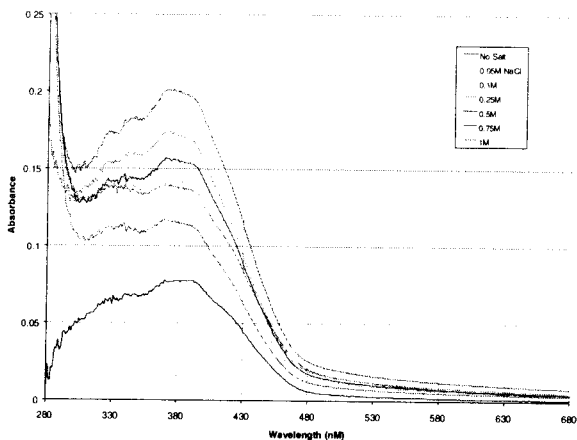


Figure 1. Preliminary study of the effects of salt content on absorbance. The spectra from bottom to top are for salt concentrations of 0.0 M, 1.0 M, 0.05 M, 0.1 M, 0.75 M, 0.25 M, and 0.5 M. The curve with highest absorbance was obtained for 0.5 M salt.

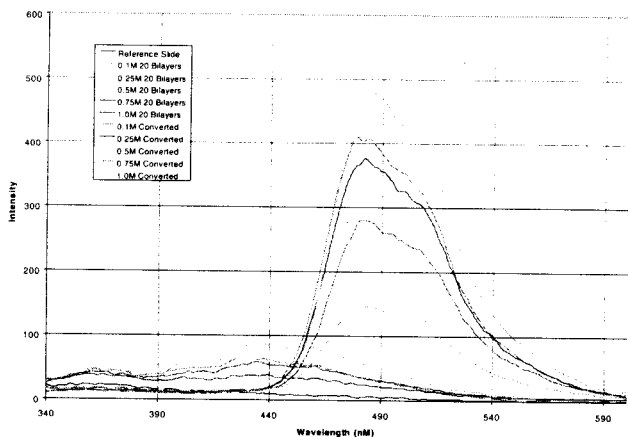


Figure 2. Pre- and post-conversion slides with a pH of 3.5 and varying salt molarity. For post-conversion, the spectra from bottom to top are for salt concentrations of 1.0 M, 0.75

M, 0.25 M, 0.1 M, and 0.5 M. The highest intensity in the fluorescence was obtained for 0.5 M salt.

The device configuration is typical for LED device. On top of the Indium Tin Oxide (ITO) layer we deposited the ISAM (PPV/PMA)_x film, and on top of the film the aluminum electrodes were deposited by resistive evaporation. **Figure 3** contains the absorption, photoluminescence, and electroluminescence spectra for a typical ISAM PPV/PMA device. The fluorescence spectrum was obtained using the excitation wavelength of 440 nm, where the maximum for absorption occurs. The electroluminescence spectrum has the maximum at 506 nm and has similar features with the photoluminescence spectrum, as expected for a good thermal conversion of the PPVpc to the fully conjugated form. Typical I-V and L-V curves for the films are presented in **Figure 4**. The low luminance values are due to the fact that we used a low concentration for the PPVpc dipping solution. More recent results from devices prepared with more concentrated solutions showed an increased value for the luminance.

Interesting results were obtained from the measurements of small (0.6 cm x 0.3 cm) and large (0.6 cm x 0.7 cm) area devices, which were fabricated on the same ITO coated glass slide. The films had 20 bilayers of (PPV/PMA). **Figure 5** (left) shows that the small devices had a higher current density for the same applied voltage, and both types of devices had the threshold voltage at around 3.5 V. **Figure 5** (right) shows that the luminance values of the devices are similar for current densities below 200 mA/cm². Beyond this value, the large area device failed during testing, while the small device sustained much higher current densities. The higher heat generation combined with the larger number of defects present in the large area devices may cause the device failure. Our smallest devices are still much larger than the typical devices described by other groups [9], which used 0.2 cm x 0.2 cm polymer LEDs.

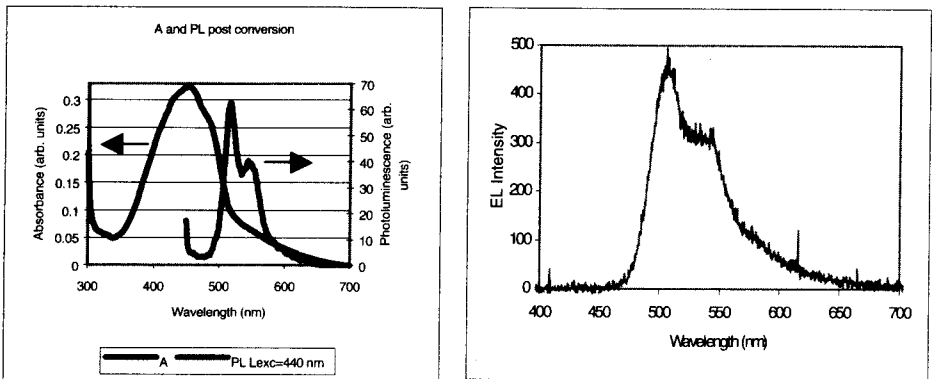


Figure 3. Absorbance, photoluminescence, and electroluminescence spectra for a typical ISAM PPV/PMA LED device.

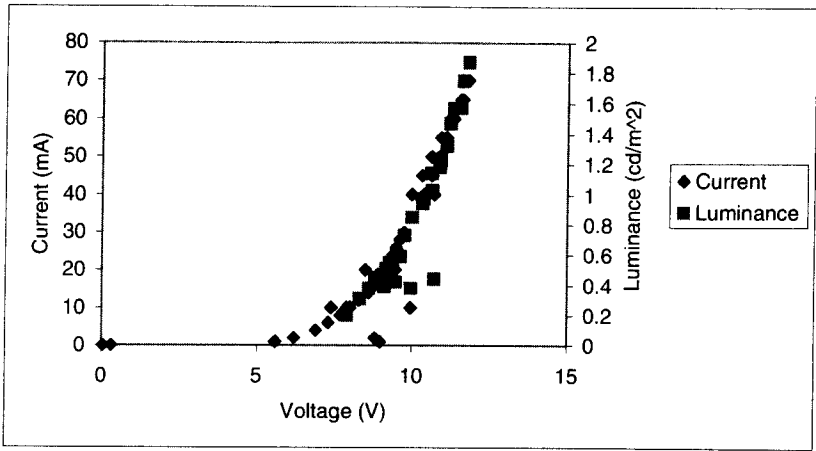


Figure 4. Current and luminance vs. voltage for ITO/(SPS/PPV)₅/(PMA/PPV)₃₀/Al₂O₃/Al.

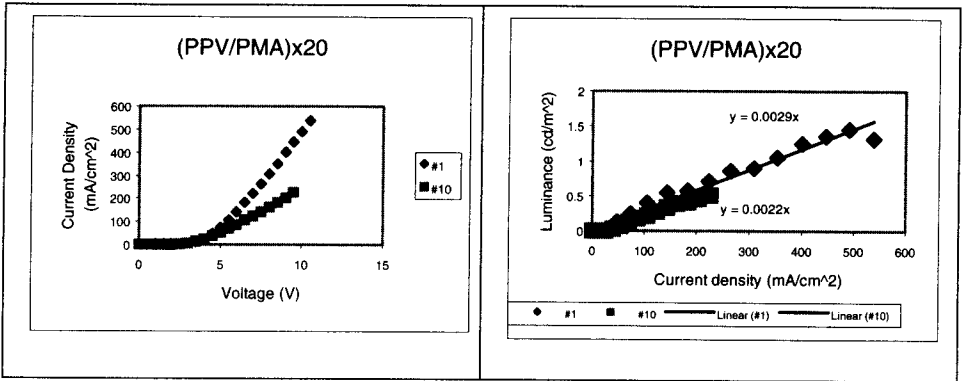


Figure 5. Current density vs. voltage (left) and luminance curves (right) for the small (#1) and large (#10) are devices made with (PPV/PMA)₂₀.

CONCLUSIONS

The ionically self-assembled monolayer (ISAM) technique can successfully be used for the fabrication of polymer light emitting diodes, yielding homogeneous deposition and buildup of monolayers. The amount of deposited PPV can be controlled through pH and salt concentration. Lastly, the efficiency of the devices can be improved through manipulation of the interface layers. The ISAM technique is appropriate for this procedure, allowing for detailed structural and thickness control at the molecular level.

ACKNOWLEDGEMENTS

The authors would like to thank Winston Matthews for the help in the preparation of the samples. This research was supported by the U. S. Navy under contract No. N00014-98-C-0161.

REFERENCES

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **347**, 539 (1990).
2. P. L. Burns, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, and R. H. Friend, *J. Chem. Soc., Chem. Commun.*, 32 (1992).
3. A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. C. Greenham, P. L. Burn, A. B. Holmes, and A. Kraft, *Appl. Phys. Lett.*, **61**, 2793 (1992).
4. D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, **58**, 1982 (1991).
5. N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, *Nature*, **365**, 628 (1993).
6. G. Decher and J. D. Hong, *Makromol. Chem., Makromol. Chem. Symp.*, **46**, 321 (1991).
7. G. Decher, J. D. Hong, and J. Schimitt, *Thin Solid Films*, **210/211**, 831 (1992).
8. A. C. Fou, O. Onitsuka, M. Ferreira, M. F. Rubner, and B. R. Hsieh, *J. Appl. Phys.*, **79**, 7501 (1996).
9. J-K. Lee, D. Yoo, and M. F. Rubner, *Chem. of Materials*, **9**, 1710 (1997).
10. J. R. Heflin, Y. Liu, C. Figura, D. Marciu, R. O. Claus, *Proc. SPIE*, **3147**, 10 (1997).
11. S. L. Clark, E. S. Handy, M. F. Rubner, and P. T. Hammond, *Adv. Mater.* **11**, 1031 (1999).
12. F. R. Denton III, P. M. Lahti, F. E. Karasz, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 2223 (1992).