

Molecular Self-Assembly of Conducting Polymers : A New Process for Fabricating Electrically Conducting Thin Films

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Abstract

A novel thin film processing technique has been developed for the fabrication of ultrathin films of conducting polymers with molecular-level control over thickness and multilayer architecture. This new self-assembly process opens up vast possibilities in applications which require large area, ultrathin films of conducting polymers and more importantly in applications that can take advantage of the unique interactions achievable in the complex, supermolecular architectures of multilayer films.

1. Introduction

Conducting polymers are generally becoming more important as semiconducting materials in new applications. Recent progress has been made in the fabrication of electronic devices based on metal-semiconductor Schottky junctions, where conducting polymers are used as active semiconducting materials.¹⁾ Particularly exciting are reports of light-emitting diodes (LEDs), based on the poly(p-phenylene vinylene) (PPV) and its derivatives.²⁻⁷⁾ Since then, a number of polymer LEDs have been reported, using different conducting polymers emitting in various portions of the visible spectrum.⁸⁻¹⁰⁾ The emission of light in the range from green-blue to orange-red can be produced with the proper chemical modifications of PPV.⁵⁾ Furthermore, fascinating properties due to the polymeric nature of the semiconducting material have been demonstrated: light sources processing mechanical flexibility and the capability of emitting polarized light and large LEDs are already being developed.^{5,11)} Although inorganic blue electroluminescent(EL) diodes consisting of III-V comp-

ound semiconductors have substantially developed,¹²⁾ a polymer emitting blue light is particularly desirable.^{9,10)}

On the other hand, ultrathin organic films are currently gaining interest in many areas such as integrated optics, sensors, electronics, etc.¹³⁾ It is most interesting and challenging to construct films with a supramolecular architecture in which the individual organic molecules are macroscopically oriented and in which molecules with different functionality can be incorporated into individual layers. For example, the Langmuir-Blodgett(LB) technique can be utilized to fabricate multilayer heterostructures from a wide variety of quite different conducting polymers. Although the LB technique provides a powerful processing vehicle for the fabrication of multilayer thin films, it is limited in terms of the types of materials that can be used, the shape and geometry of the substrates coated and the time it takes to fabricate complicated multilayer thin films.¹⁴⁾

Recently, a new technique of constructing multilayer assemblies by consecutively alternating adsorption polyelectrolyte was developed. Rubner et al. have found that it is possible to extend this exciting new technique to the manipulation of conducting polymers.¹⁵⁾ That is, recent advances in the molecular level processing of conducting polymers have made it possible to fabricate thin film multilayer heterostruc-

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tures with an unprecedented level of control over the type and thickness of the deposited layer. Since this new layer-by-layer deposition process is carried out with dilute, aqueous solutions of the charged polymers, it is an extremely simple and effective way to produce thin film structures that are controllable at the molecular level. Then, as the dimensions of the individual layers approach molecular scales, it may also be possible to realize quantum effects in these multilayer contracts.

In this paper, we describe the fabrication of self-assembled multilayer heterostructures of conducting polymers and report the EL properties of LED consisting of a multilayer thin film as an emitter material. Furthermore, we discuss that the delocalized positive charges (polarons and/or bipolarons) of in-situ polymerized conducting polymers can be used to self-assembled thin films.

2. Principles of Molecular Self-Assembly Process

The basic process used to create alternating layer thin films involves dipping a substrate into a dilute aqueous solution of a polyanion, rinsing the substrate with water and then dipping it into a dilute solution containing a polycation. Thus, in the first dip, a monolayer thick film of a negatively charged conjugated polyanion is deposited onto the surface of the substrate whereas in the second dip, a monolayer thick film of a positively charged conjugated polyion is deposited. This process can be repeated as many times as desired to build multilayer thin films in which each layer deposited is only about 0.5–2nm in thickness (depends on such parameters as solution concentration, pH, and ionic strength). Each complete cycle of deposition can take as short as 30 seconds to complete, thereby making it possible to easily and quickly form electrically conducting thin film coatings with complex multilayer organizations and controllable functionally.

For example, the self-assembly process as described by Decher and coworkers is illustrated

in Fig. 1.¹⁶⁾ In this case, a positively charged glass substrate, created by suitable silane chemistry, is first immersed into a dilute solution of a polyanion followed by immersion in a dilute solution of a polycation. The repetition of this cycle produces a multilayer thin film comprised of alternating layers of polyanions and polycations. The thickness and conformation of each polymer layer deposited are determined by the chemistry of the depositing solution.

Figure 2 shows molecular structures of typical conjugated polyions that we can successfully utilize to fabricate multilayer thin films via this process.

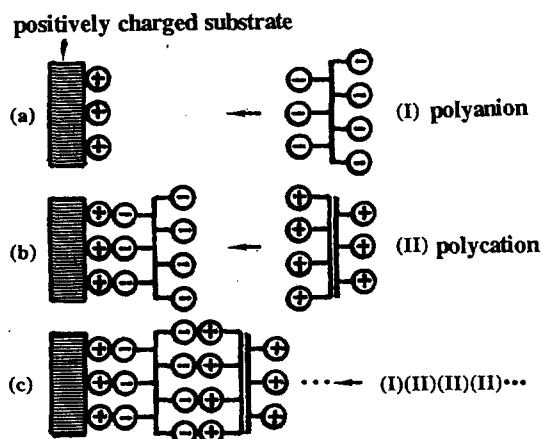


Fig. 1. Molecular self-assembly process involving the alternate deposition of polyanions and polycations. In this case, the substrate surface is positively charged.

3. Experimental Procedure

3.1. Preparation of Polyions

In this paper we discuss the use of PPV polycation precursors to fabricate multilayers of PPV with sulfonated polyaniline (SPAN) as a polyanion. PPV-precursor/SPAN multilayer films can be successfully built with a remarkable reproducibility of the amount of material delivered in each deposited layer. The precursor present in this film can also be easily thermally converted to its fully conjugated form thereby creating films with electroactive PPV layers as shown in Fig. 3.

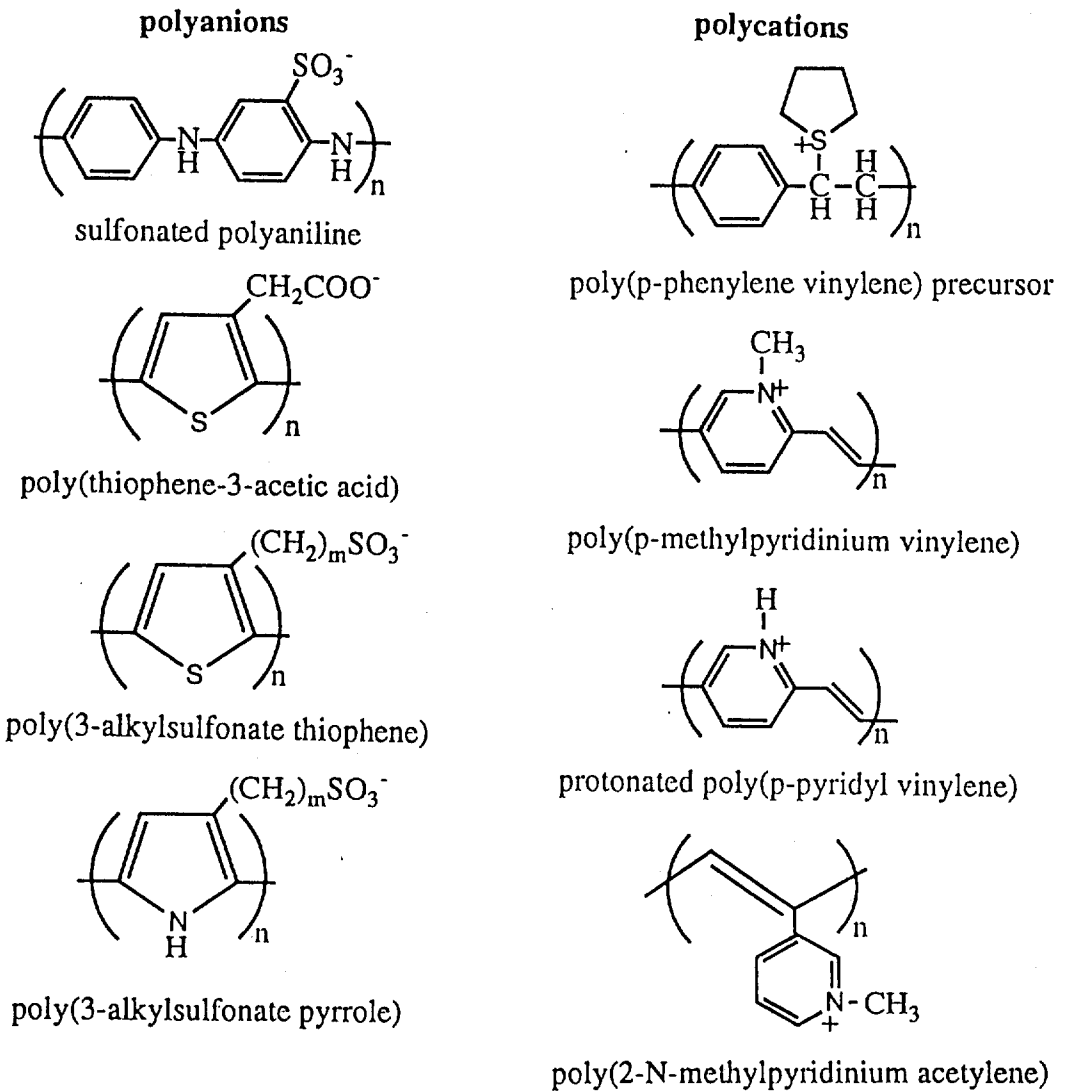


Fig. 2. A list of the conjugated polyions used to fabricate multilayer thin films via self-assembly process.

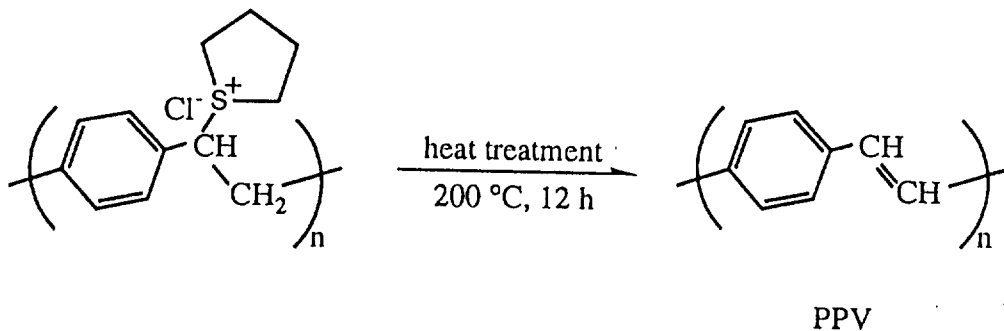


Fig. 3. Thermal conversion of the PPV- precursor to PPV.

PPV-precursor was synthesized by tetrahydrothiophene (THT) route.¹⁷⁾ SPAn was synthesized using the procedure described by Yue et al.¹⁸⁾ The SPAn solution was prepared by dissolving the polymer on a 0.1 mol/l NaOH. The acidity of the solution was then adjusted with HCl to give a measured pH of 4.5. All solutions were prepared in the concentration range of 0.001–0.1 mol/l and filtrated through a 1.0 μm filter prior to use.

3.2. Nature of the substrate surface

It should be noted that the fabrication of high optical quality and multilayer thin films with useful electrical properties can be accomplished with a variety of different substrates, including substrates that are either hydrophobic or hydrophilic. As long as the first layer deposited is a polycation, it is not necessary to use substrates that have been chemically treated to render them charged. However, the nature of substrate surface influences the deposition process and molecular organization of the deposited monolayer.

In this study, indium tin oxide (ITO)-coated conducting glass with positively charged surfaces were used as substrates for the absorption process. That is, ITO glass substrates were first conditioned successively with solutions of methanol, methanol/toluene (1/1), and toluene each for 10 min. These substrates were then treated with 5 vol% TMS (N-(2-aminoethyl-3-aminopropyl)trimethoxysilane) in toluene for 15 h. The TMS-coated substrates were then heated in a warm toluene bath for 1 h to form a physical bond between the substrates and TMS. After the heat treatment the substrates were cleaned in toluene, methanol/toluene (1/1), and methanol each for 10 min. Finally the substrates were rinsed extensively with deionized water to remove residual TMS and dried in air.¹⁹⁾

3.4. Fabrication of SPAn/PPV multilayer

The multilayer films were built up first immersing the ITO glass substrate in the SPAn solution for 15 min, rinsing with deionized water

and air drying. The subsequent dipping in the PPV-precursor solution for equal time followed by the rinsing the drying procedures puts down another layer. This cycle can be repeated as many times as desired.

Figure 4 shows a schematic illustration of a self-assembled film fabricated with alternating layers of two different polymers: SPAn (polyanion) and PPV-precursor (polycation). Thermal conversion of the SPAn/PPV-precursor to SPAn/PPV multilayer was performed in an oven at 200°C in vacuo for 12 h.

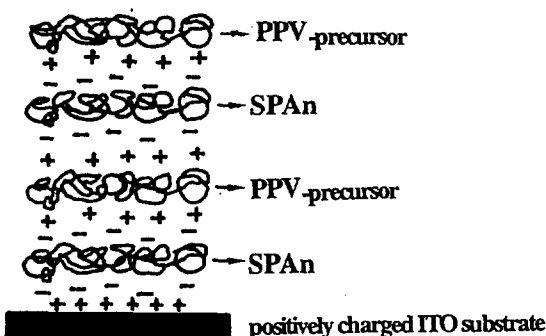


Fig. 4. Schematic illustration of a multilayer heterostructure fabricated via the self-assembly process.

3.5. Fabrication of SPAn/PPV multilayer EL device

The construction of typical SPAn/PPV multilayer EL device is illustrated in Fig. 5. A high work function metal such as ITO (about 4.8 eV) serves as the anode and is semitransparent. The self-assembled multilayer heterostructures of SPAn/PPV were deposited as a thin film on the ITO electrode and a low work function such as Al (about 4.2 eV) is evaporated on to the polymer surface by vacuum metal vapor deposition. Active areas of SPAn/PPV multilayer LED were 2 mm².

The assembled multilayer films were monitored by UV-vis absorption spectroscopy using a Hitachi 330. The thickness of the layer was determined by optical absorption measurements (i.e. the optical absorbance of the film, showed a linear relation with the film thickness). The EL emission spectra and light intensity properties

were measured by using Nikon P-250 spectrometer with a photomultiplier and a Si photodiode. For photoluminescence(PL) spectra, the polymer was excited with light at 450nm. Current-voltage curves were obtained with Keithley 990 digital multimeter and Metronics 5244 dc voltage source. All the measurements were performed at room temperature in air.

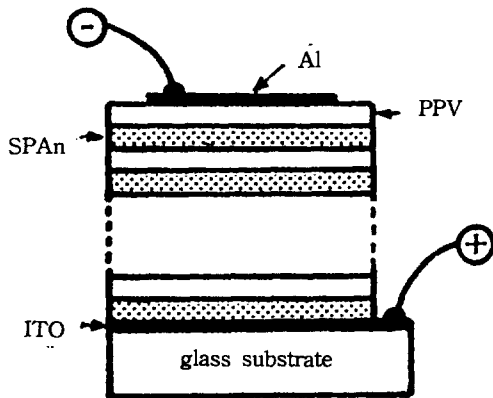


Fig. 5. Structure of the SPAn/PPV multilayer light-emitting diode.

4. Results and discussion

4.1. Self-assembled multilayer heterostructures of electroactive SPAn/PPV

Although PPV-precursor does not absorb light in the visible region, it is possible to readily monitor the growth process as the SPAn absorbs in the visible region. Figure 6 shows the optical absorption spectra of a ten bilayer film fabricated from SPAn/PPV-precursor using 0.001 mol polyion solutions before and after thermal conversion. As SPAn thin films are doped by HCl of the polyanion dipping solution (pH=4.5), the spectrum of the SPAn/PPV-precursor film shows a characteristic expected for a doped SPAn film. It is suggested that the charges on the SPAn polymer are actually in the form of delocalized polarons and/or bipolarons. After the thermal conversion, the spectrum of the SPAn/PPV shows a small broad peak at around 2.0eV due to thermal dedoping of SPAn and a strong peak which corresponds to the interband transition of the

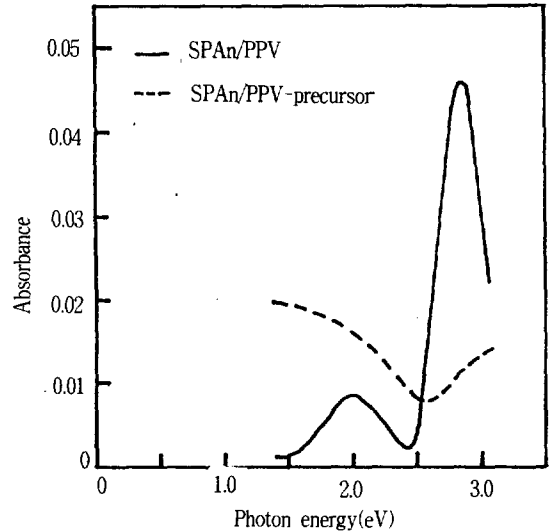


Fig. 6. Optical absorption spectrum of a SPAn/PPV multilayer thin film. Optical absorption spectrum of a SPAn/PPV-precursor multilayer thin film is also shown for reference. The multilayer structure consists of 10 periods of 20Å thick SPAn/PPV.

newly formed PPV film appears at around 2.8eV. The absorption peak at 2.0eV has been assigned to the optical absorption of polarons in partially doped SPAn. It has been reported that the interband transition peak of SPAn appears at around 3.8eV.²⁰⁾ Accordingly, the multilayer film containing alternating layers of SPAn and PPV is seen to be essentially a superposition of these two spectra indicating that both materials are successfully transferred into multilayers and suggesting that no ground state interaction is taking place between these two materials. The bandgap of the SPAn/PPV multilayer film was evaluated to be about 2.6eV from the $(\alpha h\nu)^2$ vs. $h\nu$ plot of the absorption edge of the interband absorption peak of PPV, where α , h and ν are the absorption coefficient, Planck's constant and the frequency of light, respectively. This bandgap is compatible with that of PPV film formed by spin coating.²¹⁾

The heterostructure thin films formed with these different polymers were of the same high quality as the films formed from the individual

polyions and also exhibited a perfectly linear relationship between the absorbance of the conjugated polymer and the number of layers deposited. Figure 7 shows the absorbance of SPAn/PPV multilayer film measured at 2.8eV as a function of the number of bilayers deposited from solutions with different concentrations. The linearity of these plots clearly demonstrates that each deposited monolayer contributes on average an equal amount of material to the thin film. Thus alternating polyanion (SPAn)-polycation (PPV-precursor) bilayers can be successfully assembled from conjugated-conjugated polyions and it is possible to fabricate novel SPAn/PPV multilayer heterostructures by thermal conversion. In the case of our experimental condition, preliminary results showed that the thickness contributed by each bilayer of SPAn/PPV varies from about 20Å (0.001 mol/l solutions) to 42Å (0.1 mol/l solutions) when dipping times of 15 min are used for each layer. We determined that if the dipping time is more or less than 15 minutes, the films could be made to grow thicker or thinner than the above thicknesses, respectively. Thus, by simply controlling the dipping sequence and the types of polyions

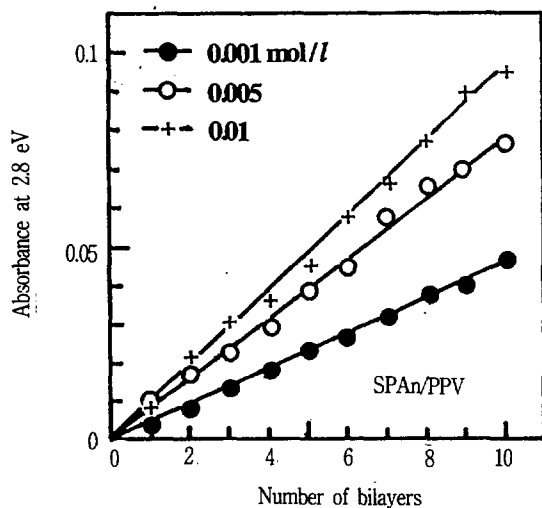


Fig. 7. Dependence absorbance at 2.8eV of a ten bilayer SPAn/PPV multilayer thin film on the number of bilayers deposited from solutions with different polyion concentrations.

deposited, it is possible to fabricate diverse collection of composition modulated heterostructures that are controllable at the molecular level.

4.2. LEDs using SPAn/PPV multilayer thin film

Figure 8 indicates the typical dark current density-electric field characteristic of the EL device with ten bilayer of SPAn/PPV thin film as an emitter material. A pronounced rectification effect was observed in this device, where the forward bias corresponds to positive on the ITO electrode. That is, the forward bias current of this device increases nonlinearly at electric field higher than about 0.7×10^8 V/m, which is nearly identical to the threshold of light emission. This threshold electric field means that substantial charge injection into an emitting layer occurs. It should be noted that the EL emission was detected only in the forward bias and the reverse bias current of this device remained small; the rectification ratio approximately $10^2 \sim 10^3$. Furthermore, the EL intensity increased drastically with increasing electric field and approximately linear with injected current. High forward bias voltage are required in order to achieve charge injection. However, reducing

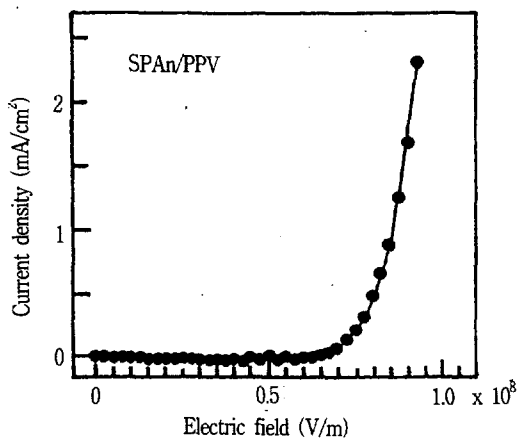


Fig. 8. Current density-electric field characteristic for a electroluminescent(EL) device having a SPAn/PPV multilayer thin film as an emitting layer. The multilayer structure device consists of 10 periods of 20Å thick SPAn/PPV. Only the forward-bias is shown.

the thickness lowers the device operating voltage. It was clearly demonstrated that the current-voltage curves depend on the electric field. This clearly points to a tunneling model for carrier injection in which one or both of the carriers(electrons and holes) are electric field emitted through a barrier at the electrode interface.

A schematic energy diagram of SPAn/PPV EL device is illustrated in Fig. 9. The ionization potential of PPV and SPAn films are about 5.7 and 5.6eV, respectively. In PPV having the bandgap of 2.6eV the bottom of the conduction band is estimated to be located at an energy higher than a Fermi level of Al by about 1.1eV. And the top of the valence band of SPAn is located at an energy lower than a Fermi level of ITO by about 0.8eV. In the SPAn/PPV EL diode, the energy of about 0.8eV is required for holes to be injected from the ITO electrode into SPAn film. Since the conduction band of PPV is located at about 3.1eV below the vacuum level, the energy barrier of about 1.1eV exists between the Al electrode and the conduction band. This means that electron injection into PPV from the Al electrode is somewhat difficult compared to hole injection into SPAn from the ITO electrode. It was assumed that the top of the valence band of SPAn is located at a higher energy state than that of PPV by about 0.1eV. The larger bandgap of SPAn by about 0.9eV compared with that of PPV indicates that the bottom of the conduction band of SPAn is located at an energy higher than that of PPV by about 1.0eV. Accordingly, it follows that the

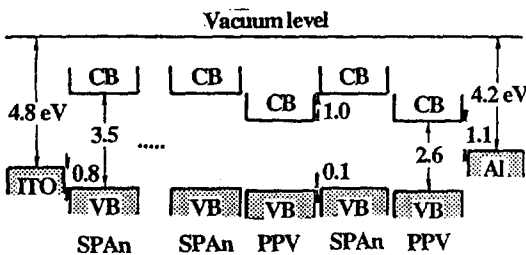


Fig. 9. Schematic electron level structure for SPAn/PPV multilayer heterostructure EL device.

accumulation of holes and electrons at the SPAn-PPV heterojunction interface is expected.

The emission spectrum of a ten bilayer(10 periods of 20Å thickness) SPAn/PPV LED device at room temperature is shown in Fig. 10. The EL spectrum of SPAn/PPV monolayer film (1 period of about 120Å thickness) formed by spin coating is also shown for comparison. The driving condition (injection current 0.6mA/cm²) is the same. Although the emission intensity of the SPAn/PPV multilayer LED is weak compared with that of SPAn/PPV monolayer LED, the emission intensities of the LEDs are normalized.

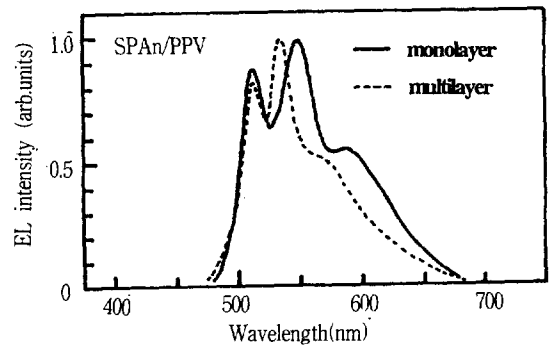


Fig. 10. EL spectrum for light-emitting diode (LED with SPAn/PPV multilayer and monolayer structure. The multilayer structure LED consists of 10 periods of 20Å thick SPAn/PPV. The monolayer LED consists of 1 period of 120Å SPAn/PPV.

The emission properties are hardly affected by the absorption of SPAn having very low optical densities at about 2.0eV. However, the presence of adjacent monolayers of SPAn may slightly weaken the EL emission of SPAn/PPV LED due to a weak reabsorption of SPAn at 2.0eV. The EL spectrum of the LED with monolayer structure is just similar to that reported Burroughes et al., with a peak near 555nm(2.23eV).²⁾ Therefore, this device emits light in the greenish-yellow range of the spectrum and can be easily seen under normal lighting even at low driving voltage. On the other hand, the peak of EL emission of the LED with multilayer structure is at about 536nm, corresponding to

the photon energy of 2.31eV;bluish-green emission can be seen with the naked eye. The light emitted from this device is also visible under ordinary room lighting. These SPAn/PPV heterostructure LEDs show an emission spectrum characteristic of a single polymer layer, in this case PPV. There is no contribution to the emission spectrum from excitons decaying in the SPAn. The EL spectrum separates into three peaks. This separation of EL spectrum is considered to be due to the Stokes shift based on the absorption and emission of phonon. Similar vibronic structure is also observed in the EL spectrum of PPV LEDs.^{2,7)}

There is a small shift of about 20nm(0.08eV) between the two spectra as can be seen in Fig. 10. This can also be observed by the eye; the EL of device with monolayer structure appears greenish-yellow while that with multilayer appears bluish-green. Figure 11 shows the shift of peak emission energy of the EL emission spectrum of SPAn/PPV multilayer LED from that of SPAn/PPV monolayer LED as a function of bilayer thickness.

The origin of this shift is not clear at present. Usually the EL emission is generated by recombination of the electrons and holes injected from opposite electrodes of the device. The EL emission of the SPAn/PPV heterostructure LEDs can be tentatively interpreted by taking the dynamics of oppositely charged polarons generated by injection of electrons and holes into consideration.

In the energy band scheme shown in Fig.9 schematically, the energy barrier for the electrons in the PPV was estimated to be 1.0eV, whereas that for the holes in SPAn is 0.1eV. Therefore, it is considered that electrons in a PPV layer are sandwiched by the SPAn energy barrier, and holes in the SPAn layer by the PPV, separately. The SPAn/PPV multilayer LEDs seem to be the Type I' superlattice structure similar to inorganic compound semiconductor. Accordingly, the confined electrons in the PPV layer localize at a higher energy states and since the state densities in the higher

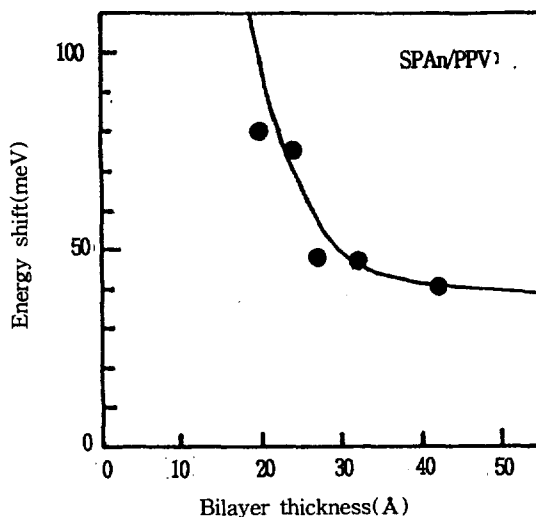


Fig. 11. Relation between peak energy shift of EL emission spectrum of the LED with multilayer structure and bilayer thickness. Solid line was estimated from Kronig-Penny model.

energy are larger than those at the lower energy, the recombination of carriers from the higher energy state is expected and should be large. That is, a small emission energy shift can be interpreted in terms of the confined carriers in the multilayer structure. Then the slight narrow emission spectrum can also be explained since the quantized energy level has a steplike state density. The energy shift was evaluated using the Kronig-Penny model for the localized electrons. As can be seen in Fig. 11, experimental results exhibit a good fit the solid line by the Kronig-Penny model which derives energy-wave number vector relationship in rectangular type potential profile by assuming $m^*=0.8m_e$, where m^* and m_e are effective electron mass and electron mass, respectively. Quantized energy levels are indicated schematically with a dashed line in Fig. 12. However, at this stage, we cannot conclude that the phenomena which we observed in the EL diodes consisting of SPAn/PPV multilayer structure arise from the same quantum size effect as discussed in inorganic compound semiconductors. Because the nature of SPAn-PPV interface is not sufficiently

clear yet and the quantized energy states may not exist due to the layer fluctuations and the imperfect crystallinity etc.

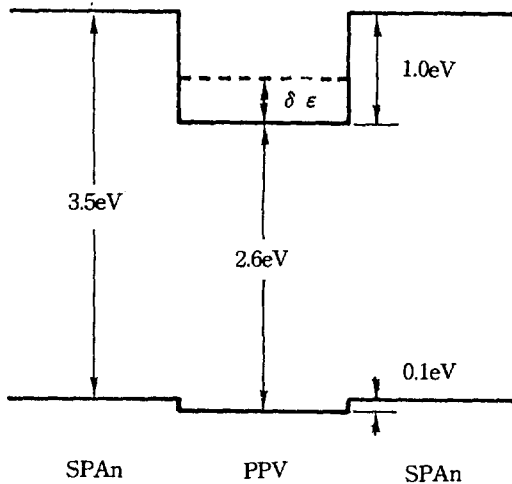


Fig. 12. Simple quantized energy level diagram of SPAn/PPV multilayer structure.

Although it cannot be explained satisfactorily at this stage that the EL emission of SPAn/PPV multilayer LED comes from only PPV layer, we speculate as follows. The generation of polaron excitons are expected to take place very close to the SPAn-PPV heterojunction. Accordingly, it is considered that the EL emission occurs when holes tunnel through the heterojunction barrier and polaron excitons were formed into PPV layer of SPAn/PPV heterostructures. That is, SPAn carries the roles of assisting the injection of holes from ITO and the transport of the injected holes to the boundary of heterojunctions.

We observed novel optical effects in the LED device with the periodic multilayer structure of SPAn/PPV thin film. Of particular interest are multilayer thin films in which layers of functionally different materials are used to control the injection, transport and recombination of electrons and holes in Schottky barrier based LEDs.

5. Ultrathin films of in-situ polymerized conducting polymers

As described in §2, the layer-by-layer molecular self-assembly technique of conducting polymers is based on the spontaneous adsorption of a charged polymer onto a surface from a dilute polymer solution. Accordingly, the delocalized positive charges (polarons and/or bipolarons) of in-situ polymerized conducting polymers such as polypyrrole and polyaniline can be used to self-assemble multilayer thin films when alternated with a suitable polyanion such as poly(styrene sulfonic acid). That is, the basis of this new process is the electrostatic attraction developed between the ionized functional groups of a polyanion and the delocalized positive charges along the backbone of a p-type doped conducting polymer.

The dipping solution of the in-situ polymerized, p-type doped conducting polymer consisted of 0.005 mol/l ferric chloride in deionized water, 0.02 mol/l p-toluenesulfonic acid, and 0.02 mol/l pyrrole monomer. The substrates were ordinary glass slides with various surface treatments. Polypyrrole was deposited onto the various substrates by a single-dip, free-growth process in which the substrate was simply immersed in the polypyrrole dipping solution for a specific amount of time, rinsed, and dried. The deposition of polypyrrole was monitored by UV-vis absorption spectroscopy using a Hitachi 330.¹⁹⁾

Figure 13 shows the optical absorption spectrum of polypyrrole thin film fabricated onto the

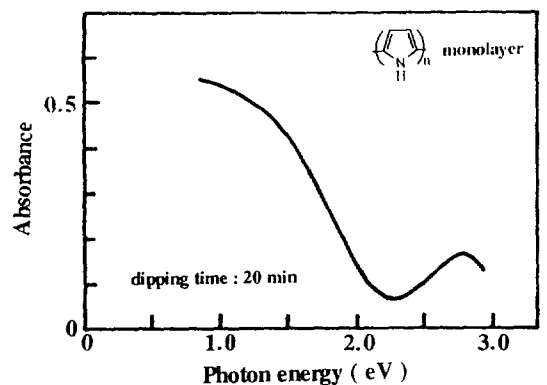


Fig. 13. Optical absorption spectrum of polypyrrole thin film fabricated onto the negatively charged substrate.

negatively charged substrate. The interband absorption peak of polypyrrole is observed at around 2.8eV and a broad absorption peak which corresponds to the delocalized positive charges (polarons and/or bipolarons) along the backbone of a p-type doped polypyrrole appears at around 1.0eV.

Figure 14 shows the growth of in-situ polymerized polypyrrole onto four different surfaces as determined by monitoring the optical absorption of the as-grown film with time. It should be noted that the nature of the substrate surface plays an important role in the early stages of the polypyrrole growth process. It can be seen that there is a linear correspondence between dipping time and the amount of polypyrrole deposited onto the negatively charged substrate. However, for surfaces that are positively charged, hydrophobic and hydrophilic, there is an induction period of 20-30min during which time no polypyrrole is deposited. After this induction period, the growth of polypyrrole onto the surface is significantly less than that observed on a negatively charged surface. That is, the fact that polypyrrole deposits in a very controlled manner on negatively charged surfaces makes it possible to use this process to

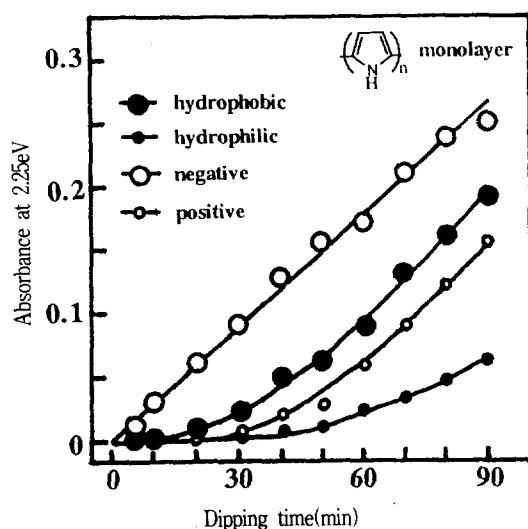


Fig. 14. Dipping time dependence of the absorbance of in-situ polymerized polypyrrole deposited onto various surfaces.

fabricate single layer and multilayer thin films with well defined layer thickness.

Figure 15 shows a schematic diagram of the polypyrrole monolayer fabricated onto the negatively charged substrate.

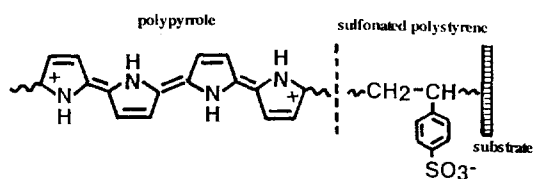


Fig. 15. Schematic diagram of the polypyrrole monolayer fabricated onto the negatively charged substrate.

6. Conclusions

Multilayer thin-film heterostructures comprised of alternating layers of PPV and SPAn were fabricated using a new self-assembly technique. We have obtained visible-light EL diode utilizing SPAn/PPV multilayer thin film. We had also demonstrated that polypyrrole, chemically produced by in-situ oxidative polymerization, can be deposited as a highly uniform, ultrathin film onto a substrate with a high level of control over thickness. Furthermore, complex heterostructures can also be fabricated by simply alternating between solutions of conjugated and nonconjugated polyelectrolytes.

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