Novel Organic Field Effect Transistors via Nano-Modification

Final Report

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In recent years, organic/polymer field-effect transistors (FETs) provide inherent advantages of low cost, large area fabrication, simple packing and compatibility with flexible substrates. The performance of organic FETs is determined primarily by the field effect mobility of the carriers in the organic semiconductor layers and by the efficiency of injecting and extracting carriers at source and drain currents. For virtually all classes of organic semiconductors, the intrinsic carrier mobility depends on the degree of molecular ordering critically and the extent of the π-π stacking in the material. Under these conditions, we propose to enhance carrier mobility by using two kinds of nano-scale films. One is to apply the photoalignment method on a nano-scale film to control the orientation of pentacene molecules as an active layer in the thin-film transistors with conspicuously anisotropic electrical characteristics. Another is to employ also a nano-scale film (polymer electrolyte) to control moving of ions in/out an active semiconductor, pentacene or conducting polymer, for improving carrier mobility. In this project, pentacene or a series of conducting polymers, such as the derivatives of PANI and P3HT will be patterned and manufactured in FETs. Nano-scale films including polyimide for photoalignment/ion beam treatment and polymer electrolyte for ion doped/dedoped modification are to achieve the high mobility.
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In recent years, organic/polymer field-effect transistors (FETs) provide inherent advantages of low cost, large area fabrication, simple packing and compatibility with flexible substrates. The performance of organic FETs is determined primarily by the field effect mobility of the carriers in the organic semiconductor layers and by the efficiency of injecting and extracting carriers at source and drain currents. For virtually all classes of organic semiconductors, the intrinsic carrier mobility depends on the degree of molecular ordering critically and the extent of the π-π stacking in the material.

Under these conditions, we propose to enhance carrier mobility by using two kinds of nano-scale films. One is to apply the photoalignment method on a nano-scale film to control the orientation of pentacene molecules as an active layer in the thin-film transistors with conspicuously anisotropic electrical characteristics. Another is to employ also a nano-scale film (polymer electrolyte) to control moving of ions in/out an active semiconductor, pentacene or conducting polymer, for improving carrier mobility. In this project, pentacene or a series of conducting polymers, such as the derivatives of PANI and P3HT will be patterned and manufactured in FETs. Nano-scale films including polyimide for photoalignment/ion beam treatment and polymer electrolyte for ion doped/dedoped modification are to achieve the high mobility.

**Phase I (4 months, from July 1 to October 31, 2004)**

The focus of this period is to enhance the carrier mobility of pentacene based OFETs. We will investigate molecules of an active layer aligned by rubbing or photoalignment on a nano-scale film (such as polyimide). Such materials must have photo-sensitive function groups in a polymer chain for photoalignment. Ion beam treatment offer the advantage that the material can be treated without any photo-sensitive function groups in a polymer chain. We will study various effects of rubbing, photoalignment and ion beam treatment the surfaces of alignment layers for pentacene based OFETs. Optical and optoelectronic measurements, including polarized Raman scattering, X-ray diffraction, atomic force microscopy, Fourier transform infrared ray spectroscopy, ultraviolet-visible spectroscopy, tunneling electronic microscopy, and semiconductor parameter analyzer will be used to characterize organic semiconductor surfaces, interface, and optoelectronic properties.

**Phase II (4 months, from November 1, 2004 to February 28, 2005)**
Conductivity, mobility and concentration of charge carriers are the prime factors, being tuned to improve the performance of OFETs assembly and evaluated. In this period, two targets will achieve. One is the molecular structure design of conducting polymers. The conformational change of conjugate polymers could exploit as an alternative approach to have high mobility. As it well known, the bandgap energies of conjugate polymers depend on their chain conformations. We expected the conformational transition of conjugate polymer chain from a “compact coil” to an “expanded coil”, leading to a concomitant increase in conductivity and mobility.

Another target is the modification in virtue of nano-scale polymer electrolyte film that renders active semi-conducting polymer doped/dedoped by ions. The on/off ratio of polymer field-effect transistors (PFETs) is a function of the doping level of conducting polymers. The doping level of conducting polymers might be due to in/out of ions provided by polymer electrolyte. In this period, we will fabricate the polymer based PFETs in which additional nano-scale polymer electrolyte is used to control ion doped/dedoped, and test in OFETs applications.

**Phase III (4 months, from March 1 to June 30, 2005)**

In this period, we will apply ion beam treated technology to PFETs. We treat polymer electrolyte by ion beam to align the polymer chains in the active layer for manufacturing PFETs. By the way, nano-scale polymer electrolyte will be also induced to control ions in/out pentacene based OFETs. The schematic cross section of field effect transistor is shown as following figures.
We expect some significant results of PFETs manufactured by treating polymer electrolyte via ion beam. Then final report having good results is expected.

Three finished papers

In the AOARD project, we have prepared three papers for the submission to
Applied Physics Letters. Two papers described the improvement of the field-effect transistor performance by ion beam treatment and insertion of nanoscale polymer electrolyte between dielectric layer (SiO₂) and channel material (poly(diphenylamine), PDPA). Ion-beam aligned silicon dioxide layers were found partially aligned the pentacene molecules and mobility was up to an order of magnitude greater than that of the controlled device. A polymer electrolyte, PDDA was employed to modulate the conductivity of conductive polymers and enable the conductive polymer to obey transistor operation. In the I-V characteristics, the source-drain currents were modulated over one order of magnitude by applying polymer electrolytes to OTFT based on conductive polymer.

Another paper described a polarized polymer light-emitting diode which can be constructed by employing poly(N-vinylcarbazole) (PVK) as an extra hole-transporting alignment layer which prevent the damages of hole-injected layer, poly (3,4 ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS), from the mechanical rubbing. By using a PVK alignment layer, a dichroic ratio of 25.7 (at 451 nm emission wavelength) was observed by finding optimum thickness of PF, such are highly polarized and enough to use an efficient light source of liquid crystal displays. The details can be referred to the following.

**Paper 1**

**Organic thin-film transistors with ion-beam-processed dielectric gate**
We have found that pentacene films can be aligned on a silicon dioxide surface bombarded to a low energy and neutral argon ion beam. Pentacene films of submicron thickness, deposited by molecular beam epitaxy, have been implemented into organic thin-film transistors and characterized using X-ray diffraction, polarized Raman spectroscopy and atomic force microscopy. Ion-beam aligned silicon dioxide layers were found partially aligned the pentacene molecules and mobility was up to an order of magnitude greater than that of the controlled device. The anisotropy in the mobility for the current flow perpendicular and parallel to the direction of the ion beam is equal to 2.4. A mechanism for this alignment is proposed.

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In recent years, organic semi-conducting materials have attracted much interest and have been demonstrated to be some of the most popular candidates for fabricating thin film transistors (TFTs). The performance of organic TFTs (OTFTs), characterized by such parameters as the field-effect mobility, modulated on/off current ratio and threshold voltage, varies with the molecular structure of the semiconducting film. The degree of molecular ordering and crystalline orientation of the organic thin film have been proven to affect significantly the performance of TFT devices.\textsuperscript{1,2} The transport efficiency of charge carriers - electrons or holes - is generally believed to increase with the molecular chain ordering or improve crystalline orientation. The orientation-controlled organic thin films have superior potential to enhanced mobility and provided more peculiar characteristics, \textit{i.e.} optical and electrical anisotropy. Anisotropic mobility is useful in isolating neighboring components to reduce the cross-talk effect in logic circuits or pixel switching elements in displays. Recently, several methods have been developed to align organic semiconducting films with anisotropic mobility, including mechanical stretching,\textsuperscript{3} liquid crystalline self-organization,\textsuperscript{4} rubbing\textsuperscript{5,6} and photoalignment.\textsuperscript{7,8}

In this study, an ion-beam (IB) alignment method, a non-contact alignment technique, is applied herein to align pentacene molecules. The so-called IB alignment method can generate an easy-orientation axis on the surface of the polymer (polyimide)
or diamond-like carbon in an liquid crystal (LC) cell upon bombardment by an argon ionic beam, as has been reported recently.\textsuperscript{9,10} LC in a bombarded region can be oriented parallel to the direction of the IB. Ion-beam alignment is a promising technology for aligning a variety of liquid crystals, especially in fabricating multiple domains using shadow masks. Pentacene is a rigid rodlike molecule that is similar to the core structure of an LC, so similar surface-induced order is expectable to be able to be imposed on it.

The pentacene films were prepared by molecular beam expitaxy as described elsewhere.\textsuperscript{7,8} The bottom-gate TFTs are fabricated with 3000 Å silicon dioxide (SiO\textsubscript{2}) dielectric layer and indium-tin-oxide (ITO) source-drain contacts. The SiO\textsubscript{2} films were then bombarded with an argon ion beam with energy of 600 eV at an incident angle of 45° to the plane of the substrate. Then, an IB-processed SiO\textsubscript{2} layer is used to control the orientation of pentacene, yielding films with conspicuously anisotropic mobility. A Keithley 4200-SCS semiconductor parameter analyzer was used to measure the electrical characteristics of the TFTs in a dark vacuum chamber.

Figure 1(a) shows the X-ray diffraction (XRD) pattern for a 100 nm-thick pentacene layer deposited onto a native SiO\textsubscript{2}. The peaks arise from the well-known “bulk” (00l) and “thin-film” (00l) phases of pentacene - with corresponding \(d\textsubscript{001}\)-spacings of 15.4 Å and 14.5 Å, respectively.\textsuperscript{11} The presence of only (00l) reflections but no other (hkl)
reflections indicated that all crystals in the film were oriented with their $(00l)$ planes parallel to the substrate. The XRD pattern of the pentacene film grown on an IB-processed SiO$_2$ surface was shown in Fig. 1(b). The pattern exhibits a strong Bragg reflection including only one “thin-film” phase. The average crystalline domain size, $T_{hkl}$, perpendicular to the $(00l)$ planes and the degree of structural disorder, $g_{II}$, were evaluated from the half width of the diffraction peaks according paracrystal theory$^{12}$ as described in detail elsewhere.$^7,8$ The obtained $T_{hkl}$ and $g_{II}$ for pentacene film grown on IB-processed SiO$_2$ were 287 Å and 1.08%, respectively. In contrast, the smaller $T_{hkl}$ of 230.9 Å and the worse $g_{II}$ of 1.38% for pentacene film directly grown on the native SiO$_2$. The atomic force microscope images [the insert of Fig. 1(b)] show that the pentacene film was partially orientated such that its elongated grains grew perpendicular to the direction of the incident IB [as shown by the arrow in the insert of Fig. 1(b)]. For comparison, a typical pentacene film grown directly on a native SiO$_2$ contains mostly disordered isotropic grains, as depicted in the Fig. 3(b) of Ref. 8. Therefore, bombarding a SiO$_2$ alignment layer with an IB of appropriate energy could dramatically increase the structural ordering of the pentacene molecules. These features indicate that the pentacene film grown on IB-processed SiO$_2$ surface exhibited partial ordering and comprised large crystals with a better crystalline quality than that grown on the native SiO$_2$. 
Figure 2(a) shows the polarized micro-Raman spectrum measured with \( y(x,x)y \) geometry: the polarizations of the laser beam and the collected Raman signals were perpendicular to the incident IB direction. The Raman peak at 1158 cm\(^{-1}\) originates from the in-plane molecular vibration of pentacene, as depicted in the insert of Fig. 2, while the peak at 1155 cm\(^{-1}\) represents the out-of-plane vibration perpendicular to the molecular axis on both sides of the pentacene molecule.\(^\text{13,14}\) Partial alignment of pentacene molecules prevents these two peaks, at 1155 cm\(^{-1}\) and 1158 cm\(^{-1}\), from being completely separated. Notably, the intensity of the Raman peak at 1155 cm\(^{-1}\) exceeds that of the peak at 1158 cm\(^{-1}\), since the electric field of the incident laser beam markedly enhances the atomic motion perpendicular to the molecular axis on both sides of the pentacene molecule. This observation implies that the axis of the molecule was aligned perpendicular to the polarizations of the laser beam and parallel to the incident IB direction.

When Raman scattering was performed with \( y(z,z)y \) geometry\(^\text{8}\) [Fig. 2(b)], the polarizations of the laser beam and the collected Raman signals were parallel to the incident IB direction. The peak intensity at 1155 cm\(^{-1}\) apparently decreases compared with that in Fig. 2(a) and that of both peaks, at 1155 cm\(^{-1}\) and 1158 cm\(^{-1}\), are almost the same, because the in-plane vibration of pentacene molecule has components in both the \( x \) and the \( z \) directions. This result reveals that the laser beam polarized along the
molecular axis or parallel to the incident IB direction did not enhance any particular atomic motion. While pentacene films typically grow on native SiO$_2$ surface the lack of an alignment layer prevented from the features associated with the in-plane and out-of-plane molecular vibrations from being resolved by varying the polarizations of the laser beam; the peaks at 1155 cm$^{-1}$ and 1158 cm$^{-1}$ were much less intense than those from the sample with an IB-bombarded dielectric layer [as in, for example, Fig. 5 of Ref 8]. The Raman spectra again demonstrated that the pentacene molecules were partially aligned using IB bombardment, and that the preferred alignment of pentacene molecules was parallel to the incident IB direction that had bombarded on the gate dielectric layer.

Figure 3 show the output current-voltage ($I$-$V$) characteristics of the three pentacene transistors at gate-source voltage ($V_{GS}$) of -80 V. The device had lower output current of only 3 $\mu$A at $V_{GS} = -80$V in the control sample (in which the pentacene film was deposited directly on top of the native SiO$_2$ without IB-processed). Field-effect mobility ($\mu$) of the control sample was about 0.02 cm$^2$/Vs that determined from transfer electrical characteristics in saturation regime. When the device whose IB-direction was perpendicular to the current flow shows a saturation that is almost 15 times larger than that of the control device. The calculated saturation mobility, $\mu_{\perp}$, is 0.14 cm$^2$/Vs. However, when the grains of the pentacene are partially orientated
perpendicular to the current, and the IB direction is parallel to the current, the device exhibited a lower saturation current (~8.38 μA) and the mobility, $\mu_{//}$, of 0.063 cm$^2$/Vs. The anisotropic ratio of the mobility, $\mu_{\perp}/\mu_{//}$, is in the range of 2.19 to 2.39. The electric anisotropy was interpreted by performing a morphological study, as presented in the insert of Fig. 1(b): inducing alignment in the pentacene films established a preferential direction along which some of the grain boundaries were eliminated.

In summary, ion-beam alignment was used successfully to generate pentacene transistors with anisotropic electrical characteristics and carrier mobility that was an order of magnitude larger than that of typical devices in which pentacene was grown directly on the native SiO$_2$ surface. The nano-structure of the grooves was responsible for elongated grains of pentacene perpendicular to the incident ion-beam. To our knowledge, these results first demonstrate that the IB alignment method is useful for preparing partially ordered organic semiconducting films with anisotropic electrical characteristics. We believe that further optimizing the IB alignment conditions in OTFTs would increase the mobility and the anisotropic electrical characteristics, and may thereby improve devices for use in circuit applications.

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Figure captions

Fig. 1 X-ray diffraction patterns from pentacene thin films deposited on surface of: (a) a native SiO₂; (b) an ion-beam-processed SiO₂. Insert of (b), corresponding AFM image of pentacene film deposited onto the surface of an ion-beam aligned silicon dioxide. The arrow shows the direction of the ion-beam.

Fig. 2 MicroRaman spectra of the C-H bending vibration of the pentacene film measured at two polarization conditions. The direction of ion-beam bombardment is parallel to the z-axis.

Fig. 3 Drain-source current – drain-source voltage characteristics of three pentacene OTFTs. The up and down triangles indicate the data from devices with ion-beam aligned SiO₂ layers, in which the alignment directions of the ion-beam are perpendicular and parallel to the direction of the flow of current in the channel, respectively, while the circles represent the data from the device without the ion-beam processing.
Fig. 1

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Fig. 2

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Fig. 3
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High Luminescence Polarized Polymer Light-Emitting Diodes Using Aligned Polyfluorene

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Abstract

We have successfully constructed a polarized polymer light-emitting diodes (PLEDs) by employing poly(N-vinylcarbazole) (PVK) as an extra hole-transporting alignment layer which prevent the damages of hole-injected layer, poly (3,4 ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS), from the mechanical rubbing. The maximum luminance efficiency 0.31 cdA⁻¹ of blue polarized PLED fabricated with the aligned polyfluorene (PF) layer is obtained. The brightness is approaching 1000 cdm⁻² at relatively low biased voltage. By using a PVK alignment

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layer, a dichroic ratio of 25.7 (at 451 nm emission wavelength) was observed by finding optimum thickness of PF, such are highly polarized and enough to use an efficient light source of liquid crystal displays. In addition, the spectrum of photon emission is narrow, characterized by its full width at the half maximum value.

Conjugated polymers are amorphous semiconducting materials with long-chain molecular structures and used for the applications of organic electronic devices like polymer light-emitting diodes (PLEDs),\textsuperscript{1,2} thin-film transistors\textsuperscript{3} and photovoltaic cells.\textsuperscript{4} However, the morphology of polymer films depend on the changes by the processing conditions. Aggregations, orientations, alignment directions, and packing conditions of the polymer chains are the few parameters that influence the stacking of \( \pi \)-electron clouds and alter the electrical and optical properties of polymer electronic devices.\textsuperscript{5} Therefore, Grell \textit{et al.}\textsuperscript{6-8} had successfully developed a rubbing process to enable the alignment of the polymer chains and observed the polarized emission from PLEDs. We regard PLEDs with the polarized electroluminescence (EL) is of great potential to be the efficient backlighting source for liquid crystal display (LCD). For the conventional LCD, 50 \% of the backlight was lost by the polarized filters.\textsuperscript{9}

In order to control the packing directions of polymer chains, the active layer of
PLED is spin-cast from its solution on a pre-aligned substrate. The details for the fabrication of above processes can be found elsewhere.\textsuperscript{6} Generally, polyimide (PI)\textsuperscript{10} layer was used as the alignment layer to manipulate the direction of molecular chains for active layer. However, the EL efficiency is poor because PI is an insulated material.\textsuperscript{8,9} Therefore, a hole-transporting alignment layer is used to integrate the function of both hole-transport and alignment properties.\textsuperscript{11,12} Poly(N-vinylcarbazole) (PVK) polymer with carbazole group is considered to be a good candidate for the above purpose.\textsuperscript{13,14}

Polyfluorene (PF) is a conjugated liquid-crystalline polymer with rigid rod/flexible spacer, which allows the rearrangement of molecular chain after achieving monodomain alignment.\textsuperscript{6,15-17} The uniaxial molecular alignment in a solid film can be achieved by the underneath alignment layer upon the thermal annealing. PF has been proved to be in highly oriented configurations in polarized device by aligning PI and poly(\textit{p}-phenylenevinylene). Neher et al.\textsuperscript{18} have quantified the emission profile in polarized device and discussed the recombination zone is independent of the device thickness. Herein, we employ PVK as an extra hole-transporting alignment layer to prevent the damages of hole-injected layer\textsuperscript{19}, poly (3,4-ethylenedioxythiophene)-poly (styrene sulfonate) (PEDOT-PSS), from the mechanical rubbing. The maximum luminance efficiency of blue polarized PLED fabricated with the aligned PF layer
reaches 0.31 cdA\(^{-1}\) at 10 mA. The brightness is higher than 1000 cdm\(^{-2}\) at relatively low biased voltage. The performance of the polarized PLED is closer to that of the device (0.53 cdA\(^{-1}\) at 10 mA) without rubbing the PVK layer. By using an extra PVK alignment layer, a dichroic ratio of 25 was observed while the polarized PLED was biased at 2 mA a brightness of 150 cdm\(^{-2}\) was noted.

Details of the synthesis and characterization of PF derivative in study is obtained from Eternal Company, Taiwan. PVK (Aldrich) and PEDOT-PSS (Baytron P, AI4083, Bayer) were used without any treatment. For fabrication of PLED devices, glass substrates pre-patterned indium tin oxide (ITO) electrode was subsequently cleaned. A 40 nm layer of PEDOT-PSS was coated onto top of the substrate and dried in clean room for 30 min as the hole-injected layer. PVK was used at a total solid content 0.8 % in 1,2-dichlorobenzene solvent at a spinning speed 4000 rpm onto the surface of PEDOT-PSS layer. After 30 min soft bake at 60 °C, the PVK thin film (58 nm) was rubbed in uniaxial direction using a rubbing machine. The rotating cylinder was covered cloth and each device was rubbed twice under the cylinder. Then, PF film prepared with p-xylene was treated with thermal annealing at 70 °C for 1 hr, after spin-coating at various speeds onto PVK alignment layer to get the film thickness of 34, 45, 60 and 76 nm. The top electrode was deposited by thermal evaporation at a pressure about 10\(^{-6}\) torr at rate of 1 Å/s for Ca electrode (600 Å) and 3 Å/s for Al
electrode (1200 Å). The current-brightness-voltage ($I$-$L$-$V$) measurements were carried by the keithley 2400 source measure units and keithley 2000 digital multimeter along with a silicon photodiodes, calibrated by Minolta LS-100 luminous meter. Photoluminescence (PL) and EL spectra were obtained by Perkin Elmer LS55 luminescence spectrometer with a remote fiber optic accessory. All experimental record was in nitrogen surrounding glove box.

The device configuration for polarized PLEDs involved in this study is presented in the inset of Figure 1(b). Figure 1(a) shows the $I$-$L$-$V$ curves of the devices with various thicknesses of PF films. The threshold voltage for charge injection was less than 3 V (right axis) and the light turn-on voltage was around 4.0 V (left axis) for the devices. From the inset of Figure 1(a), it can be noticed that device was found to have a larger leakage current and lower EL when PEDOT-PSS layer alone was used. We attribute the poor device performance to the scratch damages of PEDOT-PSS layer generated from the rubbing process. Moreover, aligned and non-aligned PF films with a thickness 60 nm showed a luminance of 1200 cdm$^{-2}$ at 7 V. Such a result indicated that the rubbing process in hole transport PVK layer did not lower the performance of the PLEDs. At an operating voltage of 7 V, the devices with various thickness (75 nm, 45 nm and 34 nm) of PF film showed a varying luminance (368, 700 and 150 cdm$^{-2}$, respectively). Most of these rubbed devices, the leakage current was still larger but the
efficiency was greatly improved due to the modification that we have made in the
device configuration. The thickness of PF as 34 nm was too thin to recombine
effectively electron-hole pair in the active layer. The luminance efficiency, 0.05 cdA⁻¹,
was the lowest among the polarized PLEDs, as shown in Figure 1(b).

PF films alignment was investigated using polarized PL measurements which
were made by use spectrometer equipped with a highly dichroic polarizer. The PL
spectra were measured with the polarizer aligned parallel and perpendicular to the
rubbing direction. Table I shows the results of PL measurements. The ratio of the PL
emission parallel to the rubbing direction to that perpendicular increases with a
decrease in film thickness of PF for the peak at 430 nm. The dichroic values increase
with decreasing the film thickness of PF, indicating that there can be improvement in
the degree of uniaxial alignment for PF with the surface of the conducting PVK layer.
The highest dichroism in PL observed with the device having 34 nm PF film was due
to emission occurring from the most highly oriented segments of the polymer in the
region near the interface between the PF and PVK. Accordingly, the maximum PL
dichroic ratio was evaluated as 5.5 at 458 nm for 34 nm PF film.

The device features and performance data at 2 mA for all PLEDs was analyzed by
the same polarizer used for the polarize PL measurement in a dry, nitrogen filled glove
box. The polarized EL spectra display in Figure 2 in terms of the emission intensity
parallel (I ||) and perpendicular (I⊥) to the rubbing direction for 45 nm thick PF film. The EL dichroic ratio, I / I⊥, had a maximum value of 25.7:1 at the 451 nm peak wavelength. Across the EL spectra range from 400 to 540 nm, the ratio of the integrated intensities of parallel to perpendicular polarized light was evaluated as 26.2:1 and the device performance with luminance efficiency of 0.31 cdA⁻¹ at a current of 10 mA measured without polarization analysis. The emission is blue for PF but its spectral is somewhat different from that of the standard EL spectra without alignment process. The peak at 451 nm and the longer wavelength shoulder match features in Figure 2, but the maximum 433 nm peak of standard PLED is weaker and peak is generally less well resolved in polarized EL spectra. We also note the highest polarized PLED device reported here reach a high brightness of 700 cdm⁻² which is suitable as the backlight in liquid crystal (LC) display with the advantages of easy process and compatibility with LC fabrication.

Table I reveals an interesting phenomenon in which the degree of dichroism observed in EL is higher than that observed in PL. Pichler et al.²⁰ reported the conjugated polymers can be aligned by alignment layers within a thin boundary region whose thickness corresponds to the interchain correlation length, so a PVK alignment layer could somewhat enhance the order parameter of the PF film within a similar distance of its surface. Because of polarization light of PL contributed mainly from the
region near the alignment layer, the dichroic ratio measured from PL increases with decreasing the thickness the PF film. The maximum dichroism of PL is 5.5 at a thickness of 34 nm. For PLEDs, we regarded the recombination region for electrons and holes are confined at PF film that is close to the interface of PVK/PF layers. Therefore, the EL was expectedly generated from the aligned PF region, resulting in the enhanced dichroic ratio. In Table I, the dichroic ratio of EL increase with the decrease of the thickness of PF film, however, dichroic ratio is only 1.5 at 34 nm because of poor EL performance.

Organic light emitting diodes with $\pi$-conjugated molecules have the advantage of color tuneability and hence they can be used to build full-color displays. Nevertheless, there is also a drawback of very broad emission spectrum that is caused by the vibrational and rotational motions of atoms inside the $\pi$-conjugated molecules. Typically, the full width at half-maximum (FWHM) of emission spectrum is ranging 50 to 100 nm. The FWHM of our polarized and non-polarized PLEDs are 41 and 47 nm, respectively, as shown in Figure 3. We note that smaller FWHM in polarized PLEDs without respect to parallel, perpendicular to rubbing directions was due to uniaxial alignment of polymer chain reducing the random vibrational motion of atoms inside the $\pi$-conjugated molecules. Further work is in progress to improve the electrical performance of the polarized EL and to narrow the emission spectrum by use
of various alignment methods.

In summary, we have successfully constructed polarized PLEDs using the rubbed PVK films to make excellent alignment layers for the blue light-emitting PF. The necessary uniaxial polymer chain alignment was accomplished by spin-coating PF onto a PVK conductive alignment layer. The hole transporting properties of the PEDOT-PSS and rubbed PVK double layer allow construction of highly polarized and bright blue PLEDs and the PL and EL dichroic ratios increase with a decreasing film thickness of PF. For an emission peak at a current density of 33 mA/cm$^2$, a polarization ratio of up to 25.7, an integrated polarization ratio of up to 26.2, and a luminance efficiency of 0.31 cdA$^{-1}$ have been completed through optimization of the PF layer thickness. To our knowledge, the 45 nm thick aligned PF film emits a polarized luminance approaching 1000 cdm$^{-2}$ which is the highest brightness for polarized PLED. Such highly polarized and luminant PLEDs are enough to use an efficient light source of liquid crystal displays. In addition, the spectrum of photon emission is narrow, characterized by its full width at the half maximum value, for the aligned PF film because of reducing of the random vibrational motions of atoms in $\pi$-conjugated molecular chain.

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Reference


Figure captions

FIG. 1. (a) $I-L-V$ curves of the devices containing PF thickness: 76 nm(□), 60 nm(○), 45 nm(■), and 34 nm(▲) on the rubbed PVK layer surface that compared to standard device(●). Inset: $I-L-V$ curve of 60 nm thick PF film on the rubbed PEDOT without PVK layer. (b) The luminescence efficiency versus current for the devices with PF thickness: 76 nm(□), 60 nm(○), 45 nm(■) and 34 nm(▲) on rubbed PVK layer and compared to standard device(●) and rubbed PEDOT without PVK(●). Inset: The device structure of polarized PLED.

FIG. 2. Electroluminescence spectra of ITO/PEDOT/PVK (58nm)/PF/Ca/Al device were measured with parallel (solid line) and perpendicular (dash line) to the rubbing direction: mechanical rubbed PVK/PF (45nm).

FIG. 3. Normalized electroluminescence spectra for standard ITO/PEDOT/PVK/PF/ Ca/Al device (solid line) and rubbed PVK for polarized devices (dash line).
Figure 1, Chung et al.
Figure 2, Chung et al.
Figure 3, Chung et al.
Table I. The features and performances of PLED devices. (Dichroic ratio is defined as $I_{PL}/I_{EL}$, in which $I_{PL}$ and $I_{EL}$ are the luminescent intensity measured parallel and perpendicular to the rubbing direction).

<table>
<thead>
<tr>
<th>Device</th>
<th>Thickness of PF (nm)</th>
<th>Dichroic ratio PL ($\lambda_{\text{max}}$)</th>
<th>Dichroic ratio EL ($\lambda_{\text{max}}$)</th>
<th>EL (Integrated)</th>
<th>Charge injection voltage (V)</th>
<th>Luminance efficiency$^{[b]}$ (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>76</td>
<td>1.6</td>
<td>2.3</td>
<td>3.2</td>
<td>2.7</td>
<td>0.32</td>
</tr>
<tr>
<td>B</td>
<td>60</td>
<td>1.9</td>
<td>10.2</td>
<td>10.3</td>
<td>3</td>
<td>0.52</td>
</tr>
<tr>
<td>C</td>
<td>45</td>
<td>3.3</td>
<td>25.7</td>
<td>26.2</td>
<td>2.9</td>
<td>0.31</td>
</tr>
<tr>
<td>D</td>
<td>34</td>
<td>5.5</td>
<td>1.5</td>
<td>1.5</td>
<td>2.7</td>
<td>0.05</td>
</tr>
<tr>
<td>E</td>
<td>60</td>
<td>1</td>
<td>1</td>
<td>1.02</td>
<td>2.8</td>
<td>0.53</td>
</tr>
<tr>
<td>F</td>
<td>60</td>
<td>1</td>
<td>1</td>
<td>1.03</td>
<td>3.5</td>
<td>0.22</td>
</tr>
<tr>
<td>G</td>
<td>60</td>
<td>2.2</td>
<td>2.5</td>
<td>2.6</td>
<td>4.0</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$^{[a]}$ The concentration and spin rate of PF on the twice rubbed PVK are 3 % and 3000 rpm for device A, 2.5 % and 3000 rpm for B, 2.5 % and 4000 rpm for C, 2.5 % and 5000 rpm for D, respectively. Standard device without any rubbing treatment for device E. Without PVK layer, PF 2.5 % with 3000 rpm on the twice rubbed PEDOT for device G and non-rubbed for F. $^{[b]}$ Luminance efficiency was obtained at a current of 10 mA.

Table 1, Chung et al.

**Paper 3**

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Electric-field induced ion-doped metal-insulator transition in the aniline derivatives, poly(dipheneamine) for the application in polymer field effect transistor

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Abstract

In recent, a single semiconducting polymer is applied to organic thin film transistors (OTFT) usually. In this work, we applied the polymer electrolytes to modulate the conductivity of conductive polymers and enable the conductive polymer
to obey transistor operation. In the I-V characteristics, the source-drain currents were
modulated over one order of magnitude by applying polymer electrolytes to OTFT
based on conductive polymer.

Much progress has been made in recent years in the field of organic thin-film
transistors motivated by the numerous advantages that organic materials can offer,
including low cost processing, mechanical flexibility, and easy property tuning by
structure modifications. These properties make them ideal materials for large area or
low cost disposable electronic products, such as identification tags, smart cards, and
electronic papers.

Many small organic semiconductors are rather rigid and planar structures, which
are generally insoluble to be incorporated into electronic devices. Polymers have
longer molecular chains, which are alternatives for solution processing. However, most
conducting polymers such as polyaniline are still insoluble owing to the stiffness of its
backbone, restricting its further applications. One approach to increase the solubility is
to modify the conducting polymer structure. Poly(diphenylamine), (PDPA) is the
derivatives of polyaniline and shows excellent solubility in common organic solvents.
Also, its structure is closed to the famous hole transporting materials, N, N-diphenyl-N,
N’-bis(3-methylphenyl)-[1,1’-biphenyl]-4-4’-diamine (TPD) and N,
N’-bis(i-naphthyl)-N, N’-diphenyl-4,4’-diamine (NPB) for application in organic light
emitting diodes. This prompted us to use PDPA as the channel material for
fabrication of polymer thin film transistor.

Brown and co-worker reported that the mobility of soluble polythiophene can be
increased by doping the conjugate polymer. The increased mobility is accompanied by an equivalent increase of the conductivity. The mobility-conductivity relationship can be described by a simple power law, $\mu \propto \sigma^\delta$, with $\delta$ around 0.7. Chen et. al.\textsuperscript{7, 8} made the electrochemical transistors by using PEDOT-PSS and reported that the conductivity switching has been successfully utilized in a low-voltage operating all-organic electrochemical transistor and electrochemical devices. Polymer electrolytes have been previously studied for application such as batteries, supercapacitors, and solid-state voltammetry.\textsuperscript{9, 10} The possibility of using a polymer electrolyte to gate a transistor was demonstrated over a decade ago for redox-active semiconductors, such as polythiophene\textsuperscript{11, 12} and polyaniline\textsuperscript{13}, as well as for p-type crystalline silicon.\textsuperscript{14} More recently, two groups have reported carbon nanotubes field-effect transistors gated and doped by polymer electrolytes.\textsuperscript{15, 16} According to their results, an additional nano-scale polymer electrolyte, poly(diallyldimethylammonium chloride) (PDDA) is introduced to provide ions in/out conducting polymers and control the electronic performance.

A schematic structure of the FET device configuration and polymer structure in this work are shown in Fig. 1. Device fabrication began with a thin film Al (~1000Å) coated on the backside of the SiO$_2$/Si substrate as the gate electrode. In the front side, the polymer electrolyte PDDA and PDPA were spun on the SiO$_2$ layer. A thin gold layer was coated by sputter through a shadow mask to define source and drain pattern. The channel length of this mask is 50 μm, and the area of source or drain is 2 × 2 mm$^2$. All devices were characterized in air, at room temperature. A representative plot of drain current, $I_D$, versus source-drain voltage (source is always grounded), $V_D$, is shown in Figure 2 as a function of the applied gate voltage, $V_G$, for a PDPA channel in a top contact FET configuration (Figure 1). The $p$-channel FET operates in an enhancing model upon application of a negative bias to the gate electrode, as the
concentration of holes contribution to $I_D$ increases. As can be seen that the device shows the leakage currents when $V_D$ is around 40 V without gate voltage applied. These leakage currents are attributed to the impurities in the silicon substrate. The evidence can be observed from the high resolution microscopy image (Figure 3). Several small spots exist in the silicon substrate. The charge carriers can be flowed through these small spots when no gate bias is applied to the device and lead to the leakage currents.

The observation of filed effect in conducting materials is an entirely unusual phenomenon as due to large density of charge carriers in conductors, the electric filed should be screened on the atomic scale and not penetrates in the sample at all. For conducting polymers, the charge concentration may be up to $\sim 10^{20}$ cm$^3$ and the Debye length could be a few nm. However, the charge transport in the conducting polymers is not that of a simple metal. It was suggested$^{17,18}$ that these conducting polymers are close to insulator-metal transition (IMT). There is a general consensus that the IMT is an Anderson disorder-driven localization-delocalization transition. In the approach to get high conductivity of conducting polymers, doping process should be involved for compensate the positive charge and delocalize the free charge carries from the main chain of conducting polymers. The large discrepancy of mobilities between the undoped and doped state is obvious. This fact is presumably derived from the polymer conformations. In the present study, a nanoscale polymer electrolyte (PPDA) is employed to insert between dielectric layer (SiO$_2$) and undoped conducting polymer (PDPA). The additional nanoscale polymer electrolyte can provide anions to compensate the positive charge under the electric field. In the present study, we can observe the maximum value for $I_D$ is $\sim 135 \ \mu A$ at $V_D = + 100$ V. Best on our knowledge, the $I_D$ current is always less than 100 $\mu$A with using conducting polymer (such as
polyaniline and polypyrrole) as channel materials for the applications in FETs. The large maximum value of $I_D$ is restatement of the fact that undoped PDPA has increased its conductivity by doping Cl$^-$ anions from PDDA under electric field.

In order to confirm the role of PDDA in the device, a device structure without PDDA layer was included to compare the electric performance of the devices. Figure 4 present the $I_D$ vs. $V_D$ plots for both devices. Obviously, the $I_D$ current of PDPA/PPDA is much higher than the device without PDPA. Bao et. al. have been mentioned that a mixture of poly(ethylene oxide) with lithium chloride or lithium trifluoromethane sulfonate with a conducting polymer such as poly(3-hexylthiophene) showed very low conductivity and no transistor behavior. In comparison with PDDA and PEO containing salts, the difference is the single mobile ions of PDDA. The pendant positive ions along polymer chain did not migrate to PDPA in comparison with two mobile ions of PEO-salt system under electric field. Based on this observation, we propose that these materials undergo ion-assisted electrochemical doping during transistor operation. Under normal operating conditions, the undoped PDPA at the semiconductor/electrode interface is reduced during charge injection. The charge transport is realized by the “hopping” along the main chain of PDPA. However, the undoped PDPA seems to the insulator in spite of the $V_G$ applied. In comparison with the traditional polymer field effect transistor, the addition of PPDA provides Cl$^-$ anions to dope with PDPA under a double layer of opposing charge. The concentrations of Cl$^-$ anions can be modulated by the applied gate voltage. With increasing $V_G$ voltages (from 0 V to -100 V), the concentrations of Cl$^-$ doped with PDPA is increased which leading to increase the conductivity of PDPA and shows the enhancement of $I_D$ current. Also, the I-V characteristic of the device is investigated at atmosphere condition without any sealing to avoid the moisture. Generally, H$_2$O and O$_2$ will be adsorbed on
the organic film just like OLED.\(^{21,22}\) Qie, et al\(^{23}\) also reported that the effect of H\(_2\)O on the stability of pentacene based organic field effect transistors. For the present study, the I-V characteristics of the device did not affect by the H\(_2\)O and O\(_2\). The reason might be related to the insertion of PPDA between SiO\(_2\) and PDPA layers. The mobile ions (Cl\(^-\)) can be easy migrated to PDPA under moisture and electric filed conditions and dispel the effect of H\(_2\)O.

**Acknowledgements:**

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**References**


Figure Captions

FIG. 1. Schematic diagram of FET and chemical structures of PDDA and PDPA. Layer
thickness are as follows: 100nm of gold for the electrodes (source and drain), for the spin-coated PDDA and PDPA, 250nm of SiO$_2$, 100nm of aluminum for gate.

FIG. 2. Current-voltage characteristics of polymer thin film transistor based on PDDA/PDPA.

FIG. 3. The defect of the dielectric layer which cause the leakage current for the polymer-field effect transistor.

FIG. 4. Current-voltage characteristics of polymer thin film transistor based on (a) PDDA/PDPA (b) PDPA.
Figure 1, Lin et al.
Figure 2, Lin et al.
Figure 3, Lin et al.
Ids (μA) vs. Vds (V) for different VG voltages: VG = 0V, VG = -20V, VG = -40V, VG = -60V, VG = -80V, VG = -100V.

Figure 4, Lin et al.