Interfacial Morphology in Polymer Light-Emitting Diodes

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This work considers the anode at the indium-tin oxide (ITO)/poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) interface in polymer light-emitting diodes (PLEDs). The surface morphology of ITO is studied by scanning probe microscopy (SPM). The mechanical properties of ITO and MEH-PPV are measured by nanoindentation. The results indicate that the surface roughness, defined as the root-mean-square of the surface height on the surface of the ITO substrate, influences the injection of hole-carriers. The injected current is dominated by the tunneling of hole-carriers at the low bias. Increasing the effect contact area at the ITO/MEH-PPV interface lowers the barrier to the injection of holes through the ITO anode to the MEH-PPV light-emitting layer.

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Organic light-emitting diodes (OLEDs) have attracted much attention because they exhibit high efficiency and high brightness. Their high efficiency results from the effective recombination of oppositely charged carriers, and their high brightness is due to the effective injection of both types of carrier. Recent investigations of the device efficiency have focused on the improvement of either the fabrication process or the materials. However, increasing evidence demonstrates an urgent need to understand the effects of interface morphology.

PLEDs in the bilayer configuration exhibit enhanced injection of charge carriers and high luminous efficiency as reported by Tang et al. In 2001, Guo et al. presented a template active surface process (TAS). They compared the surface topographies formed by TAS and the spin-coating processes. The results revealed the importance of interface topography to device performance. He et al. reported that the root-mean-square (Rq) roughness of the indium-tin oxide (ITO) surface affects device efficiency. Yang et al. reported the fabrication of highly efficient polymer LEDs (PLEDs) using an interfacial layer to modify the cathode interface. These investigations indicated that device performance is directly related to the formation of a suitable contact interface. In this study, PLEDs were fabricated with various ITO surfaces to examine the influence of the contact interface on the ITO/conjugated polymer interface. The surface contact mechanics on the microscale are reported to elucidate the relationship between the surface topography of the ITO anode and the device performance.

The device configuration herein consists of a prepatterned ITO/glass substrate as the anode, poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) as the light-emissive layer, and an aluminum (Al) electrode as the cathode. The MEH-PPV polymer layer was spin-cast onto the ITO/glass substrate from its toluene solution (concentration was 0.8 mg/cm³). Subsequently, the Al metal electrode was thermally evaporated on the substrates inside a vacuum chamber at 4 × 10⁻⁶ Torr. The current density-voltage (J-V) characteristics were obtained using a Keithley 2400 source meter. The luminescent intensity was obtained using a Konica Minolta LS100 luminosity meter.

Potassium hydroxide (KOH)/isopropyl alcohol solution (35 wt %) was used to etch the ITO/glass substrate and create various topographies. Table I summarizes the Rq roughness on the ITO/glass surface and the total effect contact area at ITO/MEH-PPV layer for samples A–C and the barrier height extracted from devices made of samples A–C. In this study, sample A was etched ITO/glass substrate for 20 min by KOH, sample B was etched for 30 min, and sample C was etched for 40 min. The Rq roughness of the etched ITO/glass substrates was determined using an atomic force microscope (AFM, Veeco) in tapping mode and is shown in Fig. 1.

Microscopically, the surfaces of the solid films are rough. The area of effect contact between two substrates or films is only a portion of the apparent contact area. Hence, the morphology of the interface results in contact impedance. Because the charge carriers in the operated PLEDs were injected through the contact interface, the interface morphology determined the efficiency of carrier injection.

Several mechanical properties of ITO and MEH-PPV layers, including hardness, Young’s modulus, and Poisson’s ratio, must be known to calculate the effect contact area between the ITO/glass anode and light-emitting polymer layer (MEH-PPV in this study). The depth-sensing technique of nanoindentation was employed to measure the material’s hardness and Young’s modulus. The average hardness of ITO was calculated to be 11.16 GPa and the average Young’s modulus was 126.75 GPa. The mean hardness of MEH-PPV was 3.7 GPa and the mean Young’s modulus was 88.55 GPa. The nanoindentation was made by Hysitron. These obtained values were substituted into Eq. 1

$$\frac{1}{E_i} = \frac{(1 - v_i^2)}{E_i} + \frac{(1 - v_f^2)}{E_f}$$

where $E_i$ is the reduced elastic modulus for film and indenter, $E_f$ is Young’s modulus of the thin film, $v_i$ is the Poisson’s ratio of the thin film, $E_f$ is Young’s modulus of the indenter, and $v_f$ is the Poisson’s ratio of the indenter ($\sim 0.2$). The Poisson’s ratios ($v_f$) of ITO and MEH-PPV were 0.2 and 0.3, respectively.

The density of aluminum was 3.96 g/cm³. The thickness of the evaporated aluminum on the device was 200 nm, and the diode area was 0.32 cm². The mass of the aluminum cathode was calculated to be 2.5 × 10⁻⁶ kg. Because the weight of the MEH-PPV film was negligible as compared to that of aluminum, the loading on the ITO film can be regarded as 2.5 × 10⁻⁶ kg. A surface-contact mechanics model was utilized to characterize the contact area between the ITO and the MEH-PPV film to understand easily the effects of contact areas and surface roughness on the barrier height of the MEH-PPV films. In this model, given the average separation of the surfaces, the total effect area of contact ($A_e$) is rewritten as

<p>| Table I. The Rq roughness on the ITO/glass surface and the total effect contact area at ITO/MEH-PPV layer for samples A–C, and the barrier height extracted from devices made of samples A–C. |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rq (nm)</td>
<td>5.58</td>
<td>5.24</td>
<td>5.17</td>
</tr>
<tr>
<td>Contact area $\times 10^{-3}$ (cm²)</td>
<td>7.21</td>
<td>6.80</td>
<td>7.17</td>
</tr>
<tr>
<td>Barrier height (eV)</td>
<td>0.12</td>
<td>0.14</td>
<td>0.13</td>
</tr>
</tbody>
</table>

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where $N$ is the total number of asperities, $A$ is the contact area of an asperity deformed elastically, $d$ is the separation obtained from the asperity heights, $\varphi(z)$ is asperity height measured from the mean of asperity heights, and $\omega$ is interference ($z - d$). The asperity distribution is assumed to be isotropic and the radius of curvature of an asperity is constructed by a uniform spherical. Because the contact behavior between ITO and MEH-PPV film is mainly elastic deformation, the result of the contact is comparable to that given by the model presented by Greenwood and Williamson. The total effect contact area of samples A–C was calculated from Eq. 2 and summarized in Table I. However, $R_q$ roughness is decreased with increased etching time of ITO/glass substrates. The surface topographies of ITO/glass samples with different etching times probably result in the difference on the calculation of the total effect contact area.

Figure 2 displays the log $J$–log $V$ plot of devices made of the ITO/glass substrates with different etching conditions (samples A–C). The log $J$–log $V$ curves at the low-voltage regime ($<2.0 \, \text{V}$) demonstrate that the current densities of the devices are related to the $R_q$ roughness of the ITO surface. The $R_q$ roughness and the device current density ($<2.0 \, \text{V}$) show a tendency to decline with increased etching time of the ITO/glass substrates. Presumably, the $R_q$ roughness of the ITO surface is an important parameter to influence the injection of charge carriers through the ITO/glass anode at the initial and the low-bias regime. The charge carriers tend to be easily accumulated on the tops of the contact peaks and probably are responsible for tunneling through the contact points.

Fowler–Nordheim (F-N) tunneling theory was used to understand the tunneling of charge carriers\textsuperscript{14,15}

\begin{equation}
J \propto E^2 \exp\left(-\frac{\kappa}{E}\right)
\end{equation}

In Eq. 3, $J$ is the current density, $E$ is the electric-field strength, and $\kappa$ is a parameter that depends on the barrier shape. Due to the much smaller injection barrier height of holes through the ITO/glass anode than that of electrons from Al cathode, the straight-line ln($J/E^2$) vs $1/E$ curves (samples A–C) as presented in Fig. 3 indicate that the holes are injected into the MEH-PPV layer through the tunneling
process at the beginning of charge injection and are the dominant charge carriers.

The charge carriers (holes) are assumed to tunnel through a triangular barrier at the polymer interfaces; the constant $\kappa$ in Eq. 3 is given by

$$\kappa = \frac{8\pi \sqrt{2m^* \varphi}}{3q\hbar}$$

where $\varphi$ is the barrier height and $m^*$ is the effective mass of a hole in MEH-PPV, $q$ is the electron charge, and $\hbar$ is Planck’s constant. The injection barriers for the tunneling of holes through the anode in the devices were calculated from Eq. 4. As presented in Table I, it is found that the estimated barrier heights for devices made of different ITO/glass substrates show an inverse trend to the total effect contact area. In the microview conception, the two contacting surfaces contact at several contact spots. The sum of the areas of the contact spots equals the effect contact area. The effect contact area determines the contact impedance, as presented in Fig. 4. A device with a lower effect contact area has a larger contact impedance and a smaller current flow.

This investigation studies the correlation between the interfacial topography, $R_q$ roughness, and the effect contact area in ITO/MEH-PPV interface. It is found that the KOH/isopropyl alcohol etching process changes $R_q$ roughness of the ITO surface and the total effect contact area between ITO/MEH-PPV. The injection barrier height for holes is related to the total effect contact area. The effect contact area at the ITO/MEH-PPV interface exhibits a correlation on the injection of charge carriers.

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