Effect of Voltage Bias at MEH-PPV Layer on SPR Wavelength observed during in-situ Measurement Method in Polymer Light Emitting Diode

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Abstract
The shifting of surface plasmon resonance (SPR) wavelength has been observed during in situ measurement in polymer light emitting diode (pLED). Examination is performed using an pLED sample which has an ITO/PEDOT:PSS/MEH-PPV/Au structure. When the voltage bias is increased from 0 to 9 volt the SPR wavelength shifts from 612 nm to 628 nm and the absorption curve shifts to lower absorbance value. From the theoretical analysis, it can be understood that the change of the SPR dip and the absorption curves correspond to the change of dielectric constant of the MEH-PPV layer. These results show that SPR wavelength depends on the metal and air dielectric constant as well as on the MEH-PPV layer. These results also imply that the SPR wavelength being evaluated can be controlled by varying the voltage bias.

Keywords: Absorption, Pled, Resonance, Wavelength shift, SPR dip

1. Introduction
In SPR (Surface Plasmon Resonance), evanescent wave generates Surface Plasmons (SP) wave propagating along the metal/dielectric interface. The field amplitude of the SP wave decays exponentially very quickly in the metal side but slightly slower in the dielectric side¹⁻³. Due to this characteristic, SPR method is widely used for characterizing very thin layer surface and metal-dielectric interface, which can be found in modern sensors and analytical systems⁴,⁵.

For practical usage for sample characterizations, a dielectric sample can be placed either on the top of the metal layer (Kretschmann configuration) or in between the prism and the metal layer (Otto configuration)⁶,⁷. However, both configurations have the same purpose, that is, to excite the SP wave in the metal-sample interface. When the resonance takes places, the incident light will be absorbed resulting in the appearance of a spectral dip in the reflection spectrum. The SPR wavelength is very sensitive to the dielectric permittivity. Therefore, the changes in the dielectric permittivity of the sample will shift the spectral dip position, which is attributed to the shift of SPR wavelength or frequency⁸. The SPR wavelength also depends on the thickness and the nanostructure of the metal layer, which is important in designing the SPR sensor⁹,¹⁰. Due to its sensitivity, SPR sensor becomes a powerful tool for real time monitoring¹¹,¹².

Although the effect of the dielectric permittivity change on the SPR wavelength shift have been widely investigated in simple configuration consisting of single layer, the same effect for the case of multilayer structure, such as in polymer light emitting diode (pLED) structure, was rarely discussed. In this paper, we report the application of SPR method to investigate the change of dielectric permittivity in the active (emissive) layer of pLED by means of in-situ technique at various bias voltages. The generation of SP wave in this case is not as simple as in the case of Kretschmann configuration, because the SP wave cannot be generated directly at the active layer-electrode interface. The experimental results were analyzed by comparing the data with the theoretical calculations for explaining the shift of SPR wavelength with respect to the change of bias voltage.

2. Theory
In the SPR method with Kretschmann configuration, light is directed to the gold thin film via a prism with refractive index $n_p$ as shown in Figure 1. The reflectance $R$ for 3 layers system ($p$-prism, $m$-metal, and $a$-air) is given by¹³

$$ R = \left| r_{pm} \right|^2 = \frac{\left| r_{pm} + r_{ma}e^{-2ik_maxd} \right|^2}{1 + r_{pm}^2r_{ma}^2e^{-2ik_maxd}}, \quad (1) $$

with the coefficients of reflection by the interface of two adjacent mediums are

$$ r_{pm} = \frac{k_{pm}c_m - k_{ma}c_p}{k_{pm}c_m + k_{ma}c_p}, \quad (2) $$

$$ r_{ma} = \frac{k_{ma}c_m - k_{mp}c_a}{k_{ma}c_m + k_{mp}c_a}. \quad (3) $$

$$ k_{pm} = \sqrt{k_{pm}^2 - k_{mp}^2}, \quad (4) $$

$$ k_{ma} = \sqrt{k_{ma}^2 - k_{mp}^2}. \quad (5) $$

where $k_{pm}$ and $k_{ma}$ are the phase constants of the wave in the metal and air, respectively.
\[ r_m = \frac{k_{m \epsilon_m} - k_{m \epsilon_a}}{k_{m \epsilon_a} + k_{m \epsilon_m}}, \quad (3) \]

and

\[ k_z = \left( \frac{\epsilon_j \omega^2}{c^2} - k_x^2 \right)^{1/2}, \quad (4) \]

\[ k_x = \frac{\omega}{c} n_j \sin \theta, \quad (5) \]

where \( \epsilon_j \) with \( j = p, m \) and \( a \) is the dielectric permittivity of the prism, metal or air, respectively, and \( k_z \) is the wave vector component perpendicular to the interface, and \( d \) is the thickness of the metal film.

3. Experiments

3.2 Instrumentation

The SPR spectroscopy system is consisted of a Tungsten Halogen light source (Ocean Optics), a polarizer (Sigma Koki), a pin-hole plate (Sigma Koki) and a motorized rotation stage (Sigma Koki) for adjusting the angles of sample and detector. A portable CCD spectrometer (USB-2000, Ocean Optics), combined with a personal computer, is used to measure the reflection spectrum.

3.2 Measurements

The schematic diagram for the SPR spectrum measurement on multilayer pLED is shown in Error! Reference source not found..

Experiment was performed by directing polychromatic light toward a BK7 prism at a fixed incident angle, namely \( \theta_i = 41^\circ \) (or \( \theta'_i = 42.37^\circ \)). The SPR spectrum was measured from the reflected beam passing through at various applied bias voltage in the range of 0-9 V.

3.3 Sample fabrication

A glass plate with 200 nm thickness of indium tin oxide (ITO) layer was cut into 2 cm × 3 cm size pieces. Etching process was carried out to obtain ITO line strips of 3 mm × 30 mm. The plate was cleaned by oxygen (2 minutes), UV light (10 minutes) and nitrogen (5 minutes). Poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonic acid) [PEDOT:PSS] layer was then deposited on the top of the substrate by means of spin casting with 5000 rpm rotation speed for one minute. The sample was then heated at 100°C for 20 minutes. Solution of 4 mg poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) [MEH-PPV] in 0.5 ml toluene was prepared by using an ultrasonic bath for 15 minutes. This solution was then deposited on the top of the PEDOT:PSS layer also by means of spin casting with
two steps rotation speeds, namely 500 rpm (5 sec) and 1500 rpm (30 sec).

Finally, gold thin layer with the thickness of only about 50 nm as the topmost layer was deposited by using an electron beam gun evaporation machine at $10^{-4} - 10^{-5}$ Pa.

4. Results and Discussions

The measured reflectance spectrum is shown in Figure 3, which exhibit the appearance of an SPR dip at 620 nm for the condition of bias voltage at 0 V. The dip position is shifted toward 628 nm as the bias voltage is increased gradually to 9 V. In addition, there is also an increment in reflectance as the bias voltage increases, which means that the layer becomes more transparent at higher bias voltage.

![Figure 3. Reflectance spectrum measured at various bias voltages: (a) 0; (b) 1; (c) 3.5; (d) 5; (e) 6; (f) 7; (g) 8 and (h) 9V. The SPR dip position shifts from 612 nm to 628 nm.](image)

The dielectric constant and the thickness of Gold can be determined from curve fitting. At the Au/air interface, by using the dielectric constants of (1.515)$^2$ for BK7 prism, $-11.74 + 1.67i$ for Gold and 1 for air, the resonance was estimated to occur at incident angle toward prism/pLED interface of $43.717^\circ$. This result is close to the experimental data, which implies that at the incident angle of $42.37^\circ$, SP wave will be excited at the Au/air interface. In the case of the Au/MEH-PPV interface (with MEH-PPV refractive index = 1.8), the incident angle was found to be $90^\circ - 49.85i$, which implies no incident angle suitable for SP excitation at Au/MEH-PPV interface.

The shift of SPR dip may indicate the change of the real part of the refractive index, which in turn implies the change in the dielectric constant of active layer inside the pLED, here the MEH-PPV emissive layer. Meanwhile, the change of dielectric constant of the electrode is neglected due to the absence of charge accumulation there.

Application of Fresnel formulation for multilayer case (e.g. prism/dielectric/Au/air structure) turns to be unable to explain the MEH-PPV influence on the shift resonance as shown in Figure 4. The change of the real part of the substrate refractive index does not shift the dip position, while the change of its imaginary part result in the change of reflection intensity only.

![Figure 4. Reflection spectrum vs. wavelength with variation of substrate refractive index.](image)

Meanwhile equation (9) demonstrates that due to the thinness of the gold layer, substrate refractive index must be taken into account, because the SP wave can reach the substrate layer. Penetration depth of the SP wave for gold in wavelength $\lambda$ is

$$z_{\text{Au}} = \left(\frac{2\pi}{\lambda} \left(\frac{\epsilon_{\text{Au}}^2}{\epsilon_{\text{Au}} + \epsilon_{\text{air}}}\right)^{1/3}\right)$$

(10)

For $\lambda = 600$ nm, $Z_{\text{Au}} = 26.5$ nm which result in effective penetration depth 133 nm. Because the thickness of the gold layer is 50 nm, the SP wave will reach the MEH-PPV layer around 100 nm. Penetration toward PEDOT:PSS layer is negligible due to the fact that very low SP energy remains after passing the MEH-PPV layer. The variation of PEDOT:PSS refractive index will not affect the SP wave vector considerably. Therefore the change of refractive index of the MEH-PPV of the pLED will shift its dip of the SPR spectrum.

If the equation (9) is applied for the multilayer pLED case, the equation of $\Delta k_{SP}$ shows its dependence to the MEH-PPV layer,

$$\Delta k_{SP} = \left(\frac{\epsilon_{\text{PPV}}}{\epsilon_{\text{MEH}} + \epsilon_{\text{Au}}}^2\right)^{1/3}\frac{e_{\text{Au}}^2}{e_{\text{Au}} + e_{\text{PPV}}}$$

(11)

with the coefficient of reflection at MEH-PPV/Au interface is

$$r_{\text{PPV} - \text{Au}} = \frac{k_{\text{PPV},z}e_{\text{PPV}} - k_{\text{PPV},z}e_{\text{EM}}}{k_{\text{PPV},z}e_{\text{EM}} + k_{\text{PPV},z}e_{\text{PPV}}}$$

(12)

where $\epsilon_{\text{PPV}}$ is the dielectric constant of MEH-PPV.

The refractive index of MEH-PPV and the dielectric constant of gold are dependent of the light wavelength. For an example, the real parts of MEH-
PPV refractive index for the 612 nm, 620 nm and 628 nm are 1.8, 1.78 and 1.76 respectively, while their imaginary parts relatively equal to zero\(^{13}\). The gold dielectric constants for those wavelengths are \(-11.2+1.41i\), \(-12.0+1.39i\), dan \(-12.8+1.36i\)^{14}. From the optical parameters of MEH-PPV and gold, the \(k_{SP}\) value can be determined, while from the experimental data, the value of \(k_x\) can be calculated as in Table 1. Ideally, the \(k_{SP}\) values are equal to \(k_x\) in accordance to the shift of resonance value of the incoming wave and the SP. When the refractive index of MEH-PPV decreases, the SP wave vector or the SP resonance condition of SP wave. Analytical consideration indicates that SPR wavelength being evaluated can be controlled by varying the voltage bias. The changes of reflectance and absorbance values against the bias voltage indicate the influence of the bias voltage upon the dielectric constant of MEH-PPV.

Absorption of light by a pLED can be observed from its absorption spectrum, Figure 6. When the bias voltage is increased, absorption spectrum at the 400-650 nm range is shifted downward, indicating the decrease in absorption. At around 510 nm, huge absorption occurs due to the MEH-PPV polymer absorption, while at above 650 nm, practically no change of absorption observed. These changes are caused by optical characteristic changes of the MEH-PPV layer when bias voltage is applied to a pLED. The imaginary part of MEH-PPV refractive index is responsible for those changes.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>(n_{\text{MEH-PPV}})</th>
<th>(\varepsilon_{\text{Au}})</th>
<th>(k_{SP} \times 10^7) (m(^{-1}))</th>
<th>(k_x \times 10^7) (m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>612</td>
<td>1.80</td>
<td>(-11.2+1.41i)</td>
<td>1.060</td>
<td>1.055</td>
</tr>
<tr>
<td>620</td>
<td>1.78</td>
<td>(-12.0+1.39i)</td>
<td>1.035</td>
<td>1.035</td>
</tr>
<tr>
<td>628</td>
<td>1.76</td>
<td>(-12.8+1.36i)</td>
<td>1.018</td>
<td>1.022</td>
</tr>
</tbody>
</table>

The c1, c2 and c3 lines in Figure 5 represent the dispersion relation of SP for pLED system at Au/Air interface for different refractive index of MEH-PPV, while c4 line is the light line in the prism. The intersection of c4 line with c1, c2 and c3 indicates the shift of resonance value of the incoming wave and the SP. When the refractive index of MEH-PPV decreases, the SP wave vector or the SP resonance frequency decreases accordingly, indicating the increase of the resonance wavelength. Each intersection represents the condition for the resonance to occur.

As an example, from Table 1, it can be seen that for 612 nm, \(\text{Re}(k_{SP})=1.060 \times 10^7\) m\(^{-1}\) is the resonance point for \(n_{\text{MEH-PPV}}=1.8\) and \(\varepsilon_{\text{Au}}=-11.2+1.41i\). At 620 nm, the refractive index of MEH-PPV decreases down to 1.78 results in the shift of resonance to \(\text{Re}(k_{SP})=1.035 \times 10^7\) m\(^{-1}\). Similarly, at 628 nm, \(\text{Re}(k_{SP})=1.018 \times 10^7\) m\(^{-1}\) is obtained. The decrease in MEH-PPV refractive index changes result in smaller changes on \(k_{SP}\) values, so that the SPR wavelength is shifted to higher value. The dip shift is related to the real part of MEH-PPV refractive index.

![Figure 5. Dispersion relation of SP for pLED system at Au/Air interface for different refractive index of MEH-PPV (c1, c2 and c3), and light line in the prism (c4).](image-url)

![Figure 6. pLED absorption spectrum vs wavelength for various bias voltages (a) 1; (b) 3.5; (c) 5; (d) 6; (e) 7; (f) 8 dan (g) 9V.](image-url)
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References