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Surface Plasmon Resonance in Organic Photovoltaic Cells with Silver or Gold Electrodes

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The enhancement of photocurrent in organic photovoltaic cells by excitation of surface plasmon resonance (SPR) is shown to be greater for Ag electrodes than for Au electrodes. Three-layer Al/tin-phthalocyanine/(Ag,Au) photovoltaic cells are fabricated by vacuum evaporation, and the current–voltage characteristics measured with and without excitation of SPR at the metal–dielectric interface. Excitation of SPR increased photocurrent in the Ag-electrode cell by a factor of 5.73, and that in the Au-electrode cell by a factor of 3.78. The intensity of the SPR-induced electric fields responsible for this photocurrent enhancement appears to be dependent on the surface roughness and electrode material.

Keywords: attenuated total reflection method; photocurrent; photovoltaic cell; surface plasmon resonance; tin-phthalocyanine

1. INTRODUCTION

Tin-phthalocyanine (SnPc) is a functional organic material consisting of π-conjugated systems and due to its high electrical conductivity is applicable as a p-type organic semiconductor to form Schottky junctions with metals having small work functions such as Al [1]. Surface plasmon resonance (SPR) can be generated at the metal–dielectric interface in such devices by attenuated total reflection (ATR) of a p-polarized laser beam. Excitation of SPR by light induces strong electromagnetic fields [2] that give rise to surface-enhanced optical phenomena, including emission, scattering, and photoconduction [3,4]. As photovoltaic cells fabricated using functional organic

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materials generally have very low photoelectric conversion efficiency ($\sim$5% max.), SPR may provide a means of increasing the conversion efficiency without changing the cell structure.

In this study, the most effective electrode material for SPR enhancement of organic photovoltaic cells is investigated by characterizing three-layer photovoltaic cells prepared with Au or Ag electrodes. The optimal dielectric constants and layer thicknesses are determined theoretically, and the surface roughness is investigated by atomic force microscopy (AFM).

2. EXPERIMENTAL

The dispersion relation for surface plasmon polaritons (SPPs) propagating along the interface between a metal and a dielectric is given by

$$k_x = \left(\frac{\omega}{c}\right)\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{\frac{1}{2}}, \tag{1}$$

where k_x is the complex wave vector of SPPs, ε_1 and ε_2 are the complex dielectric constants of medium 1 (metal) and medium 2 (dielectric), ω is the frequency of monochromatic incident light, and c is the speed of light. The complex wave vector is related to reflectance by

$$|r_{012}^{p}|^2 = |r_{01}^{p}|^2\left[1 - \frac{4\Gamma^{i}\Gamma^{rad}}{\left\{k_x' - \left[k_x^0 + \mathrm{Re}\left\{\Delta k_x^{rad}\right\}\right]\right\}^2 + \left(\Gamma^{i}+\Gamma^{rad}\right)^2}\right], \tag{2}$$

where k_x' is the wave vector of incident light, k_x^0 is the real part of the wave vector of SPPs at a semi-infinite metal/dielectric interface, Δk_x^{rad} is the displacement of the wave vector of SPPs derived from the ATR configuration, Γ^{i} is internal damping, and Γ^{rad} is radiation damping to the prism [2].

The reflectance and transmittance are calculated using Fresnel coefficients in order to determine the optimum film thickness of each layer of the photovoltaic cell for using SPR. The amplitude reflectance with p-polarized light r_{012}^{p} and the amplitude transmittance with p-polarized light t_{012}^{p} in a three-layer system (e.g., prism/metal/air) are given by

$$r_{012}^{p} = \frac{E_r^{p}}{E_0^{p}} = \frac{r_{01} + r_{12}e^{2i\alpha}}{1 + r_{01}r_{12}e^{2i\alpha}}, \tag{3}$$

and

$$t_{012}^{p} = \frac{t_{01}^{p}t_{12}^{p}e^{i\alpha}}{1 + r_{01}^{p}r_{12}^{p}e^{2i\alpha}}, \tag{4}$$

with

$$\alpha = n_1 \frac{\omega}{c} d_1,$$

where r^{p}_{ik} and t^{p}_{ik} are the reflectance and transmittance from interface media i and k (i, $k = 0,1,2$, $i \neq k$), and d_1 and n_1 are the thickness and refractive index of medium 1. The intensity of reflectance and transmittance are given by the square of r^{p}_{012} and t^{p}_{012}, respectively. The reflectance and transmittance of the photovoltaic cell, which is composed of five layers (prism/metal/dielectric/metal/air), are determined by expanding Eqs. (3) and (4) to the five-layer system. Under the present experimental conditions, Eq. (3) approximately represents the ATR spectrum [2]. Equation (4) gives the intensity of the field at each interface in the system. The ATR curve and field intensity at each interface in the photovoltaic cell depend on the layer thickness and the electrode materials (Ag and Au) according to the dielectric constants (Table 1) [5]. The optimized thicknesses of the Al, SnPc and Ag/Au layers were 10, 40 and 30 nm, respectively.

The photovoltaic cells were prepared on BK7 optical glass substrates ($30 \times 40 \times 1\,mm^3$) by vacuum evaporation. SnPc was sublimated prior to evaporation. The cell thicknesses were monitored using a quartz oscillator. As shown in Figure 1, the width of the Al, Ag, and Au electrode films was 10 mm, corresponding to an active cell area of $10 \times 10\,mm^2$. After evaporation, fine Au wire was attached to the Al and Ag/Au films using silver paste.

Figure 2 shows the ATR configuration for excitation of SPR at the metal–dielectric interface. A He–Ne laser ($\lambda = 632.8$ nm, 0.8 mW) with p-polarized beam and beam spot of 1 mm diameter was used for irradiation of the active area of the photovoltaic cell from the Al side via the prism. The reflected light intensity was measured as a function of the incident angle, and the ATR spectra were measured over the range

TABLE 1 Real Part of Complex Refractive Indices (n) and Imaginary Part of that (k) used in Reflectance and Transmittance Calculations

	n	k
Au	0.18	−3.44
Al	1.37	−7.62
Ag	0.06	−4.28
SnPc	1.91	−0.28
BK7	1.52	–
Air	1	0

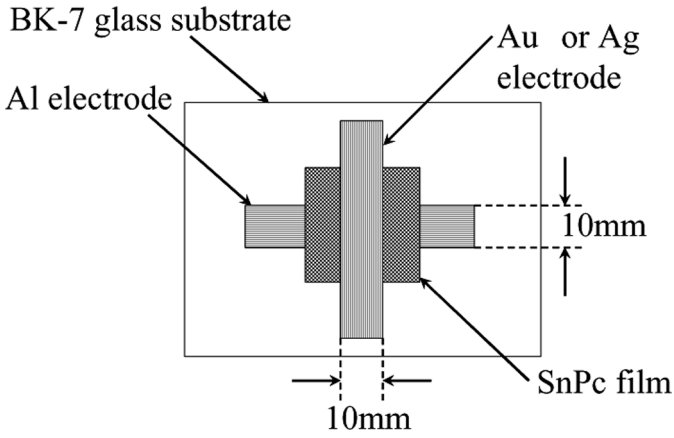


FIGURE 1 Structure of organic photovoltaic cells.

37.5–60°. The curve calculated from the Fresnel coefficients was then fitted to the measured ATR spectra. The current–voltage (*I–V*) characteristic of the photovoltaic cell was measured under three conditions: in the dark, illuminated without SPR, and illuminated with SPR.

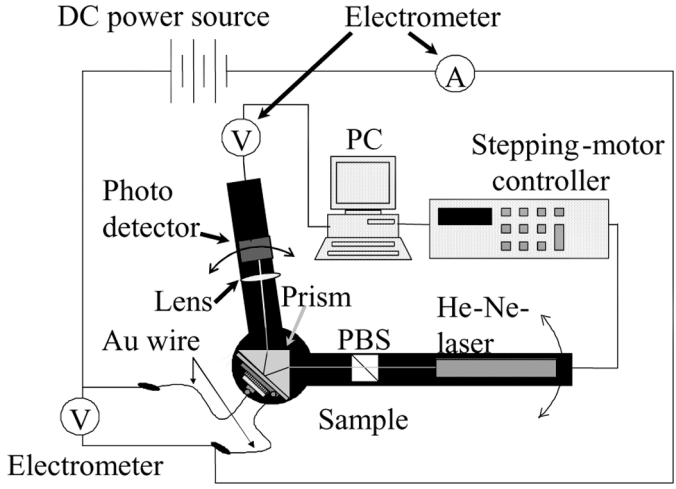


FIGURE 2 System for measurement of ATR spectra and *I–V* characteristics. A computer-controlled stepping motor was use to scan the incident angle and detector angle. In the *I–V* measurement, SPR characteristics were measured at the angle of SPR excitation and illumination characteristics without SPR were measured at an angle in the non-excitation region.

3. RESULTS AND DISCUSSION

3.1. ATR Characteristics

The ATR spectra for the Al/SnPc/Ag and Al/SnPc/Au cells are shown in Figure 3. A sharp dip can be seen at an incident angle of 43.9° for the Al/SnPc/Ag cell, while the Al/SnPc/Au cell exhibits a broad dip at 47.0°. SPPs at the (Ag,Au)/air interface can be excited at these incident angles (θ_{SPR}). In the ATR spectra for the Ag and Au cells, the reflectance reaches a minimum of 38.2% and 50.6% below the total reflectance intensity, respectively, giving the proportion of incident power transfer to SPR at these incident angles. The half-width at half-maximum (HWHM) of the dip ($\theta_{SPR}^{1/2}$) is 0.2° for the Ag cell and 2.4° for the Au cell. The fitting curves calculated from Eq. (3) are also shown in the figure. The differences between the ATR spectra and the calculated curves are assumed to be due to surface roughness of the photovoltaic cell. Figures 4 show AFM images of the Al/SnPc/Ag and Al/SnPc/Au cells, respectively. The average surface roughness (Ra) determined from the AFM images was 1.24 nm for the Ag cell and 1.40 nm for the Au cell. Such roughnesses are sufficiently high to influence the ATR spectrum [2].

Electric field intensities calculated as a function of the thickness of each layer from the Fresnel coefficients for the interfaces are shown in

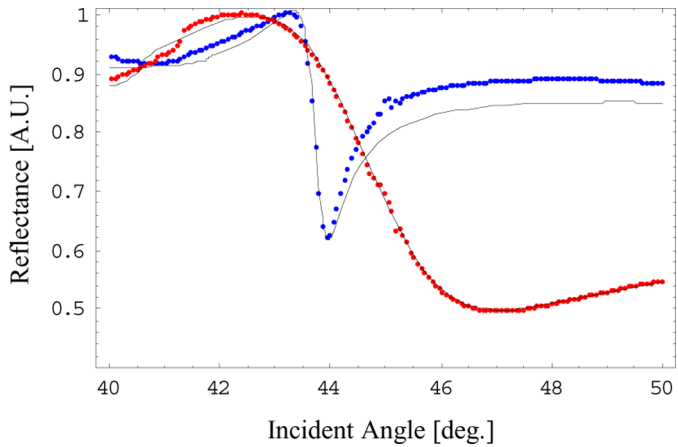
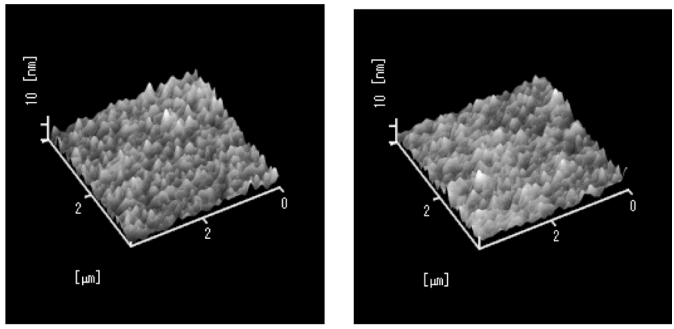


FIGURE 3 Measured ATR spectra of Al/SnPc/Ag (blue) and Al/SnPc/Au (red) photovoltaic cells. Calculated spectra are shown as solid lines. (See COLOR PLATE I)



(a) (b)

FIGURE 4 AFM images ($4 \times 4\,\mu m$) of (a) Al/SnPc/Ag and (b) Al/SnPc/Au photovoltaic cells.

Figure 5. The electric field can be determined from the intensity of transmittance by

$$\left|\frac{E(2/1)}{E_0(0/1)}\right|^2 = |t_{012}^{p}|^2 = 4\left(\frac{\omega}{c}\right)^2 |t_{01}^{p}|^2 e^{2i\alpha}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^3 \times \left(\frac{1}{\varepsilon_1-\varepsilon_2}\right)^2 \frac{1}{|k_x' - (k_x^0 + \Delta k_x^{rad})|^2}, \quad (5)$$

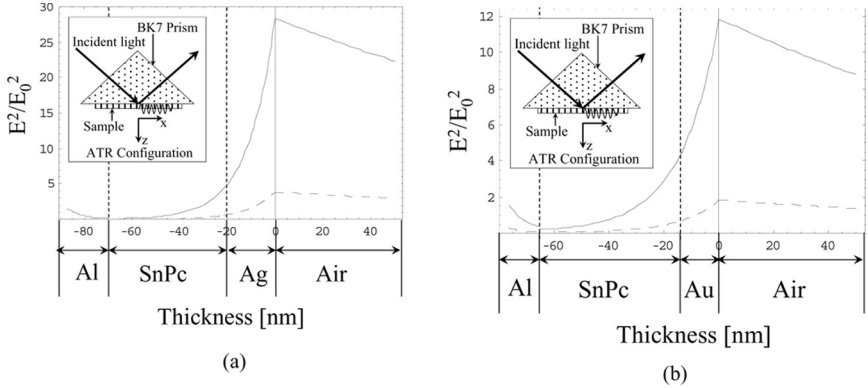


FIGURE 5 Intensity of SPR-induce field in (a) Al/SnPc/Ag and (b) Al/SnPc/Au photovoltaic cells. Dashed line represents the x components of the field, and solid lines denote z components. (Inset) Directions x and z in the ATR configuration.

where $E(2/1)$ is the electric field on the metal/air interface at the air side, and $E_0(0/1)$ is the electric field on the prism/metal interface at the prism side.

Figure 5 shows that the fields propagate in the cell from the air side to the prism side. The electric field was induced by SPR at the interface between metal (Ag, Au) and air, and affects the photoelectric conversion at the Al/SnPc interface forming the Schottky junction (i.e., the site of photoelectric conversion). For the Al/SnPc/Ag cell, the field was enhanced by a factor of 3.84 in the x direction and 28.4 in the z direction by activation of SPR. The enhancement factors were 1.85 and 11.9 in the x and z directions for the Al/SnPc/Au cell. The enhancement factor of the field in Al/ SnPc/ Ag cell was larger than that of Al/ SnPc/ Au cell. This suggests that enhancement factor of the field is determined by competition between depth and HWHM of the dip in the ATR spectrum.

3.2. *I–V* Characteristics

The *I–V* characteristic for the Al/SnPc/Ag cell is shown in Figure 6(a). The photocurrent for this cell was 8.89 nA at an incident angle of 38.4° without SPR and 50.95 nA at 43.9° with SPR. The photocurrent was therefore increased by a factor of 5.73 by activation of SPR. The open circuit voltage (V_{OC}) for this cell was 0.7 V and did not vary with activation of SPR. Therefore, SPR is therefore considered to enhance photocarrier generation. The *I–V* characteristic for Al/SnPc/Au cell is shown in Figure 6(b). The photocurrent for this cell was 2.61 nA

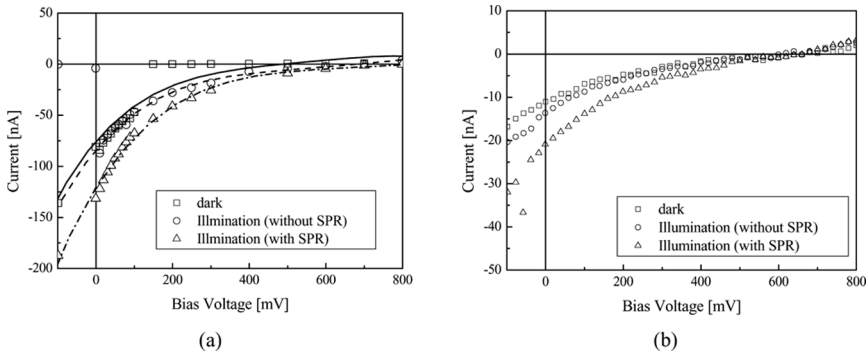


FIGURE 6 *I–V* characteristics of (a) Al/SnPc/Ag and (b) Al/SnPc/Au photovoltaic cells. Squares, circles and triangles denote measurements made in darkness, under illumination, and illuminated with SPR, respectively.

at 38.4° without SPR, and 9.87 nA at 47.0° with SPR, corresponding to an increase by a factor of 3.78. The V_{OC} was stable at 0.7 V regardless of SPR activation. The SPR enhancement of photocurrent is therefore considerably greater in the Al/SnPc/Ag cell than in the Al/SnPc/Au cell.

4. CONCLUSIONS

Photocurrent in Al/SnPc/Ag and Al/SnPc/Au photovoltaic cells was enhanced by a factor of 5.73 and 3.78, respectively. The electrical properties suggest that the SPR-induced electric fields enhanced photocarrier generation in the cells. The present results also showed that the intensity of fields induced by SPR is dependent on the surface roughness and electrode metal.

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