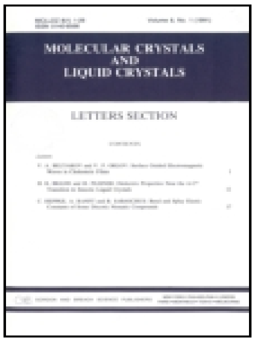

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Enhanced-Evanescent-Field Induced Photoluminescence of Rubrene Thin Films

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Photoluminescence (PL) was investigated for rubrene thin films with thickness comparable to light wavelength on silver in attenuated total reflection (ATR) geometry. The ATR properties indicate excitations of ATR modes that differ from surface plasmon resonance (SPR) in the metal. The ATR modes enabled enhancement of the PL intensity by 42 times at the peak wavelength, compared with that on glass. This enhancement is attributable to an increase of absorption in rubrene layers induced by enhanced evanescent fields. ATR-mode excitation can provide enhanced fluorescence not only for fluorescent thin films < 100 nm, but also for thicker films.

Keywords Photoluminescence; fluorescence; rubrene; attenuated total reflection (ATR); evanescent field; surface plasmon resonance (SPR)

Introduction

Fundamental optical spectroscopy for organic thin films, such as absorption and luminescence, is necessary for the development and fabrication of optoelectronic devices: organic light emitting diodes [1], organic field-effect transistors [2], and organic solar cells [3]. Recently, rubrene thin films with polycrystals have been proposed for applications in these organic devices because of their high electrical mobility [1-3]. Another characteristic of rubrene molecules is their visible fluorescence. Both high electrical conduction and effective fluorescence properties of rubrene are beneficial for electrical and optical applications.

In spectroscopic methods for organic layers, surface plasmon resonance (SPR), which is generated in an attenuated total reflection (ATR) geometry using a prism, is extremely useful for enhancing the fluorescence of molecules on metal [4]. However, enhanced fluorescence based on SPR is restricted to extremely thin molecular layers (typically, $d <$ 10 nm) on the metal thin films [4]. In addition, only *p*-polarized incident light can induce the SPR in flat interfaces on metal because surface plasmons are nonradiative longitudinal surface waves [4, 5].

An earlier report [6] has presented enhanced PL properties for fluorescent tris (8-quinolinate) aluminum (Alq_3) layers ($d <$ 100 nm) on a silver thin film, using the ATR method. Passage of *s*-polarized incident light through an ATR prism increases absorption in the Alq_3 layers at excitation of an "ATR mode [6]". The ATR mode, which we call an optical mode with an enhanced electric field using the ATR technique, differs from the SPR [5-7]. We confirmed that ATR-mode excitation provides enhanced photoluminescence

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[6]. Nevertheless, it remains unclear whether ATR-mode enhanced PL spectroscopy is applicable for thicker films ($d > 100$ nm), for example, for those with thickness comparable to a light wavelength. We have demonstrated enhanced PL characteristics for rubrene thin films comparable with light wavelength on silver thin films in ATR geometry.

Experiments

Rubrene ($C_{42}H_{28}$, 5, 6, 11, 12-tetraphenylnaphthacene, sublimed grade; Sigma-Aldrich Corp.) was used for samples without purification. On a cover glass substrate of BK-7, Ag and rubrene layers were deposited successively by vacuum evaporation at 5×10^{-4} Pa. The substrates were not heated at deposition. The rubrene films were evaporated at a deposition rate of about 1.1 nm/s.

We measured polarized ATR and PL spectra for the samples using an experimental setup for visible ATR luminescence measurements [6, 8]. The glass substrate with the film sample was attached to a hemi-cylindrical prism of BK-7 glass using immersion oil with the same refractive index as that of the glass. Light derived from a diode-pumped solid state laser ($\lambda = 473$ nm, 25 mW) was used for reflectance and PL measurements. A light beam (about 0.7 mm diameter, spread angle $< 1.2 \times 10^{-3}$ rad) was linearly p-polarized or s-polarized with a half-wave plate. The ATR and PL measurements were demonstrated at attenuated powers of incident light approximately 6 mW/cm^2. The polarized ATR measurements were performed as follows; an incident angle of p-polarized or s-polarized light to the sample mounted on a θ stage was changed by rotating the θ stage at a scanning angle of 0.1° with a controller. Light reflected from the sample through the prism was detected by a Si photodiode mounted on a 2θ stage. Therefore, we obtained the polarized ATR data as a function of incident angle θ at a fixed wavelength. The excitation light was incident at angles of the ATR dips. The emitted PL spectra were measured at a fixed angle of normal direction to the sample using a fiber-coupled spectrometer. For a control sample of rubrene/glass also, the PL spectra were measured using a similar method. The PL spectral signals were measured sensitively using an electrically cooled detector of a charge-coupled device. The PL spectral measurements were performed at 293 K.

Absorption spectra for rubrene thin films were obtained from usual transmission measurements. White light from a Xe lamp was irradiated normally through an optical fiber to the film sample. Then the transmitted light was measured using the fiber-coupled spectrometer. The absorption spectrum was estimated from the relative transmission T with respect to the bare glass substrate as $-\ln T$, where the reflected light from the sample was ignored.

Results and Discussion

Figure 1 portrays the absorption spectra of rubrene thin films on a glass substrate. The rubrene thin film thickness was 100 ± 6 nm, as evaluated using a quartz crystal microbalance in vacuum-evaporation. The rubrene thin films exhibit a characteristic absorption band in 2.2 – 2.8 eV, with three peaks at 2.35, 2.52, and 2.67 eV. The wavelength of excitation light used for the PL, $\lambda = 473$ nm (2.62 eV), is at the somewhat high energy side of the large absorption band.

Figure 2 portrays the polarized ATR for the prism/Ag ($d = 50 \pm 3$ nm)/rubrene ($d = 500 \pm 30$ nm) as a function of the incident angle: (a) p-polarized and (b) s-polarized reflectivities. Both polarized ATR curves exhibit sharp dips in all reflection angles between the glass prism and air. If the thickness of rubrene layers on metal thin films is less

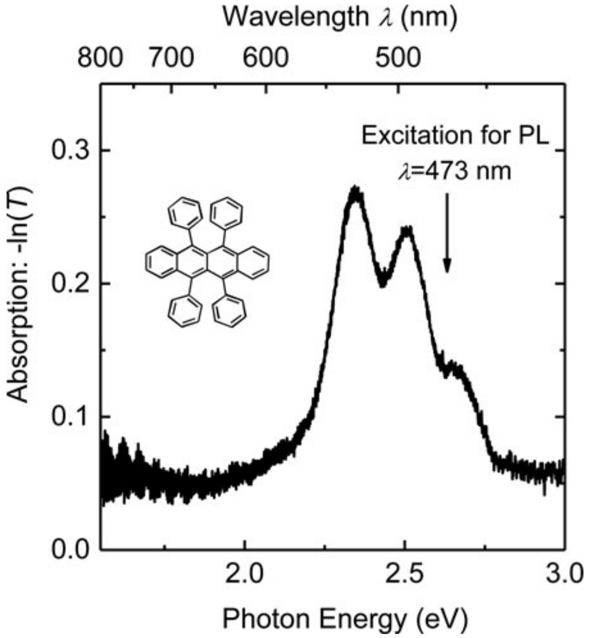

Figure 1. Absorption spectra of the rubrene thin films on a glass substrate. Inset: rubrene molecular structure.

than approximately λ/10, then only one dip in *p*-polarized ATR would be observed, and *s*-polarized reflection would have no dips.

We demonstrated that ATR-mode induced enhanced PL spectroscopy for the rubrene thin films. The PL spectrum at *s*-polarized reflection dip of $\theta_{\text{in}} = 41.9°$ in Fig. 2 (b) is depicted in Fig. 3. For comparison, the PL spectrum measured under the same condition ($\theta_{\text{in}} = 41.9°$) for rubrene layer on a glass substrate, which had the same thickness as that on the Ag thin film, is also portrayed. The PL spectrum of the rubrene sample on the glass

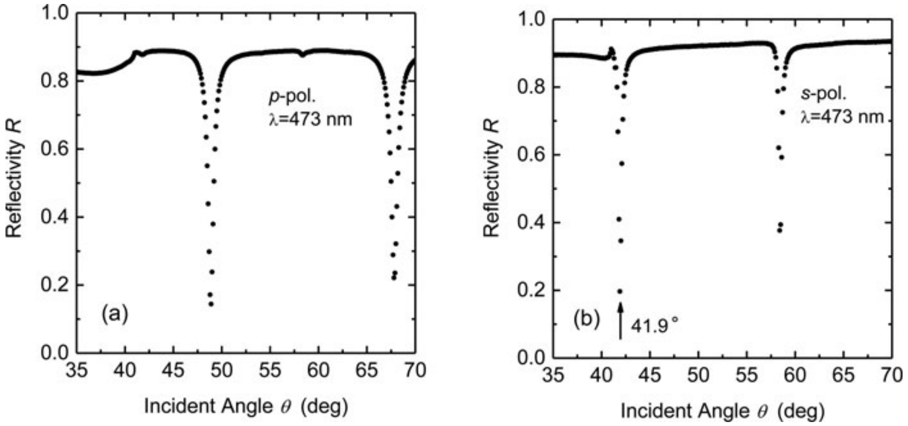

Figure 2. Polarized ATR for the prism/Ag /rubrene as a function of the incident angle: (a) *p*-polarized and (b) *s*-polarized reflectivities.

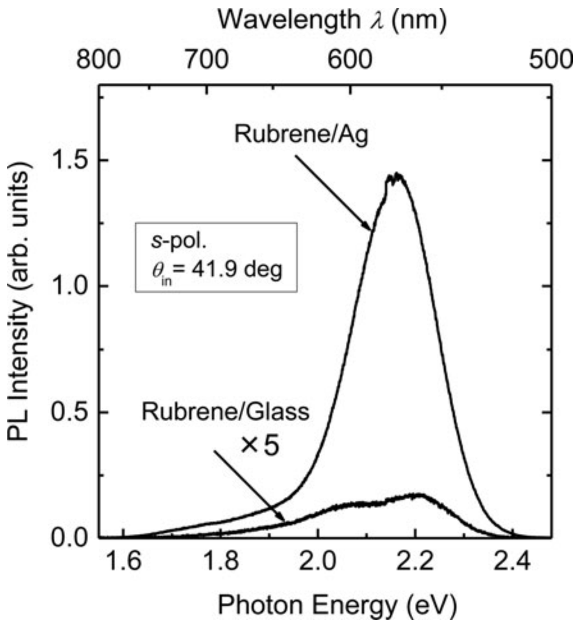

Figure 3. PL spectra at the ATR mode excited by the *s*-polarized light.

is displayed, being multiplied by five times because the signals were considerably weaker than the ATR-mode induced PL. Excitation of the ATR mode leads to enhancement of the rubrene fluorescence. The PL enhancement factors at the peak position around 2.16 eV and for the integral estimation of PL intensity are, respectively, 42 and 31 times those

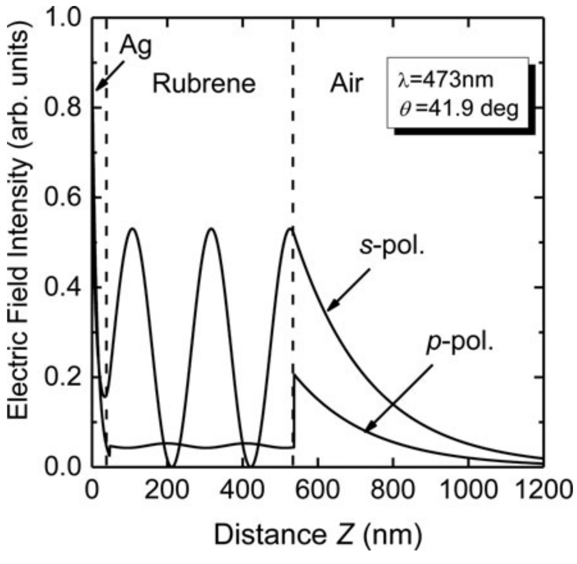

Figure 4. Calculated electric-field distributions as a function of the distance z, along the film thickness for polarized incident light.

of glass substrate. Enhancement of rubrene fluorescence at the ATR dips results from an absorption increase in the rubrene layers. Similar enhanced PL phenomena were observed at incident angles of other ATR dips: $\theta_{\text{in}} = 58.4^\circ$ for *s*-polarization; $\theta_{\text{in}} = 48.9^\circ$ and 67.8° for *p*-polarization.

The spectral shape of ATR-mode-induced florescence differs somewhat from that of rubrene on glass, as depicted in Fig. 3. The ATR-mode-induced PL spectrum has a large peak at 2.16 eV as well as the fluorescence of rubrene thin film on glass, but a sub-peak near 2.05 eV is unclear, probably because enhanced electric fields attributed to the ATR mode excitations provide fluorescence quenching in spite of weakened incident light for PL excitations.

Figure 4 portrays the calculated electric-field distributions as a function of the distance z along film thickness at $\theta_{\text{in}} = 41.9^\circ$ for polarized incident light. The curves were obtained using the fitting parameters for ATR data in Fig. 2: prism, $\varepsilon = 2.32072$; Ag thin film, $d =$ 47.0 nm, $\varepsilon = -7.70 + i\,0.440$; rubrene thin film, $d = 505$ nm, $\varepsilon = 2.31 + i0.005$ at $\lambda =$ 473 nm. At the excitation of *s*-polarized ATR mode, the field intensity is increased clearly in the rubrene layer, compared with the non-excitation of the ATR-mode (*p*-polarized incident light). The enhanced electric field induces increased absorption in the rubrene layer. This calculation result supports the enhanced PL at the ATR-mode excitations.

Conclusion

We demonstrated PL enhancement for rubrene thin films with thickness comparable to the light wavelength in ATR geometry. Results shows that ATR modes that can be excited not only by *p*-polarized light but also by *s*-polarized light provide increased absorption in rubrene thin films. For organic films that are thicker than those suitable for SPR, PL spectroscopy based on ATR-mode excitations is a powerful technique.

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