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Surface Plasmon Excitation and Emission Light properties for Prism/MgF₂/Ag/MEH-PPV Film Structure

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1. Introduction

Attenuated total reflection (ATR) method utilizing surface plasmon (SP) excitation is known as a useful way for thin film evaluation, sensing and so forth¹. In the ATR configuration, light emission due to SP excitation can be observed through the ATR prism². The emission angle almost corresponds to the SP resonance angle and depends on the film structure in the sample. We have been investigating the SP emission light for ATR Kretschmann configuration with fluorescent dyes³⁻⁵. In such configurations, near-field of excited dyes induces SP excitation at metal surface and the SP excitation depends on the dye orientation and/or distance between the dyes and the metal^{4,5}. Such energy interaction between dye and metal should be very important to improve efficiencies of organic light-emitting diode, solar-cells etc.

It is well known that SPs can be excited using Kretschmann or Otto configurations¹. However, SP emitted light properties have not been studied well for Otto configuration. In this study, SP emission light properties were investigated for prism (BK-7)/MgF₂/Ag film/MEH-PPV film configurations¹. The refractive index of MgF₂ is smaller than that of the prism. SPs can be excited at the interface between MgF₂/Ag film due to Otto configuration and at the interface between Ag film/air due to Kretschmann configuration. The SP emission lights induced by MEH-PPV were observed at various emission angles.

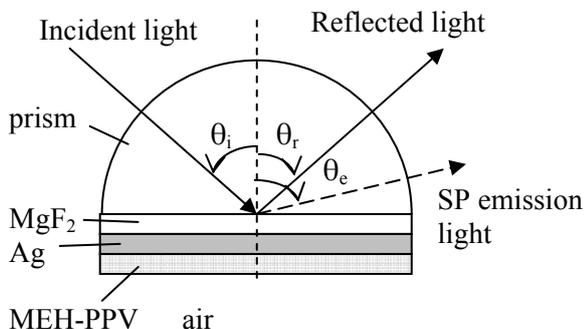


Fig. 1. The sample configuration.

2. Experimental details

Figure 1 shows the sample configuration for the measurement. MgF₂ and Ag films were fabricated using vacuum evaporation, and MEH-PPV film was fabricated using spin-coating method. The ATR curves were measured by observing the reflected light. The SP emission lights at various emission angles (θ_e s) were observed for Ar⁺ laser beam incidence from the MEH-PPV film side ($\theta_i = 180^\circ$). The ATR and SP emitted light properties were observed using an apparatus developed in our laboratory.

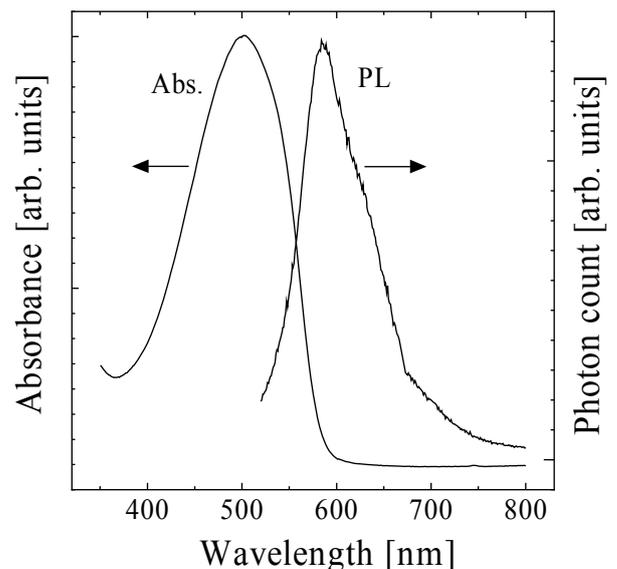


Fig.2. The UV-vis absorption spectra.

3. Results and discussion

Figure 2 shows the UV-vis absorption and photoluminescence (PL) spectra of the MEH-PPV film. The PL peak was observed at approximately 585 nm. The ATR curve for He-Ne laser beam ($\lambda = 594.1$ nm) incidence is shown in Fig. 3. The ATR dip can be observed at approximately 79° . Each thickness of the MgF₂, Ag and MEH-PPV was assumed to be 450, 88, 95 nm and the each dielectric constants of the film was obtained as 1.90, $-13.06+i0.72$, $3.24+i0.11$ from theoretical calculation. Electric field in the sample was also calculated using the above film parameters. The electric field at the MgF₂/Ag interface become strong when the incident angle was set around the ATR dip angle,

and it suggests the SP excitation at the interface due to Otto configuration. It is considered that the dip of SP excitation at Ag/MEH-PPV interface is not observed since the thickness of MEH-PPV film was large.

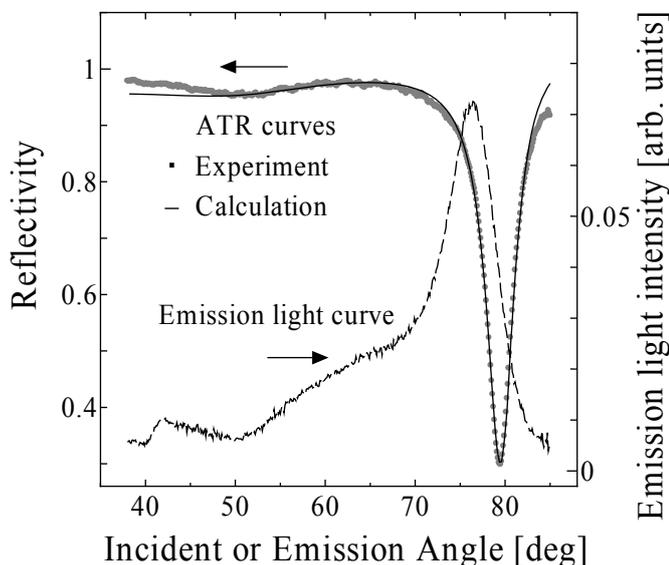


Fig. 3. The ATR and SP emission light curves.

The SP emission light curve for Ar^+ laser beam incidence ($\lambda = 488.0 \text{ nm}$, $\theta_i = 180^\circ$) was also observed. The laser beam excites MEH-PPV and the MEH-PPV induces SP excitation at the Ag surface. Figure 3 shows the SP emission light for the sample. A sharp-cut filter which eliminates the excitation laser beam was set in front of a light detector to observe the SP emission light induced only by the dye molecules. The emission light peak was observed at approximately 76° . The spectra of the emission lights were observed at the various emission angles and are shown in Fig. 4. The peak wavelengths were observed in the PL region of MEH-PPV and it suggests the emission lights are induced by MEH-PPV. Furthermore, the spectra strongly depend on the emission angles as shown in Fig. 4. It suggests the emission lights are induced by the SP excitation. Some of the SP energy is coupled out by the prism to the SP resonant angle. Since the SP resonant angle depends on the wavelength, the emission light varies with the emission angle. In general, the SP resonant angle tends to shift to lower angle for longer wavelength.

The peak angle of the emission light almost corresponded to the dip angle of the ATR curve in Fig. 3. It is considered that MEH-PPV between Ag and air induces SP excitation at MgF_2/Ag interface. However, Ag film was thick (88 nm) and PL transmission of MEH-PPV through Ag film was not observed at normal direction ($\theta_e = 0^\circ$) of the film. The mechanism of energy transfer from MEH-PPV film to Ag/MgF_2 interface has not been clarified yet. However, near-field from MEH-PPV may be related to the SP excitation and the emission light. Recently, energy transfer across a metal film mediated by the SPs was reported for glass/ polymethylmethacrylate (PMMA) with

(Alq_3)/silver film/ PMMA with Rhodamine B (RB) structure⁶. Excitation energy of Alq_3 can be transferred to RB by SP associated with each metal interface. Similar phenomena may be induced the SP excitation at the sample in this study.

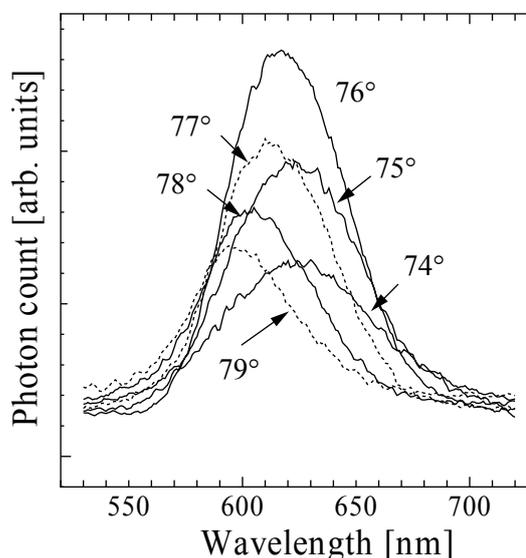


Fig. 4. The SP emission light spectra observed at various emission angles.

3. Conclusions

The SP excitation and emission light properties were investigated for Otto/Kretschmann hybrid configuration, that is, prism/ $\text{MgF}_2/\text{Ag}/\text{MEH-PPV}$ film structure. The reflection dip was observed for the ATR curve and was considered to be due to the SP excitation at the MgF_2/Ag interface. Furthermore, SP emission light due to the energy transfer from MEH-PPV was observed by the laser beam incidence from the MEH-PPV film side. Further investigation is needed to clarify energy interaction between metal and MEH-PPV.

Acknowledgements

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