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Fluorescence lifetime measurement excited with ultraviolet surface plasmon resonance

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ABSTRACT

We present an application of surface plasmon resonance in the ultraviolet region (UV-SPR) to lifetime measurement of fluorescent materials. Surface plasmon resonance (SPR) has been used to enhance fluorescence intensity and UV-SPR is important in the analysis of organic and biomolecules, including proteins and DNA, because UV light can excite many kinds of fluorescent dyes simultaneously or autofluorescence of biological specimens without any stain process. We obtained 16 times improvement of signal-to-noise ratio in lifetime measurement. We demonstrated the fluorescence lifetime of anthracene and CdSe/ZnS quantum dots using UV-SPR. The shortened fluorescence lifetime excited with UV-SPR compare to lifetime exited without SPR was analyzed.

1. Introduction

The research field of plasmonics is growing and evolving owing to their potential applications in sensors [1,2], imaging [3,4], photovoltaic [5], and photonic devices [6]. Surface plasmon resonance (SPR) has been used to enhance the surface sensitivity of spectroscopic measurements, including fluorescence [7], Raman scattering [8–11], and second harmonic generation [12] by increasing the electric field of incident light by a factor of 10 or more. SPR in the ultraviolet (UV) region is important in the analysis of organic and biomolecules [13,14], including proteins and DNA. UV light can excite many kinds of fluorescent materials simultaneously and it is possible to excite the autofluorescence of biological materials. The highly sensitive observation of dye-labeled organelles in cells using SPR in the deep UV region (DUV-SPR) has been demonstrated [15–17].

For existing SPR in the UV region (UV-SPR) it is possible to use several metals, with Al, In, and Mg showing the best optical properties. Aluminum is very technological, cheap, and good for making thin metal films [18]. There are a few methods available for making thin aluminum films such as magnetron sputtering and temperature evaporation. The thin aluminum films made by evaporation method have better quality for SPR.

Fluorescence lifetime (FLT) has been widely utilized for the characterization of fluorescence species and in biophysical studies of proteins. Since FLT is independent of the initial light intensity, FLT measurement can reduce the artifacts that are caused at stain process and non-uniformity of excitation light intensity. There are two methods of FLT measurement: the time-domain method and frequency-domain method. In the time-domain method, FLT is measured in nanoseconds (ns) by a laser with a pulse duration of a few picoseconds and a ns-level shutter because the lifetime of an excitation state is usually 1–20 ns. In the frequency-domain method, FLT is calculated by measuring the phase shift of fluorescence and the reduction of its amplitude using a detector with a gain modulator when the laser used as the excitation light source is modulated (1–200 MHz).

In general, fluorescence intensity is weak and FLT measurements require the detection of the fluorescence decay process. This means that we need to measure at least two fluorescence intensities within the lifetime. For this reason, FLT measurement intrinsically requires the detection of weaker signals and limits the signal-to-noise ratio and measurement time. In this paper, we propose the combination of FLT measurement and SPR in order to improve the signal-to-noise ratio in FLT measurements.

2. Experimental setup for FLT measurement with UV-SPR

To measure FLT, we constructed the new optical setup shown in Fig. 1, which is a combination of the setup for FLT measurement and SPR detection.

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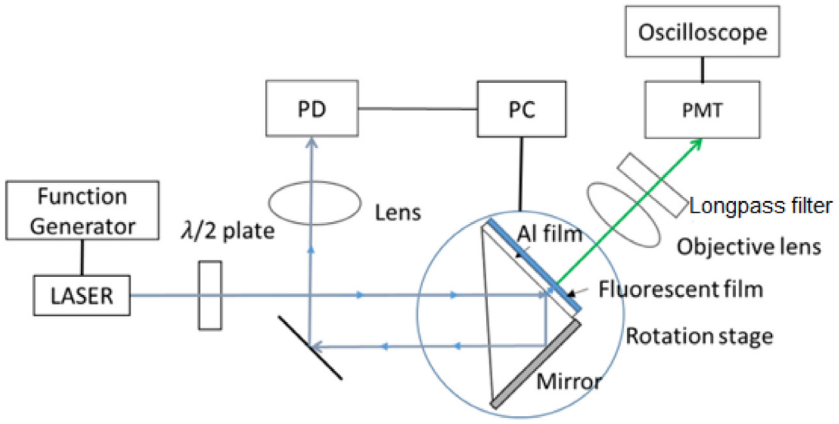

Fig. 1. Optical setup for measuring fluorescence lifetime using SPR setup in the Kretschmann configuration.

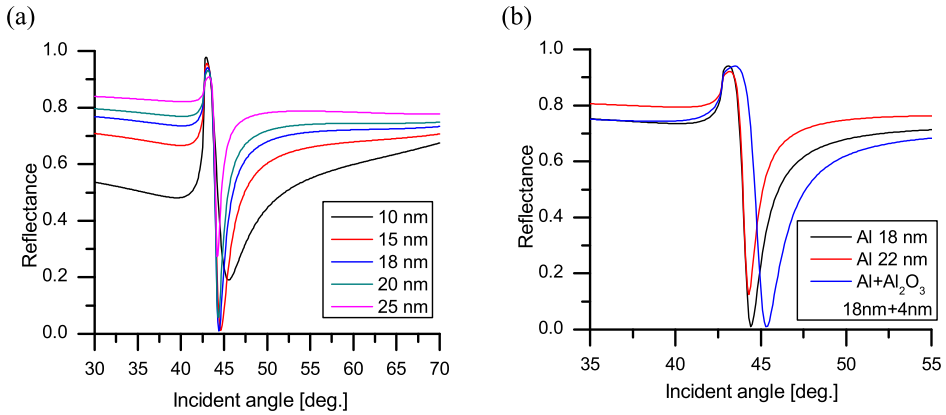

Fig. 2. Calculated incident angle dependence of reflectance on aluminum film thickness (a) and comparison with alumina (b).

Fig. 1 shows the experimental setup for measuring the reflectance, fluorescence intensity and FLT in the Kretschmann configuration. The light source was a laser diode with a wavelength of 375 nm and output power of 2 mW. The UV light with p- or s-polarization was obtained using a half-wave plate. The UV light was incident upon an aluminum film through a quartz prism in the Kretschmann configuration. The reflected light was detected using a photodiode. The incident angle of the light was changed using a rotation stage controlled by a personal computer. The samples were spin coated on the thin aluminum film. The fluorescence of anthracene and CdSe/ZnS quantum dots (QDs) on aluminum films were detected using a photomultiplier tube (PMT). The fluorescence signals from an oscilloscope were used to calculate FLT. An excitation-light cut filter was placed in front of the PMT.

3. Experimental results of FLT excited with SPR

3.1. Surface plasmon resonance

We used a thin aluminum film, which is one of the most suitable metal films for SPR. Aluminum is good metal for exciting the UV-SPR because its permittivity in the UV region has a negative real part and a small imaginary part [19]. The reflectance was calculated in order to optimize the aluminum thickness to yield the largest electric field on the film surface. We applied Fresnel equations to a four-layer system in the Kretschmann configuration. The refractive indices of quartz, aluminum, alumina, and air are 1.473, 0.432 + i4.56, 1.791, and 1, respectively, at the wavelength 375 nm. The aluminum thickness was optimized with simulation.

Fig. 2(a) shows the calculated incident angle reflectance dependence of the aluminum film thickness. The optimum aluminum film thickness for our laser wavelength is 18 nm. We improved our system by adding a thin layer of alumina because aluminum surface is easily oxidized. We assume that the alumina thickness is 4 nm [20]. Fig. 2(b) shows the reflectance dependence of aluminum thickness with 4 nm alumina film on the incident angle. The optimum film thickness for our sample is 22 nm. The dip of reflectance is shifted for aluminum with alumina film (18 nm + 4 nm) to higher incident angle compare to the aluminum films (18 nm and 22 nm).

We used the vacuum evaporation technique to make aluminum thin films and the evaporation speed was 10 nm/s. The gas pressure in chamber was 4×10^{-4} to 10^{-3} Pa. The thickness of these films was measured by a profilometer.

3.2. Sample properties

Anthracene is a solid polycyclic aromatic hydrocarbon ($C_{14}H_{10}$) that contains three fused benzene rings. Anthracene is used in the production of red dye alizarin and other dyes. Anthracene exhibits blue (400–500 nm peak) fluorescence under UV irradiation [21]. The fluorescence spectrum of anthracene is shown in Fig. 3(a), which was measured with a longpass filter at 400 nm because we excited fluorescence by a 375-nm laser diode. This is the reason why we cannot see the peak near 380 nm what shown on Fig. 3(a).

We also measured the fluorescence spectrum of CdSe/ZnS QD as shown in Fig. 3(b). The CdSe/ZnS QD has an emission peak at wavelength of 540 nm. The diameter of this QD is 6 nm. Fluorescent QDs have excellent photostability, high luminescence quantum yields, broad absorption bands, and very large one- and two-photon absorption cross-sections. These give them a wide range of applications, including biomedical applications [22].