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RESEARCH ARTICLE

Surface plasmon coupled fluorescence in deep-ultraviolet excitation by Kretschmann configuration

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We report the experimental demonstration of fluorescence of CdSe quantum dots with surface plasmon excitation in deep-ultraviolet (deep-UV) region. Surface plasmon resonance in deep-UV is excited by aluminum thin film in the Kretschmann-Raether geometry. Considering the oxidation thickness of aluminum, the experimental results of incident angle dependence of reflectance show good agreement with Fresnel theory. Surface plasmon resonance with 19 nm-thick aluminum and 5 nm-thick alumina was excited at the incident angle of 48 degrees for 266 nm excitation. Fluorescence of CdSe quantum dots coated on this aluminum film was observed by the surface plasmon excitation.

Keywords surface plasmon polarities, deep-ultraviolet light, fluorescence

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Since ultraviolet (UV) energy strongly interacts with materials, UV light of higher energy than visible has attracted much attention due to its application in photolithography, sterilization, protein analysis, and so on [1–3]. Since most of biological samples are constructed from proteins, the deep-UV excitation stimulates autofluorescence of their molecules. Aoki *et al.* reported near-field scanning microscopy in deep-UV excitation [4]. They successfully obtained fluorescence images of polystyrene and stromal cell, PA6 without staining in high spatial resolution.

In recent years, researchers have been actively involved in surface plasmon resonance (SPR) in deep-UV for enhanced Raman scattering, coupled emission fluorescence, and photoelectron emission [5–11]. Yang *et al.* demonstrated surface endhanced Raman spectroscopy and fluorescence of crystal violet in UV region by gallium nanoparticles substrate [5]. Taguchi *et al.* reported tip-enhanced Raman scattering (TERS) in deep-UV region [9]. They demonstrated TERS spectra of crystal violet with a nanoscale resolution beyond the diffraction limit of light. They have achieved that molecular analysis and imaging with nanoscale spatial resolution in deep-UV resonance Raman spectroscopy by the tip-enhancement effect. Local surface plasmon properties of aluminum nanoparticles have been investigated in deep-UV region [12–14].

In this paper, we demonstrate deep-UV SPR excitation in Kretschmann–Raether geometry and coupled fluorescence with the enhanced electric field of SPR. For the deep-UV SPR excitation, we have applied aluminum which has a negative permittivity and low imaginary part of permittivity in deep-UV region. Silver and gold are frequently used for SPR excitation in visible and near-infrared region. However, they are not applicable in deep-UV region, because their permittivities take positive in deep-UV. Therefore, aluminum is one of the suitable metal for SPR excitation in deep-UV.

Figure 1 shows calculated incident angle dependence of reflectance in Kretschmann configuration as a function of various thickness of aluminum on quartz prism, where the incident wavelength is 266 nm. The inset of Fig. 1 is the enlarged line profile in incident angle from 42 to 48 degrees, which shows a minimum reflectance at the incident angle of 44 degrees at the aluminum thickness of 20 nm. The optimum thickness of aluminum is

much thinner than that of gold or silver film, usual metal for visible SPR excitation, in Kretschmann configuration that is about 40–50 nm.

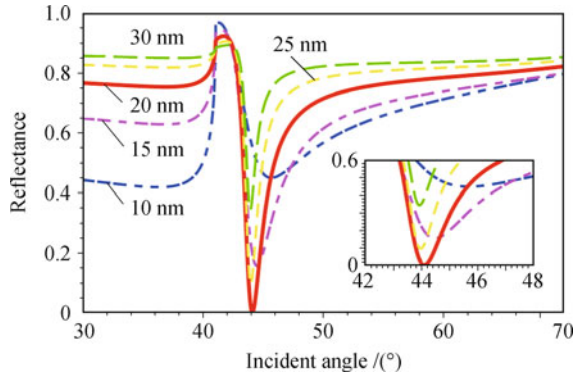

Fig. 1 Calculation results of reflectance with respect to the incident angle for various thickness of aluminum 15–30 nm with 5-nm step that is coated on quartz prism. The incident wavelength is 266 nm. The lowest dip appears at the incident angle of 44 degrees when the aluminum thickness is 20 nm.

The solid line shown in Fig. 2 indicates the measured reflectance depending on the incident angle of aluminum thin film evaporated with the thickness of 24 nm on synthesized quartz prism. A dip of reflectance appeared at 48-degree incidence. In calculation, a dip should appear at 44 degrees for the thickness of 24 nm in aluminum as shown in dashed line of Fig. 2. It departs from the experimental line profile. Considering the oxidized thickness of aluminum, it shows good agreement if we assume the 5 nm oxidization so that the aluminum thickness of 19 nm in total thickness of 24 nm. Aluminum is easily oxidized in atmosphere, and aluminum of 5–8 nm thickness is inherently replaced by alumina. The oxidized thin film around 5–8 nm is userful for the surface plasmon coupled fluorescence. Although the surface electric field intensity is decreased, the quenching of fluorescence is avoided due to the insulating film of alumina. The total thickness of

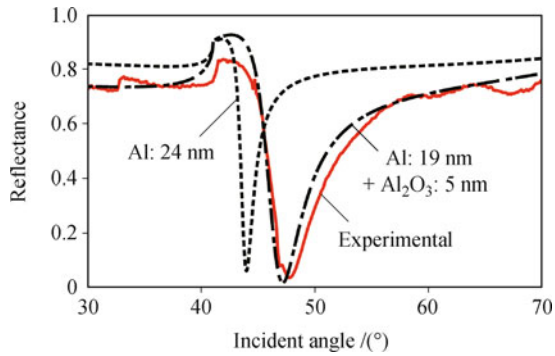

Fig. 2 Calculated (*dashed lines*) and measured (*solid line*) incident angle dependence of reflectance with aluminum thickness of 24 nm. The experimental curve shows good agreement with calculation by regarding it as containing the oxidized aluminum with 5 nm.

the evaporated aluminum film was measured by stylus surface profiler. The oxidized thickness in the total is found by fitting with the Fresnel calculation.

CdSe quantum dots are spin-coated on the aluminum thin film for the demonstration of SP coupled fluorescence. The CdSe quantum dots (Lumidot TM CdSe 560, Aldrich) have an emission peak at the wavelength of 560 nm. Figure 3 shows the experimental setup for the fluorescence measurement in Kretschmann configuration. The 4th harmonic Nd:YAG CW laser of 266 nm was employed as the excitation light. The fluorescent light intensity of CdSe quantum dots and the reflected light intensity of excitation light have been simultaneously detected by Si photodiodes with the rotation of the sample to investigate the relationship between SPR excitation and fluorescence. The output laser power was 2 mW. The incident polarization of *p*-polarization and *s*-polarization was selected by a half-wave plate.

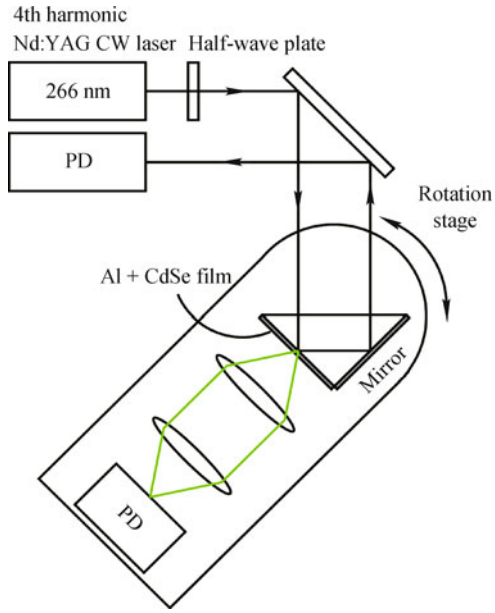

Fig. 3 Experimental setup for the measurement of reflectance and fluorescence intensity with the incident angle dependence. Fluorescence spectrum is also measured with same setup by guiding to the monochlometer using fiber at the steady angle.

The incident angle dependence of the reflectance and the fluorescence intensity of CdSe quantum dots coated on aluminum of 24 nm film thickness (Al: 19 nm, Al_2O_3: 5 nm) are shown in Figs. 4(a) and (b), respectively. In linear *p*-polarized light incidence, SPR is excited at the incident angle of 49 degrees. On the other hand, SPR is not excited for s-polarized light incidence. The fluorescence intensity is enhanced corresponding to the SPR excitation. The fluorescence is 12 times higher than that of linear *s*-polarized light incidence. The fluorescent spectrum of this sample is measured with the incident angle

fixed to 49 degrees where fluorescence intensity is maximum value. As shown in Fig. 4(c), single peak fluorescence in the spectrum was obtained at the wavelength of 560 nm. This peak wavelength is corresponding to the emission peak wavelength of CdSe quantum dots we have used. We successfully demonstrated the coupled fluorescence with deep-UV SPR.

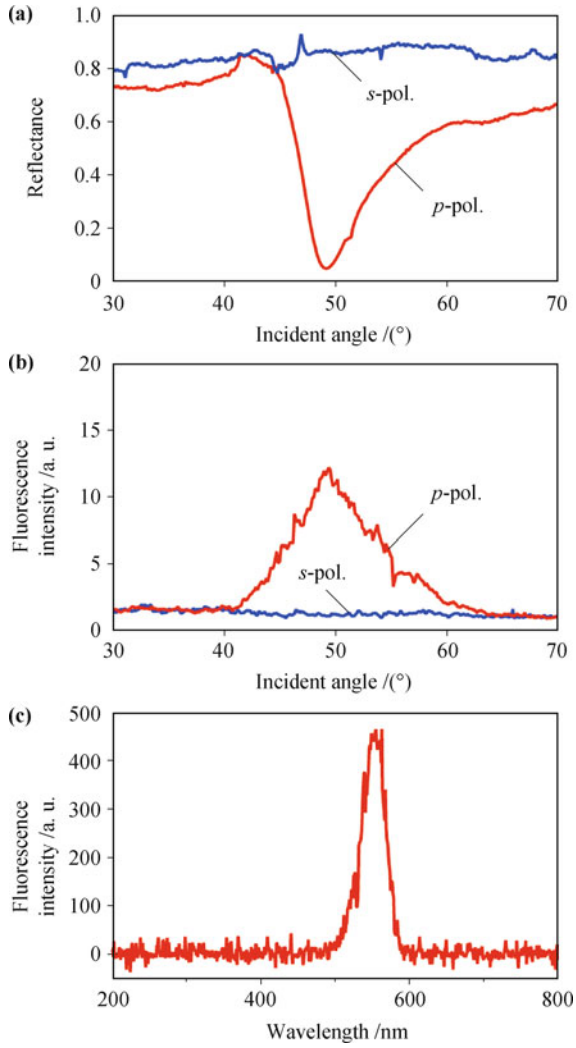

Fig. 4 **(a)** Measured reflectance depending on the incident angle with *p*-polarized and *s*-polarized light incidence. The CdSe quantum dots are coated on the aluminum. The aluminum thickness is 24 nm oxidized with 5 nm (Al: 19 nm, Al_2O_3: 5nm). Surface plasmon is excited at the incident angle of 49 degrees in *p*-polarization. **(b)** Incident angle dependence of fluorescence intensity of CdSe quantum dots coated on aluminum. The fluorescence intensity increases as the SPR excitation efficiency. **(c)** Measured spectrum of fluorescence intensity fixed at the incident angle of 49 degrees. Fluorescence peak was observed at 560-nm wavelength.

Aluminum is one of the excellent metal to be useful for the surface plasmon excitation in UV region. For the application to fluorescence by SPR, it remains a matter of quenching by the metal. There is no issue in terms of quenching for aluminum because it is obtained the insulating layer by the natural oxidization to alumina. A few nanometer of natural oxidization is very useful for the fluorescence by SP-mediated excitation. It remains to be investigated in near future that the optimal distance between the aluminum surface and the quantum dots for the fluorescence enhancement by deep-UV SPR excitation.

UV light is absorbed by the most of fluophores which have the emission wavelength in visible so that it is used as the excitation light for the fluophores. Fluorescence enhancement would be achieved by increasing the absorption efficiency thanks to the SPR. It is expected that SPR excited in Deep-UV would be applied for white light fluorescence enhancement, UV emission enhancement, and autofluorescence of biological samples.

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