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High sensitive detection of near-infrared absorption by surface plasmon resonance

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In this letter we report on an operative method for high sensitive measurement of near-infrared absorption based on a surface plasmon resonance (SPR) technique. By coupling with the SPR of a gold film, an absorption band of water near 5173 cm^{-1} assigned to a combination of the stretching and bending modes of OH groups is enhanced over 100 times compared with a case without the gold film. In addition, positive and negative enhancements of an absorption depending on the thickness of a gold film were observed as predicted by H. Kano *et al.* [Appl. Opt. **33**, 5166 (1994)]. These experimental results are mathematically well reproduced by use of Fresnel multiple-reflection theory. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1610812]

Near-infrared (NIR) spectroscopy has acquired great importance in a variety of fields such as agriculture, foods, pharmacy, polymers, and biotechnology.[1,2] NIR absorptions, arising from anharmonicity of molecular vibrations, are assigned to combinations or overtones of fundamentals observed in the infrared (IR) region. The low absorptivity of NIR allows *in situ* spectral measurements of a huge variety of materials. However, it generally means that NIR absorption measurement requires a large quantity of a sample. In this letter, we propose high sensitive NIR spectroscopy based on a surface plasmon resonance (SPR) technique in light of the widely recognized need of realizing the countermeasure against a small quantity of a sample.

The conventional SPR sensing technique gives accurate information about the refractive index of a sample owing to a sharp resonance for an incident angle. However, the SPR measurement provides not only the refractive index, but also information about molecular absorption. Pockrand *et al.* experimentally demonstrated the sensitive detection of absorption coupled with SPR in 1978.[3] The key to expand the SPR method to the absorption measurement is the introduction of the complex refractive index, $\tilde{n}=n+\kappa i$, where n and κ represent a real part of the refractive index and an extinction coefficient, respectively. The complex refractive index is also applicable to the conventional SPR theory. By use of this theory Kano *et al.* predicted an evident enhancement of absorption by SPR in the visible region in 1994.[4] Since then, although several studies have been done on the absorption-sensitive SPR in the visible region,[5–9] no attention has been paid to the NIR region. To compensate for the low absorptivity, this SPR technique should be applied to the NIR spectroscopy. Therefore, we have aimed at developing an operative method for the enhancement of absorption with a NIR spectrometer based on the absorption-sensitive SPR technique.

Our experimental setup is shown in Fig. 1. We adopted a most typical optical geometry for SPR measurement called a Kretschmann configuration,[10] which is the same as that for attenuated total reflection (ATR) except for the presence of metallic film on the surface for internal reflection. The light beam from the external port of a Fourier transform NIR spectrometer (Bruker Optics, VECTOR22/N) is sent through a quartz fiber optic (the core diameter is 0.6 mm) to a planoconvex lens, which focuses the beam on a slit. Then, the beam is collimated in a BK7 ($n_D=1.517$) hemicylinder prism to a beam width of ~ 1 mm, and the size of the beam spot on the reflective surface is less than 2 mm^2. In this study we used only one drop of pure water as a sample. By using our optical system one can reduce a sample volume from a mL range to a μL range, which is required for NIR spectral measurement. Furthermore, taking account of the penetration depth of the evanescent wave (about 300 nm in depth), the effective volume of a sample can be reduced less than 10 nL.

For handiness, a glass slide coated with a thin gold film, was placed on the prism with index matching fluid (polyethylene glycol). The gold films were prepared by vapor deposition onto microscope glass slides (IWAKI) that had been washed with pure water. The reflected beam is sent back to the spectrometer through a polarizer, a planoconvex lens and

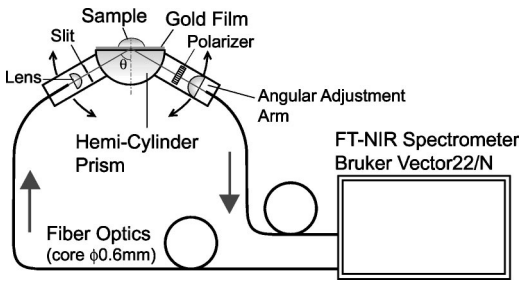

FIG. 1. Schematic of our experimental setup for measuring NIR absorbance enhanced by SPR.

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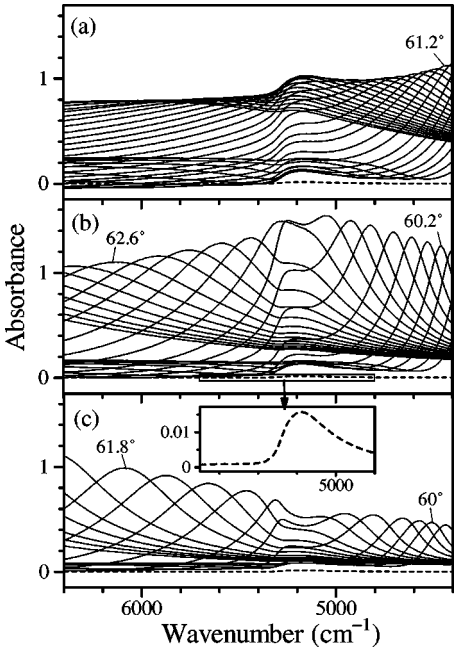

FIG. 2. SPR absorption spectra in the 6400–4400 cm^{-1} region measured over an incident angle of 59°–65° (every 0.2°) for three gold films (a), (b), and (c). Dashed lines show the spectra of water measured by single reflection ATR at $\theta=66°$.

a fiber optic. The tips of the fiber optics and optical elements are mounted on angle adjustment arms, allowing us to vary the incident angle continuously from 35° to 90°. SPR absorbance spectra were generated by background spectra, which were collected with the polarizer set to *s* polarization, and sample spectra, which were collected with the polarizer set to *p* polarization. All SPR spectra were measured at a 4 cm^{-1} resolution and 32 scans were co-added.

The thickness of gold films, d, on the glass slides were determined to be (a) 11.1, (b) 17.7, and (c) 28.6 nm by transmittance measurement at 5173 cm^{-1} and calculations based on the Fresnel formula considering the multiple reflection in the thin films.

Figure 2 shows SPR absorption spectra of water in the 6400–4400 cm^{-1} region measured over an incident angle of 59°–65° with an increment of 0.2° for the three gold films (a)–(c). Also shown is a water spectrum measured by single reflection ATR with $\theta=66°$, namely, without a gold film (dashed lines). The inset shows an enlarged ATR spectrum of an absorption band assigned to the combination of bending and antisymmetric stretching modes of water (the absorbance at 5173 cm^{-1} is 0.0157). The SPR peak can be tuned with changing the incident angle.[11] In all the cases in Fig. 2, absorption of the sample is evidently enhanced by SPR compared with that of ATR especially when the absorption peak and SPR peak overlap with each other. Furthermore, note that the envelope curves of the peak tops of SPR spectra convex upward in the cases of (a) and (b), whereas they concave downward in the case of (c), depending on the thickness of gold films in the water combination band region.

To analyze the above results mathematically, we refer to Fresnel multiple-reflection theory. The intensity of reflectance is represented as a function of the incident angle θ and the thickness of a gold film d with the amplitude reflectance

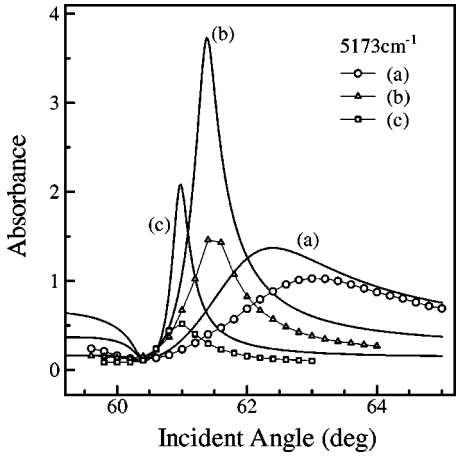

FIG. 3. SPR absorption for each gold film at 5173 cm^{-1} against the incident angle. Open symbols with thin solid lines and bold lines show experimental and calculated results, respectively.

r_{ij} at the boundary between medium i and j for light incident from i to j as

$$R(\theta,d)=\left|\frac{r_{pm}+r_{ms}\exp(2ik_{mz}d)}{1+r_{pm}r_{ms}\exp(2ik_{mz}d)}\right|^2, \tag{1}$$

where suffixes s, p, and m denote sample, prism, and metal, respectively. k_{mz} is the z component (parallel to the surface) of the wave number of the light inside the metal, given by

$$k_{mz}=\frac{2\pi}{\lambda}\sqrt{n_m^2-n_p^2\sin^2\theta}, \tag{2}$$

where n_m and n_p denote the refractive indices of the metal and the prism, respectively, and λ is the wavelength of the incident light in vacuum. Here, we assumed a smooth continuous surface for a thin gold film. The amplitude reflectance r_{ij} is defined for each polarizing direction, namely, $r_{ij\perp}$ for p-polarized light and $r_{ij\parallel}$ for s-polarized light. The reflectance for p-polarized light $R_\perp$ and that for s-polarized light $R_\parallel$ are also defined by using of $r_{ij\perp}$ and $r_{ij\parallel}$, respectively. Accordingly, the observable absorbance is represented as

$$A(\theta,d)=-\log\frac{R_\perp}{R_\parallel}. \tag{3}$$

For calculation purposes, we used data supplied by Sigma Koki Co., Ltd., for the refractive index of BK7 prism and the known value for the real part of the refractive index of water.[12] To model the absorption band of water, we assumed the extinction coefficient, $\kappa=9.69\times10^{-4}$ at 5173 cm^{-1} for the sample and $\kappa=0$ for the blank sample. As reliable data for the optical constants of gold, we employed Johnson's results.[13]

Figure 3 compares the calculated SPR absorption with the experimental result for each gold film at 5173 cm^{-1} displayed as a function of the incident angle. The thin solid lines with the open symbols and the bold solid lines denote the experimental results and calculated results, respectively. It is noted that the SPR absorptions against the change in the incident angle are well reproduced by the Fresnel multiple-reflection theory. The difference in the absorbance between the experimental and calculated results is due to the dispersion of the lens and the hemicylinder prism. Assuming that

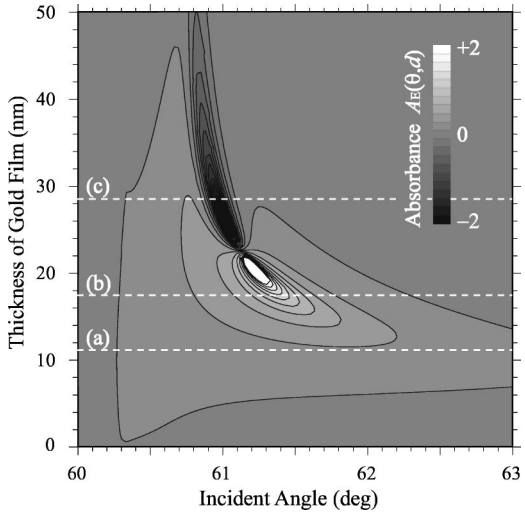

FIG. 4. Contour plot of the extracted absorption A_E as functions of the incident angle θ and the thickness of gold film d at 5173 cm^{-1}.

the incident beam profile has a Gaussian distribution through the calculation, we could confirm the broadening of the SPR peaks. Moreover, we found an obvious difference in the peak position of SPR curves for the gold film (a) between the experimental results and calculated results, because we cannot precisely determine the dielectric constants due to the surface roughness of the gold film, which is not negligible compared to its mean thickness. Although it seems from Fig. 3 that we can obtain the finest absorbance by use of the gold film with the thickness of about 20 nm, it must be noted that the observed absorbance contains components from both the absorption of a sample and the SPR. It is almost impossible to separate these two contributions experimentally because we have to prepare a blank sample, which has the same dispersion as that of water, but has no absorption. However, we can realize this procedure theoretically.

In order to examine the degree of enhancement of absorption by SPR, we subtracted the intensity of the SPR absorbance without any molecular absorption of sample $A_{\kappa=0}$ from the intensity of SPR absorbance with the absorption $A_{\kappa\neq0}$ at 5173 cm^{-1}. As a matter of fact, the observable absorption does not consist of the simple summation of these two contributions because it is a modulated SPR signal by the presence of water with absorption. Given the above, this numerical procedure is valid to extract the enhanced absorption of the sample broadly. Figure 4 shows a contour plot of the extracted absorption $A_E=A_{\kappa\neq0}-A_{\kappa=0}$ as functions of the incident angle and the thickness of gold film. In Fig. 4, strongly enhanced positive and negative absorption peaks are observed. This phenomenon was theoretically predicted for the visible region.[4] As can be seen from Fig. 4, the observed signal is due to the light that leaks back from the interface between the metal and the sample. Therefore, if the thickness of a gold film is thinner than the penetration depth of the evanescent wave, the absorption is positively enhanced and vice versa. The absorbance of the positive peak top is $A_E=56.26$ at $\theta=61.20$ and $d=20.74$, whereas the absorption of negative peak top is $A_E=-47.9$ at $\theta=61.04$ and $d=25.31$. These conditions are experimentally unrealizable, besides the double-digit absorbance makes no sense. However, we can safely say that SPR practically provides the absorption enhancement by a factor of 10^2 compared with the absorbance of ATR. To compare the calculated with the experimental results, we drew dashed lines for each gold film (a)–(c) (Fig. 4). Cross sections at each dashed line correspond to the calculated results in Fig. 3 (the bold solid lines). On the basis of the agreement between the experimental and calculated results in Fig. 3, it is considered that the absorption band of water is positively enhanced in the cases of the gold films (a) and (b) and negatively enhanced in the case of (c). These features correspond to the convex and concave envelope curves of the SPR spectra shown in Fig. 2.

In conclusion, we fabricated a setup for spectral measurement of SPR in the NIR region and observed an obvious enhancement of the absorption band at 5173 cm^{-1} due to water. The intensity of absorption is enhanced over 100 times compared with ATR, when absorption peaks due to the sample and SPR peak overlap. In addition, the reported alternative features of positive and negative enhancement of absorption depending on the thickness of gold film were observed. These results were mathematically well reproduced by use of the Fresnel multiple-reflection theory. By using our setup one can reduce a sample volume from the mL range to the nL range required for NIR spectral measurement.

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