Cambridge University Press
978-1-107-40822-7 - Materials for Nanophotonics — Plasmonics, Metamaterials and Light Localization: Materials Research Society Symposium Proceedings: Volume 1182
Editors: Luca Dal Negro, Mark Brongersma, Joseph M. Fukumoto and Lukas Novotny
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Poster Session I

Mater. Res. Soc. Symp. Proc. Vol. 1182 © 2009 Materials Research Society 1182-EE09-08

Real-Time Visualization Method of Surface Plasmon Resonance With Spectroscopic Attenuated Total Reflection

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ABSTRACT

We report the real-time visualization technique of surface plasmon resonance (SPR) with the spectroscopic attenuated total reflection (S-ATR). Using this technique, light absorption due to SPR on thin metal films by the white light were clearly visualized on a two-dimensional detector such as CCD camera in the coordination of the incident angle and the wavelength. Metal films could be distinguished even in partially oxidized condition. The real-time SPR visualization would be useful for monitoring of biochemical reactions as well as for fabricating plasmonic devices.

1. INTRODUCTION

Recently, surface plasmons resonance (SPR) is widely studied for plasmonics devices for constructing faster processor in the electronic microprocessors as well as for biochemical evaluation. SPR is a specific absorption which is sensitive to the dielectric constant and thickness of the metallic material, resulting in strong absorption of light as a function of incident angle, wavelength and polarization of light. [1-15] Since the dispersion property of SPR exists in the total reflection region, it had been studied with the attenuated total reflection (ATR) method. Kretchmann configuration[3] using a glass prism and an approximately 50 nm-thick silver or gold film was often used as sensing instruments in order to evaluate the optical constants of the film itself,[3-7] the coating layer on the film,[5,8,9] the surface process deferences,[10,11] or the ambient material.[12]. Most of SPR signals had been measured with either angular or spectral dependence with this geometry. In the case of angular dependence,[3-11,13] the monochromatic laser, e.g. He-Ne laser at 632.8 nm, is often used for the incident light. One can measure reflection loss as a function of an incident angle in the total reflection region. In the spectral dependence,[12] a white light source is used instead of a monochromatic laser in order to measure reflection loss as a function of wavelength at a fixed incident angle. In both cases, the absorption peak shifts easily due to a few nm-thick layer on the metal film.[1] Visualization technique of SPR on the thin film had been developed using a two-dimensional detector such as a CCD camera.[17-20]

On the other hand, another imaging technique, called surface plasmon fingerprinting, had been developed for visualizing surface plasmon resonance with angular and spectral dependences.[21] In Ref. 21, the angular and spectral behavior of SPR was visualized using a tilting mirror system, and it was useful to evaluate the angular and spectral shift of SPR in order to understand the phenomena on the metal surface. It is desired to visualize the SPR fingerprints in the real time when one wants to evaluate reaction on the surface. Here we report that the spectroscopic attenuated total reflection (S-ATR) technique for real-time SPR visualization in which we employed the polychrometer and the two-dimensional CCD detector to monitor SPR fingerprinting in the real time.

2. THEORY

We will briefly explain an ordinary ATR image for SPR measurement before experimental results. Figure 1 shows the Kretschmann configuration in order to excite SPR.[3] Normally, thin metal film (~50 nm-thick Ag or Au) is located on the prism surface. In this configuration, the transmitted intensity I_T through the prism is calculated by the following equation

$$I_T=(1-R_1)\,R_2\,(1-R_3)\,I_0 \quad (1)$$

, where I_0 is the incident intensity, and where R_1, R_2 and R_3 are the reflectivities at the plane in shown in Fig.1. As seen in equation (1), I_T is directly related with R_2. The relations between angles α, β and γ are expressed by the following equations

$$n_{air}\sin\alpha=n_{prism}\sin\beta \quad (2a)$$
$$\gamma=\beta+45^\circ \quad (2b)$$
$$n_{prism}\sin\gamma_c=1 \quad (2c)$$

, where n_{air} and n_{prism} are the refractive indices in the air and the prism depending on the wavelength λ of the incident light. n_{air}=1 for all the wavelength range. The total reflection occurred more than the critical angle γ_c. To simplify the situation, we consider that a 45° quartz (SiO_2) prism is located in the air and that an incident light at the wavelength of 633nm illuminates a 50 nm-thick Ag (or Au) film located on the prism. Since the critical angle γ_c=43.34° for n_{prism}=1.457, the total reflection occurs γ>43.34°, β>-1.66° and α>-2.42°.

SPR can be excited only with P-polarized light, not with the S-polarized light. The SPR dispersion between air and metal surface is expressed by the following equations,

$$K_{SP}=(\varepsilon_{r,metal}\,\varepsilon_{r,air})/(\varepsilon_{r,metal}+\varepsilon_{r,air}) \quad (3a)$$
$$k_0=\omega/c=2\pi/\lambda_0 \quad (3b)$$
$$\varepsilon^*=\varepsilon_r+\varepsilon_i=n^* \quad (3c)$$

where K_x is the wave number of SPR along the metal surface, and ε^* and n^* are the complex dielectric constant and the complex refractive index of the material, respectively. k_0 and λ_0 are the wave number and the wavelength of incident light in vacuum, ω is the frequency and c is the light speed. Since the wavelength λ and the wave number k change in the material, ε^* is expressed as a function of ω like n^*.

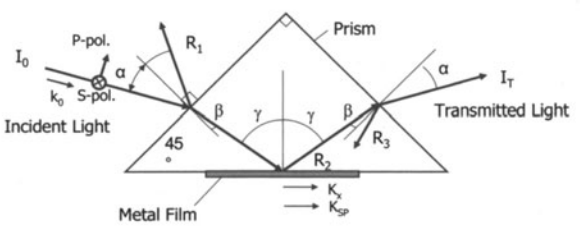

Fig.1. Kretschmann geometry of the ATR method in order to excite SPR. R_1 and R_3 are reflection at the prism surface, and R_2 is the reflectivity at the film.

Figure 2 shows the wavelength dependences of dielectric constants for silver (Ag), gold (Au) and quartz (SiO_2).[16] Normally, the real component of the dielectric constant is negative and the imaginary component is positive for metal, while the real component is positive and the imaginary component is almost zero for glass material. Since SPR has larger wave number compared with light, i.e. $K_x/k_0>1$, therefore $\varepsilon_r<-1$. As shown in Fig.2, ε_r of Ag is smaller than that of Au at the wavelength between 400 and 900 nm, which indicates that K_x/k_0 for Ag is smaller than that of Au in this wavelength range. For example, ε_r for Ag and Au at 633 nm are –17.46 and –9.62, which correspond to K_{SP}/k_0=1.061 and 1.117, respectively. The peak incident angle α for Ag must be smaller than that of Au. The reflectivity due to SPR for Kretschmann configuration is calculated including the thickness of the metal film as well as that of the coated layer on the metal film.[5]

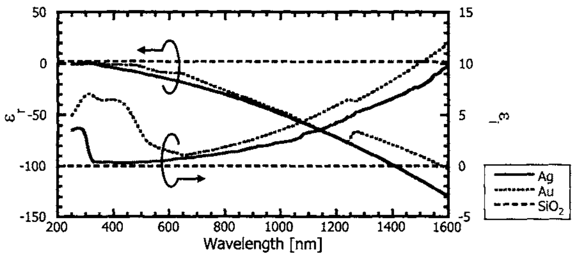

Fig.2. Dielectric constants used for the calculation. The real parts of the dielectric constants of metal films are normally negative.

In the ATR method using a prism to excite SPR, the wave number of light has to agree with the wave number K_{SP}. (See Fig.1) The wave number along the prism surface K_x is expressed by the following equation

$$K_x=(n_{prism} \sin \gamma)\ k_0 \quad (4)$$

In order to achieve above K_x/k_0, $n_{prism} \sin \gamma>1$, i.e. $\gamma>\gamma_c$. Therefore SPR will appear in the total reflection region.

Figures 3 show calculated S-ATR images passed through the configuration shown in Fig. 1. SPR absorptions are clearly seen in the total reflection region in these figures. A 50 nm-thick Ag film in Fig.3 (a) shows the peak incident angle at the incident angle of 0.1 ° for the wavelength of 633 nm. In Figs.3 (a)-(c), the SPR absorption curves are shifted toward the right direction, i.e. the larger incident angle, as the thickness of the quartz coating increases. However, 15.5 nm-thick quartz (SiO_2) coated 50 nm-thick Ag film shows the same peak angle at 2.5 ° with the 50 nm-thick gold film for this wavelength. However, the S-ATR image for Au film shown in Fig.3 (d) can be easily distinguished from the S-ATR image for Ag film shown in Fig.3 (b). Therefore, the S-ATR image is important for visualizing SPR for an unknown film.

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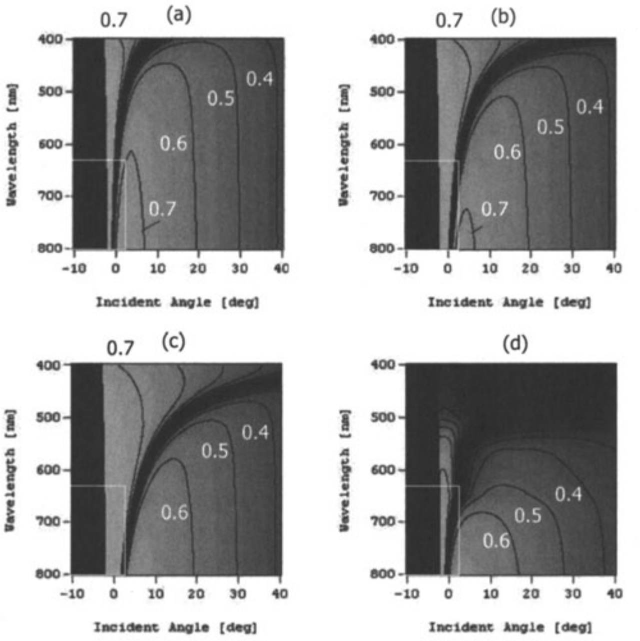

Fig.3. Calculated S-ATR Image for thin Au and Ag films. (a) 50 nm-thick Ag film, (b) 15.5 nm-thick and (c) 30 nm-thick SiO_2 coated Ag film as well as (d) 50 nm-thick Au film. The grayscale is colored for transmission I_T/I_0 from 0 (black) to 1 (white). Each contour indicates 0.1 differences in transmission. White corners in these figures show the incident angle of 2.5 ° and the wavelength of 633 nm.

3. EXPERIMENT

In order to visualize SPR, a two-dimensional CCD detector was used to detect SPR fingerprint in the coordination of the incident angle and the wavelength. Figure 4 shows geometry of the S-ATR technique. As shown in this figure, a white light source irradiatedwith wide incident angle toward a sample film located on a prism. The white light passed through the prism illuminates an entrance slit of a spectrometer in order to catch the angular distribution of the transmitted light that passed through the prism. The spectrometer is equipped with two-dimensional CCD detector. On the detector, each position of the image means a reflection property for a certain incident angle and a certain wavelength, indicating the angular-resolved and spectral-resolved ATR image, i.e. S-ATR image. The S-ATR image includes the dispersion property of SPR in the angle and the wavelength separately.

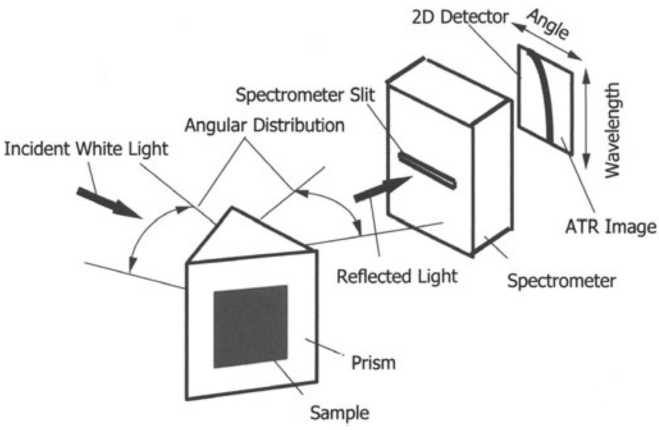

Fig.4. Schematic of the ATR imaging technique.

Figure 5 shows the experimental setup in this experiment. Vacuum evaporated 50nm-thick silver (Ag), gold (Au), and copper (Cu) films were prepared on quartz (SiO_2) substrates. A partially oxidized silver film (AgO_x on Ag) was also prepared from the 50 nm-thick Ag film by a plasma reactor. A 200 W tungsten lamp (I-150, CUDA Products Corp.) was used as a white light source. The light that passed through a polarizer (P) and through an achromatic lens (L1, f=80 mm) illuminates a pair of 45 ° quartz prisms used in order to straighten the incident beam toward the spectrometer. An achromatic lens (L2, f=80 mm) correct the dispersed light from the prism pair into the horizontal slit (S1, 100 μm-wide). A dove-prism and two achromatic lenses (L3 and L4, f=200 mm) were used to rotate the reflected light in order to send it into the vertical entrance slit (S2, 100 μm-wide) of the spectrometer. A spectrometer (Monospec 27, Jerral Ash Inc., f=270 mm) with a 150 lines/mm grating was used to diverse the transmitted light. A CCD camera (CS3330, Tokyo Electric Industries Co., Ltd.) is used as a two-dimensional detector. On the CCD image, the wavelength range from 476 to 782 nm was determined extrapolating the three He-Ne laser light at 543.5, 594.0, 632.8 nm, and the incident angle range from –3.1 ° to +6.1 ° was determined using a hard aperture between the lens (L1) and the 1st prism. The angular and spectral accuracy is 0.1 ° and 1.5nm, respectively.

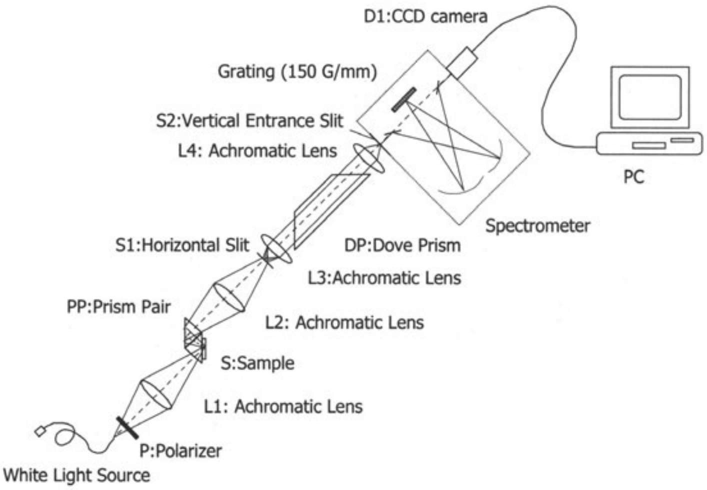

Fig.5. Schematic of the experimental setup is shown. A Dove prism (DP) is used to rotate the image of the horizontal slit (S1) in order to send it to the entrance slit (S2).

Figure 6 shows the details of the sample geometry consisting of two prisms and the substrate, which were optically connected with an index matching liquid. The transmitted intensity through this geometry system is expressed as

$$I_T = (1-R_1)\, R_{2,1st}\, R_{2,2nd}\, (1-R_3)\, I_0 \quad (5)$$

When the total reflection condition, equation (5) is same as equation (1).

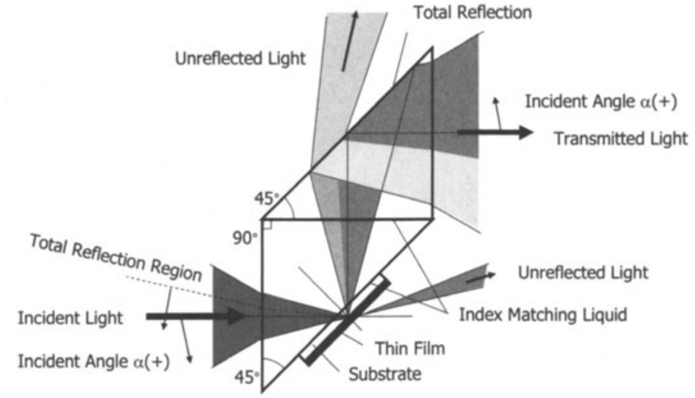

Fig.6. Top view of the pair of prisms and the substrate is shown. Index Matching Liquid is used between the two prisms and the sample substrate.

4. DISCUSSION

Figure 7 shows comparisons between a measured and a calculated S-ATR images for a 50 nm-thick Ag film with the P-polarized light. The SPR absorption is clearly observed. Dark SPR absorption curve shows good agreement.

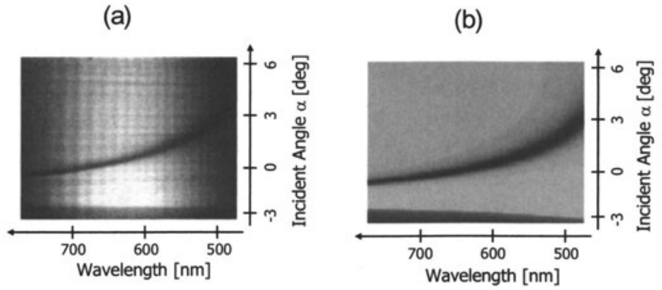

Fig.7. (a) Measured and (b) calculated S-ATR images for a 50nm-thick Ag film with the P-polarized light are shown.