Localized Surface Plasmon Resonance Sensing Properties of Ag/TiO_2 Films

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Ag nanoparticles were deposited on TiO_2 films (Ag/TiO_2 films) by photocatalytic means. When the film was immersed in various kinds of alcohols, the linear relationship was observed between the wavelength of localized surface plasmon resonance peak and the refractive index of the alcohols in the range of 1.33–1.41. The Ag/TiO_2 films can be applied to the SPR sensors.

The interesting colors observed in silver nanoparticles embedded in dielectric matrices have led to extensive study of their optical properties.[1] In recent years, nanometer-sized metal particles have attracted considerable interest for their application to sensor devices such as surface plasmon resonance (SPR) sensors,[2] immunoassays,[3] and optoelectronic devices.[4]

Conventional SPR sensors with a metal film deposited upon a glass prism are based on the principle that the SPR is highly sensitive to the refractive index of surrounding medium.[5] The index differences are detected via angle changes of a reflected laser beam. Thus, the conventional SPR sensors require the glass prism and the optics associated with the detection system for the attenuated total reflection geometry. On the other hand, the SPR sensors with metal nanoparticles do not require the complicated system.[2] The sensors are easy to fabricate and are reproducible in their performance. Furthermore, the sensors can be small and reduce the required sample amount.[2]

Recently, there have been several papers[6–9] where Ag nanoparticles were deposited on TiO_2 films (Ag/TiO_2 films). The Ag/TiO_2 films have many interesting properties; therefore, there are a variety of applications for the films such as photochromic displays,[7] catalysts,[8] and antibacterial materials.[9] In this paper, we report on the SPR sensing properties of photocatalytically prepared Ag/TiO_2 films.

A glass slide substrate was coated with TiO_2 film from anatase sol (Ishihara Sangyo Kaisha, ST-K211) by a dip-coating technique. The dip and drying procedures were repeated three times, resulting in the TiO_2 film about 300 nm in thickness on both sides of the substrate surface. The glass slide film with TiO_2 was soaked in a 20 mL of 0.01 M aqueous $AgNO_3$ solution in a petri dish, followed by irradiating UV light from above for 4 h. Thus, Ag particles were deposited on one side of the TiO_2 film. The light source used was a 15-W low-pressure mercury lamp (a germicidal lamp). The resultant Ag/TiO_2 films were dried for more than 12 h. All the preparation procedures were carried out at room temperature.

Figure 1 shows the typical XRD pattern of the Ag/TiO_2 film. In the XRD pattern, the peaks at $2\theta = 38.1$ and at $2\theta = 44.3°$ are assigned to the (111) and (200) (ICDD No. 04-0783) reflection lines of cubic Ag, respectively. The mean diameter of Ag particles was estimated to be about 39 nm from the line broadening of the diffraction band at $2\theta = 38.1°$ using Schrrer's equation. Nanosized Ag particles were successfully deposited on the TiO_2 film by the photocatalytic process. The deposited Ag nanoparticles were not washed off by distilled water and organic solvents. Thus, the nanoparticles were immobilized upon the TiO_2 film by the photocatalytic reaction even at room temperature. The nature of the chemical bonds of the Ag/TiO_2 film was investigated by XPS.[10] In the Ag 3d electron spectrum of the Ag/TiO_2 film, the spin doublet of Ag 3d, i.e., Ag $3d_{3/2}$ and Ag $3d_{5/2}$, was clearly observed. The peak positions of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ corresponded to metallic Ag. It is confirmed that the deposited Ag nanoparticles are in metal Ag, but not in Ag_2O or AgO.

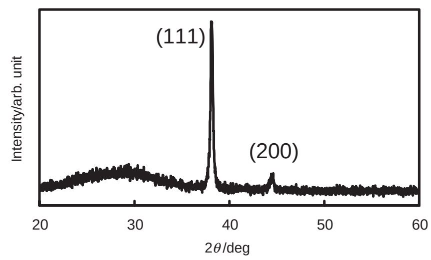

Figure 1. Typical XRD pattern of the Ag/TiO_2 film.

The colorless TiO_2 films turned brownish-gray during the UV irradiation, owing to the localized SPR absorption of the deposited Ag particles. The absorption spectra of the Ag/TiO_2 film and the film immersed in five kinds of linear alcohols were measured using a UV–vis spectrophotometer. The spectra measurements of the immersed films were carried out by using a typical quartz liquid cell with a path length of 10 mm and a window area of about 28 mm^2 (6 mm in diameter). The film was positioned on the edge of the cell and it was sequentially immersed in the five kinds of alcohols. After the immersion, the film was dried at room temperature and was again immersed another alcohol. The alcohols used were as follows: methanol ($n_D^{20} = 1.3292$), ethanol ($n_D^{20} = 1.3605$), 1-propanol ($n_D^{20} = 1.3854$), 1-butanol ($n_D^{20} = 1.3993$), and 1-pentanol ($n_D^{20} = 1.4103$). The n_D^{20} is the refractive index of the alcohol at 20 °C.

Figure 2a shows the absorption spectra of the Ag/TiO_2 film and the film immersed in the five kinds of alcohols. The color of the film was brownish-gray not transparent yellow, suggesting that the size distribution of the Ag particles was large. In the figure, the film shows an absorption peak at 382 nm, due to the localized SPR absorption of the Ag particles.

The broad absorption band of the film confirmed the large size distribution of the Ag particles. The absorption spectra of the magnified scale for the immersed film near the localized SPR absorption peak are shown in Figure 2b. In the figure, the peak absorbance of the immersed film increases and the absorption peak wavelength is clearly shifted to longer wavelengths (428–440 nm) with increasing the refractive index of the alco-

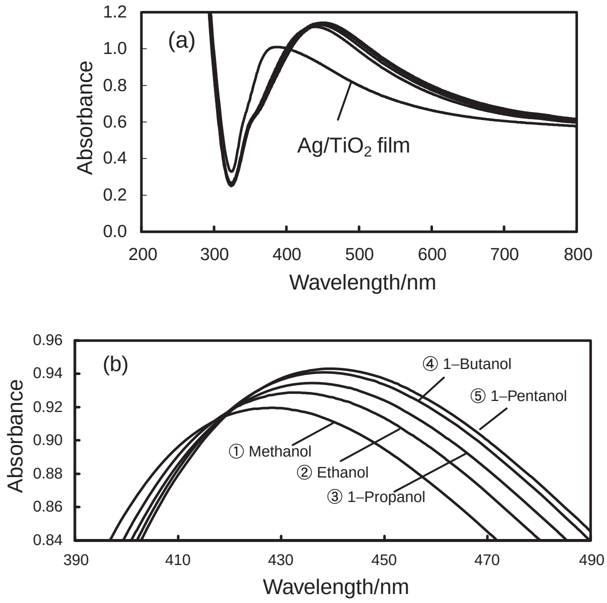

Figure 2. Optical absorption spectra of the Ag/TiO_2 film and the film immersed in five kinds of alcohols with different refractive index: (a) in the range between 200–800 nm and (b) near the localized SPR peak of the spectra for the immersed film.

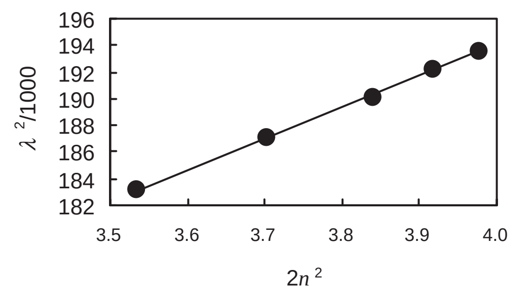

Figure 3. The square of the localized SPR peak absorbance wavelength as a function of twice the square of the refractive index of the alcohols.

hols. The linear relationship was observed between the peak wavelength and the refractive index in the range of 1.33–1.41. These absorption spectra were reproducible for all the alcohols used here. The Ag/TiO_2 film can be used many times only if they are dried at room temperature after the immersion. The Ag/TiO_2 films prepared were stable for more than six months.

According to Mie theory,[11–14] the wavelength of the localized SPR peak position, λ, is related to the refractive index (n) of the surrounding medium by the following eq 1:

$$\lambda^2 = \lambda_p^2(\varepsilon^\infty + 2n^2), \qquad (1)$$

where λ_p is the bulk metal plasmon wavelength, ε^∞ the high frequency dielectric constant due to interband and core transitions. The refractive index of the medium is directly related to its dielectric constant, ε_m, i.e., $n = \sqrt{\varepsilon_m}$. From the eq 1, the plot of λ^2 as a function of $2n^2$ will be linear. On the other hand, the absorbance maximum increases with increasing n of the surrounding medium as shown by Mulvaney et al.[13] Figure 3 shows a relation between the square of the observed peak position, λ^2, of the localized SPR of the Ag/TiO_2 film and the twice of the square of the refractive index, $2n^2$, of the surrounding alcohols. In the figure, over the range of refractive index of the alcohols studied, the linear relation ($R = 0.999$, R: correlation coefficient) is observed. The linear relation between λ^2 and $2n^2$ is indicative of the fact that the alcohol refractive index influences the localized SPR peak wavelength by Mie theory. The absorbance maximum also increased with increasing the refractive index of the surrounding alcohols as indicated by Mulvaney et al.

In summary, the Ag/TiO_2 films have been successfully prepared by the photoreduction of Ag ions on the surface of TiO_2 films at room temperature. The deposited Ag nanoparticles on the films are immobilized and the Ag/TiO_2 films are stable. When the film was immersed in five kinds of alcohols, the linear relation between λ^2 and $2n^2$ was clearly observed in the refractive index of the alcohols in the range of 1.33–1.41. These absorption spectrum changes were reproducible for all the alcohols studied here. Thus, the photocatalytically prepared Ag/TiO_2 films can be applied to the SPR sensors.

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