Optical Properties of Long-range-ordered, High-density Gold Nanodot Arrays Prepared Using Anodic Porous Alumina

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Long-range-ordered, high-density gold (Au) nanodot arrays were prepared by vapor deposition using anodic porous alumina as a mask. The optical properties of such arrays were examined. The effects of highly ordered, high density arrangements of Au nanodots on the optical properties were elucidated by the dependences of the wavelength (λ_{max}) of the absorption maximal on the dot height and the refractive index of the solvent in which the Au nanodot arrays were immersed.

Recently, the development of sensing devices utilizing localized surface plasmon resonance (LSPR) exhibited by nanometer-scale noble-metal particles has attracted considerable interest because LSPR gives rise to spectrally selective light absorption and enhanced scattering, resulting in the development of the highly sensitive devices for the detection of chemical or biological molecules.[1,2] To date, studies of LSPR on the disordered arrangement of metal nanoparticles have focused on the effects of the size, shape, and dielectric properties of the metal on the optical properties of the arrays.[3,4] Moreover, the optical properties of short-range-ordered arrays of nanoparticles fabricated by colloidal lithography have been also reported.[5] However, reports of LSPR on highly ordered arrays of nanoparticles with uniform size, shape, and spacing over large areas are limited to those with the ordered particle arrays where the spacings are much larger than the particle size and the nanoparticles have low aspect ratios (h/d; h: dot height, d: dot diameter), as determined using nanosphere lithography and electron beam lithography.[6,7] High ordering of the nanoparticles with high density is a key factor not only in understanding how nanostructure parameters influence LSPR in fundamental interest but also in maintaining and improving the optical properties, such as narrowing of the full widths at half maximum (FWHM) and increases in the absorption intensity due to the interaction between nanoparticles, in the applications.

In this study, we will report the optical properties of long-range-ordered, high-density Au nanodot arrays which have various aspect ratios of nanodots and are immersed in the solvents. The Au nanodot arrays were fabricated by a simple preparation method using highly ordered anodic porous alumina as a mask in the vapor deposition, which we have previously reported.[8] Highly ordered anodic porous alumina has porous structures with uniform nanometer-scale hole diameters and periods, and straight holes over large areas.[9] Using an ordered hole array of anodic porous alumina as a mask, an ordered nanodot array can be formed easily over large areas in which each dot has uniform size and spacing to its neighbors because of the uniform arrangement of the holes and straight channel structures on anodic porous alumina. In particular, this method using anodic porous alumina can be used to fabricate arrays composed of Au dots having an aspect ratio of more than 1, whose structures cannot be fabricated using nanosphere lithography and electron beam lithography. Here, the observed optical properties of highly ordered arrays of Au nanodots having high aspect ratios and high densities over large areas were compared with those of ordered arrays of nanoparticles having lower aspect ratios and lower densities and disordered nanoparticle arrays.

Au nanodot arrays were prepared by vapor deposition as reported previously[8] using highly ordered anodic porous alumina through-holed membrane with a hole period of 100 nm, a hole diameter of 55 nm, and a membrane thickness of 300 nm, which was prepared by two-step anodization under appropriate conditions, resulting in the formation of a self-organized hole array structure with straight through holes, uniform sizes, and an ordered hole configuration. Au was deposited on quartz plates using a vacuum evaporation apparatus. After the vapor deposition, the mask was removed mechanically. The size of the evaporation mask was usually approximately 5 mm × 5 mm. Uniform Au nanodots were formed over the area. The density of the Au nanodots was approximately 510 dots/μm^2. This density corresponded to 0.36 monolayer coverage. Transmission visible absorption spectra were measured using nonpolarized light with a Hitachi spectrophotometer, U-3300 (sampling area: 1.5 mmϕ).

Figure 1 shows the surface and cross-sectional SEM images of a Au nanodot array with a dot period of 100 nm, a dot diameter of 55 nm, and a dot height of 40 nm. The Au nanodots on the substrate are arranged uniformly over the substrate. From the cross-sectional image, it is seen that the Au dots have a uniform cone shape. The cone-shaped dots were formed because the Au deposited on the mask reduces the width of the openings on an anodic

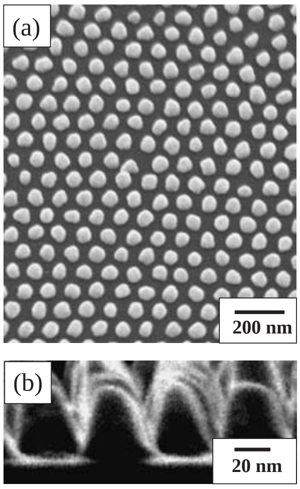

Figure 1. Surface (a) and cross-sectional (b) SEM images of a Au nanodot array with a dot period of 100 nm, a dot diameter of 55 nm, and a dot height of 40 nm, which was fabricated using highly ordered anodic porous alumina with a hole period of 100 nm and a hole diameter of 55 nm as an evaporation mask.

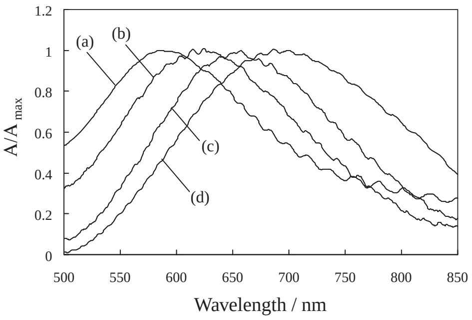

Figure 2. Transmission absorption spectra for Au nanodot arrays with a dot period of 100 nm and a dot diameter of 55 nm in dry N_2 gas. Dot heights: (a) 80, (b) 60, (c) 40, (d) 25 nm.

porous alumina with the progress of vapor deposition. The adjustment of deposition time could control the height of the nanodots from 25 to 80 nm, almost without changing the cone shape and its curvature. Au nanodot arrays with dot height of more than 80 nm could not be fabricated currently because the Au deposited on the mask closed the pores on an anodic porous alumina.

Figure 2 shows the transmission visible absorption spectra of Au nanodot arrays having different dot heights in dry N_2 gas while keeping the dot period of 100 nm and dot diameter of 55 nm constant. The peaks were normalized to the same height because the intensity markedly increased with the height of the Au nanodots. As can be seen in the figure, the LSPR peaks of the ordered Au nanodots are located in the visible light region from 550 to 700 nm. The absorption peaks show a blue-shift upon increasing the height of Au nanodots, together with a decrease in FWHM. The values of FWHM were 242 and 200 nm at the dot height of 25 and 80 nm, respectively. The relative shift ($\Delta\lambda_{max}$) in peak position was linearly dependent on the height of the Au nanodots. From the slope of the plot, the sensitivity factor ($\Delta\lambda_{max}/\Delta h$) was calculated as 1.9. A similar behavior was observed in the measurements of reflective absorption spectra using Au nanodot arrays fabricated on Si single-crystal substrates. Sensitivity to changes in Au nanodot height in nanoparticle arrays fabricated by nanosphere lithography has been reported.[6] $\Delta\lambda_{max}/\Delta h$ has been calculated to be 2 when the particle diameter and spacing have been maintained 90 and 310 nm, respectively. Nanoparticles with a smaller diameter are less sensitive to changes in nanoparticle height.[6] Therefore, the result in this study showed the same $\Delta\lambda_{max}/\Delta h$ even at dot diameters of 55 and 90 nm, and is considered to indicate one of the effects of highly ordered, high-density arrangements of Au nanodots on the optical properties.

The measured absorption spectra of the Au nanodot arrays (dot period of 100 nm, dot diameter of 55 nm, and dot height of 40 nm) immersed in samples of various refractive indexes (n) are shown in Figure 3. As n of solvent was gradually increased from 1 to 1.73, the LSPR peak shifted to higher wavelengths, together with an increase in intensity and a slight increase in FWHM. The values of FWHM were 207 and 222 nm in N_2 gas and diiodomethane, respectively. $\Delta\lambda_{max}$ was linearly dependent on n of the surrounding solvent (Figure 4). From the slope of the plot, $\Delta\lambda_{max}/\Delta n$ was calculated as 95 nm per refractive index unit (RIU). In addition, when the dot height was changed from 25 to 80 nm and the dot diameter was kept constant, the slope of the $\Delta\lambda_{max}$ versus n plot was almost unchanged. Furthermore, the optical properties of the Au nanodot array with a dot period of 63 nm, a dot diameter of 30 nm, and a dot height of 40 nm was also examined. Similar to the results of the Au nanodot array with a dot period of 100 nm, the linear relationship between λ_{max} and n showed a sensitivity factor of 116 nm/RIU. This $\Delta\lambda_{max}/\Delta n$ is relatively higher than those obtained for disordered[5] and ordered[6] arrays of nanoparticles having similar diameters and heights, and low aspect ratios. It is considered that the increase in the $\Delta\lambda_{max}/\Delta n$ in LSPR is due to the strong interaction between the Au nanodots caused by the high-density arrangements of the Au nanodots and high ordering of nanodots.

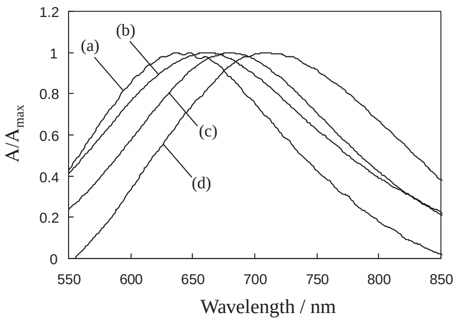

Figure 3. Transmission absorption spectra for a Au nanodot array with a dot period of 100 nm, a dot diameter of 55 nm, and a dot height of 40 nm in samples of various refractive indices. (a) dry N_2 gas ($n = 1$), (b) ethanol ($n = 1.36$), (c) glycerol ($n = 1.47$), (d) diiodomethane ($n = 1.73$).

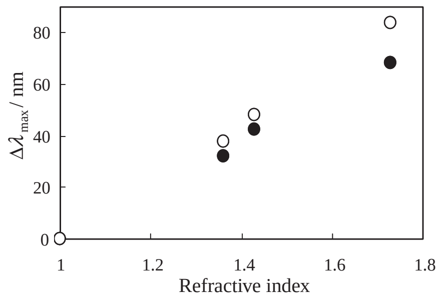

Figure 4. LSPR λ_{max} (solvent) $-$ λ_{max} (dry N_2 gas) vs refractive index of solvent for Au nanodot arrays. ●: Au nanodot array with a dot period of 100 nm, a dot diameter of 55 nm, and a dot height of 40 nm, ○: Au nanodot array with a dot period of 63 nm, a dot diameter of 30 nm, and a dot height of 40 nm.

In conclusion, the optical properties of long-range-ordered, high-density Au nanodot arrays were examined. Peaks due to the LSPR could be observed in the visible region. The peak wavelength depended on the height of the dots and the refractive index of the solvent. The absorption peak showed larger shifts than those observed on nanoparticle arrays with lower densities of particles fabricated by conventional methods and on disordered arrays. The development of optical sensors using highly ordered nanodot arrays was shown feasible.

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