Effect of heat treatment of optical fiber incorporated with Au nano-particles on surface plasmon resonance

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Abstract: To improve the sensitivity of the surface plasmon resonance (SPR) sensor based on the specialty optical fiber incorporated with Au nano-particles (NPs) in the cladding region, the effect of heat treatment (800 °C - 1000 °C) of the fiber on sensing capability of refractive index (n = 1.418 - 1.448) was investigated. The SPR appeared at a particular wavelength around 390 nm for the corresponding refractive indices regardless of the heat treatment temperature and the SPR wavelength increased with the increase of the index. The SPR sensitivity was found to increase with the increase of heat treatment temperature, 178 nm/RIU, 299 nm/RIU, and 945 nm/RIU at 800 °C, 900 °C, and 1000 °C for an hour, respectively. On the other hand, the SPR absorption intensity decreased with the increase of heat treatment temperature due to the increase of the propagation loss of the incident light and the SPR band became spread due to the increase of the size distribution of the Au NPs at the various refractive indices.

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References and links


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1. Introduction

Recently, optical fiber sensors based on surface plasmon resonance (SPR) due to the excitation of electron density oscillations from thin film or nano-particles (NPs) of metals such as Au, Ag, and Cu as the plasmonic materials have drawn much attention for measurements of various chemical, physical, and biological quantities such as concentration of gas, temperature, pressure, electrical current, and bimolecular [1–24]. Also, it has attractive advantages of compactness and remote sensing capability for all-optical applications [1–9]. Various types of optical fiber such as polished fiber, tapered fiber, grated fiber, and coated fiber have been suggested and used for size, thickness, shape, and composition of plasmonic materials have mainly been studied for SPR fiber sensor applications [1–4, 10–12, 25–42]. Previously, we have presented a new type of SPR fiber sensor using a novel optical fiber incorporated with Au NPs in cladding region, which is called the Au NPs(cladding)-doped optical fiber [9]. The optical properties of the Au NPs(cladding)-doped optical fiber depend mainly on the size, shape, formation, and spatial distribution of the Au NPs [30–44]. Thus, the size increase of the Au NPs in glass matrix can be easily controlled by a heat treatment, enabling tunability of operation range of sensing wavelength of the SPR.

In this work, enhancement of the SPR absorption and sensitivity was demonstrated by controlling the size of the incorporated crystalline Au NPs in the fiber cladding through heat...
treatment. The heat treatment of the fiber was carried out in the image furnace equipped with halogen lamp as a heat source to minimize the surface contamination as well as the oxidation of the fiber [45, 46].

2. Experimental

The Au NPs(cladding)-doped fiber preform was fabricated by using the modified chemical vapor deposition (MCVD) with solution doping process. A detail description of the fiber fabrication process was described in our previous work [9]. To incorporate Au NPs in the cladding region of the optical fiber, the porous germano(0.2 mole %)-silicate layers which will be cladding later, onto the inner surface of a silica glass tube were formed and deposited by the MCVD process. GeO$_2$ was doped in the cladding for a light to propagate into the cladding region of the fiber to induce surface plasmon waves at the interface between the cladding glass and Au NPs [4, 47]. The porous deposition layers for cladding were soaked for two hours in an Au doping solution, which was prepared by dissolving 0.025 mole of reagent grade Au(OH)$_3$ powders (Aldrich Chem. Co. Inc., 99.9%) in nitric acid solution (Junsei Co., 70%). Then the glass tube with the deposited layers was dried and sintered to incorporate Au NPs. Then a pure silica glass rod (refractive index, $n = 1.4571 \, @ \, 633 \, nm$) was inserted in the tube and consolidated into a jacketed preform. Then the outer part of the jacketed preform, which was the originally silica glass tube, was etched off using a hydrofluoric acid solution (J. T. Baker, 49%) for revealing the doped layers to become a new surface of the rod as a cladding. The final preform consisted of the germano-silicate glass cladding doped with Au NPs and the pure silica glass core as shown in Fig. 1. Finally, the fiber preform was drawn into a fiber with 124.3 $\mu$m in diameter using the draw tower at 2150 °C. During the drawing process, the fiber was coated with lower refractive index polymer (EFIRON UVF PC-375, $n = 1.3820 \, @ \, 852 \, nm$) than that of the germano-silicate glass of the cladding to induce total internal reflection for light transmission. Also, for enabling a light to propagate into the cladding region not into the core, the refractive index of the cladding region was larger than 0.00125 that of core region. The cladding width and total diameter of the optical fiber were 2.6 $\mu$m and 124.3 $\mu$m, respectively.

Fig. 1. Schematic diagram of the optical fiber incorporated with Au NPs in cladding region.

The fabricated Au NPs(cladding)-doped preform and the fiber were examined by transmission electron microscope (TEM; Technai, G2 S-Twin 300 KeV) to confirm formation and distribution of Au NPs in the cladding. Optical absorption of the preform and the fiber was measured to verify again the existence of Au NPs by the UV-VIS-NIR spectrum and by the cut-back method using the Optical Spectrum Analyzer (Ando AQ 6315B) and white light source (Ando AQ 4305), respectively. To investigate the effect of heat treatment on the SPR sensing capability of the Au NPs(cladding)-doped fiber, the coated polymer of 3 cm length were stripped off using acetone and then the bare part of the fiber was heat treated using the image furnace equipped with the halogen lamp at 800 °C, 900 °C, and 1000 °C for an hour. It is noticed that the temperatures of the heat treatment were chosen by considering the melting
point (1064 °C) of bulk pure Au and the effect of heat treatment on possible damage of the fiber surface [45]. The heat treatment was carried out by focusing the light from the lamp onto the stripped part of the fiber in the image furnace, in which the linear light was obtained by the elliptical mirror [45]. The surface morphology of the fiber before and after the heat treatment was examined by using the scanning electron microscope (SEM; Hitachi, S-4700 FE-SEM). To characterize SPR sensing property, the change in optical absorption of the fiber was measured by putting small drops of the refractive index matching oil with various refractive indices (n = 1.418 - 1.448) on the surface of the stripped part (3 cm) of the fiber of total length 20 cm before and after the heat treatment as shown in Fig. 2.

3. Results and discussion

The existence and size distribution of Au NPs in the cladding region of the fabricated optical fiber preform were verified by TEM morphology as shown in Fig. 3. The average diameter of Au NPs in the cladding of the fiber preform was 2.4 nm (size distribution: 1.4 nm ~3.4 nm), which was crystalline, to be roughly spherical and uniformly distributed. Figure 4 compares the UV-VIS-NIR spectra of the fiber preforms incorporated with and without Au NPs. The absorption bands at 261 nm and 576 nm appeared in the preform after the incorporation of Au NPs [48–50]. The absorption band at 261 nm is known to be due to Au NPs dispersed uniformly in the preform cladding, while the broad absorption band peaking at 576 nm may be due to the coupling effect of the Au NPs from the dipole–dipole interactions of the aggregates of the Au NPs as shown in Fig. 3 (Enlarged image) [18, 22, 32, 51]. Note that the absorption peak of the appearing at 244 nm in the preform without Au NPs is attributed to a GeO defect center [51]. The optical absorption below 200 nm is due to the interaction with electrons of Si-O bonds, absorption by impurities, and the presence of OH groups and point defects such as Si-Si bonds, and strained Si-O-Si bonds [52].
After drawing the fiber from the preform at high temperature of about 2150 °C, the existence and size distribution of the Au NPs in the cladding region of the fiber were also verified by TEM analysis as shown in Fig. 5. The average diameter of Au NPs in the cladding region of the fiber increased to 3.8 nm (size distribution: 2.5 nm ~ 5.2 nm) from 2.4 nm in the preform, but they still remained as crystalline particles with spherical shape. Note that the density of the Au NPs decreased as compared with those in the preform because the fiber was elongated during the drawing process. The existence of the Au NPs in the fiber was verified again by optical absorption spectra of the fiber as shown in Fig. 6. The absorption bands due to the SPR of the incorporated Au NPs in the fiber appeared at 392 nm and 790 nm, which were red-shifted from 261 nm and 576 nm of the fiber preform, respectively. The red-shift of the SPR bands may be due to the increase in the size of the Au NPs after the drawing process [9, 31, 50, 52–57]. These bands shift can be attributed to growth or recrystallization of the Au NPs during the fiber drawing process about 2150 °C. From the results of the optical absorption spectra of the optical preform and the fiber as shown in Fig. 4 and 6, respectively, we also found that the intensity of the absorption band corresponding to single Au NPs at 392 nm (α = 0.018 cm⁻¹) in the fiber slightly increased as compared with that at 261 nm (α = 0.012 cm⁻¹) in the preform (after baseline correction). Also, the proportion of the absorption from single Au NPs between two absorption bands in the fiber (Fig. 6) was relatively large as compared with that in the preform (Fig. 4). It is because the Au NPs was distributed more homogeneously in the fiber and thus the ratio of the aggregated Au NPs decreased (Fig. 5).
Using the Au NPs(cladding)-doped fiber, effect of the heat treatment on the SPR sensitivity was investigated by varying the refractive index of the matching oils. Figure 7 shows the surface morphologies of the stripped portion of the Au NPs(cladding)-doped fibers before and after the heat treatment at 1000 °C for an hour. Note that no surface defects, fiber bending or distortion due to any temperature fluctuation or crystallization of the optical fiber were found, indicating the usefulness of the heat treatment by the light energy in the image furnace [45].

Then the SPR absorption and sensitivity of the Au NPs(cladding)-doped fiber was measured by dropping the index matching oils onto the stripped and heat treated portions of 3 cm with total fiber length of 20 cm. Figure 8 shows the SPR spectra obtained by dropping the matching oils of different refractive indices before and after the heat treatment. The SPR was
found to occur at particular wavelengths around 390 nm for the corresponding refractive indices from 1.418 to 1.448, increased with the increase of the refractive index. However, there was no SPR peak detected around 790 nm. From the results of the SPR spectra as shown in Fig. 8, the variation of the SPR peak wavelength and the SPR sensitivity of the SPR spectrum upon the heat treatment were summarized in Fig. 9. The SPR peak wavelengths increased with the increase of the corresponding refractive indices regardless of the temperature of the heat treatment (Fig. 9(a)). The red-shift of SPR peak wavelength with the increase of the refractive index is related to the resonance wavelength of the incident light due to the increase of the wave vector of the surface plasmon mode [1, 4–7, 10–13, 21]. Also, the SPR peak wavelength showed a tendency to shift towards longer wavelength with the increase of the heat treatment temperature regardless of the corresponding refractive indices due to the increase in average size of the Au NPs in the fiber cladding region after the heat treatment. The SPR sensitivities increased to be 178 nm/RIU, 299 nm/RIU, and 945 nm/RIU after heat treatment at 800 °C, 900 °C, and 1000 °C, respectively, as shown in Fig. 9(b). However, the SPR sensitivities decreased after the heat treatment until 900 °C as compared with the measured SPR sensitivity (407 nm/RIU) at room temperature (at 25 °C). It may be possible because the SPR sensitivity of the optical fiber depends not only on the size of the Au NPs but also on the nature, shape, concentration, and stability of the Au NPs in cladding region [58–62].

![Fig. 8. The SPR spectra obtained by dropping the matching oils of different refractive indices (a) before and after the heat treatments at (b) 800 °C, (c) 900 °C, and (d) 1000 °C for an hour.](image-url)
Figure 9 shows the variation of the SPR peak wavelength as a function of the refractive index of the matching oils (The lines were linearly-fitted) and the SPR sensitivity of the SPR spectrum before and after the heat treatments at 800 °C, 900 °C, and 1000 °C for an hour (The line was exponentially-fitted for a guideline).

Figure 10 shows the variation of the SPR absorption intensity with the FWHM of the SPR spectra of the fibers after the heat treatment. The baseline corrected SPR absorption intensity decreased with the increase of heat treatment temperature, due to the increase of the signal propagation loss through the fiber cladding region but the FWHM increased due to the increase of the size distribution of the Au NPs. Furthermore, with the increase of the refractive indices, the SPR absorption intensity showed a tendency to increase regardless of the heat treatment temperature due to leaking out of more divergent light beam from the cladding of the fiber [11, 22, 23]. The broadening of the SPR, i.e., the increase of the FWHM was found with the increase of the refractive index regardless of the heat treatment temperature because of the spatial spreading and scattering of the conduction electrons [7, 35, 63]. As the heat treatment temperature increased, even though the change of the SPR absorption intensity decreased due to the decrease of the SPR absorption by increasing the propagation loss according to the change of the medium refractive indices, the change of the FWHM increased due to the increase of the size distribution of the Au NPs. As the temperature increased from 800 °C to 900 °C and 1000 °C, the SPR sensitivity increased from 178 nm/RIU to 299 nm/RIU and 945 nm/RIU. The average SPR absorption intensity and the average FWHM were changed from 1.2 dB to 0.3 dB and 0.2 dB and from 58.1 nm to 69.6 nm and 200.4 nm, respectively. The SPR sensitivity, the average absorption intensity, and the average FWHM with various heat treatment temperatures are listed in Table 1.
Table 1. The SPR Sensitivity, the Average Absorption Intensity, and the Average FWHM of the Optical Fiber Incorporated with Au NPs in Cladding Region after the Heat Treatment

<table>
<thead>
<tr>
<th>Heat treatment temperature</th>
<th>Sensitivity</th>
<th>Average absorption intensity</th>
<th>Average FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit  °C</td>
<td>[nm/RIU]</td>
<td>[dB]</td>
<td>[nm]</td>
</tr>
<tr>
<td>Fiber 800</td>
<td>178</td>
<td>1.2</td>
<td>58.1</td>
</tr>
<tr>
<td>Fiber 900</td>
<td>299</td>
<td>0.3</td>
<td>69.6</td>
</tr>
<tr>
<td>Fiber 1000</td>
<td>945</td>
<td>0.2</td>
<td>200.4</td>
</tr>
</tbody>
</table>

4. Conclusion

The SPR sensor based on specialty optical fiber incorporated with Au NPs in cladding region has been investigated. The enhancement of the SPR absorption and sensitivity was demonstrated by controlling the size of the incorporated crystalline Au NPs in the fiber cladding through heat treatment. The average diameter of Au NPs in the cladding of the fiber increased from 2.4 nm to 3.8 nm due to growth or recrystallization of Au NPs during the high temperature fiber drawing process. The absorption bands peaking at 261 nm and 576 nm of the preform were found to shift toward longer wavelength of 392 nm and 790 nm in the fiber, respectively, confirming the growth of the Au NPs during the drawing process. The SPR band was found to appear around 390 nm for the corresponding refractive indices (n = 1.418-1.448), increased with the increase of the index regardless of the heat treatment temperature. As the temperature of the heat treatment increased, the SPR peak wavelength showed a tendency to shift towards longer wavelength regardless of the corresponding refractive index due to the increase in the size of the Au NPs. The SPR sensitivities increased from 178 nm/RIU to 945 nm/RIU after the heat treatment from 800 °C to 1000 °C, respectively. While the SPR absorption intensity decreased from 1.2 dB to 0.2 dB when heat treatment temperature increased from 800 °C to 1000 °C, the FWHM increased from 58.1 nm to 200.4 nm, respectively. The decrease of the SPR absorption intensity was due to the decrease of the SPR absorption by increasing the propagation loss of the light through the fiber cladding region and the increase of the FWHM was due to the increase of the size distribution of the Au NPs.

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