Localized surface plasmon sensor using a hetero-core structured fiber optic with gold island films

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Abstract. This paper reports the effect of applying a gold islands film to the hetero-core structured optical fiber, which is fabricated by annealing thin Au films of 3 nm and 5 nm thicknesses and its sensing performance for the RI changes. We experimentally observe that novel LSPR spectra for 1.333 RIU appear in the visible-to-near-infrared region depending on the shape of Au islands. The absorbance and spectral sensitivities for a given refractive index region of the tested solvents were obtained to be 4.81 AU/RIU and 517 nm/RIU, respectively, in the range of 1.333–1.384 RIU in the case of 5-nm-thick Au film annealed at 900 °C.

1. Introduction
Recently, localized surface plasmon resonance (LSPR) [1, 2] has been proposed as a way to minimize the size and cost of SPR sensors. A localized surface plasmon is generated by a light wave trapped within metallic nanoparticles (NPs) smaller than the wavelength of light. This effect leads to strong light absorption and scattering, in the appearance of surface plasmon absorption bands, for which the resonant frequency strongly depends upon the size and composition of the NPs. Therefore, a large number of optical fiber-based LSPR sensors for chemical sensing have been developed, including unclad [3] and tapered [4] optical fibers, which have advantages in terms of thin size, immunity to electromagnetic interference, and resistance to corrosion. The majority of these optical fiber-based LSPR sensors were fabricated by immobilizing Au NPs on the decladed fiber core surface by means of organic linkage [5]. However, these films are often non-uniform, with many agglomerates of deposited NPs for which it is difficult to control the density; this leads to poor stability and reproducibility of fiber surfaces and measurements.

Au island films are another possible way to produce plasmonic sensors with LSPR ability. As compared to Au NPs, Au island films are directly contact with the substrates and are easy to fabricate. Therefore, a number of studies have been reported to reveal the influence of such simple thermal treatments on the morphology of the Au layer evaporated on the glass substrates, as well as on its biosensing performance. Gupta et al. [6] revealed that for thinner Au films and higher annealing temperatures, the shape of the gold islands should be approximately spherical, with the shape becoming flatter at lower annealing temperatures. In order to construct LSPR sensors optical fiber-based LSPR sensors, Au island films have been applied to the unclad fiber [7] or the end of the fiber [8, 9]. Meriaudeau et al. [7] have firstly demonstrated the LSPR sensor effect in Au islands with an extra dielectric layer based on an unclad fiber. Beyond this, they proposed an LSPR sensor using Au island films deposited on the end of the fiber, and measured the absorption spectra for RI changes.
However, the ends of the fiber must be polished as its light intensity is affected by the end-face angle, resulting in a lower absorbance peak level for RI changes. Moreover, morphology and absorption spectra of the annealed Au layer coated on the unclad fiber surface has been rather limited, being mainly subject to sensor sensitivities for refractive index changes [10].

In this paper, we have reported the effect of applying a Au islands film to the cylindrical cladding surface, which is fabricated by annealing thin Au films of 3 nm and 5 nm thicknesses coated around the hetero-core structured optical fiber at temperatures of 500 °C and 900 °C, and have obtained the absorption spectra for the RI changes. Ever since the hetero-core technique [11] has been demonstrated by this paper’s authors, a variety of hetero-core structured fiber optic SPR sensors for refractive index measurement and gas detection have been developed, owing to this technique’s practical advantages in terms of simplicity of structure and its interesting sensing principle that requires no removal of cladding. Its structure consists of a short segment of single-mode optical fiber inserted between two multimode fibers. Because of the difference between the diameters of the fiber cores, the transmitted light is guided to the cladding region of the single-mode fiber, which works as a sensing interface. Most of the leaked light travels as an evanescent wave and can interact with metallic NPs on the cladding surface. The SEM images of Au island films on the fiber surface are obtained to estimate the size, shape, and density variations of the Au islands.

2. Sensor fabrication and operation principle

The fiber sensor used in this experiment is made with a hetero-core fiber structure, as shown in Fig. 1, which has previously been reported for use in SPR sensors [12, 13]. As mentioned above, this structure consists of an inserted fiber segment that works as a sensing region, the core diameter of which is smaller than that of the transmission fiber. The hetero-core sensor used here consists of an inserted single-mode (SI) fiber, with a 15 mm length and 3.1 μm core diameter, and spliced multimode (GI) fibers with core diameters of 50 μm at both ends. The outer diameters of both fibers are 125 μm, and the refractive index of the SI fiber used as a sensing surface is 1.4613. The SI sensor element is inserted by means of a thermal-fusion splicer (FSM-100M, Fujikura Ltd.). In this structure, due to the core diameter difference, most of the light propagated in the multimode fibers leaks into the cladding of the SI sensor element. An evanescent wave is generated at the surface of the cladding layer of the SI fiber when it is bounced off the boundary between the cladding region and the surroundings under a condition of total internal reflection. At the other end of the SI sensor element, some lights are re-coupled to the core of the multimode fiber. When metallic NPs are deposited onto the surface of the sensing region, they interact with the evanescent wave, resulting in a decrease of the reflection light corresponding to the RI of the surrounding medium.

![Figure 1. A hetero-core structured fiber optic LSPR sensor and experimental setup to analyze the response of gold island films fabricated on the hetero-core fiber to RI changes.](image-url)
Thin Au films of thicknesses of 3 and 5 nm were cylindrically coated around the hetero-core region using an RF sputtering machine (CFS-4ES-231, Shibaura Mechatronics Corp.), in which a specially designed rotating mechanism was devised to achieve symmetrically uniform deposition on the cladding surface. The Au film’s thickness is determined by the thickness of the deposited film on a glass substrate. After the film coating, the fibers were annealed at temperatures of 500 °C and 900 °C in an argon atmosphere for 1 h.

To characterize the propagated light spectrum of the LSPR sensors, a white light source, which emits continuous light waves in the range 400-1800 nm, and a spectrum analyzer (AQ6315A, Ando Electric Co., Ltd.) were used, as shown in Fig. 1. The hetero-core fiber structure was mounted on a stretching support, where the sensing portion was in a straight line. In the series of experiment, various glycerin solutions were prepared as test liquids with concentrations of 0%-40% by weight, corresponding to refractive indices ranging from 1.333 to 1.384. Spectrum measurement was carried out by immersing the entire sensing portion in the different RI solutions to be tested.

3. Results and Discussions

Figures. 2(a)–(d) show SEM images of 3- and 5-nm-thick Au films annealed at 500 °C and 900 °C. As shown in Figures. 2(a) and (b), 3-nm-thick Au annealed films form small particles with high island density and sizes (diameters) of 30 and 40 nm for 500 °C and 900 °C, respectively. In the case of annealed 5-nm-thick Au films, differently shaped islands are generated at the different annealing temperatures. In Figure. 2(c), the particles seem to be rather circular in shape with sizes of 60 to 80 nm for the case of 5-nm-thick Au films annealed at 500 °C. On the other hand, Numerous irregular particles with non-circular shapes are seen on the entire surface of the 5-nm-thick Au film annealed at 900 °C, as shown in Figure. 2(d). These results indicate that the sizes of the islands in the SEM images become larger than reported in the previous study by Gupta et al. [6], who found that circular particles ranged from 15 nm to 40 nm in diameter for Au-film thickness of 2 to 5 nm on a quartz substrate with an annealing time of 2 h. Therefore, it is estimated that the large size of the particles may stem from the annealing time effect.

The light intensity of each sensor in air is used as a reference signal, I_ref. The transmitted light intensity of each sensor through the liquid sample is I_t. The experimental absorbance (-log(I_t/I_ref)) is then obtained for various refractive index (1.333-1.384 RIU).

Figure 3(a) and (b) shows the absorbance experimentally obtained for the 3-nm-thick Au film annealed at 900 °C, and 5-nm-thick Au film annealed at 900 °C, as a function of wavelength for refractive indices of 1.333, 1.345, 1.358, 1.371, and 1.384, which correspond to glycerin concentrations of 0, 10.0, 20.3, 30.9, and 39.9 wt.%, respectively. It can be seen from Figure. 3(a) and
3(b) that as a result of the increasing refractive indices, the resonance wavelength is redshifted, and the light intensity decreases. The absorption spectra for all annealed sensors were similarly changed according to alternating glycerin concentrations. The absorbance at 627 nm and 720 nm was chosen to plot the LSPR response to the refractive index of glycerin solutions, as shown in Figure. 3(a) and (b).

**Figure 3.** Experimental absorbance spectra for (a) 3 nm-thick Au films annealed at 900°C and (b) 5 nm-thick gold films annealed at 900°C for refractive index changes. The each inset shows the absorbance at 627 nm and 720 nm as a function of refractive index of glycerin solutions.

These wavelengths are selected in the plot because maximum sensitivities are found at those wavelengths. The sensitivity and linear correlation coefficient (R) are 4.41 absorbance unit (AU)/RIU (R =0.995) for annealed 5-nm-thick Au film and 4.81 AU/RIU (R = 0.993) for annealed 3-nm-thick Au film. These experimental results have proved that annealed sensors have high sensitivities compared to a conventional fiber-based LSPR sensor with Au-colloid film [14]. As can be obtained from the slopes in Figure. 4(a) and (b), the spectral sensitivities and limits of detection for the sensors with 3-nm-thick Au film annealed at 900°C, and 5-nm-thick Au film annealed at 900°C are found to be 385 nm/RIU and 1.3 × 10⁻³ RIU, and 517 nm/RIU and 9.7 × 10⁻⁴ RIU for the 1.333-1.384 RIU range, considering that the wavelength resolution of a spectral analyzer is 0.5 nm.

**Figure 4.** Resonance shifts as functions of the refractive index for (a) 3 nm-thick gold film annealed at 900°C and (b) 5 nm-thick gold film annealed at 900°C.
On the other hand, Figure 5(a) shows that it is difficult to clearly read out the resonance peaks because of broad absorbance spectra in the cases of the 5-nm-thick Au sensor annealed at 500°C in the range of 1.333–1.384 RIU. However, refractive index measurements can be realized using a simpler scheme with a monochromatic light source and an optical power meter based on light-intensity-mode operation, because the obtained near-infrared spectrum region finds appreciable difference in their intensities as the given refractive index change. The tested sensor was found to have linear sensitivities of 2.93 AU/RIU for the 5-nm-thick Au sensor annealed at 500°C, as can be seen from Figure 5(b).

The presence of an experimentally obtained LSPR absorbance peak is evidence that the evanescent field of the SI element interacts with the Au island film fabricated on the cylindrical cladding surface. In addition, the resonant wavelengths are redshifted and absorbance is linearly changed as the refractive index increases for all annealed Au film cases. The measured spectra show that it is possible to tune the absorption region in the case of an island film by controlling the shapes of the islands through Au-film thickness, annealing temperature, and annealing time during simple sensor fabrication.

![Figure 5](image)

Figure 5. Experimentally obtained LSPR absorbance spectra for 5 nm-thick Au films annealed at (a) 700°C for RI changes (a: 1.333 - e: 1.384). Plot of absorbance at (b) 1100 nm for 5 nm-thick Au films annealed at 500°C as a function of refractive index of glycerin solutions.

4. Conclusion
In this paper, the effect of Au island films prepared by annealing thin Au films at high temperatures upon LSPR-based refractive index sensors has been experimentally demonstrated using a hetero-core structured optical fiber technique. The Au island films fabricated by annealing Au films with thickness of 3 and 5 nm at temperatures of 500°C and 900°C for 1 h were characterized. As a result, novel LSPR spectra for 1.333 RIU appeared in the visible-to-near-infrared region depending upon the shapes of the Au islands. The results indicated that for thinner Au films, the Au islands are hemispherical, whereas they are spheroidal for thicker films. In addition, lower annealing temperatures generate larger particles. The experimental results for refractive index measurements show that the resonant wavelengths were redshifted as the refractive index increased for all annealed Au film cases. Additionally, the 5-nm-thick Au film annealed at 900°C was found to be preferable from the viewpoint of sensitivity. The absorbance and spectral sensitivities for a given refractive index region of the tested solvents were obtained to be 4.81 AU/RIU and 517 nm/RIU, respectively, in the range of 1.333–1.384 RIU. This fiber-sensing structure will be attractive for practical sensor probes due to its sensitivity and simple sensor fabrication, and the controllability of its absorption region.

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