Au "Edged Hole Array" for Sensor Application

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This paper described the design and fabrication of precursor for Au hole structure with four edges (edged hole array: EHA) for sensor application. In this paper, effect of the gap length of opposite edges \( g \) and hole side length \( l \) was investigated systematically by simulation. As the result, optimal design of EHA that shows strong light absorption (> 90%) and electric field (1.79×10⁵-fold increase against the incident light) at \( \lambda = 785 \text{ nm} \) was revealed. Finally, the precursor resist pattern for EHA was fabricated using electron beam lithography and cold development. As the result, the precursor structure that was expected to generate strong electric field at \( \lambda = 785 \text{ nm} \) was successfully fabricated.

Keywords: Cold development, Electron beam lithography, Localized surface plasmon resonance, Surface enhanced Raman scattering

1. Introduction

On the surface of metal nanostructures, the optical phenomenon “Localized surface plasmon resonance: LSPR” is observed [1-5]. LSPR is the resonance of electric field of light and collective oscillation of free electrons on the surface of metal nanostructures. The oscillation of free electrons (plasmon) derives a strong polarization on the metal surface and that gives specific optical characteristics. Especially, based on light absorption at specific wavelength and strong electric field generation around the nanostructures, metal nanostructures have studied for application to highly sensitive biosensors [6-10].

Surface enhanced Raman scattering (SERS) is known as highly sensitive label-free sensing method [11-13]. Since the enhancement factor of Raman signal depends on the electric field intensity, various studies for strong electric field generation have been reported. By using hot-spot [14,15] and lightning-rod effect [16,17], electric field is strongly integrated to the small area (< 100 nm). As the result, strong electric field intensity enhancement has been achieved by these approaches. However, when the concentration of analytes was extremely low, analytes have to be collected into the electric field for the successful detection.

In this work, Au hole array with edge structure (edged hole array: EHA) was designed for SERS application (Fig. 1). Using this structure, molecular recognition elements can be limitedly bounded to the surface of glass substrate based on the difference of surface chemical condition between substrate and Au layer [18]. Here, EHA was designed to adjust resonance wavelength to 785 nm, the wavelength of excitation laser source for SERS application [19-22]. In addition, fabrication of resist pattern for EHA using electron-beam lithography was performed.

![Fig. 1. Schematic design of EHA, consists of Au quadrate holes with four edges inside each hole. The surface oxide silicon was used as substrate.](image-url)
2. Experimental

The optical simulation was carried out using FDTD solutions (Lumerical Solutions Ltd.). In the simulation process, the optical characteristics depending on two parameters of EHA; $g$ (gap between opposite edges), $l$ (hole length) in Fig. 2 were investigated. In this study, the thickness of Au was fixed at 30 nm, and the interval of hole structures $a$ was twice as long as hole length $l$ to avoid the strong interaction between adjacent holes. In addition, to enhance the absorption intensity of EHA, surface oxide silicon was used as substrate. First, absorption spectra and maximum electric field intensities for each $g$ and $l$ were systematically analyzed. Since the $g$ strongly affected to the fabrication accuracy, this investigation was focused on the maximization of electric field enhance effect for each $g$.

![Fig. 2. Structural parameters of EHA for optimization of optical characteristics. The parameter $g$ indicates the gap size between opposite edge structures and $l$ indicates the length of the side of hole. $a$, distance of each holes was set twice as long as $l$.](image)

Following the systematic analysis, $l$ was optimized for each $g$.

In the fabrication process, electron-beam lithography and cold development were performed. The Silicon used as substrate was purchased from Nilaco Corporation (Tokyo, Japan). Acetone was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and hydrogen peroxide and sulfuric acid for piranha solution used to clean the silicon substrate surface was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan), respectively. For fabrication of the nanopattern using electron beam lithography (EBL), ZEP520A and ZED-N50 purchased from Zeon Corporation (Tokyo, Japan), were used as electron beam resist and developer, respectively. The supposed fabrication process of EHA is shown in Fig. 3. The shape of EHA is strongly dependent on the resist structure. Hence, fabrication of the fine resist pattern using cold development method was carried out (Fig. 3(1)). First, silicon substrate was cleaned by ultrasonication in acetone. After that, the substrate was washed by ultrapure water and dried in air. HMDS was spin-coated on the cleaned substrate and baked at 180 °C for 3 min to make the surface of substrate hydrophobic. Then, ZEP520A diluted by anisole to be dilution rate of 2.0 was spin-coated (5000 rpm, 60 s) on the substrate and baked at 180 °C for 3 min. From this coating condition, approximately 100-150 nm thickness of resist layer was coated on the substrate. Thereafter, electron beam was exposed at 50 kV, 304 μC/cm² dose amount and the 5 nm dot pitch. After electron beam exposure, resist was developed using ZED-N50 at the cold condition; 4 °C for various developing time (0.5, 1, 5, 10 min). After that, shape of resist pattern was observed by field-emission scanning electron microscope (FE-SEM) (JSM-7610F) from JEOL Ltd. (Tokyo, Japan).

![Fig. 3. Fabrication process of EHA. The process flow is as follows. (1) Electron beam lithography, (2) etching of Si and mold formation, (3) nanoimprint to the substrate, (4) Au deposition and lift off. The red square indicates the process worked on in this study.](image)

3. Results and discussion

3.1. Parameters $g$ and $l$ dependence

Figures 4 and 5 show the optimized absorption spectrum and electric field intensity distribution at $\lambda$.
= 785 nm for \( g = 40 \) nm, \( l = 120 \) nm. From these figures, light absorption reaching about 90% and strong electric field (1.79×10^5-fold increase) at the tip of edge structure were observed in this condition. These results indicated that absorption peak and the maximum electric field intensity could be optimized for certain wavelength by varying \( g \) and \( l \) values.

After that, the optical characteristics of EHA depending on the structural parameters were investigated. 2D-mapping of absorption intensity and maximum electric field intensity at \( \lambda = 785 \text{ nm} \) is shown in Fig. 6 and Fig. 7, respectively.

As the figures show, the favorable \( l \) for the usage at \( \lambda = 785 \text{ nm} \) becomes larger for larger \( g \). From these results, in the EHA structure, two factors for LSPR wavelength change were indicated to exist.

One is the interaction between opposite edge structures. As previous works show, the interaction of bowtie-like pillar pair structure gets weak as the pillars become distant and LSPR wavelength becomes shorter [18]. This tendency is considered to be occurred also in EHA. The blue shift of LSPR peak for larger \( g \) and constant \( l \) also indicates this trend (Fig. 8).

The other is the effect of hole perimeter size. It has been reported that when the side length of Au hole structures become larger LSPR wavelength becomes larger [23]. This tendency was also observed in EHA, for larger \( l \) and constant \( g \) (Fig. 9).

From these properties, the mode of plasmon on the EHA is considered to be following; the free electrons oscillating around the hole is “trapped” at the edge structure and large polarization is created. As the result, EHA structure can generate strong enhanced electric field (1.79×10^5-fold increase against the incident light).
Fig. 8. The $g$-dependent absorption spectra for constant $l$ (=120 nm). The arrow indicates the shift of the absorption peak derived from the change of $g$ from 20 nm to 60 nm.

Fig. 9. The $l$-dependent absorption spectra for constant $g$ (=40 nm). The arrow indicates the shift of the absorption peak derived from the change of $l$ from 80 nm to 160 nm.

3.2. Electron-beam lithography

Figures 10 (a)-(d) show the SEM images of resist pattern for each developing time. In addition, the structure designed on the software (Wecas.exe) is shown in Fig. 10 (e).

From the SEM images, fabricated resist patterns were widened compared to the designed pattern. The estimated $g$, $l$, $a$ for each developing time and designed structure are shown in Table 1.

The SEM images and estimated values indicated that developing time have to be shorter than 1 min for minimizing the fabrication error (about 10 nm), in this condition. To overcome the error in $g$, (1) optimization of dose, (2) reducing the size of designed structure are necessary.

Figures 11 and 12 show the absorption spectrum and electric field intensity distribution at $\lambda = 785$ nm for $g = 70$ nm, $l = 151$ nm, $a = 277$ nm. From these figures, the structure fabricated by 0.5 min developing time is expected to exhibit light absorption reaching about 90% and strong electric field (1.70×10^5-fold increase) at the tip of edge structure. Based on the results, the precursor resist pattern for EHA fabrication was successful.

Fig. 10. SEM images of resist pattern with different developing time; (a) 10 min, (b) 5 min, (c) 1 min, (d) 0.5 min, respectively. For comparison, designed structure is also shown in (e).

Table 1. Estimated value of $g$, $l$, $a$, for each developing time and designed structure.

| Developing time [min] | g [nm] | l [nm] | a [nm] |
|-----------------------|--------|--------|--------|
| 0.5                   | 72     | 151    | 277    |
| 1                     | 90     | 156    | 276    |
| 5                     | 159    | 193    | 274    |
| 10                    | 158    | 190    | 276    |
| Designed structure    | 0      | 140    | 280    |

4. Conclusion

Structural design of EHA was investigated by simulation analysis and resist pattern fabrication of EHA using electron beam lithography was performed.

From the investigation of parameters $g$ and $l$ dependence on optical characteristics, strong absorption of light and electric field generation was observed at appropriate balance of $g$ and $l$ values.
Fig. 11. Simulated absorption spectrum of EHA (g = 70 nm, l = 151 nm, a = 277 nm). The strong absorption peak was observed in 793 nm. The dashed line indicates $\lambda = 785$ nm.

Fig. 12. Simulated electric field intensity distribution of at the boundary of glass layer and Au layer of EHA ($\lambda = 785$ nm). Here, g = 70 nm, l = 151 nm, a = 277 nm. The enhanced electric field observed at the tip of edge structures (yellow dashed circle).

Based on the investigation, optimal design for each $g$ was determined. Here, absorption peak was successfully adjusted to $\lambda = 785$ nm. As the result, strongest absorption peak intensity was observed at $g = 20-40$ nm and strongest electric field intensity was observed at $g = 40-60$ nm.

Finally, precursor resist pattern that had the parameters; $g = 70$ nm, $l = 151$ nm, $a = 277$ nm, which is expected to be useful for fabrication of high-performance EHA.

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