Development of Au nanoparticles with continuously changing gap size

Kaichi Yatsugi[1‡], Nozomi Watanabe[1], Keishi Suga[2], Nobutomo Nakamura[1*]
([1]Osaka Univ.; [2]Tohoku Univ.)

1. Introduction

In recent years, it has been suggested that control of the gap size between nanoparticles on the order of nanometers can lead to the development of new functions. For example, in the field of nanodevices, it has been suggested that it may be possible to develop single molecule-sized electronic devices by utilizing the nanogap[1)]. In the field of photonics, such as optical sensing, the use of nanogaps may enable the development of new devices because the properties of surface plasmon resonance can be controlled by tuning the gap between metal particles[2)]. The application of nanogaps is also expected to open up new possibilities in the development of biosensors used in fields such as biology, medicine, and pharmacology[3,4)].

To precisely investigate the relationship between the gap size and the functions, it is necessary to fabricate several nanogaps with different gap sizes under the same conditions and accurately determine the fabricated nanoparticles' gap size. In this study, we developed a method to fabricate metallic nanoparticles with continuously varying gap sizes on a substrate and to identify the gap size after the fabrication. In this method, Au nanoparticles were formed on a glass substrate using an RF magnetron sputtering system. The gap size of the fabricated Au nanoparticles was evaluated using a non-contact piezoelectric resonance method. The non-contact piezoelectric resonance method is a technique that utilizes a resistive spectroscopy method[5)] and an antenna-driven ultrasonic method[6)] to evaluate the gap size between nanoparticles fabricated on a substrate. Finally, Raman spectroscopy was performed using the nanoparticle substrates to confirm the availability of the fabricated nanoparticle substrate.

2. Method for fabricating Au nanoparticles

When metal atoms are deposited on the substrate by sputtering, a three-dimensional growth mode called the Volmer-Weber type[7)] is observed. In this growth mode, atoms deposited on the substrate aggregate with each other by surface diffusion, and clusters are formed. These clusters are called nanoparticles in this study. As the nanoparticles grow, they contact, and a semi-contact state, a mixture of contacting and non-contacting nanoparticles, is formed. Further sputtering results in a contact state where the nanoparticles are in full contact with each other. Therefore, the nanogap nanoparticles focused in this study can be fabricated by interrupting the sputtering process just before the nanoparticles come into contact, and gap size can be controlled by changing the sputtering time around it.

In this study, we developed sputtering equipment that incorporates a substrate transfer system and mask to limit the area to be sputtered on the substrate as shown in **Fig. 1**. Using this equipment, it is possible to fabricate multiple nanoparticle substrates in a single sputtering operation, and it is also possible to fabricate Au nanoparticles with different gap sizes on a single substrate.

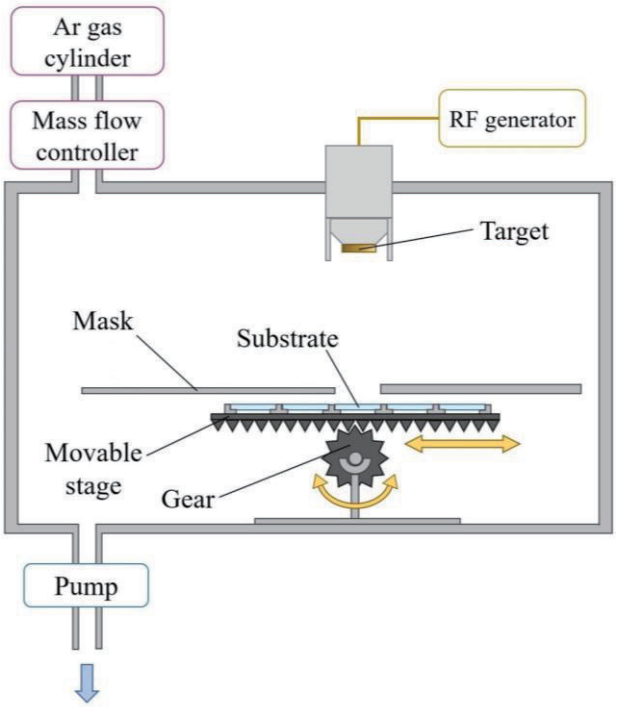

Fig. 1 Schematic drawing of the RF magnetron sputtering equipment.

E-mail: ‡yatsugi@dfm.mech.eng.osaka-u.ac.jp,
*nakamura@mech.eng.osaka-u.ac.jp

3. Method for measuring the gap size

The gap size of the fabricated Au nanoparticles was evaluated using the non-contact piezoelectric resonance method. A schematic diagram of the measurement setup is shown in **Fig. 2**. When the piezoelectric material placed below the substrate is vibrated at a resonant frequency using the electric field created by the antennas, an oscillating electric field is formed around the piezoelectric material due to the piezoelectric effect. When a substrate is located in the field and nanoparticles are formed on it, the electric field is affected by the conductivity between the nanoparticles, causing changes in the attenuation of the resonant vibration as follows. When the metallic nanoparticles are in a non-contact state, the transfer of electrons between the nanoparticles hardly occurs, and the resonant spectrum of the piezoelectric material is comparable to that measured before nanoparticles are formed. As the nanoparticles grow and a semi-contact state is formed, tunnel conduction between the nanoparticles occurs, resulting in energy loss and increase in the attenuation of the resonant vibration. In the contact state, the electrical conductivity becomes high, allowing electrons to move freely and the energy loss becomes small. Therefore, the attenuation becomes small again. Such a change in the attenuation can be detected by measuring the full width at half maximum (FWHM) of the resonant spectrum. Therefore, the gap size distribution on the substrate can be evaluated by measuring the resonant spectra while moving the nanoparticle substrate relative to the piezoelectric material as shown in Fig. 2.

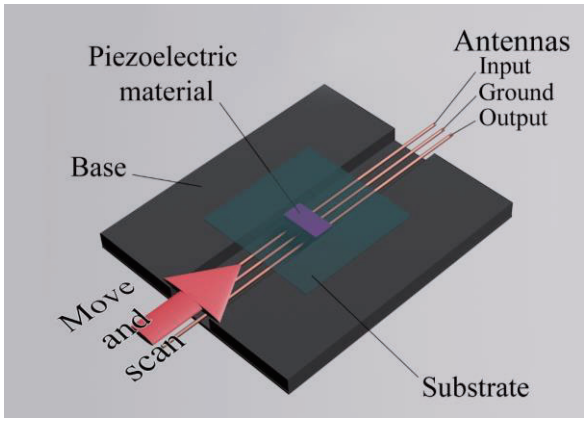

Fig. 2 Schematic drawing of resonance measurement.

4. Experimental results

Nanogap Au nanoparticles were fabricated on a glass substrate. By moving the substrate relative to the mask during the sputtering, time from edge to edge was varied from 80s to 320s. Then, gap-size distribution was measured using the non-contact piezoelectric resonance method. Lithium Niobate ($LiNbO_3$) was used as the piezoelectric material, and a resonant mode around 1.2395 MHz was measured. **Figure 3** shows the resonant spectra measured at different locations on the substrate. The FWHM increased temporarily with increasing sputtering time, indicating that the gap size becomes narrower monotonically in the measured area, and the change from the non-contact state to the contact state was confirmed.

To confirm the availability of the developed nanogap Au nanoparticles, Raman spectroscopy was performed. After organic compounds are attached to the nanoparticles, Raman spectra were measured at different locations on the substrate. As a result, the intensity of the scattered light changed depending on the location. It is well known that the intensity of the surface-enhanced Raman scattering (SERS) changes depending on the gap size. Therefore, the change in the Raman intensity at different locations indicates that the nanoparticles with different nanogaps were fabricated on the substrate, and it can be applicable for investigating the relationship between the nanogap and functions.

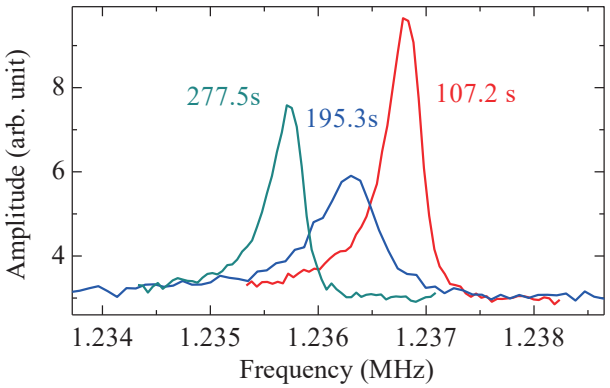

Fig. 3 Resonant spectra of a piezoelectric material measured at different locations on nanoparticle substrate.

References

1) T. Li, W. Hu, and D. Zhu, Adv. Mater., **22**, 286 (2010).
2) E. Hutter, and J. H. Fendler, Adv. Mater., **16**, 19 (2004).
3) V. Shukla, N. K. Jena, A. Grigoriev, and R. Ahuja, ACS Appl. Mater. Interfaces, **9**, 39945 (2017).
4) C. -H. Kim, C. Jung, K.-B. Lee, G. Park, and Y.-K Choi, Nanotechnology, **22,** 135502 (2011).
5) N. Nakamura and H. Ogi, Appl. Phys. Lett., **111**, 101902 (2017).
6) H. Ogi, K. Motohisa, T. Matsumoto, K. Hatanaka and M. Hirao, Anal. Chem., **78**, 6903 (2006).
7) K. Reichelt, Vacuum, **38**, 1083 (1988).