# Development of nanogap Ag nanoparticle using noncontact piezoelectric resonance method for surface enhanced Raman scattering

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## 1. Introduction

Since the discovery of Raman scattering in 1928 as a type of light scattering phenomena<sup>1</sup>), it has attracted attention as one of the methods for materials characterization. Currently. Raman spectroscopy is widely and practically used in various fields such as medical, pharmaceutical, biological, and material science fields because of its advantages such as non-destructive detection of molecules and high reactivity to biological samples. For example, there is a report in the biological field that Raman spectroscopy has been used to observe cellular activities with high spaciotemporal accuracy<sup>2</sup>). In the field of material science, there are reports of Raman spectroscopy being used to identify purity, defects, and alignment in multi-walled carbon nanotubes<sup>3,4)</sup>. However, the intensity of the Raman scattering light is generally weak. Therefore, the surface-enhanced Raman scattering technique has been developped for enhancing the intensity of Raman scattered light.

Surface-enhanced Raman scattaring is a phenomenon in which Raman scattered light is significantly enhanced by surface plasmons formed on the surface of nanoparticles and other microstructures of noble metals. In previous studies, nanoarchitectures, in which target molecules can stably attach to the hot spot where the Raman scattering light intensity is enhanced, have been developed. For example, nanostars, in which noble metal nanoparticles are grown into a shape with numerous pricks, can provide stronger Raman scattered light than spherical nanoparticles due to the presence of numerous hot spots within a single nanostar<sup>5)</sup>. Another study reported the development of core-shell nanoparticles that have nanogaps inside the particles that serve as strong hotspots, generating a large Raman enhancement effect<sup>6</sup>. Various other methods have been proposed to develop for surface-enhanced nanoparticles Raman scattering. However, the attempt to form hot spots by fabricating metal nanoparticles on a substrate with an appropriate gap size has not received much attention. In this study, we propose a method composed of sputtering and non-contact piezoelectric resonance method to fabricate Ag nanoparticles optimized for

the surface-enhanced Raman scattering. Ag nanoparticles are fabricated on a glass substrate using the radio frequency magnetron sputtering system, and the gap size between nanoparticles is continuously changed by changing the sputtering time. After the fabrication, the gap size is evaluated using the non-contact piezoelectric resonance method. The method is a technique that utilizes the resistive spectroscopy method<sup>7</sup>) and the antennadriven ultrasonic method<sup>8</sup>) to evaluate the nanogap size between metal nanoparticles on a solid surface. Raman spectroscopic measurements are then performed at different positions on the glass substrate with Ag nanoparticles, and the optimum gap size for the surface-enhanced Raman scattering was evaluated from the intensity of the Raman scattered light.

## 2. Method for making Ag nanoparticles

When metal atoms are deposited on a substrate by sputtering, they exhibit a three-dimensional growth mode called the Volmer-Weber type<sup>9)</sup>. In this growth mode, atoms that reach on the substrate surface aggregate with each other by surface diffusion and form clusters. These clusters are called nanoparticles in this study. As the nanoparticles grow, the distance between the nanoparticles becomes smaller, and the gap becomes of the order of nanometers. With further sputtering, the nanoparticles are in complete contact with each other. This morphological change of the nanoparticles can be observed using the non-contact piezoelectric resonance method. A schematic image of the measurement setup is shown in Fig. 1. When a piezoelectric material placed under the substrate is vibrated at a resonant frequency using the electric field created by the antennas, an oscillating electric field is excited around it due to the piezoelectric effect, and the oscillating electric field also reaches the substrate surface. The nanoparticles on the substrate affect the intensity and distribution of the oscillating electric field, and the resonant frequency and the attenuation coefficient of the resonant vibration are changed depending on electrical conductivity of the nanoparticles. The metal nanoparticles are insulators in the non-contact state and transform into conductors as the nanoparticles grow into the nanogap state and into the contact state. The conductivity change accompanied with the

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morphology change is detected from the changes in the resonant frequency and attenuation coefficient. Using this technique, the gap size between nanoparticles can be adjusted arbitrarily by observing the state of the growing nanoparticles and controlling the sputtering time.

In this study, nanoparticles with different gap sizes were sputtered on a glass substrate. The substrate was continuously moved under the mask with a hole during the sputtering, and the sputtering time was changed to control the gap size. After the sputtering, the gap size was evaluated using the noncontact piezoelectric resonance method using the setup in Fig. 1. This allows us to precisely evaluate the relationship between the Raman scattering intensity and the nanogap size.



Fig.1 Schematic drawing of the measurement setup of the noncontact piezoelectric resonance method.

### 3. Results and discussion

Raman spectroscopic analysis was performed on the Ag nanogap nanoparticles on a glass substrate. 4-mercaptobenzoic acid (PMBA) was used as the sample molecule. A laser with a wavelength of 785 nm was used as an incident light, and a diameter of the confocal hole was 100 µm. The obtained Raman spectrum showed a Raman peak at 1070 cm<sup>-1</sup>, which originates from the benzene ring. In this study, the intensity of the Raman peak was measured at different positions on the substrate, and the Raman intensity was compared with the full width at half maximum (FWHM) of the resonant peak obtained by the non-contact piezoelectric resonance method. Representative Raman spectra and the resonant spectra at different positions (a, b, and c) are shown in Fig. 2, which indicates that the Raman intensity becomes stronger when the FWHM becomes larger. The gap size around this position is considered to be comparable to the size of the detecting molecule. This result suggests that Ag nanoparticles around this position is suitable for the surface-enhanced Raman scattering, and an optimized nanoparticles can be

fabricated using the non-contact piezoelectric resonance method.



Fig.2 Raman spectra (upper) and resonant spectra (lower) measured at different positions (a, b, and c).

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