Electric field analysis around nano-gap metallic nanoparticles fabricated by ultrasonic resonance method

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1. Introduction

Raman spectroscopy is the optical method to characterize materials using Raman scattering of light and has been utilized in several fields such life science, material science, and so on. Raman scattering is inelastic scattering caused by irradiating a material with light, and difference in the inverse of the wavelength between the incident light and Raman scattered light corresponds to the energy of vibrational modes of the irradiated material. Therefore, by measuring the wavenumbers and peak patterns of Raman scattered light, the structure and state of materials are identified.

Although Raman spectroscopy is a useful method for materials characterization, the intensity of the Raman scattered light is greatly weak; about 10^{-6} times weaker than that of Rayleigh scattered light, which is elastic scattering caused simultaneously with Raman scattering. Therefore, detection of the Raman scattered light is not straightforward. To overcome this difficulty, surface-enhanced Raman spectroscopy (SERS) has been studied[1]. SERS is a phenomenon in which the Raman scattered light emitted from a molecule is enhanced by localized surface plasmon resonance (LSPR). When metallic nanoparticles are irradiated with light, plasmons caused by plasma oscillations are localized on their surfaces. LSPR generates a strong electric field near the surface of the nanoparticles and induces a particularly strong electric field at the nano-scale gap between nanoparticles. Since the intensity of Raman scattered light depends on that of the electric field at which a molecule is located, LSPR increases the intensity of the Raman scattered light. Therefore, when a molecule is adsorbed on nanoparticels, intensity of the Raman scattered light becomes significantly large, especially at the gap between nanoparticles. This is the mechanism of SERS, and nanostructures for SERS are being studied. Purpose of our study is to develop nanoparticles with nano gap by deposition for SERS measurments, and in this study, we analyze the electric field around metallic nanoparticles using the finite element method.

2. Metallic nanoparticles with nano gap

Nanoparticles with nano gap have been fabricated using deposition[2] and molecules with functional thiol group such as DNA[3]. In this study, we focus on the former technique. Using deposition, nanoparticles with nano gap is fabricated by interrupting deposition of metal on substrate at a certain timing. During deposition, nanoparticles are formed on the substrate in the early stage of deposition. The nanoparticles become larger as the deposition progresses, and they contact each other, forming a continuous film. Therefore, by interrupting deposition just before nanoparticles contact, nanoparticles with nano gap can be fabricaed. However, it is not straightforward to identify the proper timing and to control the gap distance at the nanoscale, because gap size is not measurable during deposition.

In our previous work[4], we have developed ultrasonic resonance method to evaluate the gap size during deposition. The method combines the resistive spectroscopy method[4] and the antenna transmission resonance method[5]. When a piezoelectric material installed under a substrate is vibrated at a resonance frequency, an oscillating electric field is generated around it due to the piezoelectric effect. When metal is deposited on the substrate and isolated nanoparticles are formed, the oscillating electric field does not cause the transfer of electrons between the nanoparticles, and the resonant vibration is not affected. As the gap becomes narrowed, the vibrating electric field causes the transfer of electrons between nanoparticles, and the energy loss occurs, which increases the attenuation of the resonant vibration of the piezoelectric material. When nanoparticles are in contact with each other, the electrical resistance of the substrate surface decreases greatly, and the energy loss becomes small due to the free movement of electrons. Then, the attenuation becomes small. Therefore, by monitoring the change in the attenuation of the resonant vibtarion during deposition, the gap size can be evaluated. In the experiments, the attenuation is evaluated by measuring the full width at half maximum (FWHM) of a resonance spectrum. The larger the attenuation, the larger the FWHM, and the FWHM becomes maximum when the nanoparticles are just before contact each other.

In our previous work[6], Au nanoparticles were fabricated on glass substrate using the ultrasonic resonance method, and 4-

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mercaptobenzoic acid (PMBA) was detected using the Raman spectroscopy. As a result, we observed that intensity of Raman scattered light changed with the gap size, and it was supposed that there was an optimized gap size which maximizes the Raman scattered light. In this study, we analyze electric fields around Au nanoparticles excited by irradiation with light using the finite element method, and evaluate the relationship between the gap size and intensity of the electric field for fabricating Au nanoparticles with an optimized gap size.

3. Finite element analysis of electric field around Au nanoparticles

For understanding the relationship between the gap size and the electric field around Au nanoparticles, and electric field was simulated using the finite element method. We considered two-dimensional model as shown in **Fig. 1**. Two circles indicate Au nanoparticles, and they are surrounded by air. Size of the model is large enough to ensure that the electric field around Au nanoparticles was not affected by the boundaries of the model. Distribution of the electric field was calculated by applying oscillating electric potential at the edge of the model, which simulates the irradiation of nanoparticles with a laser.

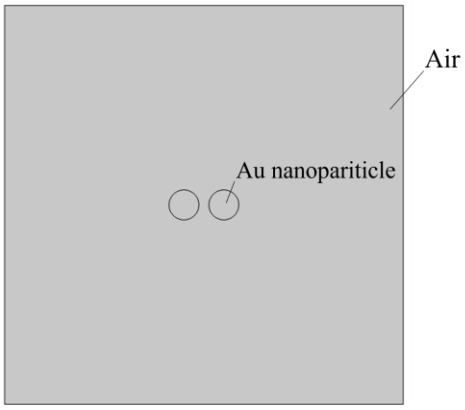

Fig. 1 Analytical model of Au nanoparticles surrounded by air.

Figure 2 shows an example of the simulation results, and intensity of the electric field is shown. Diameter of Au nanoparticles is 30 nm, and gap size is 2 nm. It is clearly observed that the intensity of the electric field is higher around the Au nanoparticles, and it is notably higher at the gap between the nanoparticles. Considering that the intensity of the Raman scattered light becomes higher when an electric field at which a molecule is located is higher these results indicate that intensity of the Raman scattered light from molecule becomes higher when the molecule is adsorbed on Au nanoparticles, and it will be maximum when the molecule exists at the gap. **Figure 3** shows the simulation results of Au nanoparticles with 10 nm gap. When the gap size became larger, the intensity of the electric field at the gap became weaker, and it was confirmed that it is important to control the gap size for fabricating nanoparticles for SERS experiments.

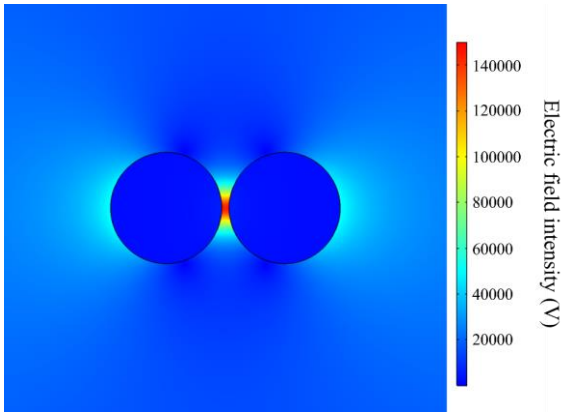

Fig. 2 Electric field around Au nanoparticles with a gap size of 2 nm.

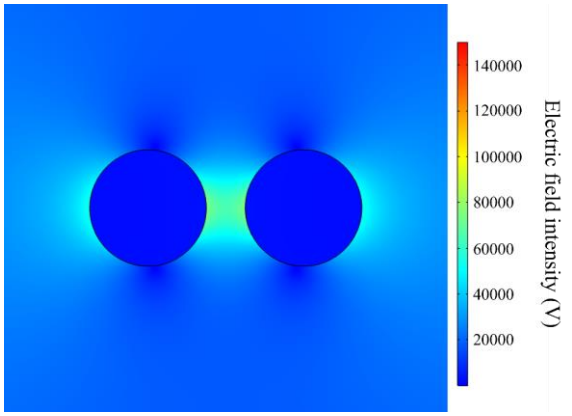

Fig. 3 Electric field around Au nanoparticles with a gap size of 10 nm.

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