Development of surface-enhanced Raman scattering substrate using ultrasonic resonance method

超音波共鳴法を用いた表面増強ラマン散乱用基板の開発

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1. Introduction

When a material is irradiated with light, elastic and inelastic scattering occur. The former one is called Rayleigh scattering, and its frequency is the same as that of the incident light. The latter one is called Raman scattering, and the frequency is different from that of the incident light. In the Raman scattering, the incident light interacts with vibrations of molecules, and the frequency of scattered light varies depending on the vibration modes of molecules. Therefore, Raman scattering is used for identifying molecules, and Raman spectroscopy technique has been used in various fields. For example, Raman spectroscopy was successfully used to visualize the structure and distribution of lycopene in tomatoes[1]. Raman spectroscopy can be used for diagnosis: by analyzing the Raman spectra of the plasma from patients with sepsis and leucemia, the patiants with those diseases are distinguished from healthy individuals[2].

The intensity of Raman scattered light is about 10^{-6} times weaker than that of Rayleigh scattered light. Therefore, it is important to enhance the intensity of Raman scattered light to detect it efficiently. To solve this problem, surface-enhanced Raman scattering (SERS) has been studied. The SERS is a phenomenon in which the Raman scattering from molecules is enhanced when they are adsorped on noble metals such as Au and Ag. Generally, SERS is successfully induced when molecules are adsorped on an extremely narrow gap between metal nanoparticles. The purpose of this study is development of such narrow gap between nanoparticles for SERS.

Narrow gap between nanoparticles can be fabricated on substrate by deposition. In a previous study, Au clusters were fabricated by deposition, and it was obserbed that intensity of Raman scattered light changes depending on the morphology of the clusters[3]. However, it is not straightforward to control the gap distance between nanoparticles at nanoscale. In this study, we fabricate Au nanoparticles on glass substrate as SERS substrate by using the originally developed ultrasonic resonance method. The ultrasonic resonance method combines the resistance spectroscopy method[4] and the antenna transmission resonance method[5]. Because the method can measure the gap distance between nanoparticles during deposition, we can fabricate Au nanoparticles with different gap distances. Using the SERS substrates with different gap distances, Raman spectrum is measured and availability of the ultrasonic resonance method is discussed.

2. Method for fabricating metal nanoparticles

Au nanoparticles were fabricated by interrupting deposition of Au at a certain timing. When a metal is deposited on a substrate by sputtering, a three-dimensional growth occurs[6]. First, nanoparticles are formed on substrate (island structure). As the deposition progresses, the nanoparticles grow, and a semi-continuous structure, in which some nanoparticles are in contact with each other and others are not, is formed. We expect that Au nanoparticles with a semi-continuous structure should be suitable for Raman scattering measurements, because gaps between nanoparticles are extremely narrow in this structure.

A schematic diagram of the ultrasonic resonance method is shown in **Fig. 1**. When the piezoelectric material installed under the substrate is vibrated at a resonance frequency, an oscillating electric field is generated around it due to the piezoelectric effect. As the structure of the metal nanoparticles changes from island structure to a semi-continuous film, the electrical resistance between nanoparticles decreases drastically, because the electrical conduction changes from the tunneling conduction to the bulk conduction. According to this structural change, the attenuation of the piezoelectric material changes. When the metal nanoparticles show island structure, the oscillating electric field does not cause the transfer of electrons between the nanoparticles, and the attenuation of the piezoelectric material does not change. As the distance between the nanoparticles decreases, the vibrating electric field causes the transfer of electrons between the nanoparticles (tunneling conduction), and the energy loss occurs,

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which increases the attenuation of the piezoelectric material. When the metal nanoparticles are in contact with each other, the electrical resistance of the substrate surface decreases greatly (bulk conduction), 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 during deposition, the gap distance between nanoparticles can be evaluated. In the experiments, the attenuate is evaluated by measuring the full width at half maximum (FWHM) of a resonance spectrum. The larger the attenuation, the larger FWHM. FWHM shows a maximum, when a semi-continuous structure is formed.

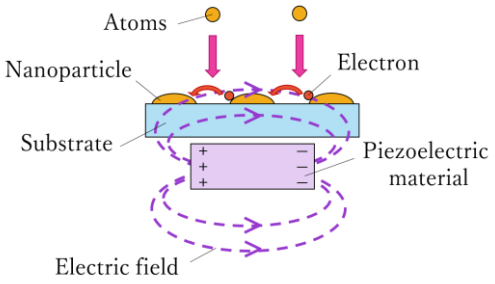

Fig. 1 Schematic diagram of the ultrasonic resonance method. An electric field around piezoelectric material is drawn.

3. Experimental results

Au nanoparticles were fabricated on the glass substrate by RF magnetron sputtering. **Figure 2** shows the change in the FWHM during deposition. In this experiment, the deposition was interrupted just after the FWHM showed a maximum to fabricate a semi-continuous Au nanoparticles.

4-Mercaptobenzoic acid (PMBA) was used as the detection molecule. A PMBA solution (10 μM in acetone) was dropped onto the SERS substrate. Then, Raman spectrum was measured for the substrate. The wavelength of the incident light was 785 nm. **Figure 3** shows the measured Raman spectrum. As control experiment, PMBA solution (100 μM in acetone) was dropped on a glass substrate. The result is shown in **Fig. 4**. It is reported that the Raman peaks from PMBA appear at around 1070 cm^{-1} and 1580 cm^{-1} [7]. The peaks are clearly observed in SERS substrate, while no peaks are observed in glass substrate. It should be noted that the PMBA concentration used in the control experiment is 10 times higher than that used for SERS substrate. These results indicate that Raman scattering is strongly enhanced by fabricating Au nanoparticles on a glass substrate.

We also fabricated SERS substrates with different gap distances, and observed that the intensity of the Raman scattered light changes depending on the gap distances. These results indicate that an optimized SERS substrate can be fabricated by using the resonant ultrasound method.

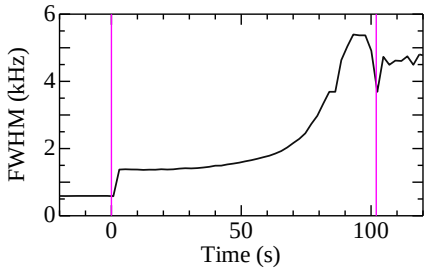

Fig. 2 Change in the FWHM during deposition of Au on a glass substrate.

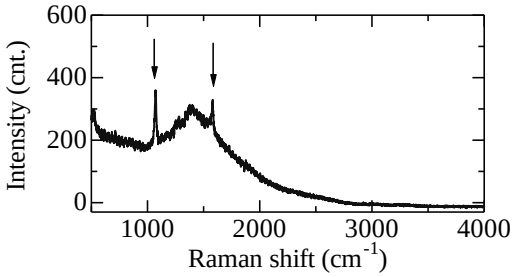

Fig. 3 Raman spectrum measured for the SERS substrate at 10 μM of PMBA. Arrows indicate Raman peaks from PMBA.

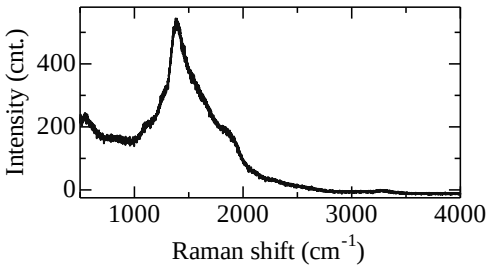

Fig. 4 Raman spectrum measured for the glass substrate at 100 μM of PMBA .

References

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