金属ナノ粒子と金属基板間の伝搬性及びギャップモード プラズモンを複合した超高感度ラマン分光

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実験方法: Different samples were used; (1) a Dove prism/Ag film (thickness of Ag films, t_{Ag} =5-20 nm)/PATP-SAM for localized surface plasmon (LSP) excitation, (2) a Dove prism/Ag film (t_{Ag} =45 nm)/PATP-SAM for PSP excitation, and (3) a Dove prism/Ag film (t_{Ag} =45 nm)/PATP-SAM/AgNPs for PSP and gap mode excitation. PATP-SAM was prepared by immersing the prism/Ag film samples in 1 mM PATP aqueous solutions. Here the pH of PATP solutions was adjusted to ~3.0 to protonate PATP, suppressing photochemical reaction of PATP [3]. Surface residuals like citrate anions on AgNPs were replaced by Cl⁻ anions, which leave negative charge on Ag surfaces [4]. Thus, AgNPs were immobilized by electrostatic interaction between positively charged amino groups in PATP on Ag films and negatively charged AgNPs. We found by SEM measurements that the surface coverage of AgNPs (with a size of 40-50 nm) on PATP/Ag films/prism to be ~4% (~35 AgNPs per 1 μ m² of Ag film). We mounted the prism/Ag films/PATP samples with and without AgNPs on a rotation stage to tune the angle of incidence for a laser (532 nm, 20 mW with p-pol.).

結果と考察: (1) LSP-SERS: Ag island films (t_{Ag}=15 nm at an AOI of 74.2°) provided pronounced SERS enhancement of 1.5×10⁵ compared to PATP on a bare prism (without Ag films) under the same optical configuration. (2) PSP-SERS: Ag continuous films (t_{Ag}=45 nm) on a Dove prism showed a pronounced reflectivity dip R_{min} ~0.2 at AOI=43.6° in accordance with theoretical value of 43.2°. SERS intensity of PATP showed the maximum enhancement of 5.7×10^3 at this resonance angle using a PSP. (3) PSP and gap mode SERS: Immobilization of AgNPs on a Dove prism/Ag film (t_{Ag}=45 nm)/PATP-SAM provided additional SERS enhancement of 370 at a resonance angle of 45.0°. The addition of AgNPs slightly increased the resonance angle by ~2°. Also AgNPs significantly broadened the reflectivity dip from 1.5° to 3.2° in FWHM. These features are probably due to increased scattering (out-coupling) of a PSP, evanescent wave, via AgNPs as anticipated by theoretical evaluations using Fresnel equations and effective medium theory. Overall SERS enhancement using both a PSP and a gap mode was 2.1×10⁶, which is apparently larger than that obtained solely by LSP in Ag island films. Furthermore, the above enhancement factor of 2.1×10⁶ is an averaged value over entire Ag films, where surface coverage of AgNPs is only ~4 %. By using the surface coverage (4 %) and by presuming a size (diameter) of hot spot to 5-6 nm in a gap mode [4], we estimated the actual enhancement of 3.4×10^9 for adsorbed molecules under each AgNP. Details in FDTD simulations of reflectivity and spatial distribution of local electric field for the prism/Ag film/PATP/AgNPs with different coverage will also be presented.

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Highly-sensitive Raman Spectroscopy using a Propagating Surface Plasmon and a Gap Mode Plasmon

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To realize single molecule sensitivity and spatial resolution of a few nanometers in Raman spectroscopy, it is crucial to utilize surface plasmons most efficiently. For this purpose, we investigated the coupling of a propagating surface plasmon (PSP) and a gap mode plasmon for a prism/Ag film/adsorbed molecule/Ag nanoparticle (AgNP) sample. An attenuated total reflection configuration assures efficient excitation of a PSP and a gap mode using an evanescent wave with electric field mostly perpendicular to the Ag film. Indeed, both a PSP and a gap mode were simultaneously excited by tuning an angle of incidence to the prism/Ag film interface. At a resonance angle of ~45.0°, we obtained an enhancement factor of 2×10^6 , as an averaged value for entire Ag films, for Raman scattering of p-mercaptoaminothiophenol. The observed value corresponds to an enhancement of 10^9-10^{10} at a nanogap area under each AgNP.