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学位論文名	Plasmon Hybridization for Tip-Enhanced Raman Analysis of Nanomaterials （プラズモンハイブリダイゼーションによるナノマテリアルの先端増強ラマン分析）
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論文内容の要旨

In this dissertation, plasmon hybridization in the gap between a metallic nanotip and a metallic nanofilm was discussed. It was demonstrated that the energy of the hybridized plasmon modes depended on thickness of the metallic nanofilm, which was utilized for increasing field enhancement of light in the gap of the tip-film system. By utilizing this phenomenon in tip-enhanced Raman scattering (TERS) experiments, it was proved that the enhancement in Raman scattering from a sample placed at the gap of a tip-film system could be well tuned by changing the thickness of the nanofilm.

In Chapter 1, fundamentals of Raman spectroscopy and microscopy are explained. Raman scattering was interpreted by the classical theory and quantum theory. Then, Raman analysis of molecules using optical microscopy combined with Raman spectroscopy was introduced.

Chapter 2 explains that the enhancement of Raman scattering by metallic nanostructures. When a metallic nanostructure is illuminated by light, light resonantly couples with plasmons on surface of the nanostructure and the surface plasmon polaritons (SPPs) are excited, resulting in the generation of strongly enhanced evanescent light near the nanostructure. This enhanced field is confined in a volume of a few tens of nanometer adjacent to the nanostructure. Thus, if a sample is placed near such nanostructure, Raman scattering from the sample can be strongly enhanced. The enhanced Raman scattering is called surface enhanced Raman scattering (SERS), and TERS is based on localized SERS at a metallic tip apex. SERS is also excited through chemical effect attributed to charge-transfer between a metal and a molecule. The mechanism of SERS was discussed and analyzed by Raman measurement in terms of the plasmonic effect and chemical effect. Moreover, SERS intensity can be dramatically increased at a nanogap between metallic nanostructures due to SPP coupling in them. The field enhancement in the gap was discussed.

In Chapter 3, some examples of TERS spectroscopy and TERS microscopy are discussed through nanoscale Raman analysis of multilayer graphene. Raman modes of graphene represent physical properties, such as defects, crystal direction, and interaction forces between the layers. The number of graphene layers and defect distribution on multilayer graphene on a glass substrate is visualized by Raman imaging of the multilayer graphene. TERS imaging of multilayer graphene is also performed, and the nanoscale analysis of the number of graphene layers and defect distribution were imaged at the resolution of ~35 nm.

Chapter 4 shows nanoscale Raman analysis of single-walled carbon nanotubes (SWNTs). Fundamental Raman modes of SWNTs depending on the diameter, defect, electric properties, and orientation are explained. In Raman scattering of SWNTs, the resonance Raman effect must be considered because SWNTs are resonant with visible light and show strong Raman scattering. Since the resonance condition depends on the diameter of SWNTs according to van Hove singularity of the energy level population, SWNTs having particular physical properties can be selectively detected. With the use of 532 nm and 442 nm excitation laser, selective Raman imaging of isolated SWNTs on a glass

substrate was obtained according to the resonance Raman effect. Also, strain induced in SWNTs can be analyzed from energy shift of the Raman modes, where the energy shift is attributed to the perturbed bond length and angles between carbon atoms in the lattice. The strain distribution in manipulated SWNTs was visualized by TERS microscopy at the nano-scale resolution.

Chapter 5 discusses the hybridization of plasmons in gap-mode of tip-film system. When a metallic tip is approached onto a metallic nanofilm, SPPs on the tip and SPPs on the two surfaces of the nanofilm interact with each other and result in hybridization. The SPPs on the nanofilm depend on the film thickness due to the Coulomb interaction between them. Therefore, the hybridized SPP modes in tip-film system rely on the film thickness. To understand the SPP modes, numerical analysis was performed using finite-different time-domain (FDTD) method. In the calculation, an Au-coated silicon tip with the apex size of 30 nm and an Au nanofilm coated on a glass coverslip were utilized. The gap distance was kept at 2 nm. When the thickness of the nanofilm was varied from 4 to 20 nm, and the SPP modes shifted from 820 to 530 nm. The phenomena was also confirmed experimentally by measuring scattering spectra from a gap in the tip-film system. It was found that the SPP modes shifted from 855 to 550 nm, when the nanofilm thickness was varied from 4 to 20 nm. The experimental results matched closely to the theoretical predictions.

In chapter 6, TERS measurement of gap-mode of tip-film system is discussed. Raman scattering of 4-aminothiophenol (4-ATP) self-assembled monolayer sandwiched in a gap of tip-film system was analyzed in order to estimate Raman enhancement in the gap. With the use of 642 nm excitation laser, the field enhancement was estimated varying thickness of the nanofilm from 4 nm to 16 nm. Consequently, the maximum Raman enhancement was obtained at the film thickness of 12 nm, and it was estimated to ~ 1.2 x 10^7. The resonant condition of the SPP in the tip-film system at the film thickness of 12 nm corresponds to the energy of 642 nm excitation wavelength, therefore it was concluded that field enhancement in the tip-film system could be improved by tuning energy of hybridized SPP in a gap of tip-film system. Finally, the outlook of the thesis is shown in the last chapter.

論文審査の結果の要旨

近年、金属ナノ構造表面に生じる表面プラズモン・ポラリトンに関する研究が活発である。二つ以上の金属ナノ構造体がナノメーター・オーダーの近距離に存在するとき、近距離電磁場を介して互いのプラズモンは相互作用し混成モードを形成し、共鳴エネルギーはぞれぞれの構造が持つエネルギーと異なる。本学位申請論文は、金チップ先端の局在プラズモンが金薄膜の表面プラズモンと結合して生成されるハイブリダイズド・プラズモンに関する研究をまとめたものである。その成果は以下のとおりである。

- 金ナノ粒子の局在プラズモンと金薄膜の表面プラズモンが結合したハイブリダイズド・プラズモンの共鳴エネルギーと散乱スペクトルについての考察を行い、それらが金薄膜の膜厚に依存することを計算から示している。また実際に、先端径30 nmの金探針を4-20 nmの膜厚の金薄膜に近接させて散乱スペクトルを取得し、計算結果と実験が一致することを示している。金探針の先端径を小さくすると、プラズモンの共鳴エネルギーが高くなることも見出している。
- プラズモンハイブリダイゼーションによる電場増強効果を利用し、先端増強ラマン分光が行える可能性について検討を行っている。実際に金探針先端と金薄膜のナノギャップに4-aminothiopheonl分子の単分子膜を配置し、励起波長642 nm (1.93 eV)を用いて先端増強ラマン分光を行い、金薄膜の膜厚によってラマン散乱強度が変化する結果を示している。膜厚が12 nmにおいてそのラマン強度が最大となることを示し、これはハイブリダイズド・プラズモンの共鳴エネルギーが膜厚12 nmにおいて励起波長のエネルギーにほぼ一致することを見いだしている。これによって金属膜厚によってラマン増強度を最適化できることを示している。プラズモンハイブリダイゼーションにより、先端増強ラマン分光の効率を４千倍程度向上できることを実証している。
- 走査型先端増強ラマン散乱（ＴＥＲＳ）分光顕微鏡を作製し、スコッチテープ法を用いて作製したグラフェンを観察し、取得したＧバンドのラマン散乱強度像からＴＥＲＳ分光顕微鏡の空間分解能が36 nmより小さいことを示している。またＧバンドと２Ｄバンドのラマン散乱強度比からグラフェンの層数分布、Ｄバンドのラマン散乱強度から欠陥分布を画像化し、グラフェン試料の構造について考察している。
- カーボンナノチューブにＡＦＭプローブを使って人工的に形成させた歪み分布をＴＥＲＳ分光顕微鏡で観察し、ＡＦＭ像とＧバンドのラマン散乱強度像及びＧバンドのピークシフト量像を示し、歪みとラマンピークとの関係について考察している。

以上のように、本学位申請論文はプラズモンハイブリダイゼーションについて理論及び実験的に新たな知見を得ておりラマン分光分析への応用を通してナノ材料科学分野での貢献が期待できる。これらの成果は応用物理学、特にプラズモニクスにおいて寄与するところが大きい。よって本論文は博士論文として価値あるものと認める。