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学 位 論 文 題 目	

Study on Nonlinear Optical Properties of Ag Nanoparticles: Effect of Size Quantization and Excitation Power Modulation
(銀ナノ粒子の非線形光学特性:量子サイズ効果及び光強度変調に関する研究)

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論 文 の 要 旨

The thesis is composed of 6 chapters. Chapter 1 gives introduction including the background and the objective of this work. Nonlinear optical properties of metal nanoparticles have been extensively studied. These particles play an important role in nanophotonics because they exhibit plasmonic effects that greatly enhance its effective optical nonlinearities. This enhancement is obtained through coherent oscillations of conduction electrons, phenomenon known as localized surface plasmon resonance (LSPR). Experimental studies of nonlinear properties of metal particles have been investigated by means of Z-scan, degenerate four-wave mixing, and pump-and-probe method. The evaluations in these papers were often performed for only one wavelength. This treatment restricts the understanding of the mechanisms underlying the optical nonlinearities. Also, these studies have been leading to conflicting results from experiments, with several reports of saturable absorption (SA) and reverse SA. In this work, Ag particles embedded in silica glass with diameter sizes of 3.0 to 16 nm were systematically investigated. By using spectroscopic ellipsometry and pump-and-probe spectroscopy with white-light continuum probe, the transient transmission changes and effective (Ag particles composite) and intrinsic (Ag particles) nonlinear third order susceptibilities were evaluated and discussed. This work is also motivated by the fragmented and conflicting previous experimental results of third order optical susceptibilities.

Chapter 2 represents fabrication of Ag nanoparticles and the linear optical property. Ag nanoparticles embedded in silica glass were fabricated by using negative ion implantation. To control the particles size, the total fluence was varied. Structural characterization was carried out by using small-angle x-ray

scattering. Average particle sizes were evaluated by using Guinier approximation. Effective thickness and Ag volume fraction of the implanted Ag particles layer were analyzed by using a variable angle spectroscopic ellipsometer. From MG effective-medium approximation (EMA), the dielectric function of Ag particles layer was modeled by fitting the dielectric function of silica glass and Ag particles. The absorption band is attributed to LSPR and its redshift with increasing particle size are due to quantum size effects of conduction electrons. Transmission and reflection spectra measured by microscope spectrometer show a single peak, which indicate a distinct particle size distribution and a single particles layer. These results clearly indicate that these Ag particles samples are suitable for nonlinear characterization of size and power modulation effects.

Chapter 3 represents characterization of dispersion of effective third-order optical susceptibility of Ag nanoparticle composites. Optical nonlinearities were measured by using a femtosecond- pulse pump-and-probe technique with white-light continuum probe. The candidate successfully evaluated the dispersion of the real and imaginary components of the effective third order susceptibility of Ag nanoparticles embedded in silica glass. Around the LSPR, the dispersion of the third order susceptibility strongly reflects the local electric field enhancement owing to the relative separation distance between the plasmon resonance and interband transition edge in contrast to other metal nanoparticles, i.e. Au and Cu. The discrepancy between the experimental and calculated dispersions at higher photon energy than the resonance peak is due to the contribution of the intrinsic nonlinearity dispersion of the Ag nanoparticles

Chapter 4 represents the particle size dependence of intrinsic third-order optical susceptibility of Ag nanoparticles. From the experimental results, the third-order susceptibility showed a strong intensity increase as the Ag nanoparticles diameter decreases from 15 to 3.0 nm. The real and imaginary parts show spectral dependence in the vicinity of the LSPR. This spectral dependence is increased as the Ag nanoparticles decrease. The intensity and spectral dependence mostly reflect the discretization of the electron transitions owing to the quantum finite-size effects. The critical Ag particle size for the quantum effects was found at 15 nm. The experimental results also show that the interband plays an important role to determine the optical nonlinearities around the LSPR.

Chapter 5 represents the characterization of the optical nonlinearities of Ag nanoparticles on excitation intensity, particle size and photon energy. The results clarified the apparently conflicting previous findings based on Z-scan measurements. In contrast to conclusions based on single photon energy results, the candidate has shown that the dispersion of the transient transmission changes reflects mainly the local field enhancement and its nonlinear modulation. For all Ag particle sizes, the transient transmission changes show negative and positive values at lower and higher photon energy in the vicinity of the LSPR. For particle sizes larger than 9.6 nm, the transient transmission changes peak position and change of sign redshift with excitation intensity increase. This result demonstrates the modulation of the resonance condition by optical nonlinearities.

Chapter 6 summarizes this work and future works are mentioned.

審　　査　　の　　要　　旨

〔批評〕

本論文では、金属ナノ構造材料の特徴的な光学的性質のひとつである非線形性に関して、従来は断片的なデータしか報告されていなかった 3 次非線形光学特性を Ag ナノ粒子材料に関して系統的に詳細に評価解析し、波長分散特性と物理的要因やその非線形特性が及ぼすナノ構造での局所場への影響に関して明らかとしたものである。分光エリプソメトリーとフェムト秒ポンププローブ分光を用いた詳細な光学計測解析により、3 次光学感受率について波長分散特性を明らかとし、波長分散が構造要因である局所場因子に強く依存していることを明らかとした。さらに、粒子径 3-16nm の Ag ナノ粒子自身の材料定数としての 3 次光学感受率の波長分散の評価に成功し、その分散特性、サイズ依存性が、量子サイズ効果を強く反映していること、その発現臨界粒子径が 15nm であることを明らかとしている。また 3 次の非線形性による局所場の変調についても実験的に明らかとして、従来の様々な断片的なデータに関して、統一的な見解を与えることに成功している。

以上の点で本論文は、非線形光学応答に対する量子効果発現を定量的に解明し学術的に重要な結果であり、サイズ効果を含む 3 次光学感受率の波長分散を明らかとし工学的にも価値が高いと評価される。

〔最終試験結果〕

平成 27 年 1 月 14 日、数理物質科学研究科学位論文審査委員会において審査委員の全員出席のもと、著者に論文について説明を求め、関連事項につき質疑応答を行った。その結果、審査委員全員によって、合格と判定された。

〔結論〕

上記の論文審査ならびに最終試験の結果に基づき、著者は博士（　工学　）の学位を受けるに十分な資格を有するものと認める。