博士論文（要約）

Tooth-shaped plasmonic multilayer structures for light emission and SERS detection

（SERS 検出と光放出のための歯状多層膜プラズモン構造体）

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Surface plasmons (SPs) are coherent free electron oscillations that can be excited at the boundary between a dielectric layer and a metal layer. Due to the optical unique properties of surface plasmons, light can be confined on the metal surface or between metallic nanoparticles. For different situations of light confinement in the nano-structure, two types of surface plasmons can be obtained: surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR). SPRs propagate along the interface between metal and dielectric layers. The decay length of the electric field of SPR is about 100 nm and long propagation length can be obtained. SPR has been widely applied in lithography, chemical and biosensing applications. LSPRs are excited in metallic nano-particles or nano-structures, which supports strong enhancement and confinement in the electric field. LSPRs have been used in surface-enhanced Raman scattering (SERS), biomolecular interaction detection, and more generally in sensing at the nanoscale. Some nanostructures, like nano-cavity and metal-dielectric multilayer structures, sustain standing wave in their structure; this optical phenomenon is called standing wave plasmon resonance (SWPR). Due to SWPR mode coupling with LSPR mode, the enhancement can be higher than LSPR mode. The plasmonic structure with SWPR mode should be useful in applications requiring strong light confinement, such as SERS and light emission.

Plasmonic structure for SERS or light emission applications need strong light confinement. In order to obtain high enhancement, nanofabrication technologies have been developed to create efficient LSPR and SWPR modes. The strong LSPR can be observed between two metal nanostructures, such as nanogap or nano-hole. There are two main nanofabrication methods for plasmonic nanostructures to obtain strong light confinement, including top-down and bottom-up approaches. For top-down approach, lithography process is a key technique. Three kind of lithography, direct writing lithography, imprint lithography, and colloidal lithography have been developed with different advantages. The writing lithography techniques, including optical lithography, E-beam lithography, and focus ion beam lithography have high create for the nanostructure (excitation wavelength control). However, the writing lithography techniques suffer from high cost. The imprint lithography techniques, include soft lithography and nanoimprint lithography, have high efficiency of the fabrication but require a one-time and high-quality template and suffer from limitation in the pattern scale and aspect ratio of the structure. The colloidal lithography techniques, such as the block copolymer lithography technique, have lower cost

and no stringent requirement for the fabrication environment, but it is limited in the shape and size of the structure. For the bottom-up nanofabrication approaches including synthesis self-assembled and physical deposition process has simple and low cost fabrication process. The main disadvantages of the bottom-up approaches are the inhomogeneity of the structures, low reproducibility for the measurement, and the difficulty for the excitation wavelength control. In summary, plasmonic structures obtained with a simple fabrication process at low cost and sustaining strong enhancement are desired.

In this dissertation, we propose a nanogaps structure that can be fabricated by using thin film technique and selective wet etching. A multilayer with different materials is deposited on a flat substrate by thin film technique. The thickness of the multilayers can be controlled accurately in the nanometer range. Subsequent selective wet etching is used to form the nanogaps in one of the material constituting the multilayer, and the depth of the nanogaps is controlled by the wet etching time. It is noted that the multilayer structure supports a standing wave plasmon resonance (SWPR). In the SWPR, incident light can be confined in the nanostructure and the strong standing wave resonance mode coupled with LSPR mode is excited. The multilayer structure with SWPR mode with high enhancement, small excitation area and angular independency is suitable for SERS, light emission, and sensing applications.The Ag/Si multilayer structure is first designed and fabricated as a tooth-shaped structure for SERS applications in the visible to near-infrared range. Due to the standing wave plasmon resonance mode coupled with LSPR mode in a few nano-scale-gap size, strong electric field enhancement can be obtained in nanogaps. This standing wave resonance is highly related to the depth of the gaps. The SERS performance is evaluated using the vibration intensity of the measured Raman signal from an adsorbed thiophenol monolayer (the 998 cm-1 vibration is used). The 10 nm gap of tooth shaped multilayer structure with 10 s etching gives 35 times larger SERS signal than that of a flat silver surface, and 16 times larger than the multilayer structure before etching. Tooth multilayer structure realizes few nanogaps with strong enhancement field and tunable resonance wavelength for SERS.

Based on the standing wave resonance mode in the multilayer structure, a multilayer grating array with multi narrow absorption band in the infrared range is proposed for thermal emission applications. Due to the light incident from the side of the multilayer grating structure, lateral standing wave resonance in the multilayer structure is excited. The absorption spectrum shows that the resonance

mode is governed by the multilayer width, which provide a means to tune the absorption band. Measured reflectance spectrum of the multilayer structure with a width of 620 nm gives a reflectance dip at 6.3 μm with a 60 % reflectance. Moreover, the effect of the incident angle on the measured reflectance spectrum was examined for a range of incident angle from 0 to 15 degrees and the results confirm the weak dependency of the resonance wavelength with the incident angle. The measurement reflectance spectrum shows a good agreement with the simulation absorption spectrum. Finally, the emission spectrum shows an emission peak around 5.2 μm close to the dip wavelength of the reflectance spectrum.