Plasmonic Nanostructured Devices for Chemical and Biological Sensing

NSF NIRT Grant ECS-0403865

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The focus of this NIRT project is to investigate the fundamentals of plasmonic phenomena in nanoscale metallic structures and to explore the use of plasmonic chip technologies in bio-chemical sensing. We investigate metal nanoaperture arrays as a medium for effective interactions among photons, plasmons, and anlytes, and also as a base structure that provides wavelength-dependent transmission of light. The plasmonic interaction in chemically functionalized nanoaperture arrays offers a new strategy for massively parallel detection of chemical and biological analytes. Modulation of the nanoaperture array's optical response by adsorbed analytes is expected to offer improved sensitivity and selectivity over conventional surface plasmon resonance (SPR) methods, which are widely used and commercialized for analysis in detecting biological and chemical agents. The conventional SPR measurement usually involves bulky optics and high-precision mechanics for angular or wavelength interrogation of metal films in contact with analytes. As such, it is difficult to implement and automate the conventional SPR technique in compact instrumentation. We investigate a new approach to SPR sensing of biochemical agents by exploiting the recent breakthroughs in plasmonics that involve metallic nanostructures. The devices being developed in this program are amenable to miniaturization and integration with a photodetector chip so that chip-scale sensor arrays, which will enable massively parallel detection of many analytes and on-chip processing of information in the electronic domain.

Research in the first year of this NIRT project has focused on investigating the fundamental physics of optical interactions in nanoapertured metal layers and on chemically modifying the metal surfaces for bio-chemical sensing.

Plasmonic Phenomena in Metal Nanoapertures:

We have analyzed the spatial and temporal evolution of surface plasmon resonances occurring in various regimes of transmission spectra. The finite-difference-time-domain (FDTD) analysis of plasmonic fields, charges and energy flow reveals that different modes of surface plasmon resonances involve different sections of metal surface, an important finding for optimally designing plasmonic nanoaperture structures for sensing applications [2]. In experimental studies, we have measured the distributions of the fields (in the near- to far-field regime) emanating from the apertures by employing an interference technique in conjunction with a scanning nanoprobe. Figure 1 shows an SEM image of a silver three-slit array structure (slit spacing of 360 nm and slit width of ~50 nm).

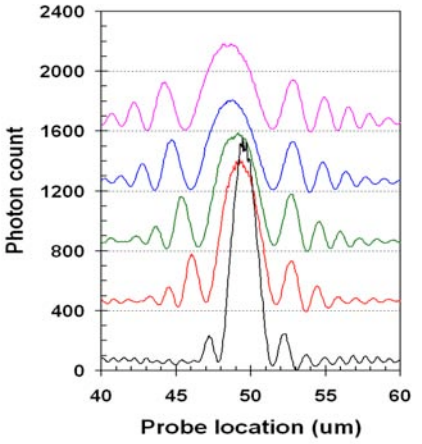

Figure 1. *SEM image of a silver three-slit array (right bottom). Optical transmission measured with a scanning nanoprobe (top): an interference pattern between a freely transmitting wave and a wave propagating through the nanoslits.*

The metal thickness was properly designed such that a directly transmitting wave component interferes with the beam transmitting through the nanoapertures. A scanning nanoprobe then records the interference pattern of the two waves. Similar to holographic recording, this interference pattern reflects both the amplitude and phase information of the subject wave with reference to the incident beam. This technique allows beam profiling with nanometer resolution in the near- to far-field regime, and provides valuable information to understanding detailed mechanisms of plasmonic interactions in metal nanoapertures.

We have also imaged the plasmon dynamics (spatio-temporal evolution) by recording a movie with an unprecedented time resolution (330 attosecond per frame) [3,4]. Figure 2 (left) shows a photo-emission electron microscopy (PEEM) image of two-photon photoemission (2PP) excited with a 10 fs, 400 nm laser pulse from a 780 nm period Ag grating. The image reveals hot spots of photoemission, which correspond to localized surface plasmon modes excited in nanometer scale surface roughness features in the Ag film. The dynamics of such localized modes was studied by recording time-resolved PEEM movies with a variable delay between pump-probe pulses in _ optical cycle steps. The pump-induced polarization wave localized in each hot spot interferes with the polarization induced by the phase related probe pulse. Initially (delay of 0 and 5 optical cycles) the plasmon modes oscillate at the driving frequency, after 10 to 20 cycles the modes evolve at their natural frequency, and beyond, the coherent interaction ceases due to dephasing of all modes. The retardation (blue) and advance (yellow) of modes A and C in the 10 - 20 cycle (13.3 - 26.7 fs delay) range is indicated. Quantitative interferometric measurements at each spot give dephasing times of 5-6 fs with the time constants decreasing with increasing plasmon frequency. This imaging technique allows us insights on fundamentals of plasmon characteristics, such as energy dissipation and concentration, decoherence, spatial propagation and plasmon-plamon interferences, important for designing plasmonic sensor devices.

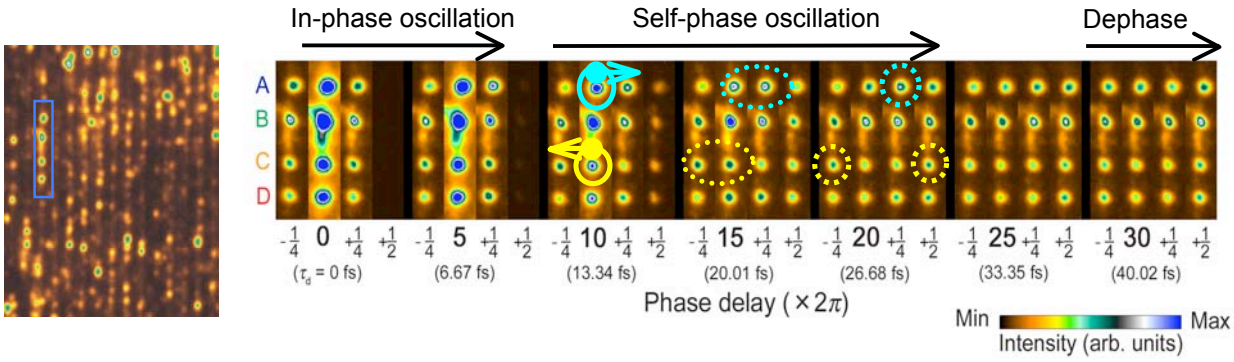

Figure 2. *PEEM image of a silver nanoslit array (left) and selected frames from a TR-PEEM movie showing (right) the phase and amplitude evolution of individual plasmon modes in 330 attosecond/frame segments.*

Chemical Modification of Metal Surfaces and Transmission SPR Sensing

We have developed chemical methods for modifying the surface of metal nanostructures in a manner that allows the identification of analyte molecules through their impact on the nanostructures spectral signature. The guiding principle for our approach in the first year of the

project has been to exploit our current expertise with thiol-based chemistry and to adapt that to the chemistry suitable for nanoaperture-based SPR sensing. To this end we have defined the following tasks: 1) Prepare self-assembled monolayers (SAM) on the metal nanostructures and demonstrate that this adsorption of a monolayer film (~1 nm thick) causes changes in the spectral signature of the device. 2) Exploit the terminal chemical functionality of a SAM film to electrostatically adsorb polyelectrolytes that are designed to bind biomolecules. 3) Exploit the chemical functionality of a SAM film to immobilize dextrans, which can later be modified for selective immobilization of biomolecules, oligonucleotides, and antibodies.

We have modified the metal nanoslit array surface using thiol-based chemistry, and studied the surface binding effects on the optical transmission. We have observed a major redshift (15nm) of plasmon resonance wavelength when a self-assembled monolayer of carboxyl-terminated alkanethiol (~1nm thick) was formed on Au-coated Ag nanoslit array surface (Figure 3) [5]. The sensitivity of this nanoslit-array-based SPR technique is measured ~1000nm/RIU (RIU: refractive index unit), which is significantly better than the conventional grating-based SPR (400nm/RIU) and the nano-hole array case (500nm/RIU). The small size at which the nanoapertured sensing element can be constructed enables the creation of an array in which different assays are simultaneously performed. This capability will allow for the testing of multiple identifiers, as well as the incorporation of redundancies and control assays.

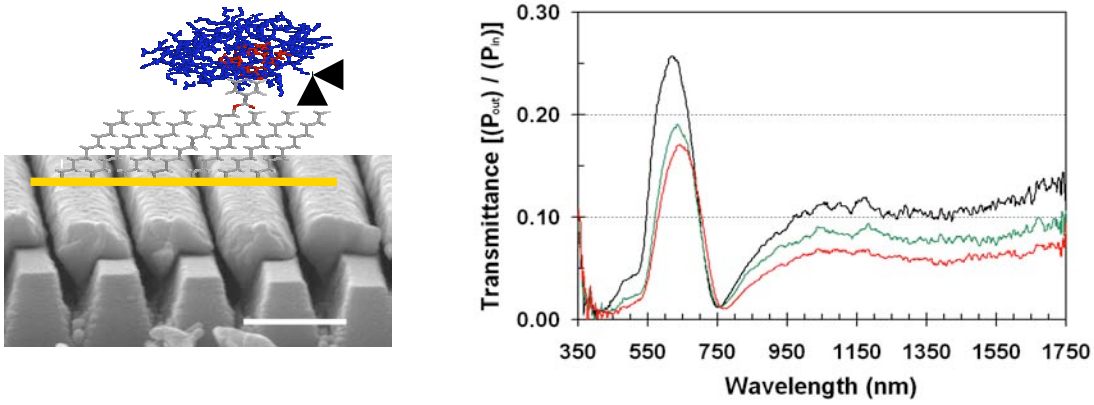

Figure 3. *Chemical modification of metal surface (left). Transmission spectra of a Au-coated Ag nanoslit array (right): before modification (black) and after formation of a thiol-based SAM (green) and a poly-L-lysine layer (red).*

References

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