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Ultrafast STM-tip Localized Responses from Nanostructured Surfaces

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Abstract: Spatially correlated reactivity and femtosecond time-scale responses from mesoscopic rough films are reported. The STM-tip spatially-localized transient SHG dynamics of nanometer scale metallic structures are used to establish localized surface plasmon dynamics.

The relationship between structure and functionality (or reactivity) is an underlying principle for the molecular biological and chemical sciences. The structure–function paradigm also applies to observables related to excitation of collective modes of materials as exemplified in the sensitivity of surface plasmon polaritons (SPP) to the structural and chemical nature of the interface.[1] The coupling of photons into the SPP mode of a material and the resultant large local electromagnetic fields are central to realizing surface enhanced spectroscopy (SES). Experimental support for the types of surface topographies that give rise to the largest predicted field enhancements came through measurements of SERS signals from structured surfaces.[2-4] Rough surfaces result in greater signal enhancement over smooth ones;[4] metal islands resulting from the formation of regular features (*i.e.,* hemisphereoids or spheroids) in quasi-periodic patterns yield greater enhancements still.[2] By contrast, theoretical studies of SES have established the local field enhancements for particular geometries on model surfaces.[3,5] These high local electromagnetic fields affect the local propensity for higher order processes like multi-photon ionization (MPI) and harmonic generation. MPI from metal films is, therefore, a representative measure of the electromagnetic contribution to SES processes since, under appropriate conditions, it is a direct result of SPP excitation.[4,6,7]

This paper reports on two types of measurements that directly correlate metal structural features with surface plasmon-induced responses. The first, correlated optical reactivity and scanning tunneling microscopy (CORSTM), measures SPP-induced reactivity initiated with femtosecond pulses and the near-field local plasmon dynamics on femtosecond time scales and nanometer length scales. A spatially localized probe (*i.e.*, STM) is used for simultaneous characterization of local surface topography and detection of the local field enhancement via SPP-mediated MPI from the metal surface. The second approach is the STM-tip localized excitation of nanometer Au features probing the SHG response as a function of tip position or interferometric time delay.

In both cases, the excitation geometry, with the pump and probe beams from the femtosecond pulse laser and STM interrogating the surface from opposite sides, facilitates excitation of SPP-modes. The optical source is a home-built cavity-dumped Ti:Sapphire laser that produces 25-30 fs pulses, centered at 780 nm, with energies up to 30 nJ. Focusing conditions yield peak intensities at the Au and Ag films of 30 MW/cm^2 and 1 GW/cm^2 for t he SHG and CORSTM experiments, respectively. The short duration pulses and high peak powers are critical for successful simultaneous measurement of the surface topography and reactivity.

The surface topography of the rough Ag films was determined by measuring the STM DC tunneling current. Simultaneous determination of the photo-induced signal component is achieved by lockin amplifier demodulation of the output of a second pre-amp located in the STM head. Topography photo-reactivity correlations[8] are found for three qualitatively different surface structures: from tens of nanometer length scale roughness, the edges of oblate ellipsoids, and from the gaps between prolate ellipsoids in close parallel proximity. These experimental results confirm the predictions of SPP-reduced electromagnetic field enhancements. Spatial resolution in these unique photo-induced surface reactivity measurements is achieved through the favorable interaction of several factors: the close proximity (~1 nm) of a sharp metallic tip to the surface, tip-surface field focusing, and the highly nonlinear nature of the process being studied.[6]

The temporal response associated with SPP-mediated MPI can be established using a pump-probe scheme; *i.e.*, detection of the local ionization response as a function of the temporal separation between two excitation pulses. The spatially localized pump–probe response shown in Figure 1 is dominated by the ultrafast pulse width-limited feature at the zero of time with a smaller amplitude component extending well beyond the pulse duration that decays to a baseline level of ~325 fA (that was subtracted in the figure). The ultrafast peak results from an “instantaneous” three photon ionization response. The longer decay component is exponential with time constants of 500-700fs. By comparison with an all-optical measurement that established that the thermalization of hot electrons created by SPP excitation in Ag occurs with a time constant of 670(70) fs,[9] the decays in Figure 1 are attributed to the relaxation of hot electrons by inelastic electron-phonon collisions. The asymmetry of the decay times is attributed to small asymmetries in the intensities and spatial overlap of the beams relative to the STM tip.

A second approach for examining spatial and time-resolved electronic dynamics of mesoscopically-structured films employed tip-localized SHG responses of individual mesoscopic scale metal particles. The surface feature selection scheme utilizes the local field enhancement that results from the plasmon resonance from the STM tip–material junction, where local field enhancements of 100-fold are possible.[10] We have already observed tip- enhanced SHG signals from structured Au and Ag films with ~100nm size particles. Tip-localized 2-pul interferometric measurements of localized plasmon dynamics have been obtained, as shown in Figure 2. Since the electronically interacting particles (and interactions with the Au or Ag tip) give rise to another plasmon resonance that is on-resonance with the fundamental wavelength, temporally broadened, fringe-resolved autocorrelation are obtained. Although position-dependent variations in the response are observed, spatial drift of the tip results in large signal changes that have prevented

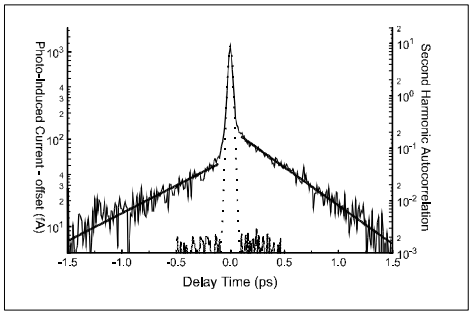

Figure 1. Semi-log plot of temporal SPP-MPI data from Ag films (solid lines) and SHG autocorrelation (dashed lines). Exponential component temporal decay constants of 680 and 490 fs. Signal was obtained with 50 KHz pulse repetition rate.

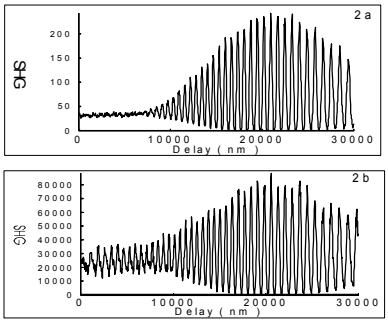

Figure 2a Interferometric SHG response from 100 μm KDP crystal.

Figure 2b Interferometric SHG from Ag particle film. Spatial variations of this signal are observed.

systematic analysis. Nevertheless, temporal broadening of the autocorrelation response suggests particle plasmon dephasing times of about 30 fs for Ag but much shorter for Au.

CORSTM measurements have been used to directly image the surface plasmon local electric field on rough Ag surfaces and establish localized plasmon and hot electron relaxation dynamics. The tip-localized SHG responses from Ag and Au nanoparticle films indicate particle plasmon resonance dephasing times of more than 30 fs for Ag nanoparticles.

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