Metal Adhesion Layer Induced Damping of Surface Plasmons Probed by Photoelectron Emission

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Nanoparticles exhibiting localized surface plasmon resonance (LSPR) have been investigated for use in a variety of applications including surface-enhanced Raman spectroscopy, high-resolution optical imaging and lithography, optical metamaterials, sensors, and photocathodes. For lithographically fabricated plasmonic nanostructures, adhesion promoting metals such as Cr and Ti are often used, while they have been shown to induce damping of LSPR, reducing the extinction cross-section, near-field enhancement, and Q factor[1,2]. In this work, we studied Ti adhesion layer induced plasmon damping of Au nanorods by numerical simulation and recently proposed photoelectron emission testing[3].

Electromagnetic simulation was performed via finite element based software *COMSOL Multiphysics* and the results are shown in Figure 1. Au nanorods were placed on indium tin oxide (ITO) substrate, an electrode in photoemission whose low index has weak perturbation on LSPR, with or without a Ti adhesion layer. Nanorod geometry was designed to exhibit LSRP when driven by 800 nm wavelength laser used in photoemission testing. Both the spectral response and near-field distribution indicate Ti adhesion layer increases damping of LSPR and reduces optical field enhancement. In fabrication, ITO was sputter-coated on Si or sapphire substrate, and nanorods were defined by electron beam lithography (Elionix F-125), followed by metal evaporation and lift-off. For samples without an adhesion layer, only Au was evaporated at a slow rate to reduce stress, prevent delamination and improve adhesion. SEM images (Figure 2(a)&(b)) show that nanorod arrays were prepared with similar yield, though in the absence of adhesion layer more interstitial particles and poorer line-edge-roughness were observed. In photoemission, nanorods were actuated by 35 fs, 800 nm pulsed Ti:sapphire laser in normal incidence and polarized along nanorod axis to excite longitudinal LSPR mode. Measured photoemission current is illustrated in Figure 2(c). At low pulse energy, photocurrent is decreased by more than 20 times by the Ti layer. Field enhancement, estimated via transition point from multiphoton emission (linear regime) to optical field tunneling (sublinear regime), is improved by 50%-80% in the absence of Ti layer, consistent with simulation.

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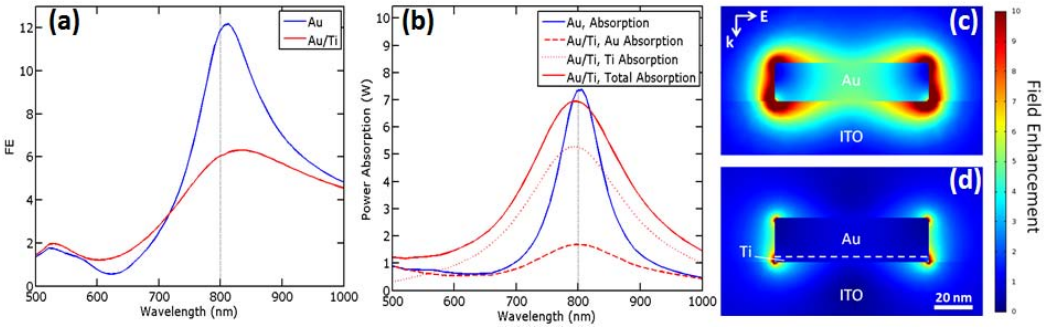

*Figure 1: Electromagnetic simulation of Au nanorods with and without a Ti adhesion layer: (a)*Field enhancement (FE) spectra. Ti layer reduces FE by a factor of 2. Dashed vertical line indicates 800 nm wavelength. *(b)* Power absorption spectra. Ti layer broadens LSPR peak and dissipates 75% of total power absorption. *(c)&(d)* Optical near field distribution. Au nanorods have 80 nm length, 20 nm width (4:1 aspect-ratio), and 20 nm thickness. They form a square array with 200 nm pitch and are placed on ITO substrate, with or without a 3 nm Ti adhesion layer. Illuminating light has normal incidence and is polarized along nanorod long-axis to excite longitudinal LSPR mode, illustrated in (c) with vectors showing propagation (**k**) and polarization (**E**) directions.

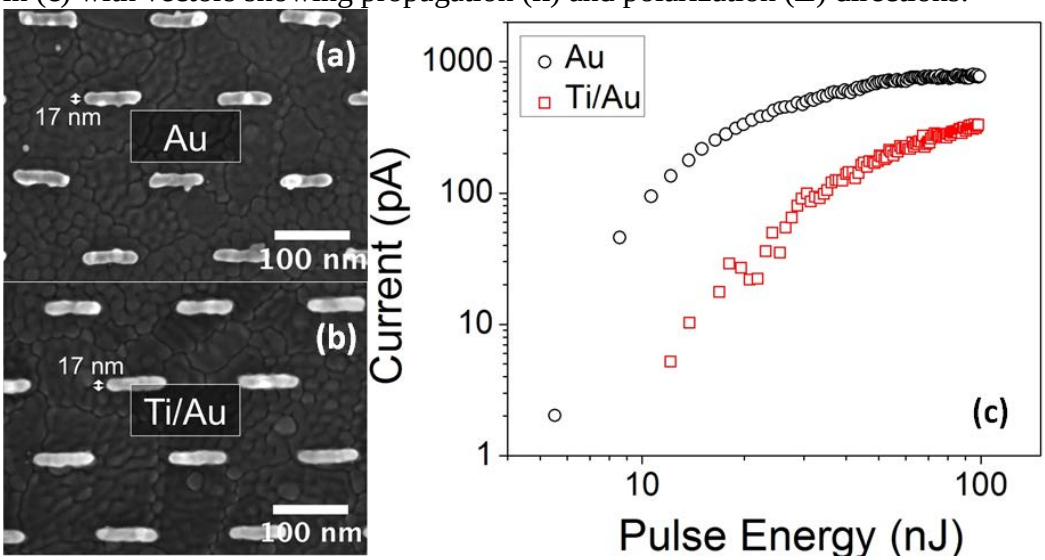

*Figure 2: Fabricated Au nanorods and photoelectron emission measurement: (a)(b)*SEM images of Au nanorods (20 nm thick) with and without a Ti adhesion layer (3 nm thick) on ITO coated (50-200 nm thick) substrate. Images were acquired using an FEI Helios Dual Beam SEM-FIB equipped with a high-resolution magnetic immersion lens allowing a resolution of < 1 nm. *(c)* Log-log plot of photoemission current against incident laser pulse energy for nanorods with and without a Ti adhesion layer. Au nanorods were optically actuated using a pulsed Ti:Sapphire amplifier (pulse duration 35 fs, wavelength 800 nm, spectral bandwidth 38 nm, linear polarization, repetition rate 3 kHz). The pulsed light source was focused to a spot (FWHM 90 μm) at the surface of the nanostructured cathode, which was mounted at an angle of 90° with respect to the direction of propagation of the laser pulse (normal incidence) within a high-vacuum chamber (~10^{-8} mbar).