Hyperspectral Nanoscale Imaging on Dielectric Substrates with Coaxial Optical Antenna Scan Probes.

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Supporting information

Summary of Experimental Set Up

To investigate the basic properties of planar coax antennae, 120nm of Au was evaporated on a standard 175 um-thick glass cover slip with a 2nm Ti adhesion layer. Coax structures with various dimensions were then milled into the Au film via Focused Ion Beam (FIB) milling (ZEISS X-beam; resolution of 12nm with 1 pico-ampere milling current). The (far-field) resonant behavior of the coax antennae were observed via transmission spectroscopy, where white light is incident on the air side of the sample and the light transmitted through the coaxial antennae is sent to a spectrometer equipped with a liquid nitrogen cooled charge-coupled device (CCD) camera. The spectra were source and background corrected. Antennae structures optimized for a resonance at 633 nm were then fabricated on the apices of NanoSensors SiN contact mode tips by evaporating 2 nm of Ti and 120 nm of Au on the tip followed by FIB milling. Subsequent near-field optical measurements were done with a modified WITec on carbon nanotubes that were grown via CVD directly on fused silica cover slips using Fe nanoparticles obtained by dropping a ferritin solution of 0.1g/L (horse spleen ferritin, Sigma) on the samples for 10 min, washed with deionized water and blow dried with nitrogen gas. Followed by a thermal oxidation step at 700°C in air to eliminate all the organic matter. Finally, the CVD was carried out at 900°C for ~30 min with a mixture of Ar (~100 sccm), H₂ (~30 sccm) flew through a bubbler containing ethanol (used as the carbon feedstock) at 1 atm (ask Ariel). The tips were mounted to the microscope's AFM attachment and approached to the sample in contact mode. The optical antenna tips were excited through the sample using a HeNe laser via a 100x 1.4NA oil objective. Signal was collected through the same objective, a dichroic mirror, and long pass filter, then directed onto either a spectrometer or a photo multiplier tube (PMT).

Resonance measurement of coaxial antennae

The resonances of the optical antennae was performed as follows: The sample with the coaxial antennae FIB milled into the planar 2nmTi/120nm Au layer was placed in a confocal microscopy setup. The individual spectra of each coaxial antenna within a matrix were taken, where they were illuminated from one side and the transmitted signal was collected on the other side by a 100x 1.4NA oil objective. The sample was placed on a closed loop piezo drive translation stage enabling a confocal scan over the sample area. Each antenna size was milled 16 times, five microns apart, into the Au film to test reproducibility and provide statistics. The 16 spectra were subsequently compared with scanning electron microscope (SEM) images. Spectra with deviations correlated to visual defects in the coaxial structure were discarded from the analysis. The remaining spectra of equivalent coaxial antennae were averaged.

Theoretical modeling

Finite Difference Time Domain (FDTD) simulations were performed for cylindrical coax structures in flat films (Fig. S2). All the simulated spectra show a peak at 505 nm corresponding to the Au material-related mode, which we also detect experimentally (compare Fig. 1a-c). FDTD simulations predict geometry-dependent peaks at 604 nm, 660nm and 671nm for the small, medium and large pin diameters. The theoretical and experimental results agree very well for the 160nm coax, whereas the 45nm and 60nm coax experimental spectra are both blue-shifted by ~50nm relative to the FDTD values. In the FDTD simulations, changes in taper angle and curvature at the end of the coax did not significantly affect resonance wavelengths. Therefore, we hypothesize that the differences between experimental and simulated peak wavelengths for the smallest two coax diameters may be due to Ga contamination from the FIB milling process, but further investigation is required and is currently underway.

Figure S1. FDTD simulation of coaxial antennae in 120nm Au film. Each of the three simulated pin diameters shows the Au Plasmon peak at ~500nm and a secondary peak due to the antenna resonance.

Fabrication of coaxial antennae on SPM tip

To obtain 120nm thick Au on the apex as well as a large enough tip area on which to mill a working coaxial structure, a 50-60nm diameter mesa was milled in the end of the tip before the Au was evaporated. The coaxial structures were subsequently milled into the tip apex with milling parameters comparable to those optimized for the flat substrates.

Topography-independent optical intensity variations

Deconvoluting topography and optical information is very important to assess the optical resolution of a near field optical image. To show clearly the independence of spatial intensity variations of the D- and G-mode from topographic effects, we show in Fig. S3b the near-field D-mode intensity map and a linescan over the intensity variations along the CNT bundle. In Fig. 3Sa the corresponding topography image with the equivalent line scan is illustrated. The topographic line-scan shows height variations on the order of $\sim 1\text{nm}$ over the CNT structure, however, these variations do not reflect the variations observed from the optical signal. Based on the optical intensity variations independent of the topographic variations we assume that optical and topography resolution were deconvoluted and we achieve an optical resolution below 23nm . In addition, the inset in figure S3b shows a line scan over a

Figure S2 corresponding topography a) and image of the CNT structure's Raman D-mode b). The line-scan over the equivalent area in both images show 2nm height variations in the topo line-scan, which do not correspond to the intensity variations observed in the line-scan in the D-mode map.

catalyst, which shows a strong D-mode signal due to probably a CNT that began to grow from it. The optical linescan reproduces again a resolution on the order of 22nm . In this case optical and topographic information are convoluted, however the resolution is comparable to the optical linescan along the CNT bundle.