Supporting Information

Intracellular Delivery of Top-down Fabricated Tunable Nano-plasmonic Resonators

Sadao Ota, Sheng Wang, Jongeun Ryu, Yuan Wang, Yong Chen, and Xiang Zhang

Methods

The TNPRs were fabricated using nanoimprinting lithography since it allows one to efficiently fabricate massive number (16 × 10^8/sample) of uniform nanostructures. Briefly, a hard mold of silicon or quartz designed for the imprinting was first fabricated by e-beam lithography, followed by etching process. On the other hand, 100 nm PMMA (polymethyl-methacrylate) and 100 nm ultraviolet (UV) cross-linking polymers were sequentially spin-coated on a 26 mm × 24 mm silicon wafer. The pre-made nanostructured hard mold then transfers its pattern to the polymers while applying the UV irradiation for cross-linking the UV polymer (at 17 mW/cm for 120 seconds, Fig 1a). The residual UV polymer and the PMMA layer were selectively removed by reactive ion etching (RIE) steps with CF4 and O2 plasma (Fig 1b-c). 4 mTorr CF4 20 sccm flow rate and O2 2 sccm flow rate gave 0.9 nm/sec etch rate for the UV polymer, and 4 mTorr O2 20 sccm flow rate gave 1.8 nm/sec etch rate for the PMMA. Onto this imprinted mold, we sequentially deposited 20 nm Au, 5 nm SiO2, and another 20 nm Au using an e-beam evaporator (CHA, CA, USA) (Fig 1d). After lift-off in acetone, we finally obtained the uniform TNPR array with TNPR diameter of 150 nm and periodicity of 500 nm on the silicon surface (Fig 1e as well as Fig 2a for a SEM image of the fabricated TNPR array pattern).

Before TNPR releasing procedure, weak oxygen plasma was first applied to remove the residual polymers and clean the sample surface. In the dry-etch process using the xenon-difluoride gas, the sample was placed inside PDMS chambers that prevented XeF2 gas-flow from directly blowing the sample. Thus, the gas approached the sample via slow convection or diffusion such that we could keep the TNPRs on the substrate at high-yield. In the sonication process for transferring the weakly attached TNPRs on substrate into a solution, the sample was placed on top of a floating boat in the sonicator and a drop of solution (~50 μL) was then placed on the sample. After sonicating them for 5 minutes, the solution containing released particles was transferred to a glass bottle and another droplet was placed on the sample to repeat the procedure.