Plasmonic Nanostructures using Cell-less Liquid-Phase Electron Beam Induced Deposition

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Certain metallic nanostructures, typically silver and gold, support localized surface-plasmon resonances (LSPR) that confine electromagnetic fields at the nanoscale. Electron-beam induced deposition (EBID) is appealing for rapid-prototyping of such structures and for deterministically placing them in more complex devices.[1, 2] However, the low purity of gold from organic precursors, the limited availability and handling difficulties of inorganic gold precursors, and the complete absence of silver precursors have limited gas-phase EBID for plasmonics applications. To address this, we previously studied EBID of silver nanostructures from bulk liquids.[3] The structures supported LSPR; however, they were deposited on the membrane of a liquid cell, an impractical geometry for most applications. Subsequently, we deposited silver on bulk substrates from aqueous solutions in an environmental SEM,[4] and Fisher et al. achieved a similar result using electrospray injection of ethylene glycol solutions.[5] Both approaches greatly improve the practicality of liquid-phase EBID.

Here we show that silver nanostructures deposited from liquid precursors on bulk substrates support LSPR. Specifically, an aqueous silver nitrate solution was used to deposit silver on oxidized silicon substrates. The solution also contained a surfactant, sodium dodecyl sulfate (SDS), to improve wetting and reduce the liquid layer thickness. Deposition was conducted with a 20kV accelerating voltage in a FEI Quanta 250 FEG ESEM. Energy-dispersive x-ray spectroscopy was used to estimate the liquid thickness and to quantify the purity of deposits. Figure 1 shows an array of silver dots deposited with a dose of 800 pC/dot. Figure 2 plots the optical dark-field scattering spectra from one dot. Enhanced scattering occurs at wavelengths consistent with the excitation of localized surface-plasmon resonances in silver. The observation of multiple resonances is not surprising given the size of the particle, the presence of the dielectric substrate, and the use of un-polarized illumination and detection. These results suggest that, after additional refinement of the patterning process, liquid-phase EBID may prove practical for fabricating plasmonic devices.

This material is based upon work supported by the National Science Foundation under Grant Numbers CMMI-1125998, CMMI-1538650, and ECCS-1542164.

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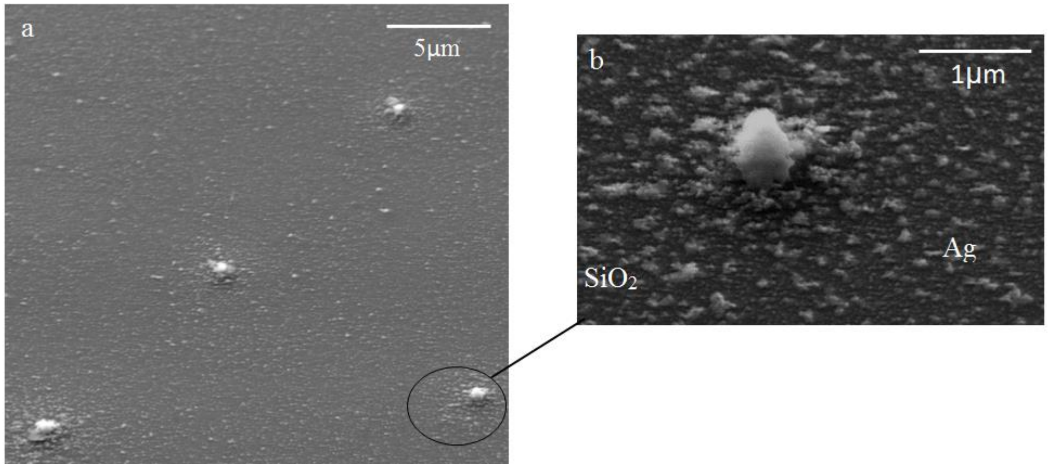

Figure 1: (a) Tilt-view of silver dots deposited from $AgNO_3$ (aq) with SDS as a surfactant. (b) Magnified view of the lower right dot in (a) deposited with a dose of 800 pC. The substrate is silicon with a 1.7-µm thick thermally grown SiO_2 layer.

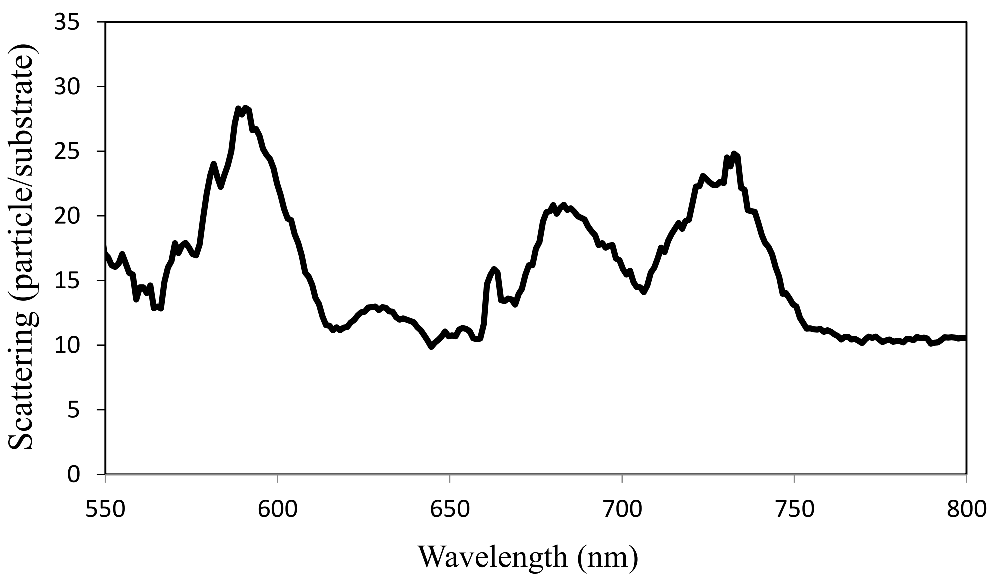

Figure 2: Optical, dark-field scattering spectrum showing a strong resonance near 580 nm and weaker resonances at longer wavelengths. These features are consistent with localized surface-plasmon excitation of silver nanostructures on a dielectric substrate.