Fabrication of ultrafine plasmonic Au nanostructures on dielectric supports using 10 keV EBL

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Plasmonic nanostructures, which commonly consist of noble metal structures interfacing a dielectric, possess unique properties. In particular, exposure of such nanostructures to light produces oscillations of electron density, known as surface plasmons. Under proper conditions, this leads to a conversion of the energy of light into different useful forms[1]. This opens paths for numerous applications, from ultrasensitive surface-enhanced Raman scattering (SERS) characterization of materials to heterogeneous photocatalysis and green energy harvesting. However, plasmonic nanostructures should meet a number of requirements for their potential could be realized. In addition to nanoscale dimensions, a high uniformity and compatibility with existing microelectronics settings are required.

Electron beam lithography (EBL) offers an unmatched control over nanoscale geometries, and also a flexibility to allow for various designs. However, careful co-optimization of EBL exposure and development is required to fabricate periodic patterns with deep nanoscale dimensions[2]. Usage of dielectric substrates is particularly challenging due to the accumulation of charge during EBL exposures. In this work, we have optimized a 10 keV EBL process using a Raith 150$^{\mathrm{TWO}}$ instrument to fabricate periodic arrays of 50 nm pitch dots on fused silica (FS) supports. To avoid distortions due to charging, a conductive layer (Electra 92, Allresist GmbH) was applied on the surface of EBL resist, PMMA (Fig.1a). For comparison, we have fabricated 50 nm pitch arrays of dots on Si substrates that do not require a conductive coating (Fig.1b). Fig.2a,b shows the dots (pits) in PMMA after development (IPA:water, 7:3) of the respective samples. In addition, we used the EBL simulator[3,4] to calculate the probability of PMMA main-chain scission in these two cases (Fig.2c,d). Despite significant broadening of the 10 keV electron beam that reaches PMMA after traveling through the conductive layer (Fig. 2c), quality arrays of dots were obtained (Fig.2a). However, the required EBL exposure doses are 2.5-2.7 times higher than the minimal dose needed to fabricate 50 nm pitch dots on a Si substrate without the conductive layer (Fig.2b).

Next, we used the patterned PMMA to fabricate 50 nm pitch arrays of Au dots on FS (Fig.3). In order to verify the performance of these Au/FS structures, we used them for SERS bio-detection (Fig.4). For this purpose, the samples were bio-functionalized with thiolated DNA aptamers that bind specifically to an important biomarker, protein interleukin 6 (IL-6). These samples were loaded with IL-6 from a solution. Distinct Raman bands in Fig. 4 suggest that the Au nano-dots produce a significant SERS enhancement. Further optimization of ultrahigh-resolution, low-kV EBL processes for the fabrication of plasmonic nanostructures on dielectric substrates will include adjustments of the design for resists and coatings, as well as co-optimization of both the exposure and development processes.

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[1] K-Te Lin, H Lin, B Jia; Nanoplasmonics 9 (10), 3135–3163 (2020).
[2] MA Mohammad et al., Nanofabrication Techniques and Principles (2012, Springer, Wien) p.11.
[3] EBL simulator, www.nanofab.ualberta.ca/2016/news/electron-beam-lithography-simulator/
[4] R Peters, et al. Vac Sci Technol B, 31(2013)06F407 (2013)

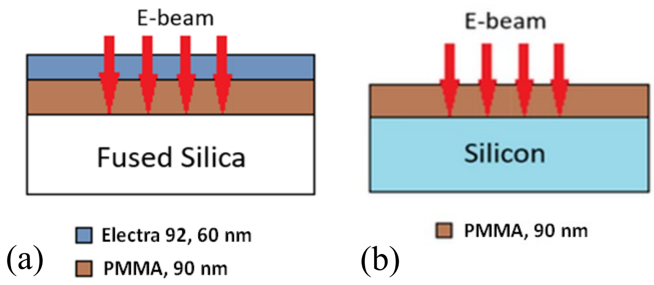

Figure 1:
(a) - Scheme of samples for EBL fabrication of periodic, 50 nm pitch arrays of dots on fused silica (FS) substrates.
(b) - Scheme of samples for EBL fabrication of similar arrays on silicon substrates for comparison.

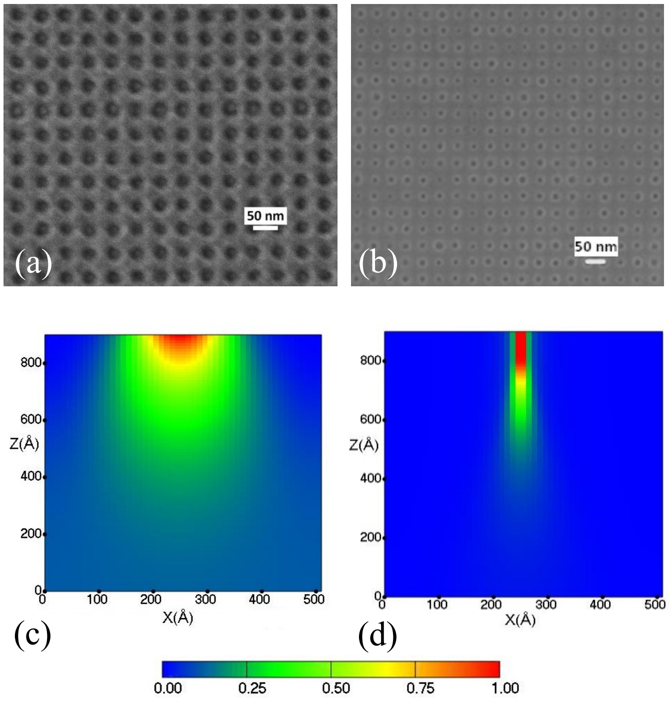

Figure 2:
(a) - HIM image (Zeiss Orion NanoFAB) of an array of 50 nm pitch dots (pits) in PMMA on FS after a 10 keV, 2.7 fC/dot exposure and development.
(b) – SEM image (Zeiss Sigma FESEM) of a similar array in PMMA on Si after a 10 keV, 1.0 fC/dot EBL exposure and development. (c,d) - simulated[3] probability of PMMA's main-chain scission per monomer at the conditions corresponding to (a) and (b), respectively. The images present cross-sections of the 3D scission patterns in the periodic, 50 nm pitch arrays of dots, where X is width and Z is depth in the PMMA layer.

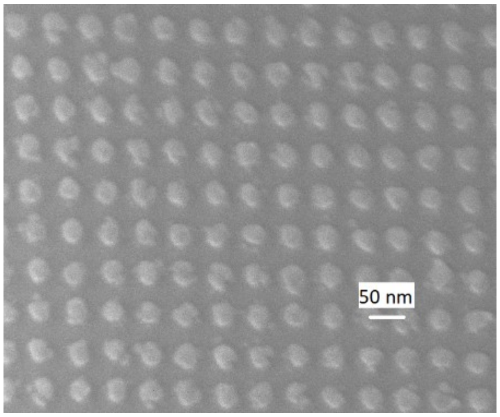

Figure 3:
HIM image (Zeiss Orion NanoFAB) of a 50 nm pitch array of Au dots on FS after metallization (10 nm) and liftoff.

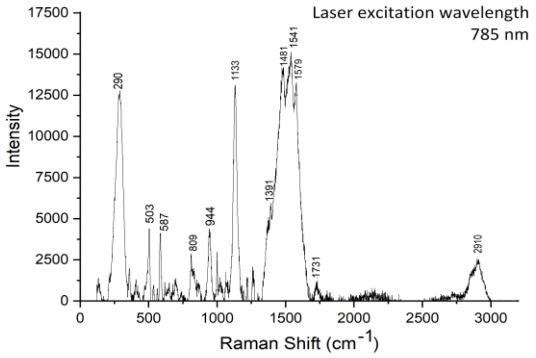

Figure 4:
SERS spectrum of the IL-6/DNA complex immobilized on Au dots on a FS support (Renishaw inVia Qontor Confocal Raman Microscope, 785 nm laser excitation).