HRTEM and EELS of nanoantenna structures fabricated using focused ion beam techniques

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Abstract. This paper describes the use of focused ion beam (FIB) techniques to fabricate Au nanoantenna structures for plasmonics applications. High-resolution transmission electron microscopy (HRTEM), diffraction and electron energy-loss spectroscopy (EELS) techniques are applied to investigate the structures of the initially patterned film, fabricated nanoantenna structures, and to map localized surface plasmon resonance (LSPR) modes in the nanostructures.

1. Introduction

Metal nanostructures can act as light concentrators in the visible and near-infrared regime due to the excitation of localised surface plasmons (LSPs), which are resonant waves of the free electrons in the metal coupled to the electromagnetic field [1,2]. Such nanostructures show considerable potential for applications ranging from optical sensing to enhancing the absorption in thin-film solar cells [3-7].

The nanoantenna structures described in this paper were produced using the “top-down” technique of FIB-lithography. They were characterised using a (scanning) transmission electron microscopy ((S)TEM) owing to the latter’s ability to resolve objects to the sub-nanometre level. Because LSPs can also be generated by high energy electrons, a STEM equipped with an EEL spectrometer and monochromator is also a powerful method to map out the underlying LSPR modes in these nanostructures with high energy (~ 0.2 eV) resolution.

2. Method

Au nanoantennas were fabricated using a dual beam FIB/scanning electron microscopy (SEM) system (Tescan Lyra). The process begins by the patterning of Au film of thickness 20 nm on a silicon-supported Si3N4 membrane of dimensions 0.5mm × 0.5mm and thickness 50 nm. A 100μm × 100μm region was then identified on the membrane, within which arrays of nanoantennas were created by milling away parts of the Au film using FIB. Analyses of the nanoantennas were carried out using an

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FEI-Titan (S)TEM operated at 300kV. TEM imaging and diffraction techniques were applied to
determine the nanostructure morphology and film quality after ion-milling. EELS spectrum imaging
(SI) [8] was performed in monochromated mode (with energy resolution 0.2eV) and focusing on the
low energy-loss regime to map out the LSPR modes of the nanostructures.

3. Results and Discussion

3.1. Nanoantenna structure fabrication

Figures 1(a) is a 30kV secondary electron (SE) image showing the 3mm-diameter Si frame and the
0.5mm × 0.5mm Si₃N₄ membrane after the deposition of Au film with thickness 20nm. The optical
image in the reflectance mode (Figure 1b) shows that the membrane was distorted after deposition,
possibly due to the stresses induced during the process. TEM bright field (BF) images of the Au film
(Figure 1c) reveal that it is non-continuous and consists of random lines of voids. Selected area
diffraction (SAD) analyses (Figure 1c inset) show that the film is polycrystalline in nature and of fcc
structure. After deposition, a 100µm × 100µm region was identified for nanoantenna structure
fabrication (Figure 1d). Arrays comprising three-by-three cells (Figure 1e) were created by milling
the Au-Si₃N₄ substrate with 30keV Ga⁺ ions. The cell sizes in the arrays are of different sizes
ranging from 500nm to 1µm. The nanoantenna structures are residual Au film in the middle of the
cells that had been retained after the ion milling process. They are supported by the silicon nitride
membrane which is still retained after the ion milling process. It is estimated that 10nm of Si₃N₄ film
was removed from the ion milling step.

![Figure 1](image)

**Figure 1.** (a) SE image at 30kV showing 3mm-diameter Si frame with a 0.5mm×0.5mm SiN window
on which Au had been patterned. (b) Optical reflectance image showing distortions in the membrane
after Au patterning. (c) TEM BF image of a region of patterned Au. The SAD pattern (inset) shows
that the film is polycrystalline. (d) SE image at 30kV, showing a 100µm×100µm region of the Si₃N₄
membrane in which fiducial markers had been made by ion milling. The sample has been tilted by
55°. (e) SE image at 30kV showing arrays, each comprising nine cells, which had been ion milled.

3.2. TEM Analyses of Nanoantenna structures
TEM analyses were performed to determine the structure and morphology of the nanoantennas. Figure 2(a) shows a low-magnification, BF image of an array consisting of nine cells. Figure 2b(i) to (ix) are higher-magnification TEM BF images of the nanoantenna structures found in the cells. At the present, the discontinuity of the patterned Au film (as seen in Figure 1(c)) may have an influence on final nanostructure morphology, and improvements in the film patterning process are being developed. Diffraction contrast in these images suggests that polycrystallinity of the Au film was largely preserved after ion milling.

3.3. EELS analyses of structures

Monochromated STEM-EELS SI was applied to map up the underlying LSPR modes in the nanoantennas. Figure 3(a) shows a high angle annular dark field (HAADF)-STEM image of a structure on which EELS SI was performed. The SI comprises 18 pixels by 27 pixels, with pixel size of 1.4nm × 1.4nm. The acquisition time per pixel was 300ms. The ZLP was removed by applying the Reflected Tail Model using Digital Micrograph. Figure 3(d) shows the extracted EELS spectra (after zero loss peak removal) from (1) Si₃N₄ membrane, (2) edge and (3) core of the nanostructure. The extracted spectra show different LSPR modes at each of these areas. However, signal-to-noise ratios were found to be low, possibly due to specimen damage during its initial fabrication process. Below 1.2eV, the falling tail of the ZLP still remained in the extracted EEL spectra, as this routine is not sufficient to completely remove the ZLPS. Investigations to accurately fit and remove the ZLPS are currently underway.
4. Conclusion
In summary, we have shown that FIB techniques can be used to fabricate nanoantennas for plasmonics applications. TEM analyses show that the patterned Au film is not continuous and can be amorphised during ion milling. We have since taken steps to improve the quality of the deposited film (via the introduction of a seed layer), and will report our findings in a separate publication. While different LSPR modes can be distinguished from various parts of a nanostructure using EELS SI, their signal-to-noise ratios and tunability can be improved upon refinements in the fabrication process.

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