Fabrication of nanostar array by nanoimprint lithography

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Surface enhanced Raman scattering (SERS) has found applications in detecting hazardous chemicals, explosives, chemical warfare agents, as well as biomolecules [1-2]. Ideal SERS substrates should offer a tunable resonance wavelength with high sensitivity and reproducibility. While spherical nanoparticles are easily fabricated by chemical methods, it lacks tunability and reproducibility. Nanolithography is essential to overcome these limits. Previously, nanosphere lithography (NSL) has been employed to fabricate ordered Ag nanoprism arrays into the gaps between adjacent spheres [3]. However, any deviation from perfect arrangement in NSL leads to uncontrolled voids and larger metal structures. This lack of control becomes even more evident for sub-500 nm spheres. In this paper we will report the fabrication of nanostar array by nanoimprint lithography (NIL) that has higher resolution and better control than NSL.

Nanostar array is ideal for SERS application. First, by varying the height/size of the nanostar, the resonance wavelength can be readily tuned from visible to near-IR that covers the biological window (~700-1400nm) and is important for *in vivo* applications. Second, the sharp tips of the star result in extreme subwavelength focusing and thus greatly enhance the local electromagnetic field [4]. Finally, the small gaps between two adjacent stars further increase the local field by creating "hot spots".

Similar to NSL, the nanostars are defined by the gaps between (four) adjacent nanodisks. In the fabrication (Fig. 1), a hole array with 200 nm period and ~100nm hole diameter was first created into PMMA by NIL using a pillar array mold. The pattern was then transferred into the SiO_2 and ARC by RIE. Next, the holes in ARC was widened by prolonged oxygen RIE until its diameter was equal to that of the array period. After removing the SiO_2 cap by diluted HF, the holes were etched through the very thin Si by SF_6 RIE then into the underneath PMGI by O_2 RIE. A Cr nanodisk array was resulted after standard evaporation/liftoff by PMGI in MIF-319 developer. Following etching into the silicon substrate with large undercut by SF_6 RIE, an array of nanostar was finally achieved by Ti/Au evaporation and its liftoff by Cr using Cr-4S that etches Cr but not Ti and Au.

Fig. 2 shows a typical nanostar array after liftoff of Ti/Au. As shown in Fig. 3, the current technique is capable of producing nanostars with sub-10 nm apex and gaps, which is well beyond those attained by NSL.

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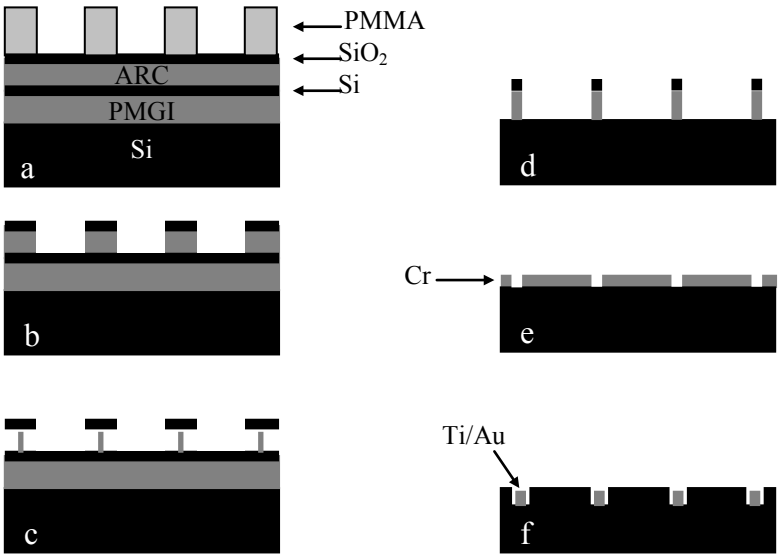

Fig. 1. Schematic representation of the process for metal nanostar fabrication. a) NIL into PMMA using a pillar array mold; b) RIE pattern transfer into SiO_2 and then into ARC (anti-reflection coating); c) Over etch to enlarge the holes in ARC to ~200 nm, the array period; d) Remove SiO_2 and RIE pattern transfer into Si/PMGI; e) evaporate Cr and liftoff; f) RIE into Si and liftoff Ti/Au by dissolving Cr using Cr etchant that doesn't attack Ti/Au.

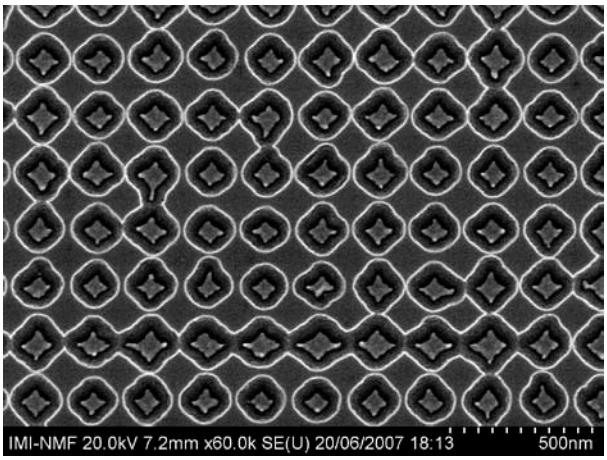

Fig. 2. SEM image of 200 nm period nanostar array of 5nm Ti/15nm Au on silicon.

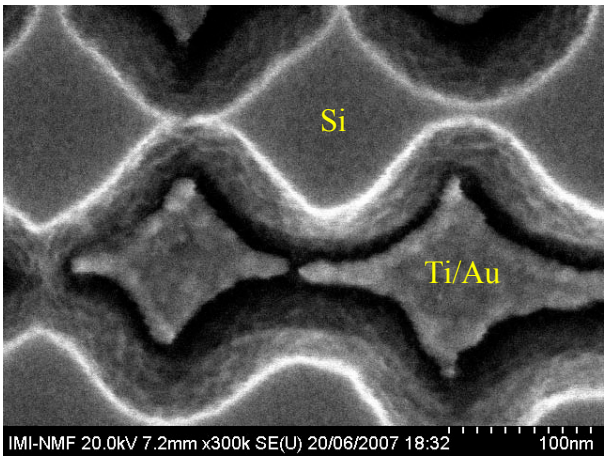

Fig. 3. SEM image of nanostars with sub-10 nm apex and gap between adjacent stars.