

# Silicon nanowire and hole arrays by a combination of self-assembly, laser ablation, and wet chemical etching

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We present two unconventional particle-based routes for the fabrication of periodic micro- and nanostructures with tunable feature sizes on a silicon wafer.

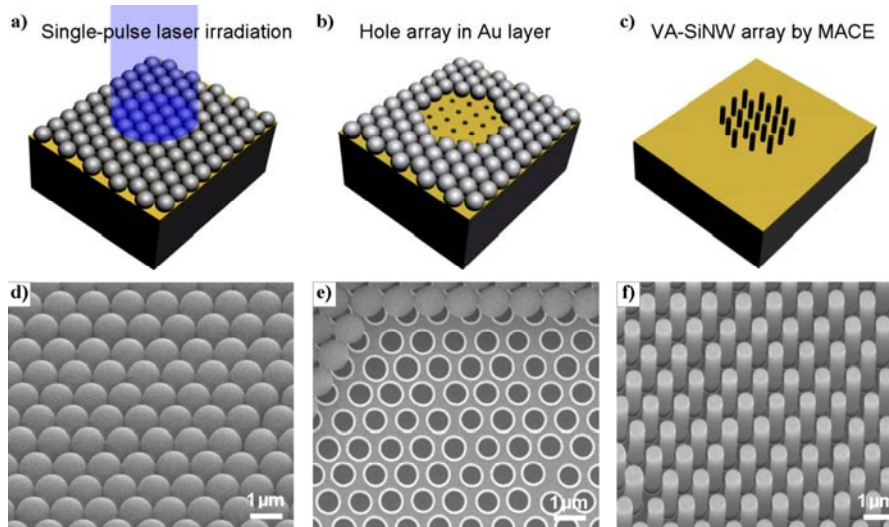
In a first approach, a monolayer of transparent microspheres ( $500 \text{ nm} < D < 1 \text{ }\mu\text{m}$ ) was convectively assembled onto a gold-coated silicon surface to serve as a microlens array (Figure 1a).<sup>1</sup> By irradiation with single-pulse nanosecond laser (Nd:YAG,  $\lambda=355 \text{ nm}$ ), the gold beneath each focusing microsphere was ablated in the near field, leaving behind a hexagonal pattern of holes (Figure 1b). The holes in the metal layer were homogenous, with diameters readily tuned within large limits ( $250 \text{ nm} < D < 600 \text{ nm}$ ) by simply adjusting the laser fluence. We achieved holes with diameter five times below the laser wavelength owing to the near-field effects. The patterned gold layer was then used as catalyst in a metal-assisted chemical etching (MACE) to produce an array of vertically-aligned silicon nanowires with smooth walls and controlled lengths (Figure 1c). This strategy combines the advantages of laser parallel nanopatterning using microlens arrays with the benefits of laser direct-writing, and together with MACE can yield nanowire arrays with controlled geometry at arbitrary locations on a same silicon wafer.

With a different strategy, arrays of gold discs prepared via self-assembly and sputter etching were used as catalysts in a MACE process to achieve well-defined pores with sub-micron diameters in silicon (Figure 2). The pores were exceptionally straight with smooth walls and aspect ratio up to 5, while the gold discs were still present at their flat base. The array spacing, pore diameter and depth could be tuned over a wide range via particle size, sputter etching and MACE processing times, respectively. We show that our pore arrays can be applied as platforms for surface-assisted laser desorption/ionization (SALDI) mass spectrometry (MS). When used for replica molding, the porous silicon templates yielded fibre arrays of polydimethylsiloxane (PDMS) and polycarbonate (PC) with exceptional density, suitable for surfaces with controlled adhesion.<sup>2</sup>

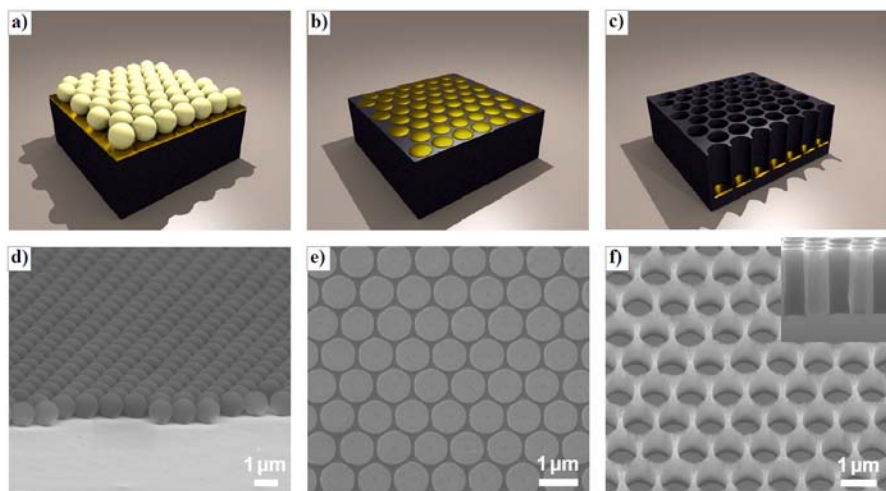
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<sup>1</sup>D. Brodoceanu, H. Alhmod, R. Elnathan, B. Delalat, N. H. Voelcker and T. Kraus, *Nanotechnology* 27, 075301 (2016)

<sup>2</sup>D. Brodoceanu, R. Elnathan, B. Prieto-Simón, B. Delalat, T. Guinan, E. Kroner, N. H. Voelcker and T. Kraus, *ACS Appl. Mater. Interfaces* 7, 1160 (2015)



*Figure 1: Process flow for the fabrication of VA-SiNW arrays. (a)–(c) Schematic illustration of the main steps. (d) Scanning electron microscopy (SEM) image of a PS microlens array convectively assembled on a silicon wafer coated with 30 nm gold layer. (e) Top-view SEM image of a hole array generated in gold layer by irradiating the microlenses with a single laser pulse ( $\lambda=355$  nm,  $\tau=10$  ns,  $f\approx 30$  mJ cm $^{-2}$ ). (f) Tilted SEM image of the array of VA-SiNW after 13 min MACE.*



*Figure 2: Pore array fabrication process. (a) Schematic illustration of hexagonally close-packed polystyrene monolayer convectively assembled on a gold-coated silicon wafer. (b) Schematic illustration of metal disc array after sputter etching process and subsequent removal of the remaining PS particles. (c) Schematic view of dense array of pores etched into silicon via MACE using gold disc array as catalysts. (d–f) SEM micrographs of the corresponding steps. (inset, f) The typical cross-section profile of the pores.*