

High aspect ratio and high resolution nanofabrication using self-assembly of salt-polymer nanocomposite film

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Due to its low cost compared to top down method, bottom up method is preferred for applications that does not require long range ordering and precise placement of the nanostructures, such as antireflective (AR) structure for photovoltaic and display applications and super-hydrophobic surface for lab-on-chip applications.^{1,2} The most popular self-assembly is the so-called nano-sphere lithography, yet it is very challenging to achieve a mono-layer and uniform sphere array when its size is less than ~200 nm. Metal film and CsCl can also be self-assembled into nanostructures due to thermal annealing or humidity, yet vacuum deposition for film coating is a costly process.^{3,4} Alternatively, nanostructure “grass” can be obtained by maskless reactive ion etching, yet the process only works for a few materials including silicon.⁵

Previously, we have reported a simple process to obtain nanostructures using a low-cost spin-coating method and RIE pattern transfer.⁶ As shown in Figure 1, we first dissolved metal salt and polymer in a solvent; and after spin-coating to form a thin film and thermal annealing to attain a phase separation, the nanocomposite film was etched with oxygen plasma to remove the polymer matrix, leaving behind nanoscale salt islands on the substrate that can be used as a hard-mask to dry-etch the substrate or sub-layer.

Here, we extended the metal salt to aluminum (III) nitrate nonahydrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (ANN), and chromium (III) nitrate nonahydrate $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (CNN), as Al and Cr are more microfabrication compatible. We dissolved the metal salt and PMMA in a polar solvent dimethylformamide (DMF) with different salt-polymer weight ratios. Figure 2 showed the final structures etched into the silicon substrate, with resolution down to 60 nm and aspect ratio up to 15:1. Smaller pillars down to 40 nm diameter are possible by using lower metal salt concentrations.

¹ E. Stratakis, A. Ranella and C. Fotakis, *Biomicrofluidics* **5**, 013411 (2011).

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⁴ J-Y Chen, C. Con, M-H Yu, B. Cui and K-W Sun, *ACS Appl. Mater. Interfaces*, **5**, 7552–7558 (2013)

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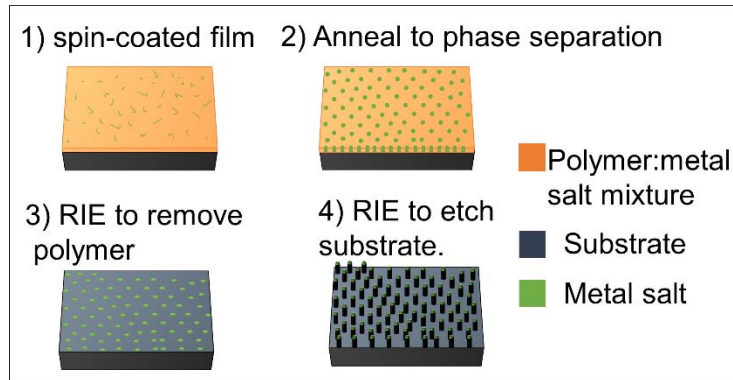


Figure 1. Schematic view of the low cost fabrication process to pattern the substrate.

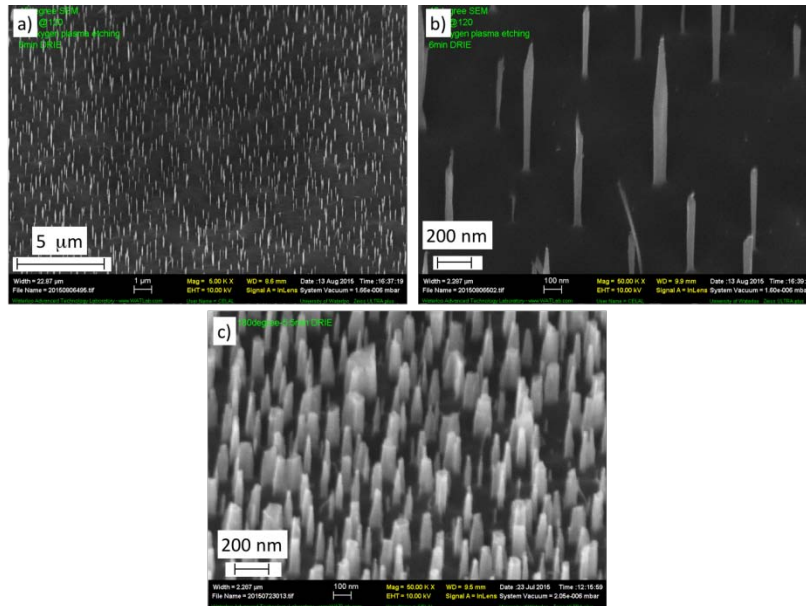


Figure 2. SEM images of silicon pillar array fabricated using self assembly of metal salt-PMMA nanocomposite film. (a-b) Using aluminum nitrate salt, imaged with low and high magnification, showing pillar diameter down to 60 nm and aspect ratio up to 15:1; (c) Using chromium nitrate salt, with 1:10 weight ratio (1 g salt and 10 g PMMA dissolved in DMF).