Ultra-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 do 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 like silicon and is not very reproducible.[5]

Here, we report a simple process to obtain nanostructures using the low-cost spin-coating method and RIE pattern transfer. We 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 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.

The key challenge for our process is to identify a solvent or solvent mixture that can dissolve both the salt (commonly soluble in water) and polymer (commonly soluble only in organic solvent). After extensive testing, we found that nickel (II) nitrate hexahydrate and PMMA can be dissolved in DMF (dimethylformamide) and form a uniform film by spin-coating when salt-polymer weight ratio is 1:10. $Ni(NO_3)_2$ is a suitable salt since nickel is a very hard mask for RIE using both F- and Cl- plasmas, and it has a low melting temperature of 56.7 ^oC. Figure 2 showed the structure etched into the silicon nitride substrate, which demonstrated that the current method is capable of achieving a very high resolution of down to 20 nm at low cost as it is a wafer-scale high throughput method.

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[1] E. Stratakis, A. Ranella and C. Fotakis, Biomicrofluidics, 5, 013411 (2011).
[2] T. Taguchi, H. Hayashi, A. Fujii, K. Tsuda, N. Yamada, K. Minoura, A. Isurugi, I. Ihara and Y. Itoh, SID Int. Symp. Dig. Tech. Pap. 41, 1196 (2010).
[3] W. Liu, M. Ferguson, M. Yavuz and B. Cui, J. Vac. Sci. Technol. B, 30, 06F201 (2012).
[4] J-Y Chen, C. Con, M-H Yu, B. Cui and K-W Sun, ACS Appl. Mater. Interfaces, 5, 7552 (2013).
[5] M. Gharghi and S. Sivoththaman, J. Vac. Sci. Technol. A, 24, 723 (2006).

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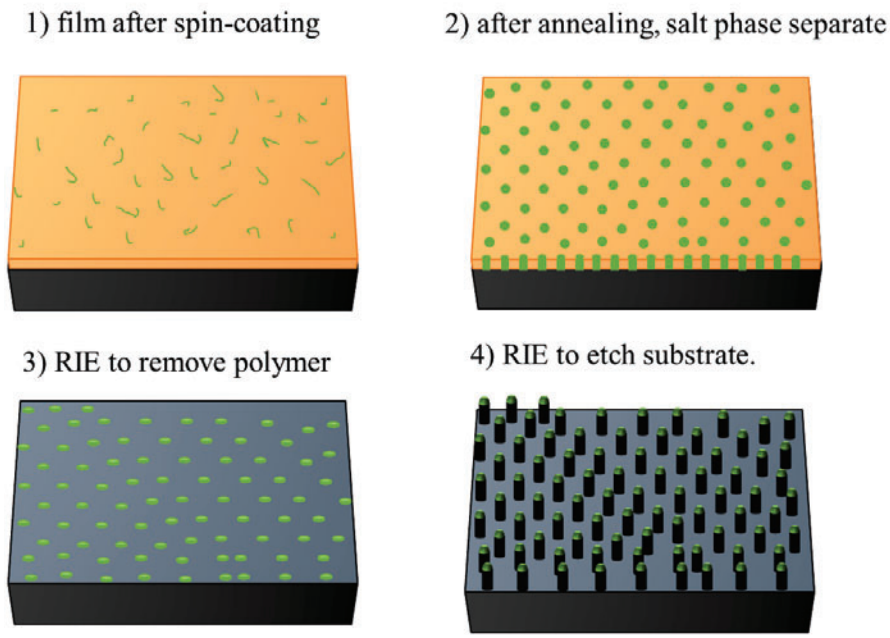

Figure 1. Schematic view of self-assembly of salt-polymer nanocomposite film, and pattern transfer process.

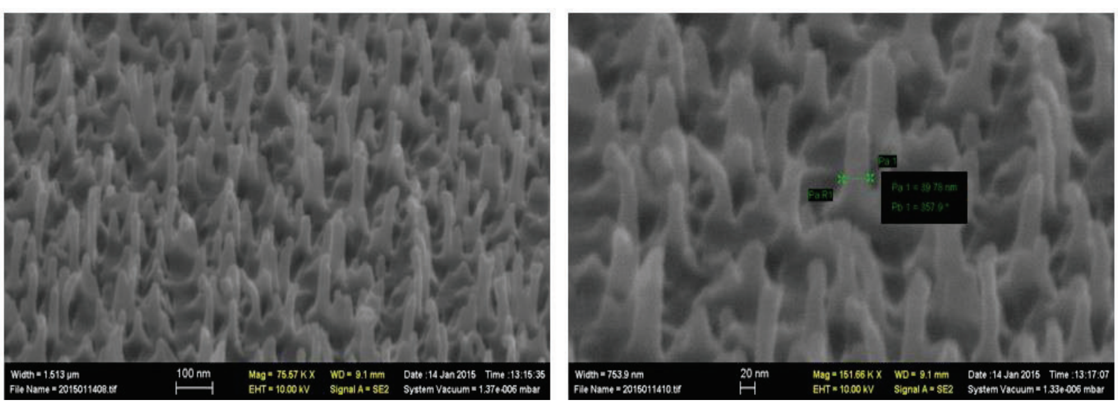

Figure 2. SEM images of 100 nm height and sub-50 nm diameter silicon nitride pillars fabricated by RIE using CF4 gas with self-assemblyed nickel nitrate islands as hard mask.