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# Nanofabrication of high aspect ratio structures using an evaporated resist containing metal

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## Abstract

Organic electron beam resists are typically not resistant to the plasma etching employed to transfer the pattern into the underlying layer. Here, the authors present the incorporation of a metal hard mask material into negative resist polystyrene by co-evaporation of the polystyrene and the metal onto a substrate. With a volume ratio of 1:15 between Cr and polystyrene, this nanocomposite resist showed an etching selectivity to silicon one order higher than pure polystyrene resist. Silicon structures of 100 nm width and 3.5  $\mu\text{m}$  height (aspect ratio 1:35) were obtained using a non-switching deep silicon etching recipe with  $\text{SF}_6$  and  $\text{C}_4\text{F}_8$  gas. Moreover, unlike the common spin coating method, evaporated nanocomposite resist can be coated onto irregular and non-flat surfaces such as optical fibers and AFM cantilevers. As a proof of concept, we fabricated high aspect ratio structures on top of an AFM cantilever. Nanofabrication on non-flat surfaces may find applications in the fields of (AFM) tip enhanced Raman spectroscopy for chemical analysis and lab-on-fiber technology.

Keywords: electron beam lithography, electron beam resist, polystyrene, evaporated resist, high aspect ratio, plasma etching

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Among all nanolithography techniques, electron beam lithography (EBL), which can generate arbitrary patterns without the need of mask or mold, is the most popular method for R and D as well as for device prototyping and the production of photomasks and nanoimprint molds. In a typical nanofabrication process using EBL, upon resist exposure and development, pattern transfer is commonly carried out either by direct etch using the resist as mask or by liftoff. The most popular resist, polymethyl methacrylate (PMMA), has a poor plasma etching resistance, and is thus suitable for liftoff but not for direct etch. The next most popular resist ZEP-520A is more resistant to plasma etching than PMMA due to its stable phenyl group, but it is still far from being ideal for pattern transfer by direct etching to fabricate high aspect ratio structures. The same is true for other organic resists including polystyrene

(PS), calixarene, ma-N 2403 and SU-8 [1–4]. The popular inorganic resist hydrogen silsesquioxane (HSQ) is resistant to oxygen plasma but not to the fluorine-based plasma used for etching silicon and its compounds [5]. Other inorganic resists such as metal halide (notably  $\text{AlF}_3$ ) are resistant to plasma etching [6–10], but applications are very limited due to the extremely low sensitivity and the inability to define structures other than lines and dots.

To pattern deep structures using the direct etching method, obviously one can use a very thick resist layer. Yet the resist structure may collapse due to capillary force during rinsing and drying upon development, and the critical dimension (CD) loss may be significant due to lateral etch of the resist structure. Alternatively, an intermediate hard mask layer, such as Cr or Al, which can be etched by chlorine-based plasma using the resist as mask, is sometimes employed to etch the sub-layer using fluorine-based plasma. However, this adds extra process

steps with increased complexity and cost. As a consequence, it is desirable to use a resist that contains metal and thus has a high dry etching resistance.

Four metal-containing resist systems have been previously demonstrated. Apparently one can use a resist that contains metal in its chemical structure, such as polyferrocenylsilane (PFS) and its derivatives containing Fe and Si [11, 12]. However, besides its low sensitivity and resolution (for PFS, 25 mC cm<sup>-2</sup> and 700 nm, respectively), it is challenging and costly to synthesize such resist. One exception is the recently studied negative resist poly(sodium 4-styrenesulfonate) that is inexpensive and readily available [13], but its etching resistance is still not high enough, possibly because sodium is not an ideal hard mask. The second method is to introduce metal or metal oxide nanoparticles into the resist as a filler, with nanoparticle contents up to 80% leading to very high dry etching resistance, but the final resolution (and line edge roughness) is limited by the size of the filling nanoparticles [14]. The third method employs the sol-gel process to synthesize the so-called 'hybrid organic-inorganic' resist with high content of metal oxide [15]. The main issue is the huge volume shrinkage (e.g. from an initial thickness of 200 nm to a final film of 30–40 nm) after development and subsequent thermal annealing, which makes critical dimension control difficult and renders it unsuitable for patterning dense structures.

The fourth method to incorporate metal into e-beam resist is the sequential infiltration synthesis (SIS) of metal oxide (Al<sub>2</sub>O<sub>3</sub>) using an atomic layer deposition (ALD) system [16–19]. In SIS, a thin film of resist is infiltrated with Al<sub>2</sub>O<sub>3</sub> by alternating the exposures to trimethyl-aluminum (TMA) and water in an ALD chamber. Once precursors are diffused into the bulk of the resist layer and are in complete chemical reaction with the resist polymer, the resist becomes more resistant to plasma etching. However, in addition to process complexity, the SIS procedure increases line edge roughness and resist swelling, and reduces resist contrast and thus resolution to ~100 nm.

In this work we demonstrate that metal can be incorporated into polystyrene (PS) resist by co-evaporation, which is possible for polystyrene resist since it can be thermally evaporated just like most metals. PS is an organic negative e-beam resist that offers ultra-high resolution for the low molecular weight polymer [1] and ultra-high sensitivity for the high molecular weight one [2]. In addition, like PMMA, it is a simple polymer with very low cost and practically unlimited shelf life. We have previously shown that low molecular weight PS can be thermally evaporated, and is hence capable of coating onto any irregular non-flat surface [20]. Evaporated resist also avoids some issues of spin-coated resist, such as swelling or dissolution if the sub-layer is an organic material, or the edge-bead problem if the wafer is of small size [21]. Since exposed and thus cross-linked PS is difficult to dissolve, liftoff is challenging and direct etching is therefore the preferred pattern transfer process. Here we achieved a high dry etching selectivity of 1:35 to silicon by using co-evaporated polystyrene-chrome (PS:Cr) composite resist, which was used to pattern high aspect ratio structures on an AFM cantilever. Nanofabrication on irregular non-flat surfaces, such as AFM cantilevers and optical fibers, may find applications in the fields of (AFM) tip enhanced Raman spectroscopy for chemical analysis [22] and lab-on-fiber technology [23].

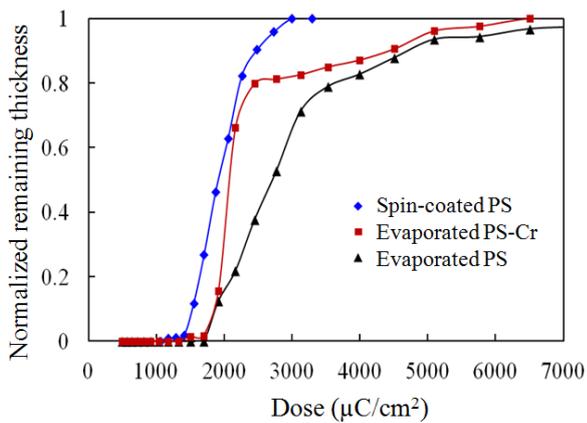
## 2. Experimental methods

We chose polystyrene (PS) with molecular weight of 1.2 kg mol<sup>-1</sup> (Scientific Polymer Products Inc.), as it was found that high molecular weight PS decomposed before vaporization and thus did not give a film. We used a thermal evaporator (Intlvac Inc.) to co-evaporate PS and Cr, with the deposition rate individually monitored for each source. The chamber background vacuum was 5 × 10<sup>-6</sup> Torr. The two sources were 10 cm apart, which was much smaller than the distance between the source and the wafer (about 40 cm). The temperature for each source was not monitored. The power was gradually increased until the desired deposition rate was reached for each source, after which the shutter was opened to start the deposition. The evaporation rate for PS was 1.8 Å s<sup>-1</sup>, and that for Cr depended on the target PS:Cr ratio. Other metals suitable for thermal evaporation, such as Al, can also be introduced to the PS film. PS powder was put inside a boat with holes in the cover. For Cr evaporation, we used a tungsten wire (R D Mathis Company) covered with a thick layer of electrodeposited Cr, which allowed a lower evaporation temperature than putting Cr pieces inside a crucible due to the intimate contact of the Cr with the heating tungsten wire. As Cr adheres well to the substrate and cannot be removed by the solvent developer, we first evaporated a very thin (20 nm) layer of PS before co-evaporation of the two materials with a total thickness of 200 nm, in order to ensure that the Cr was not in direct contact with the substrate.

After co-evaporation with different PS:Cr ratios, electron beam exposure was carried out using a Raith 150<sup>TWO</sup> system with 5 keV acceleration voltage and 0.2 nA beam current. Development was carried out by 1 min soaking with xylene in an ultrasonic bath, followed by 2-propanol (IPA) rinsing. Ultrasonic agitation helped to dissolve the unexposed composite resist, which is more difficult to dissolve than pure PS resist. For pattern transfer into the underlying silicon, we used an Oxford Instruments ICP380 dry etching system with a non-switching process (22 sccm SF<sub>6</sub> and 38 sccm C<sub>4</sub>F<sub>8</sub>, 10 mTorr, 1200 W ICP power and 20 W RF power, etching rate 370 nm min<sup>-1</sup>) [24, 25], though a Bosch process with a very short cycle time may also be employed to etch high aspect ratio silicon nanostructures [26, 27].

## 3. Results and discussion

Figure 1 shows the contrast curve measured by atomic force microscope (AFM) for the evaporated PS-Cr resist as well as for the pure (no Cr) evaporated polystyrene resist. The two curves followed each other well, implying that the incorporation of Cr did not affect significantly the resist properties due to its low concentration. The volume ratio of PS and Cr was controlled by the quartz crystal thickness monitor for each source, and is here 15:1, leading to a weight ratio of ~2:1 (Cr density 7.2 g cm<sup>-3</sup>, polystyrene 1.0 g cm<sup>-3</sup>), or roughly one Cr atom per PS monomer. However, Cr would not distribute uniformly in the PS matrix and a certain degree of phase-separation was expected. Immediately after the 'gel point' (the dose where the contrast curve starts to rise), the slope of

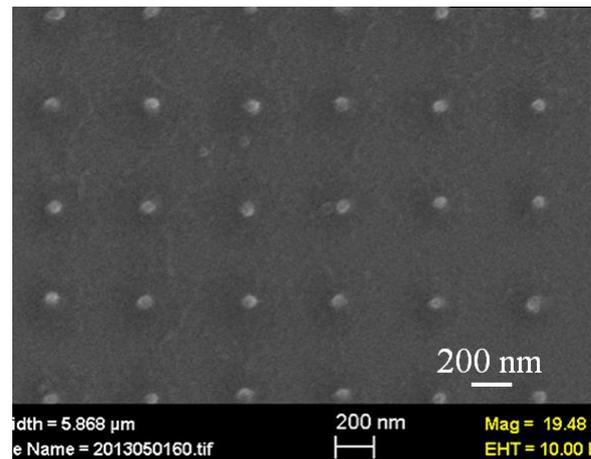


**Figure 1.** Contrast curves exposed at 5 keV and developed by xylene for spin-coated polystyrene with molecular weight of  $1.2 \text{ kg mol}^{-1}$ , co-evaporated polystyrene–Cr and evaporated (pure) polystyrene (source material with molecular weight  $1.2 \text{ kg mol}^{-1}$ ).

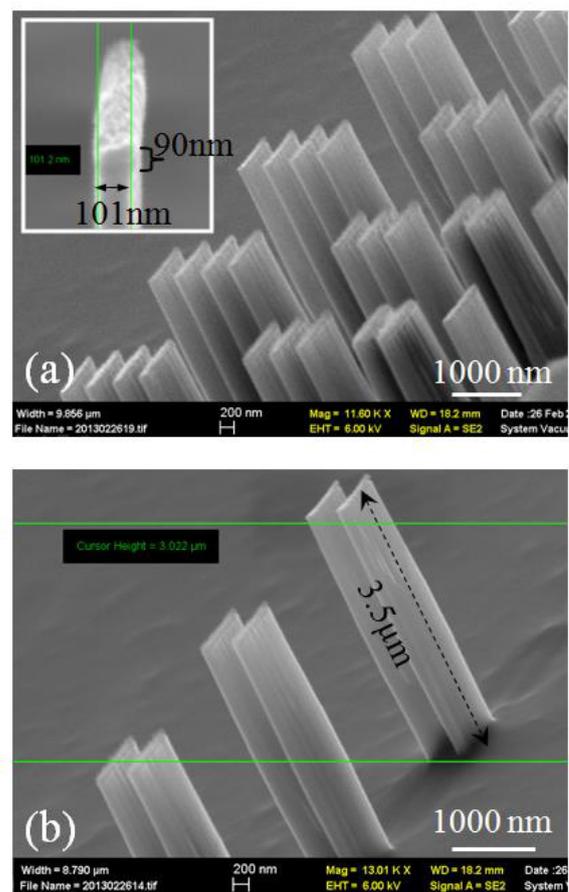
the contrast curve for the resist containing Cr is more abrupt than pure PS; this may be because the Cr-enhanced PS is more difficult to dissolve once cross-linking occurs. The contrast for the PS–Cr resist is 11.9, that is a very high value. However, the sensitivity is around  $2000 \mu\text{C cm}^{-2}$ , which is very low due to the low molecular weight; as for simple cross-linking resist its sensitivity ( $\mu\text{C cm}^{-2}$ ) is inversely proportional to molecular weight ( $\text{kg mol}^{-1}$ ) according to the Charlesby theory [28]. The sensitivity is lower than spin-coated resist of the same molecular weight, presumably because the evaporated resist actually has lower molecular weight than the source material due to thermal decomposition.

With a high contrast, the PS–Cr resist is capable of achieving high resolution. Figure 2 shows a pillar array with a diameter of 55 nm exposed in PS–Cr resist at 5 keV. Smaller pillar diameters (down to 30 nm, not shown) could be defined, but the pillars (200 nm height, aspect ratio 6.7:1 for 30 nm diameter) all collapsed due to capillary force during drying of the rinsing solvent. Here the ratio of nominal thickness between Cr and PS was 1:15. Obviously a higher Cr:PS ratio would offer higher dry etching resistance, yet resist development became more difficult. It was found that the exposed nanostructure could still be properly developed at a ratio of 1:10, but at a higher ratio of 1:5 the (unexposed) film could not be dissolved by the developer even with ultrasonic agitation for 10 min.

The metal-containing resist structure was used as the mask to transfer the pattern to the silicon substrate by ICP-RIE with  $\text{C}_4\text{F}_8$  and  $\text{SF}_6$  gases. As seen in figures 3(a) and (b), silicon structures of a high aspect ratio of 35:1 were obtained. Our measurement on blank film showed an etching rate selectivity between silicon and PS–Cr (15:1 volume ratio) resist of 1:33, compared to 1:2.6 for pure PS under the same etching conditions. Thus the incorporation of Cr into polystyrene improved its etching resistance by one order. One major advantage of evaporated resist, as compared to spin-coated resist, is its capability of coating on irregular non-flat surfaces. As a proof of concept, we coated PS–Cr resist onto an AFM cantilever, and followed the same lithography and pattern

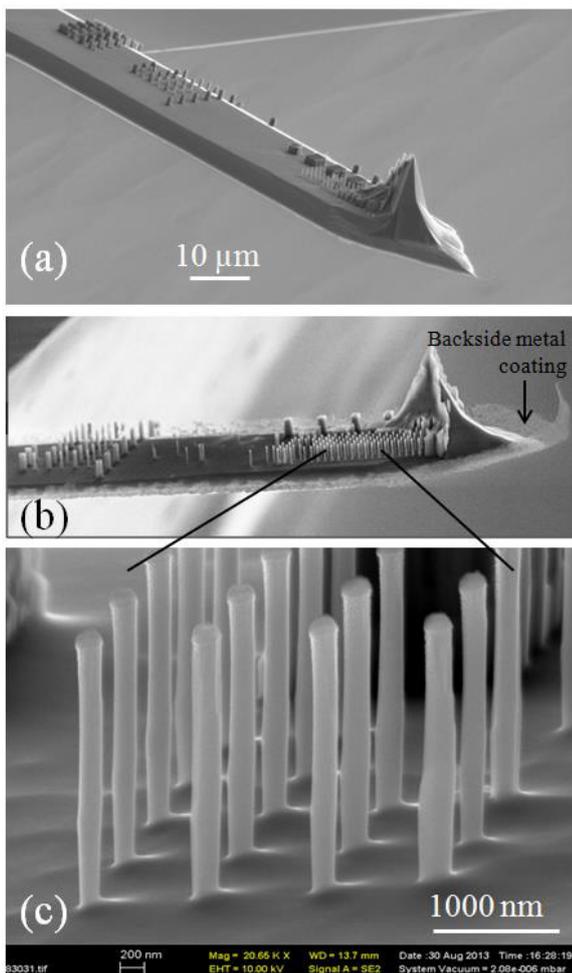


**Figure 2.** Pillar array exposed in PS–Cr resist by electron beam lithography at 5 keV and developed using xylene for 1 min. The pillar diameter is 55 nm and height is 200 nm.



**Figure 3.** SEM images of high aspect ratio silicon structures patterned by EBL using PS–Cr resist and ICP-RIE. The width of the short lines is about 100 nm and height is  $3.5 \mu\text{m}$ . The remaining PS–Cr mask is 90 nm thick as shown in the inset of (a).

transfer procedure. The high aspect ratio silicon structure patterned on the AFM cantilever is shown in figures 4(a)–(c). It would be straightforward to employ the same process on other



**Figure 4.** SEM images of high aspect ratio silicon structures patterned on AFM cantilever. (a), (b) Images taken at low-magnification for two AFM cantilevers; (c) zoom-in of the silicon pillar array in (b).

non-flat surfaces, such as the side or end of an optical fiber for photonics application [23, 29]. Compared to focused ion beam milling that is also capable of patterning on irregular surfaces, EBL using evaporated resist is faster (since the electron beam can be well focused even for an nA beam current, which is not the case for a Ga ion beam), and free from Ga contamination.

#### 4. Conclusions

To improve its dry etching resistance, here we showed that metal can be incorporated into PS resist by co-evaporation of the two materials onto a substrate. With a volume ratio of 1:15 between Cr and polystyrene, this nanocomposite resist showed an etching selectivity to silicon one order higher than pure polystyrene resist. Its contrast was also higher than pure PS resist by thermal evaporation. Silicon structures of 100 nm width and 3.5  $\mu\text{m}$  height (aspect ratio 1:35) were obtained using a non-switching deep silicon etching recipe with  $\text{SF}_6$  and  $\text{C}_4\text{F}_8$  gases. Moreover, as evaporated nanocomposite resist can be coated onto irregular and non-flat surfaces such as optical fibers and AFM cantilevers, we demonstrated the fabrication

of high aspect ratio structures on top of an AFM cantilever. Nanofabrication on non-flat surfaces may find applications in the fields of (AFM) tip enhanced Raman spectroscopy for chemical analysis and lab-on-fiber technology.

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#### References

- [1] Ma S, Con C, Yavuz M and Cui B 2011 Polystyrene negative resist for high-resolution electron beam lithography *Nanoscale Res. Lett.* **6** 446
- [2] Con C, Dey R, Ferguson M, Zhang J, Mansour R, Yavuz M and Cui B 2012 High molecular weight polystyrene as very sensitive electron beam resist *Microelectron. Eng.* **98** 254–7
- [3] Dey R K and Cui B 2013 Effect of molecular weight distribution on e-beam exposure properties of polystyrene *Nanotechnology* **24** 245302
- [4] Bilenberg B, Schøler M, Shi P, Schmidt M S, Bøggild P, Fink M, Schuster C, Reuther F, Gruetzner C and Kristensen A 2006 Comparison of high resolution negative electron beam resists *J. Vac. Sci. Technol. B* **24** 1776–9
- [5] Grigorescu A E and Hagen C W 2009 Resists for sub-20 nm electron beam lithography with a focus on HSQ: state of the art *Nanotechnology* **20** 2922001
- [6] Muray A, Scheinfein M, Isaacson M and Adesida I 1985 Radiolysis and resolution limits of inorganic halide resists *J. Vac. Sci. Technol. B* **3** 367–72
- [7] Muray A, Isaacson M and Adesida I 1984  $\text{AlF}_3$ —a new very high resolution electron beam resist *Appl. Phys. Lett.* **45** 589–91
- [8] Kratschmer E and Isaacson M 1986 Nanostructure fabrication in metals, insulators and semiconductors using self-developing metal inorganic resist *J. Vac. Sci. Technol. B* **4** 361–4
- [9] Kratschmer E and Isaacson M 1987 Progress in self-developing metal fluoride resists *J. Vac. Sci. Technol. B* **5** 369–73
- [10] Macauley J M, Allen R M, Brown L M and Berger S D 1989 Nanofabrication using inorganic resists *Microelectron. Eng.* **9** 557–60
- [11] Clendenning S B et al 2004 Direct writing of patterned ceramics using e-beam lithography and metallopolymer resists *Adv. Mater.* **16** 215–9
- [12] Ramanathan M and Darling S B 2013 Nanofabrication with metallopolymers—recent developments and future perspectives *Polym. Int.* **62** 1123–34
- [13] Abbas A S, Yavuz M and Cui B 2013 Water soluble and developable electron beam resist PSS *The 39th Int. Conf. on Micro and Nano Engineering (MNE)*
- [14] Greci G, Giustina G D, Pozzato A, Brustin G and Tormen M 2011 Boehmite filled hybrid sol–gel system as directly writable hard etching mask for pattern transfer *Microelectron. Eng.* **88** 1964–7

- [15] Greci G, Giustina G D, Pozzato A, Zanchetta E, Tormen M and Burstin G 2012 Negative hybrid sol–gel resist as hard etching mask for pattern transfer with dry etching *Microelectron. Eng.* **98** 134–7
- [16] Tseng Y-C, Peng Q, Ocola L E, Czapslewski D A, Elam J W and Darling S B 2011 Etch properties of resists modified by sequential infiltration synthesis *J. Vac. Sci. Technol. B* **29** 06FG01
- [17] Tseng Y-C, Peng Q, Ocola L E, Elam J W and Darling S B 2011 Enhanced block copolymer lithography using sequential infiltration synthesis *J. Phys. Chem. C* **115** 17725–9
- [18] Tseng Y-C, Mane A U, Elam J W and Darling S B 2012 Enhanced lithographic imaging layer meets semiconductor manufacturing specification a decade early *Adv. Mater.* **24** 2608–13
- [19] Peng Q, Tseng Y C, Darling S B and Elam J W 2011 A route to nanoscopic materials via sequential infiltration synthesis on block copolymer templates *ACS Nano* **5** 4600–6
- [20] Zhang J, Con C and Cui B 2014 Electron beam lithography on irregular surfaces using evaporated resist *ACS Nano* [at press](#)
- [21] Gerbedoen J-C, Aliane A, Giguère A, Drouin D, Ares R and Aimez V 2013 All evaporation submicron lift-off lithography process with negative e-beam QSR-5 resist *Microelectron. Eng.* **103** 123–5
- [22] Yeo B S, Stadler J, Schmid T, Zenobi R and Zhang W H 2009 Tip-enhanced Raman spectroscopy—its status, challenges and future directions *Chem. Phys. Lett.* **472** 1–13
- [23] Consales M, Ricciardi A, Crescitelli A, Esposito E, Cutolo A and Cusano A 2012 Lab-on-fiber technology: toward multifunctional optical nanoprobe *ACS Nano* **6** 3163–70
- [24] Henry M D, Walavalkar S, Homyk A and Scherer A 2009 Alumina etch masks for fabrication of high-aspect-ratio silicon micropillars and nanopillars *Nanotechnology* **20** 255305
- [25] Khorasaninejad M, Walia J and Saini S S 2012 Enhanced first-order Raman scattering from arrays of vertical silicon nanowires *Nanotechnology* **23** 275706
- [26] Morton K J, Nieberg G, Bai S and Chou S Y 2008 Wafer-scale patterning of sub-40 nm diameter and high aspect ratio (>50:1) silicon pillar arrays by nanoimprint and etching *Nanotechnology* **19** 345301
- [27] Nakamatsu K, Okada M and Matsui S 2008 Fabrication of high-aspect Si structures by deep reactive ion etching using hydrogen silsesquioxane masks replicated by room temperature nanoimprinting *Japan. J. Appl. Phys.* **47** 8619–21
- [28] Ku H Y and Scala L C 1969 Polymeric electron beam resists *J. Electrochem. Soc.* **116** 980–5
- [29] Liu Y, Meng C, Zhang A P, Xiao Y, Yu H and Tong L 2011 Compact microfiber Bragg gratings with high-index contrast *Opt. Lett.* **36** 3115–7