Water soluble and developable e-beam resist sodium PSS

Sondos Alqarni, Arwa Saud Abbas, Mustafa Yavuz and Bo Cui
Waterloo Institute for Nanotechnology (WIN), University of Waterloo
200 University Ave. West, Waterloo, ON, N2L 3G1,
bcui@uwaterloo.ca

In electron beam lithography, exposed resist is typically developed in solvent or base solution; and for spin-coating the resist is usually dissolved in a strong solvent. However, for some applications such as nano-patterning on top of a semiconducting polymer, solvent or strong base solution may attack or degrade the sub-layer material. Here we will show that, poly(sodium 4-styrenesulfonate) (sodium PSS), which is soluble in water due to its ionic nature, can be used as a negative electron beam resist developed in water. This is not surprising given that its chemical structure is similar to that of polystyrene, which is a popular negative tone electron beam resist [1-3]. Note that PEDOT:PSS (here PSS is an acid, rather than a salt) is one of the most popular conducting polymers [4].

In the experiment, we dissolved 70 kg/mol sodium PSS in DI water to make a 7-10 wt/vol% solution. After exposure, the resist was developed in DI water for 1-10 sec at room temperature. Figure 1 shows the contrast curve measured by AFM. The sensitivity of sodium PSS (defined as D_{50}) is approximately 2800 $\mu C/cm^2$. This is about one order lower than that of PMMA, but we expect much higher sensitivity for sodium PSS when using higher molecular weights such as 1000 kg/mol, if its exposure property is similar to that of polystyrene whose sensitivity ($\mu C/cm^2$) is inversely proportional to its molecular weight (kg/mol). Though with a low contrast, feature size down to 40 nm was achieved for sparse patterns, as shown in Figure 2. Moreover, since sodium PSS contains metal sodium, it is far more resistant (by 17×) to O_2 plasma etching than PMMA.

Lastly, as an application for the current process, we carried out lithography using ultra-low energy electron beams on sodium PSS coated on P3HT that is one of the most popular conducting polymer materials, followed by development and liftoff of 10 nm Cr, both with water. Here the low energy exposure is essential because: 1) it has a low penetration depth and does not cross-link the lower part of the resist, making liftoff using water possible; 2) the un-cross-linked lower part can be developed laterally, leading to an under-cut profile ideal for liftoff; 3) the sub-layer is not significantly exposed thus with minimal radiation damage [5]. Figure 3 shows the Cr pattern on P3HT film, fabricated without using any solvent or strong chemicals.

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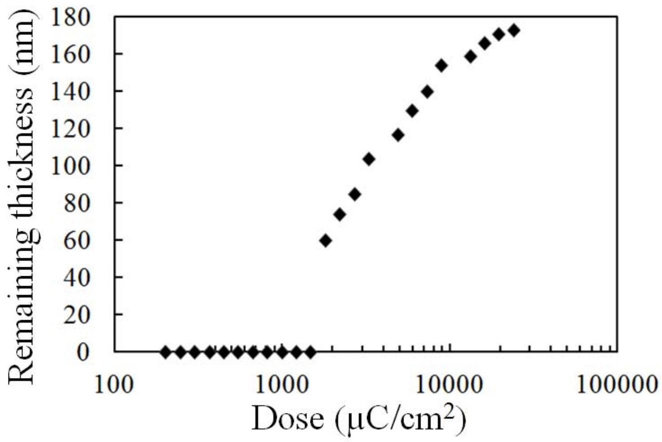
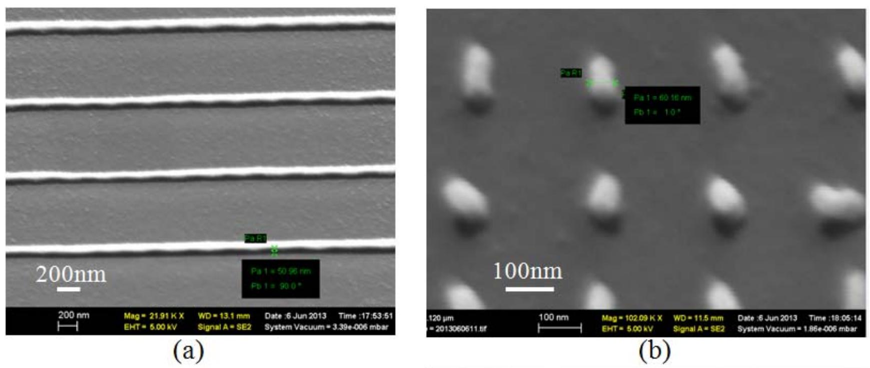


Figure 1. Contrast curve for sodium PSS exposed at 20keV and developed in DI water for 10 sec. The sensitivity (D_{50}) and contrast are derived as 2800 μC/cm^2 and 0.8, respectively.



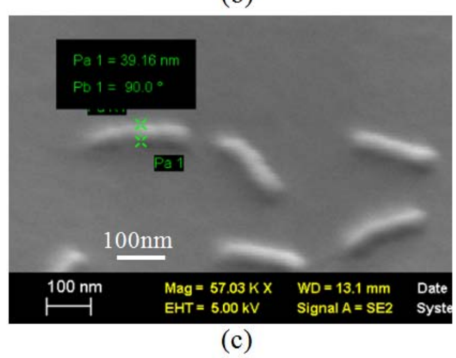


Figure 2. High resolution pattern in sodium PSS by electron beam lithography at 20keV. (a) Line array with line-width ~50 nm. Narrower lines were found collapsed. (b) Pillar array with diameter 60 nm and height close to 150 nm. (c) Pillar array with diameter 40 nm, which collapsed due to capillary force during drying.

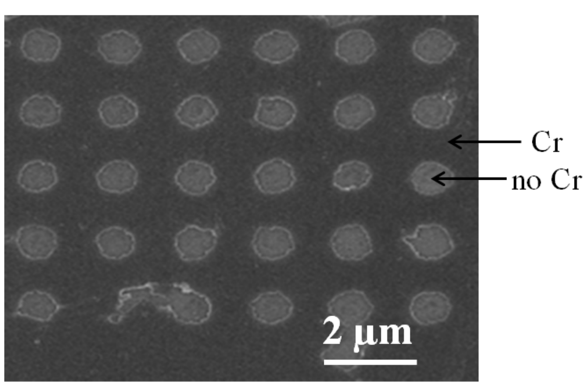


Figure 3. Cr pattern on top of P3HT fabricated by electron beam lithography at 2 keV and liftoff using water.