Water soluble and metal-containing electron beam resist poly(sodium 4-styrenesulfonate)

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Arwa Saud Abbas, Sondos Alqarni, Babak Baradaran Shokouhi, Mustafa Yavuz and Bo Cui

Waterloo Institute for Nanotechnology (WIN), University of Waterloo, 200 University Ave. West, Waterloo, ON, N2L 3G1, Canada
E-mail: bcui@uwaterloo.ca

Abstract

Popular electron beam resists such as PMMA, ZEP and HSQ all use solvent or base solutions for processing, which may attack the sub-layers or substrate that are made out of organic semiconducting materials. In this study we show that water soluble poly(sodium 4-styrenesulfonate), or sodium PSS, can be used as a negative electron beam resist developed in water. Moreover, since PSS contains metal sodium, its dry etching resistance is much higher than PMMA. It is notable that sodium PSS's sensitivity and contrast is still far inferior to organic resists such as PMMA, thus it is not suitable for patterning dense and high-resolution structures. Nevertheless, feature size down to 40 nm was achieved for sparse patterns. Lastly, using very low energy (here 2 keV) electron beam lithography and liftoff process using water only, patterning of metal layer on an organic conductive material P3HT was achieved. The metallization of an organic conducting material may find applications in organic semiconductor devices such as OLED.

Keywords: electron beam lithography, water soluble resist, electron beam resist, sodium PSS

1. Introduction

Electron beam lithography (EBL) [1], focused ion beam (FIB) lithography [2], and nanoimprint lithography (NIL) [3] are currently the three most widely employed nanolithography techniques. Amongst them, EBL is undoubtedly the most popular for R&D. Sensitivity and contrast are the two primary resist properties. High sensitivity leads to short exposure time, whereas high contrast enables high resolution patterning of dense structures. The secondary desirable resist properties include: 1) resistance to dry etching when the patterned resist is used

as etching mask for pattern transfer; 2) use of environmentally friendly chemicals to dissolve the resist for spin-coating and develop the exposed resist; 3) low cost and long shelf life. In this paper we will show that poly(sodium 4-styrenesulfonate) (sodium PSS) behaves as a negative resist with excellent performance in these three aspects.

For the first aspect, namely dry etching resistance, most polymer electron beam resists such as PMMA and ZEP-520A have low resistance to plasma etching, with typical selectivity of ~1:1 to silicon using fluorine based etching gas. One obvious approach to greatly boost the resist's etching resistance is to incorporate metal into the resist. Sodium PSS has been deliberately chosen to meet this condition. Previously, metal halides such as AlF_3 were reported to be self-developing resists containing metal, but they have extremely low sensitivity and cannot pattern arbitrary structures such as a large square, due to the limited lateral diffusion range of the resulting metallic Al upon exposure [4–6]. Metal salt of methacrylic acid (MAA) can also be incorporated into PMMA by copolymerization [7]. Another example of metal containing resist is polyferrocenylsilane (PFS) and its derivatives that contain Fe and Si [8], and PFpP [9]. It is very challenging to synthesize these resists, and they all have low sensitivity and contrast. Alternatively, the sol–gel process can be employed to synthesize the so-called 'hybrid organic–inorganic' resist with high content of metal oxide, for which the main issue is the large volume shrinkage after development and subsequent thermal annealing [10]. Metal or metal oxide nanoparticles can also be mixed with the organic resist to improve its etching resistance, but it is challenging to achieve homogenous distribution of the nanoparticles inside the resist and the resolution is limited by the particle size [11]. Yet another method to incorporate metal to the resist is co-evaporation of the resist and metal to form a film on the substrate. Obviously this method will work only if the resist can be coated by evaporation, and very recently polystyrene–chrome resist has been demonstrated with very high dry etching resistance [12]. Lastly, metal can be incorporated into the developed resist structure (rather than to the resist formulation) through the so-called sequential infiltration synthesis (SIS) of metal oxide such as Al_2O_3 using an atomic layer deposition (ALD) system [13, 14]. However, SIS makes the lithography process more complicated since it has to be carried out after each exposure. Compared to the previously mentioned metal containing resist systems, sodium PSS is a very stable and low-cost resist with a rather straightforward lithography process, though sodium is not as resistant to dry etching as many other metals.

For the second aspect, due to its ionic nature, sodium PSS can be dissolved and developed using water, rather than a solvent that may pose health or environmental problems. Several other water soluble resists have been developed previously. The first such resist is 'PanAquas™' developed by IBM, which is based on conducting polyaniline incorporated with cross-linkable functionality on the aromatic ring of the aniline monomer, and resolution down to $1\,\mu$m has been reported [15, 16]. Polyvinyl alcohol (PVA) is also water soluble but does not behave as a resist [17]. Nonetheless, when it is mixed with an oxidizing metal salt (e.g. $AgNO_3$, $HAuCl_4$, and mixture of $La(NO_3)_3$ - $Sr(NO_3)_2$ - $Mn(NO_3)_2$), the PVA can be oxidized and cross-linked upon electron beam exposure (or thermal annealing), accompanied by the reduction of the metal salt to produce elemental metal within the polymer matrix [18–20]. As such, just like sodium PSS, the mixture is a metal containing and water soluble negative resist, with demonstrated resolution down to 120 nm and 180 nm, respectively, for Ag and Au-containing resist. One issue is that the reduced metal agglomerates to form nanoparticles that would affect the pattern transfer process when used as an etching mask, whereas for sodium PSS the metal sodium is homogenously distributed in the exposed film.
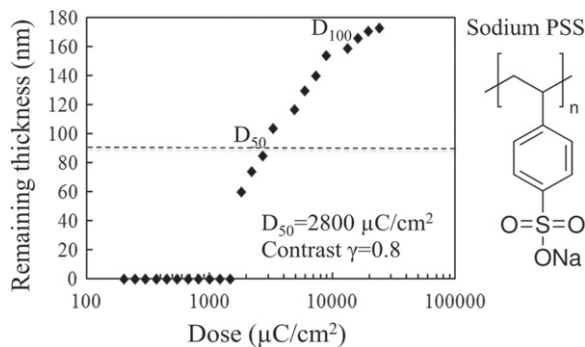
Figure 1. Chemical structure and contrast curve for sodium PSS exposed at 20 keV and developed by water for 10 s with the dose in log-scale. The resist sensitivity, defined as D_{50}, is 2800 μC cm^{-2}; and contrast, defined as $[\log_{10}(D_{100}/D_0)]^{-1}$, is 0.8. The contrast curve was measured by AFM.

In this work we will first report the exposure and dry etching properties of sodium PSS, then we will describe the fabrication of metal nanostructure on top of an organic conducting polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) by low energy electron beam lithography and liftoff using water.

2. Experimental

We dissolved 70 kg mol^{-1} PSS (Sigma Aldrich) in DI water to make a 7 wt/vol% solution that gave a ~180 nm film by spin coating. The film was then baked on a hotplate at 90 °C for 5 min to drive off the water. Afterwards, the resist was exposed at 20 keV using Raith 150$^{\text{TWO}}$ electron beam lithography system. Finally, the resist was developed in DI water for 10 s at room temperature, and was dried by N$_2$ gun. To compare the dry etching resistance, sodium PSS and PMMA film were etched using a Trion Phantom II RIE system with 20 sccm O$_2$, 20 mTorr, 20 W RF power, and 0 W ICP power; and 20 sccm CF$_4$, 20 mTorr, 100 W RF power, and 0 W ICP power. The etching rate was measured with a Veeco Dektak surface profilometer.

Next, as an application of sodium PSS for its water processable property, we demonstrated metallization of the conducting polymer P3HT. In the experiment, P3HT (1-Material Inc., Dorval, Quebec, Canada) was dissolved in chlorobenzene for spin-coating. After baking the P3HT film, 215 nm of sodium PSS was spin-coated atop, baked, and exposed at a very low energy of 2 keV that would just cross-link the upper part of the resist. After development for a very brief time of ~2 s, 10 nm Cr was evaporated and lifted off in water, thus resulting in a metal pattern on top of the P3HT film. Here liftoff in water was possible because the sodium PSS at the bottom part of the film was not fully cross-linked and was thus soluble in water. The structure was characterized using a Zeiss Ultra SEM.

3. Results and discussion

Figure 1 shows the contrast curve of sodium PSS exposed at 20 keV and developed using water for 10 s at room temperature. The resist sensitivity, defined as the dose for 50% remaining thickness (D_{50}), is approximately 2800 μC cm^{-2}; and the resist contrast, defined as
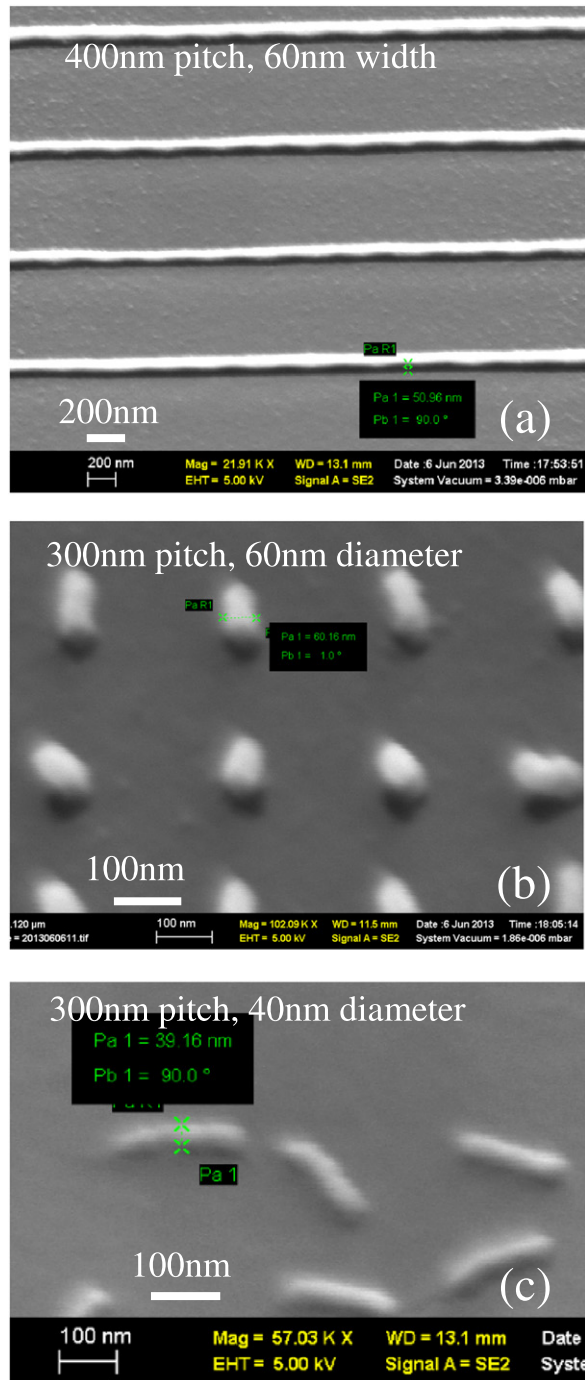
Figure 2. High resolution pattern in sodium PSS by electron beam lithography at 20 keV. (a) Line array with line-width ∼60 nm. Narrower lines were found collapsed. (b) Pillar array with diameter 60 nm. (c) Pillar array with diameter 40 nm, which collapsed due to capillary force during drying the water developer. The array periodicity is 400 nm for (a), and 300 nm for (b) and (c).

$\gamma = [\log_{10}(D_{100}/D_0)]^{-1}$, is calculated to be 0.8. The sensitivity is similar to that of low molecular weight polystyrene [21], and may be improved drastically by using higher molecular weight

sodium PSS, as for chain cross-linking polymer resist the sensitivity (μC/cm^2) is expected to be roughly inversely proportional to its molecular weight (kg mol^{-1}) [22]. The polydispersity of our sodium PSS is unknown, but it is not expected to have a significant effect on its exposure property [23]. As for the resist contrast, one way to enhance it is to use lower molecular weight, but at the cost of reduced sensitivity. Therefore, given the low sensitivity and low contrast, sodium PSS is not suitable for defining a dense pattern with high resolution. However, as seen in figure 2, for sparse line or dot array pattern where proximity effect is insignificant, line-width down to 60 nm and pillar diameter down to 40 nm were achieved, though the high aspect ratio (180/40 = 4.5) pillars collapsed due to capillary force while drying the water developer. Even higher resolution is possible by using higher energy exposure for which proximity effect is further reduced. In fact, another negative resist SU-8, has been shown to have a low contrast similar to the sodium PSS, and was reported to be able to define lines as narrow as 24 nm at 300 nm pitch when exposed at 100 keV [24].

Since sodium PSS contains metal sodium, it is expected to be more resistant to dry etching than other polymer resists such as PMMA. We first measured the RIE etching rate with O$_2$ plasma (20 sccm O$_2$, 20 mTorr, 20 W RF power), and found that sodium PSS is 17$\times$ more resistant than PMMA ($\sim$6$\times$ more resistant than negative resists polystyrene and SU-8). However, the selectivity relative to PMMA is reduced to 3.5$\times$ with CF$_4$ gas (20 sccm CF$_4$, 20 mTorr, 100 W RF power, room temperature) that is widely used to etch silicon or its compound. The etching product of the sodium component should be NaF, which has a high melting temperature of 993 °C and thus is not volatile at room temperature. Therefore, this relatively low selectivity with CF4 gas is believed to be primarily due to the low weight percentage 11.2% of sodium in sodium PSS.

Lastly, as an application for the current resist, we fabricated metal nanostructure on top of a conducting polymer, which is an important (for organic semiconductor devices) yet challenging task since most organic conducting materials are sensitive to solvents commonly used for lithography and pattern transfer process. Here we carried out electron beam lithography at a very low energy of 2 keV 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 thus does not fully cross-link the lower part of the resist, making liftoff using water possible; 2) the unexposed or under-exposed lower part can have quick lateral development, forming an under-cut profile ideal for liftoff (see figure 3(a) for schematic drawing and [25] for SEM images of undercut resist profile); 3) as most electrons are stopped in the resist layer, the sublayer is not significantly exposed, thus there is minimal radiation damage. In addition, since the resist sensitivity (μC/cm^2) is roughly proportional to the exposure energy (keV) as predicted by the Bethe equation for electron energy loss ($E_{\text{loss}} \propto 1/E \cdot \log(\alpha E)$ with α being constant), lower energy exposure offers faster exposure of the pattern. Figure 3(b) shows the Cr pattern on P3HT film, fabricated without using any solvents or strong chemicals that may attack or degrade the conducting polymer. However, we were unable to achieve sub-500 nm sodium PSS structure using this low energy exposure because they were found to be washed away by water developer even at a short development time of $\sim$2 s. This is in contrast to high energy exposure, as shown in figure 2, for which the nanostructures were not washed away after 10 s development. This is because, with low energy exposure, water can penetrate through the fully cross-linked upper layer and swell/weaken the linear or partly cross-linked lower layer at the resist/P3HT interface,
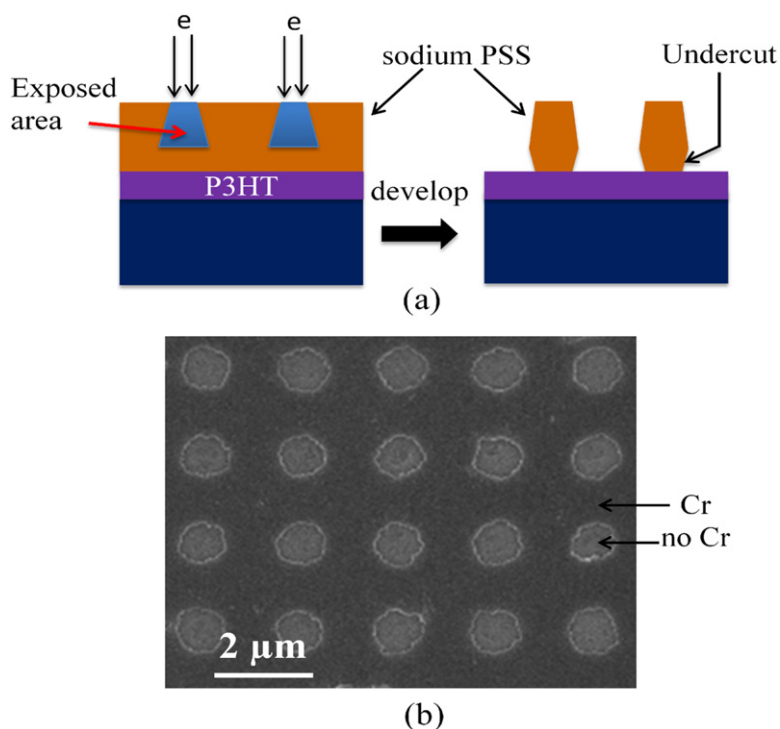
Figure 3. (a) Schematic profile of the resist with low energy exposure. Here the upper part is tapered due to electron forward scattering, whereas the lower part has an undercut profile due to fast lateral development of un-/under-exposed resist. (b) Cr pattern on top of P3HT fabricated by electron beam lithography at 2 keV using 215 nm thick sodium PSS resist, followed by liftoff with water.

which leads to a very weak adhesion. Similarly low resolution is also reported for low energy exposures of polystyrene resist [25].

Metallization of an organic conducting material utilizing a solvent-free process can also be realized using stencil lithography [26], which duplicates the pattern on the stencil (shadow) mask by evaporation of the metal through the stencil mask onto the sub-layer or substrate. However, the gap between the mask and the substrate is difficult to control, leading to blurring (an enlargement of the initial pattern) [27]. More importantly, continuous metal structure like a mesh employed as a transparent and conducting electrode for organic light-emitting diodes (OLED) [28] cannot be patterned by stencil lithography since the stencil mask must not contain any isolated structure without a support. Alternatively, 'cold welding' can be utilized to pattern metal on an organic layer, in which the metal (pre-coated on the organic layer) directly in contact with the protruded feature on the mold is peeled off upon de-molding, due to the weakening of the metal film at the feature edge [29], but extremely high pressure (>1000 atm) is needed. As a result, our method of metallization using water processable resist and low energy exposure is advantageous for the fabrication of organic semiconductor devices that are insensitive to water.

4. Summary

In this study we showed that water-soluble poly(sodium 4-styrenesulfonate) (sodium PSS) can be used as a negative electron beam resist developed in water. As it contains metal sodium, its dry etching resistance is much higher than PMMA. However, its performance in terms of sensitivity and contrast is still far inferior to an organic resist such as PMMA, and thus it is not suitable for patterning dense structures with high resolution. Nevertheless, feature size down to 40 nm was achieved for sparse patterns. Lastly, using very low energy (here 2 keV) electron beam lithography and liftoff process that involved water only, sodium PSS was employed to pattern metal on an organic conducting material (here P3HT) that is insensitive to water yet sensitive to solvents or strong chemicals. The metallization of an organic conducting material may find applications in organic semiconductor devices such as OLED.

Acknowledgments

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