Enhanced etching resistance of e-beam resist Na-PSS by adding metal compound into resist or developer

Celal Con and Bo Cui
Waterloo Institute for Nanotechnology (WIN), University of Waterloo
200 University Ave. West, Waterloo, ON, N2L 3G1,
ccon@uwaterloo.ca

In electron beam lithography, exposed resist is typically developed in solvent such as PMMA resist in MIBK:IPA, or base solution such as HSQ resist in aqueous TMAH. And for spin-coating, the resist is usually dissolved in a strong solvent such as anisole. However, for some applications such as nano-patterning on top of a semiconducting polymer or a common polymer substrate like PMMA, solvent or the strong base solution may attack the substrate material. Recently, Abbas et al. showed that poly (sodium 4-styrenesulfonate) (sodium-PSS, Na-PSS), which is soluble in water due to its ionic nature, can be used as a negative electron beam resist developed in water with sub-100 nm resolution capability [1]. Moreover, since sodium-PSS contains metal sodium, it is more resistant to plasma etching than PMMA using oxygen plasma. However, its resistance to F-based plasma is still low; and more importantly, it was found that the etching resistance after development using water is lower than the as-spun film, implying that sodium is lost to water during the development process.

Here, we report two approaches to enhance its resistance to dry etching. In the first approach, we dissolved Na-PSS and aluminum nitrate nonahydrate ($Al(NO_3)_3.\ 9H_2O$) in water, noting that Al is a better hard etching mask material than sodium. After spin-coating and electron beam lithography using water developer, it was found that the composite film retained the resist property and was able to define nanostructures (Figure 1).

Another approach is to compensate the loss of sodium into water developer by using a developer containing metal ions. Table I compared the etching resistance for different salts or bases dissolved in water for resist development. It showed that dry etching resistance can be enhanced by a factor of 2 when using water developer containing 10% KNO_2, or a factor of 10 for 25% NaOH.

[1]. Abbas AS, Alqarni S, Shokouhi BB, Yavuz M, and Cui B, “Water soluble and metal-containing electron beam resist poly(sodium 4-styrenesulfonate)”, Mater. Res. Express, 1, 045102 (2014).

Enhanced etching resistance of e-beam resist Na-PSS by adding metal compound into resist or developer

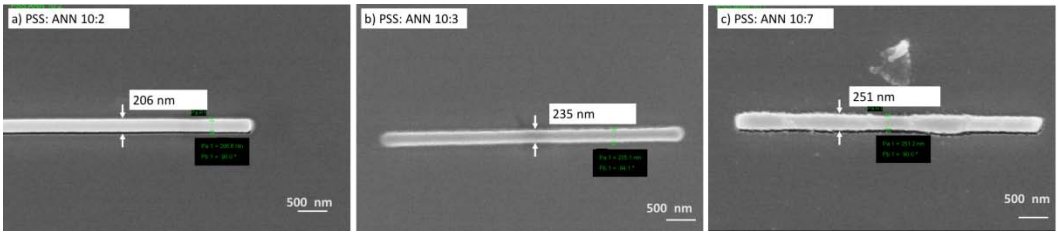

Figure 1. SEM images of line structures defined in Na-PSS e-beam resist containing aluminum nitrate nonahydrate (ANN) at various weight ratios. a) 200 nm line-width obtained from Na-PSS : ANN = 10:2; b) 235 nm line-width obtained for 10:3 weight ratio; c) 251 nm line-width obtained for 10:7 weight ratio.

Table I. Etching rate of Na-PSS structures defined by electron beam lithography and developed using water containing different salts/bases. Also shown at right is the rate for as-coated film and silicon. KNO_2 and NaOH both enhanced etching resistance, whereas $AgNO_3$ and ANN both reduced the resistance (implies they facilitated sodium loss from the resist to the developer)
RIE recipe: 50 W RF power (no ICP power), 20 mTorr, 20 sccm CF_4, 3 sccm O_2

Etching rate of PSS film with different developers (nm/min)						**Etching rate of film/substrate (nm/min)**			
	Developer type					without development			
Development time (sec)	DI water	10 % KNO_2 solution	10 % $AgNO_3$ solution	10 % ANN solution	25 % NaOH solution	Silicon	PMMA	ARC film	Unexposed Na-PSS film
10	35	14	42	54	-	38	200	200	13
30	31	14	40	60	-				
60	30	16	40	53	3.7				