PMMA resist containing metal salt for enhanced dry etching resistance

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Poly(methyl methacrylate) (PMMA) is the most popular electron beam lithography (EBL) resist due to its low cost, high resolution and ease of processing. However, it suffers from very low dry etching resistance, and is thus unsuitable for pattern transfer via direct etch. A natural solution is to incorporate metal into it since metal is typically very resistant to dry etch. Generally speaking, metal can be incorporated into organic polymer resist via sequential infiltration synthesis,[1] co-evaporation of metal and the resist,[2] and mixing nanoparticle with the resist. However, the first two methods induce high cost associated with vacuum deposition, whereas the third one suffers from inhomogeneous nanoparticle distribution and low resolution limited by particle size. Yet another approach is to use copolymer of PMMA and (metal salt of) PMAA (poly(methacrylic acid)), but the metal content is rather low and its dry etching resistance was not studied.[3]

Here we investigate the possibility of adding metal salt into PMMA resist. 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 chloride hexahydrate and PMMA can be dissolved in DMF (dimethylformamide) to give a uniform film after spin coating. $NiCl_2$ is a suitable salt since nickel is a very hard mask for RIE using both F- and Cl- plasmas, and it has a relatively high melting temperature of 140 ^oC to minimize phase separation during film baking.

As expected, the etching rate by oxygen RIE of the nanocomposite film was found to be 40 nm/min, which is 4× slower than pure PMMA film. The nanocomposite film was exposed at 20 keV and developed with MIBK:IPA 1:3 mixture. Figure 1 showed line array with 500 nm period.

Besides nickel chloride, aluminum nitrate nonahydrate (ANN) was also found able to be dissolved in DMF with PMMA. Figure 2 showed 200 nm wide line array patterned in the nanocomposite film with PMMA:ANN weight ratio of 10:3. Aluminum is an excellent etching mask against F-based plasma (but not Cl-based plasma) that etches silicon and its compound.

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[1] Y-C. Tseng, Q. Peng, L. E. Ocola, D. A. Czaplewski, J. W. Elam and S. B. Darling, J. Vac. Sci. Technol. B, 29, 06FG01 (2011)
[2] C. Con, J. Zhang and B. Cui, Nanotechnology, 25, 175301 (2014)
[3] D. J. Webb and M. Hatzakis, J. Vac. Sci. Technol., 16, 2008 (1979)

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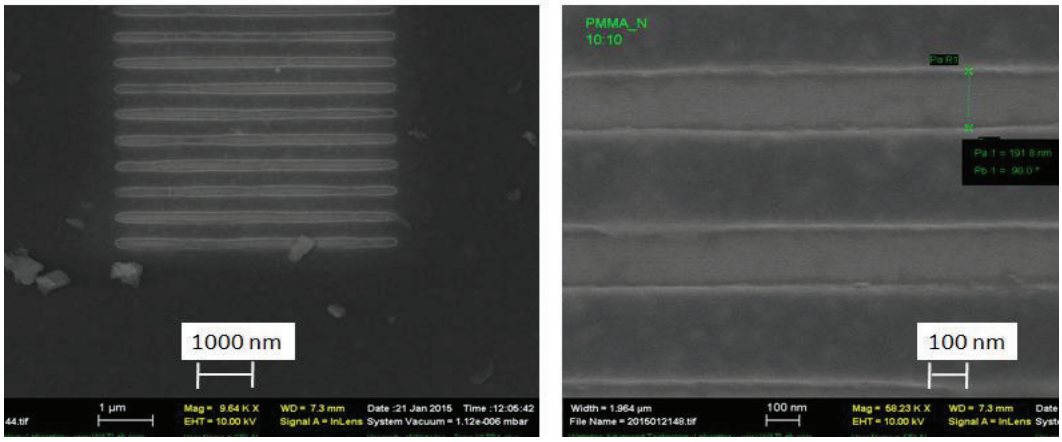

Figure 1. SEM images of 200 nm-wide lines (500 nm period) exposed in nanocomposite resist consisting of PMMA and nickel chloride hexahydrate at 1:1 weight ratio dissolved in DMF for spin-coating.

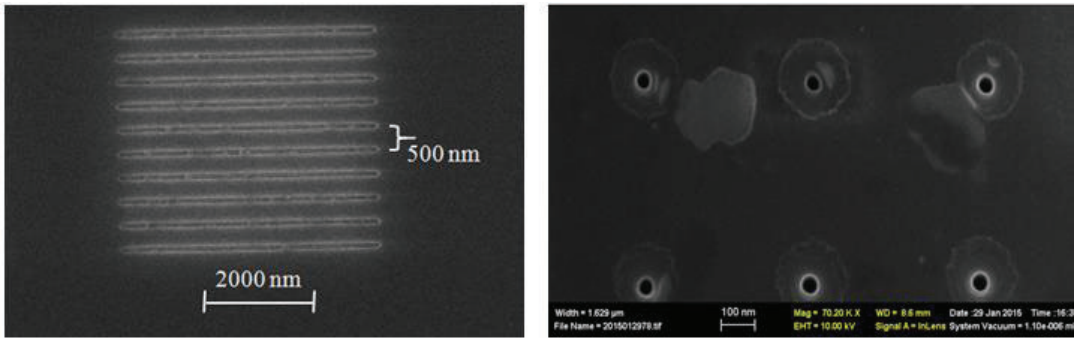

Figure 2. SEM images of line and hole arrays with 500 nm period exposed in nanocomposite resist consisting of PMMA and aluminum nitrate nonahydrate at 10:3 weight ratio dissolved in DMF for spin-coating.