Improving the Sensitivity of Metallic Organic Resists

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New resists are required to advance the nanoelectronics industry to keep up the demands of Moore's law. A new class of high dry etch selectively electron beam resist materials have been developed that are based on a family of heterometallic rings. It has been demonstrated that negative tone resists provide high resolution (18 nm half pitch¹) and ultra-high etch selectivity for silicon (130:1 has been demonstrated) when subjected to a pseudo-Bosch inductively coupled plasma–reactive-ion etch (ICP–RIE).²

Figure 1a shows a metal-organic compound [NH₂Allyl₂]Cr₇NiF₈(Pivalate)₁₆ (denoted as 1) that can be used at a resist where seven chromium(III) centers and a nickel(II) form an octagon. The exterior of the compound entirely of *tert*-butyl groups, giving high solubility in casting solvents suitable for preparing films on silicon substrates. Using our latest Monte Carlo simulation software exhibited a resolution of 20 nm half pitch (Figure 2a). While this resist produced a high resolution (Figure 2b) it came at the expense of a low sensitivity (11351 pC cm). Further Monte Carlo simulations (Figure 2c) suggested that the sensitivity could be dramatically improved by substituting the nickel atom for a cadmium atom making [NH₂Allyl₂]Cr₇CdF₈(Pivalate)₁₆ resist (denoted as **2**). The immediate observation is that the cadmium atom increases the total number of secondary electrons (SE) (14 SE/spot) that are emitted to expose the resist in the immediate write area by 1.4 times, when compared with resist 1 (10 SE/spot). Therefore, the number of primary electrons used to expose the resist can be reduced by 1.4. Figure 2d showed that resist **2** was determined to have a sensitivity of 7995 pC cm while maintaining high resolution. The increased sensitivity illustrates strong agreement between the simulation and the experimental results.

¹ S. M. Lewis et al., Angew. Chem. Int. Ed. 2017, 56, 6749.

² S. M. Lewis, et al., *Nano Lett.*, 2019, **19**, 6043.



Figure 1 a) [NH₂Allyl₂]Cr₇NiF₈(Pivalate)₁₆, b) [NH₂Allyl₂]Cr₇CdF₈(Pivalate)₁₆. The structure of the molecules in a crystal, in ball-and-stick representation. Cr atoms are green, Ni atoms are green with a blue band and Cd atoms are green with a red band. F atoms are yellow. H atoms are omitted for clarity.



Figure 2 a) Monte Carlo simulation of the performance of $[NH_2Allyl_2]Cr_7NiF_8$ (Pivalate)₁₆. b) Top down view of 20 nm half pitch patterns fabricated in $[NH_2Allyl_2]Cr_7NiF_8(Pivalate)_{16}$ resist on a Si. c) Monte Carlo simulation of the performance of $[NH_2Allyl_2]Cr_7CdF_8(Pivalate)_{16}$. d) Top down view of 20 nm half pitch patterns fabricated in $[NH_2Allyl_2]Cr_7CdF_8(Pivalate)_{16}$ resist on a Si. For the Monte Carlo simulations, the black lines represent the primary electrons, and the red lines are secondary electrons generated from collisions with resist during the writing with energies >500 eV. Purple, cyan, and green lines are further secondary electrons with associated energies below 500 eV generated by first-, second-, and third-order collisions, respectively. The blue lines are backscattered electrons.