Direct Writing of Metal-Organic Resists for Alignment Marker Fabrication in Electron Beam Lithography

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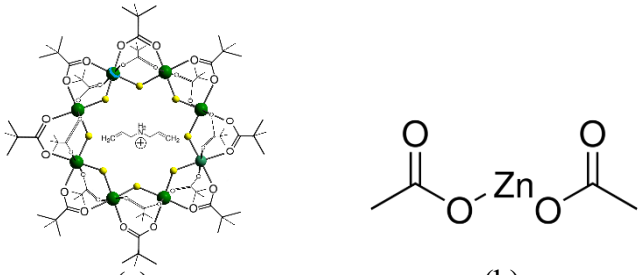
We have found that $[NH_2(CH_2\text{-}CH{=}CH_2)_2]$ $[Cr_7NiF_8(O_2C^tBu)_{16}]$ and Zinc Acetate (Figure 1a and b) and are denoted as resist **1** and **2,** respectively, can be decomposed under electron beam to form nano patterns. This is of particular interest because it demonstrates that markers for pattern placement in electron beam lithography are simple to produce with no photomasks or etching steps being required. This presentation will describe how these materials can be directly written using electron beam lithography and discuss our marker detection process. To achieve this we used our Monte Carlo simulation software called Excalibur[1] to design these markers. Figure 2 shows point spread functions for resist **1** and **2**. It was calculated that resist **1** produced 5710 secondary electrons (SEs) while resist **2** produced 458132. These electrons are responsible for exposing the resist in the marker fabrication process and are required for the marker for detection. It is clear that both of these resists need to produce the same number of SEs in order to be detected. To match the number of SE generated in Resist **1** with that of resist **2** the thickness need to be increased. Figures 2c and d show point spread functions of resist **1** and **2** respectively where their thickness are 1700 and 650 nm. These simulations predicted that both resists would generate 170236 and 172458 SEs.

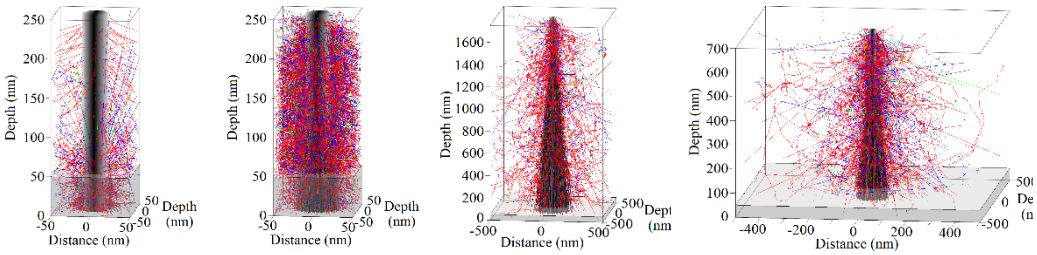
We determined that the number density of SE which is sufficient to allow the marker to be detected by the backscattered electron detector as can be seen in Figure 3. This shows a close agreement between the simulation and experiment. The X-ray photoelectron spectra of Figure 4 shows that while the electron beam is exposing each resist, the carbon bonds in the pivalate (resist **1**) and acetate (resist **2**) regions in the molecule are being broken up via the scission process and is diffused out of the film to form a mixture gases of carbon monoxide (CO) and carbon dioxide (CO_2). This reduces Resist **1** and Resist **2** into $CrNiO_xF_y$ compounds and a zinc oxide (ZnO) semiconductor, respectively. It is evident that the ZnO is more efficient at producing SEs than $CrNiO_xF_y$ compounds because of its semiconducting state where there are more electrons that are readily available to be emitted into the vacuum chamber and can be detected by the detector.

[1] S. M. Lewis et al., *Adv. Funct. Mater.* 2022, **32**, 2202710.



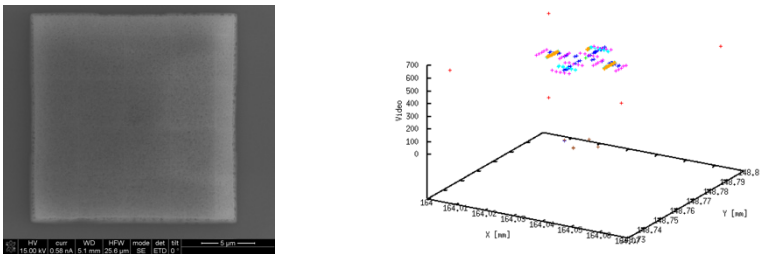
(a) (b)

Figure 1: (a) resist **1**, $[NH_2(CH_2\text{-}CH{=}CH_2)_2][Cr_7NiF_8(O_2C^tBu)_{16}]$, (b) resist **2**, Zinc Acetate. Cr green, Ni green with a blue band, F yellow, C gray. H atoms omitted for clarity.



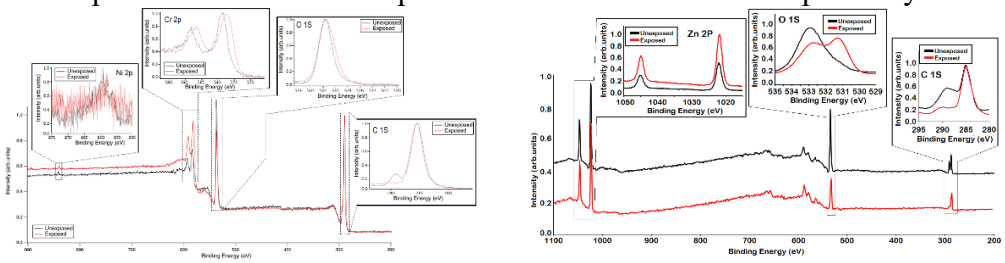
(a) (b) (c) (d)

Figure 2: Point spread function: (a) Resist **1**; (b) Resist **2;** (c) Resist **1**; (d) Resist **2**. The acceleration voltage is 100 KeV. The black lines are primary electrons, secondary electrons above 500 eV are represented by the red lines. The secondary electrons which have the associated energies below 500 eV which were generated by first, second and third order collisions are indicated purple, cyan and green. The blue lines are backscattered electrons. 1 million electrons are inserted into a single spot.



(a) (b)

Figure 3: (a) SEM image of 20 µm marker in resist **1**; (b) 20 µm marker detection result in resist **2**. Both resists were spun at 1500 rpm and soft baked at 100 °C and exposed using an accelerating voltage of 100 kV using a current of 100 nA, and a beam step size of 25 nm. Developed in hexane and methanol respectively for 20 s.



(a) (b)

Figure 4: X-ray photoelectron spectra of (a) resist **1** and (b) resist **2** materials before and after exposure to the electron beam.