Additive Nano Manufacturing of Insulators and Semiconductors Grown by Direct-Write 3D Nanoprinting

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This presentation will describe how $Cr_8F_8(O_2C^tBu)_{16}$ and Zinc Acetate materials (see Figure 1a and b) can be transformed into insulating and semiconductor materials when exposed to an electron beam. The X-ray photoelectron spectra of Figure 2 shows that while the electron beam is exposing each material, the carbon bonds in the $Cr_8F_8(O_2C^tBu)_{16}$ and Zinc Acetate 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 oxide (CO_2). This reduces the $Cr_8F_8(O_2C^tBu)_{16}$ into an insulating CrO_xF_y compound and reduces the Zinc Acetate into a zinc oxide (ZnO) which is a wide band gap semiconductor[1] (for more details see ref 1). This is of particular interest because it demonstrates that active semiconductor devices such as field effect transistors can be simple to produce with no photomasks or etching steps or impurity doping being required. We have also discovered that both materials can be sublimed at low temperatures and low pressures[2]. To date, this has been achieved by subliming them into a reaction chamber which forms a film onto a substrate, this is then exposed to an electron beam which writes the pattern into the material. This is process is repeated to produce 3D nanostructures. This has led us to design a stage that allow each material to be sublimed in an SEM chamber while the E-beam writes the pattern simultaneously, hence we can write 3D-nanostructures directly. To understand this nano-manufacturing process, our Excalibur Monte Carlo simulation tool[3] has been adapted to model these 3D nanopatterns. Figure 3 shows a 3D Monte Carlo simulation of the $Cr_8F_8(O_2C^tBu)_{16}$ and Zinc Acetate. It shows that both materials can produce high-resolution 3D nanostructures. The nanobridge have supports with a width of 50 nm and a height of 500 nm, exhibiting a 10:1 aspect ratio. The SEM images of Figure 4 shows that both $Cr_8F_8(O_2C^tBu)_{16}$ and Zinc Acetate materials can produce high-resolution 3D nanostructures. Just like the simulations in Figure 3, the nanobridges have supports with a width of 50 nm and a height of 500 nm, exhibiting a 10:1 aspect ratio. This shows strong agreement between the simulation and the experimental. It must be noted that in both cases the high aspect ratio structures that are not supported have collapsed, however, it can be seen that the nano-bridges have increased structural integrity by providing support to the lower high aspect ratio structures. Thus the pattern has been successfully resolved.

[1] A. Chaker et al., *ACS Appl. Nano Mater.* 2021, **4**, 1, 406–413.
[2] D. Goldfarb et al., J. Micro/Nanopatterning Materials and Metrology, **21**, 4, 041406 (2022).
[3] S. M. Lewis et al., *Adv. Funct. Mater.* 2022, **32**, 2202710.

(a)

Figure 1: Crystal structure of (a) $Cr_8F_8(O_2C^tBu)_{16}$ and (b) Zinc Acetate. Cr green, Ni green with a blue band, F yellow, C gray. H atoms omitted for clarity.

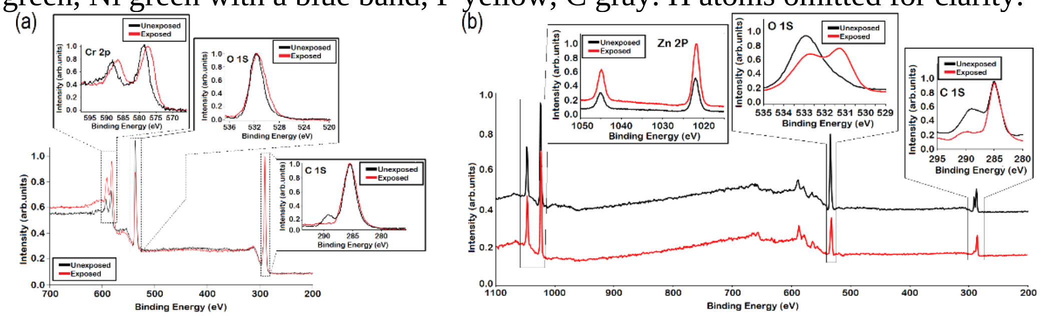


Figure 2: X-ray photoelectron spectra of (a) $Cr_8F_8(O_2C^tBu)_{16}$; (b) Zinc Acetate materials before and after exposure to the electron beam.

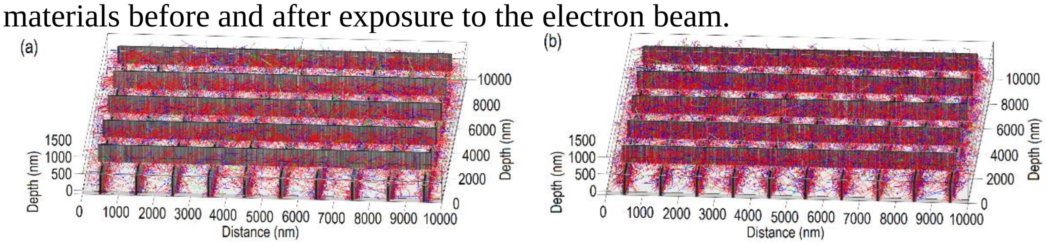
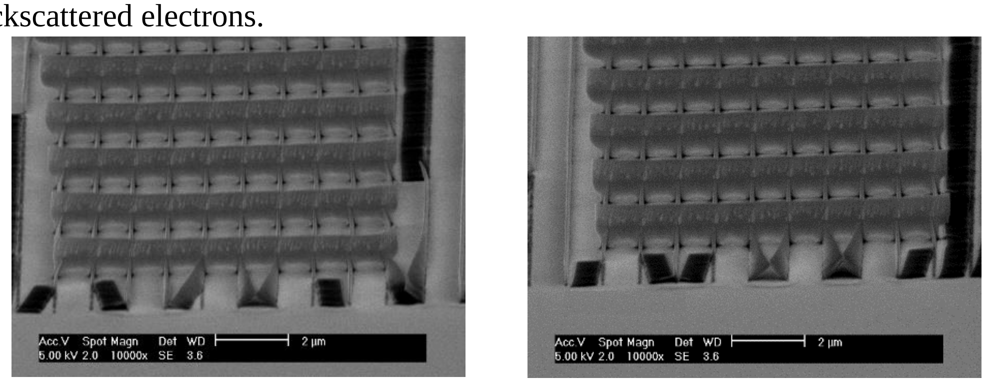


Figure 2: (a) $Cr_8F_8(O_2C^tBu)_{16}$; (b) Zinc Acetate. The acceleration voltage is 30 KeV. The black lines are primary electrons, secondary electrons above 500 eV are represented by the red lines. The secondary electrons which have the associated energies below 500 eV which were generated by first, second and third order collisions are indicated purple, cyan and green. The blue lines are backscattered electrons.



(a) (b)

Figure 3: (a) $Cr_8F_8(O_2C^tBu)_{16}$ and (b) Zinc Acetate nanobridges that have been 3D printed using an acceleration voltage of 30 keV using a current of 50 pA, and a step size of 4 nm. The nanobridge has a width of 50 nm and a height of 500 nm, exhibiting a 10:1 aspect ratio. $Cr_8F_8(O_2C^tBu)_{16}$ and Zinc Acetate materials were developed in Hexane and Methanol respectively for 20 s.