Direct Writing of Tris(xanthato)Bi(III) Precursors for use in Future Optoelectronic Devices

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Bismuth(III) sulphide (Bi_2S_3) is a non-toxic semiconductor with a direct band gap of 1.3 to 1.7 eV, and a high absorption coefficient in the order of 10^5 cm^{-1}. These physical properties are desirable for applications in thermoelectric, memory, and photodetector devices.[1] We have found that [$Bi(S_2COCy)_3$] and [$Bi(S_2COEt)_3$] (see Figure 1a and b), 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 devices 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 further applications for this material. The Monte Carlo simulations[2] of Figure 2 shows point spread functions for resist **1** and **2**. It was calculated that resist **1** produced 346175 SEs while resists **2** produced 779180. These electrons are responsible for exposing the resist. Therefore, it is expected that the exposure dose required to render the resist insoluble would be approximately 2.2 times lower than resist **1**. Figures 3a and b show Monte Carlo simulations of top down of 30 nm half pitch in resist **1** and **2** respectively. These simulations predicted that the sensitivity of resist **2** would increase by a factor of 2.2. Figures 3c and d shows that both resists can produce high-resolution structures at a pitch of 30 nm half pitch. We have found that resist **1** has a sensitivity of 76437 pC/cm, while we have observed a sensitivity increase to 33189 pC/cm for resist **2**. This shows a sensitivity factor increase of 2.3 times which shows a close agreement between the simulation and the experimental. It is evident that the ligands used affects the sensitivity of each resist. We observe with an increase in chain molecular weight decreases the resist sensitivity. This is due to the requirement of more electrons to break the increased number of carbon bonds compared to the ethyl chain in resist **2**. It is proposed that while the electron beam is exposing the molecule, the carbon bonds are being broken up via the scission process and is diffused out of the film to form gases of carbon monoxide (CO) and carbon dioxide (CO_2). This reduces the xanthate molecules to Bi_2S_3.

[1] V. Kaltenhauser et al., *J. Mater. Chem. C*, 2013, **1**, 7825-7832.
[2] S. M. Lewis et al., *Adv. Funct. Mater.* 2022, **32**, 2202710.

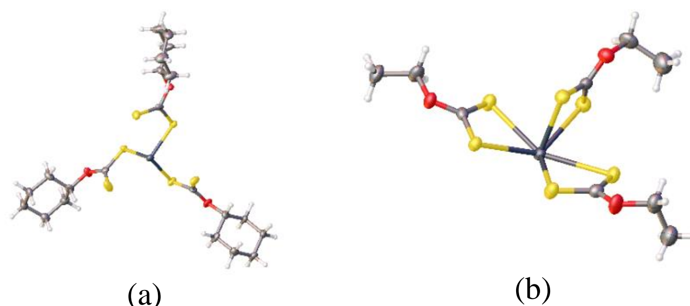

Figure 1: (a) resist **1**, $[Bi(S_2CO^iPr)_3]$, (b) resist **2**, $[Bi(S_2COEt)_3]$. The structure of the molecules in a crystal. Bi atom is black, S atoms are yellow, C atoms are grey, O atom is red, and the H atoms are white.

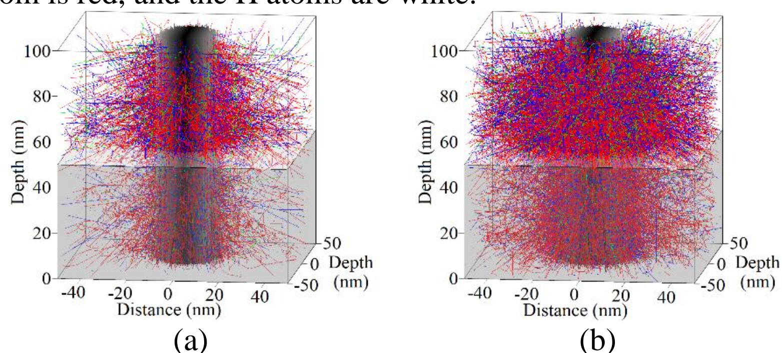

Figure 2: Point spread function: (a) Resist **1**; (b) Resist **2**. The acceleration voltage is 30 KeV. The black lines are primary electrons, secondary electrons above 500 eV are represented by the red lines. The secondary electrons which have the associated energies below 500 eV which were generated by first, second and third order collisions are indicated purple, cyan and green. The blue lines are backscattered electrons. 1 million electrons are inserted into a single spot.

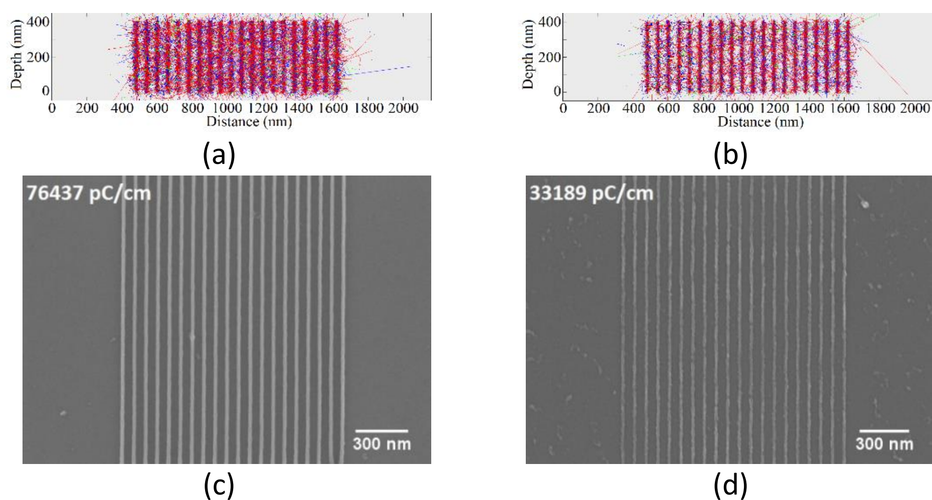

Figure 3: (a) Experimental exposure dose for resist **1** at 60 nm pitch; (b) experimental exposure dose for resist **2** at 60 nm pitch. Both resists were spun at 2000 rpm and exposed using an accelerating voltage of 30 kV using a current of 29.8 pA, and a step size of 4 nm. Both resists were developed in tert-butyl methyl ether for 20 s.