Band Gap Engineering: Direct Writing of Lead cyclohexylxanthate and Lead isopropylxanthate Precursors to Produce Lead Sulfide for Next Generation Photodetector Devices

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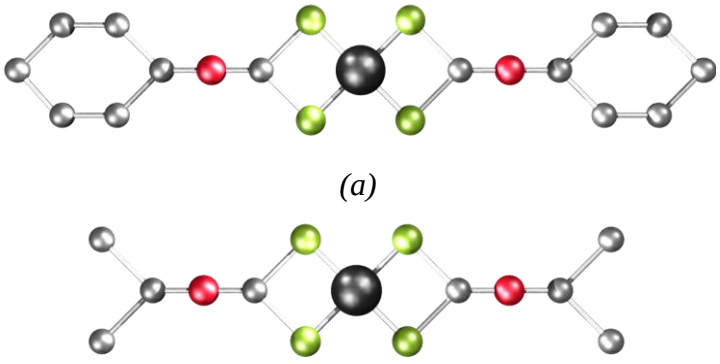
Lead sulfide (PbS) has shown interest due to its narrow band gap (~0.41 eV), being easily manipulated as either a p- or n- type semiconductor. These properties provide potential electronic and optoelectronic applications, such as photodetectors[1]. We have found that lead cyclohexylxanthate and lead isopropylxanthate (Figure 1a and b respectively) can be decomposed under electron beam to form 80 nm pitch structures. This is of particular interest due to it demonstrating that devices are simple to produce because photomasks and etching steps are not required. This presentation will describe how these materials can be directly written using electron beam lithography and discuss further applications for this material.

Figures 2a and b show that both materials can produce high resolution structures at pitch 100 to 80 nm. At the pitch of 80 nm, line doses of 54108 pC/cm and 30030 pC/cm for lead cyclohexylxanthate and lead isopropylxanthate respectively were determined.

Figure 3 shows the comparison in line dose trend and pitch for lead cyclohexylxanthate and lead isopropylxanthate. It is evident that the ligands used affects the dose for each pitch and significantly increased for writing lead cyclohexylxanthate compared to lead isopropylxanthate. This is due to the cyclohexyl group requiring more energy to break the increased number of bonds compared to the isopropyl group. At pitch 80 nm there is a dose reduction of 1.8x for lead isopropylxanthate compared to lead cyclohexylxanthate. These results show we have chemical control of the exposure dose. We have found that while the electron beam is exposing the molecule, the carbon bonds are being broken up via the scission process and it diffused out the film to form gases of CO and CO_2, reducing the molecule to form PbS, this is demonstrated by Figure 3b as the band gap has greatly been reduced from a direct band gap of 3.4 to 1.15 eV. We will present XPS analysis of this process.

Monte Carlo simulations are to be implied to further characterise these materials for secondary electron pathways[2,3] as well as demonstrating full photodetector and electrical characterization.

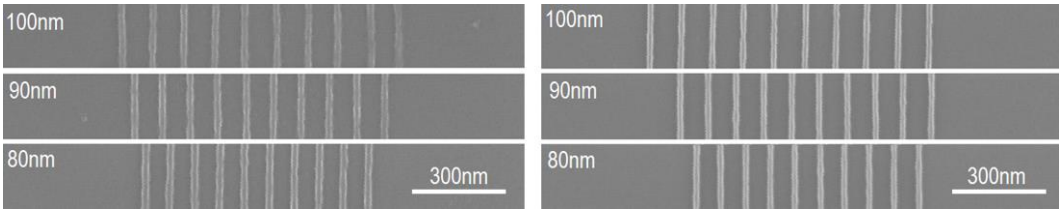
[1] J. M. Clark et al., *Dalton Trans*., 2011, **40**, 6893–6900.
[2] S. M. Lewis et al., *Angew. Chem. Int. Ed.* 2017, **56**, 6749.
[3] S. M. Lewis, et al., *Nano Lett.,* 2019, **19**, 6043.



(a)

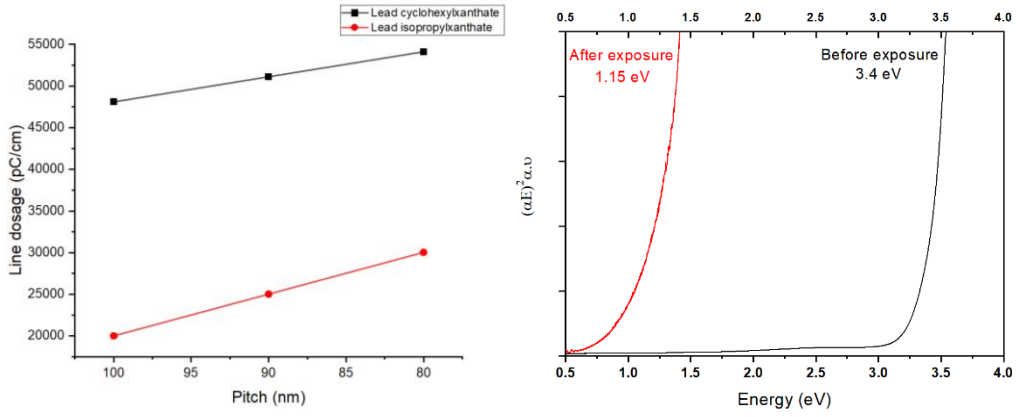
(b)

Figure 1: (a) Lead cyclohexylxanthate, (b) Lead isopropylxanthate: The structure of the molecules in a crystal, in ball-and-stick representation. Pb atom is black, S atom is green,C atoms are grey, and O atoms are red. H atoms are omitted for clarity.



(a) *(b)*

Figure 2: (a) Patterned lead cyclohexylxanthate resist. (b) Patterned Lead isopropylxanthate resist. Both films were developed for 10 seconds in Tert-butyl methyl ether. Both materials were exposed using 30 KV acceleration voltage, a current of 35 pA and step size was 4 nm.



(a) *(b)*

Figure 3: (a) Line dosage vs pattern resolution for lead cyclohexylxanthate and isopropylxanthate. (b) Band gap of lead isopropylxanthate before and after exposure with electron beam.