Development of hybrid gas-source MBE to make thin films of sulfide perovskites and related complex chalcogenides

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Ternary sulfides and selenides in the distorted-perovskite and related structures ("complex chalcogenides") are predicted by theory to be semiconductors with band gap in the visible-to-infrared and may be useful for optical, electronic, and energy conversion technologies [1-4]. We will present progress towards growing films of complex chalcogenides by hybrid gas-source MBE, including thermodynamic modeling and gas-source optimization.

We use computational thermodynamics to predict the pressure-temperature phase diagrams for select chalcogenide perovskites [5-6]. We highlight the windows of thermodynamic equilibrium between solid chalcogenide perovskites and the vapor phase. For $ABCh_3$ (*Ch* = S, Se) materials with B = transition metal, the growth windows lie at very high temperature and low pressure (*e.g.* $T > 1000$ °C and $P < 10^{-9}$ torr) that are challenging for most MBE chambers. The growth window becomes much more accessible for materials for which the quasi-binary phase diagram includes a compound (*e.g.* SnS) with high vapor pressure.

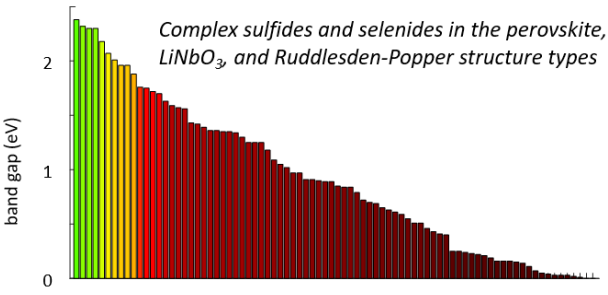

Figure 1: Survey of theoretically-predicted band gap of complex chalcogenides. Colors approximate band gap values in the visible, from $Ca_3Hf_2S_7$ (green) to $CaSnS_3$ (red). Materials with band gap below the visible (near-IR to metallic) are represented as dark red.

We then report on the effect of hydride gas source placement in our growth chamber on the growth of chalcogenide films using hydrogen sulfide (H_2S) and hydrogen selenide (H_2Se) gas sources. Taking a cue from the history of complex oxides, we hypothesize that the location of the gas injectors is quite important for optimizing film growth, more so than the chamber growth pressure read by a remote pressure gauge. We test this hypothesis by measuring gas cracking by a heated substrate and the growth of binary sulfides MoS_2 for two different gas injector positions. We support our experimental measurements by Monte Carlo simulations of gas flow in our chamber. The results highlight the importance of gas source location for optimized hybrid MBE.

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