ABSTRACT

With the rearing of a global energy crisis and the ever-exacerbating effects of climate change, the need to supplant fossil fuels with renewable energies, including solar photovoltaics, has never been more apparent than now. Silicon-based PV continues to lead the market with continuing advancements to device architecture pushing efficiencies ever closer to the single-junction ceiling. To surpass this limit, the next generation of solar generators must adopt tandem or multi-junction structures. Thin-film absorbers are poised to fit into this next wave of PV, and through solution-processing low-cost, high-throughput manufacturing may be realized, improving access to solar energy and limiting the impact of its production.

The $(Ag,Cu)(In,Ga)(S,Se)_2$ material system has been well studied, with it's tunable bandgap and relative ease of formation making it ideal for tandem architectures. Solution-processed films of this material are commonly produced using the amine-thiol reactive solvent system to coat a nanocrystalline $(Ag,Cu)(In,Ga)S_2$ precursor film which is then selenized. Absorber layers prepared in this way are plagued by a fine-grained layer which has been connected to carbon impurities and the sulfide-to-selenide conversion process. Selenide absorber layers have been coated directly from the amine-thiol system, but contain trace carbon and sulfur and have exhibited poor performance.

Alkylammonium polyselenides are species derived from the amine-thiol system and are notably sulfur-free. When dissolved in an organic solvent, they can be used to facilitate the reactive dissolution of a host of metal species. Using this chemistry, low-carbon, sulfur-free precursor solutions were formulated and used to cast fine-grain-free $CuInSe_2$ absorber layers. These polyselenide films were compared to past amine-thiol selenide precursors, and their morpholoigcal evolutions during grain coarsening were studied in-depth. Photovoltaic devices were prepared from the polyselenide precursors, showing a peak efficiency of 11.2%, a 9.4% improvement over previously reported selenide precursors. By iterating upon the synthesis of alkylammonium polyselenides, an aqueous ammonium polyselenide analogue was prepared using a biphasic solvent system to passively separate organics and inorganics. Using

this completely carbon- and sulfur-free species, Copper- and Zinc-selenium binaries were prepared, and syntheses of $CuInSe_2$ nanoparticles and molecular precursors were attempted.

Through modeling of the heat and mass transfer during film selenization, a quantitative understanding of selenium flux and thermal gradients has been achieved. In this work, the impact of selenium flux is studied over a range of temperatures and past relationships were verified under different conditions. Previously unobserved relationships between the selenium flux and selenization duration or sodium doping were shown. Insights from these experiments were applied back to the the amine-thiol selenide precursors, realizing a peak efficiency of 8.6% from the 1.8% device that was previously reported, with stark improvements in the photoluminescence and short-circuit current.

Experimental selenizations were performed using a sealed system to maintain a low-pressure selenium vapor phase. The vapor pressure and stoichiometry of selenium vapor was estimated up to saturated conditions by fitting reported experimental data. By using Cu-rich precursor films and carefully tuning the system pressure and temperature, the effects of a CuSe liquid phase vs a Se liquid phase on film morpholgy were investigated. Conditions favorable to rapid sintering were shown to limit the formation of $MoSe_2$ at the film-substrate interface. Enhanced morphology of Cu-poor films was demonstrated with a multi-micron thick film comprised of top-to-bottom grains and no fine-grained layer.

Last, the synthesis of $CaLa_2S_4/\gamma\text{-}La_2S_3$ is described. $CaLa_2S_4$ is a ceramic window material of interest, with transparency in the range of 8-14 μm. Typically formed via high-temperature sulfurizations, 650°C is the lowest reported synthesis temperature, yielding a phase-impure product. Organometallic precursors were modified by a CS_2 insertion reaction and used to prepare Ca-poor $CaLa_2S_4$ nanoparticles, containing only trace CaS, at 300°C, the lowest temperature synthesis reported to date.