

ABSTRACT

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Title: Synthesis and Characterization of Copper Arsenic Sulfide for Solution-Processed Photovoltaics

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Global warming poses an existential threat to humanity and is inevitable unless significant efforts are made to eliminate its root causes. The need to replace fossil fuels with renewable energy resources has been obvious for many years, yet the world still sources the vast majority of its energy from non-renewable reservoirs. Harnessing solar radiation is the most promising route to ensure a carbon-free energy future, as the sun is the sole source of energy that can meet humankind's energy demands for generations to come.

The most widely recognized technology associated with the sun is a photovoltaic (PV) cell, which converts electromagnetic radiation directly into electricity that can either be used immediately or stored for later use. Silicon-based solar cells currently dominate (>90% market share) the global PV market, driven in part due to parallel research on wafer purification and fabrication techniques for the microelectronics industry. However, silicon is an indirect bandgap material, resulting in thick and inflexible PV modules, and it requires high capital expenditures and high energy inputs for terawatt scale manufacturing.

The remainder of the commercial PV market consists of thin-film technologies based on Cu(In,Ga)Se_2 (CIGSe) and CdTe. These materials have a direct bandgap, so they can be used in flexible applications, and they are readily scalable due to their amenability to low-cost, roll-to-roll manufacturing. The power conversion efficiencies of CIGSe and CdTe cells have exceeded 20% and are nearing those of silicon cells, but concerns over the long-term supply of indium and tellurium cast doubt on whether these materials can be deployed at large scales. Alternative materials, such as $\text{Cu}_2\text{ZnSnS}_{4-x}\text{Se}_x$ (CZTSSe), have been researched for many years; the allure of a material with earth abundant elements and properties similar to CIGSe and CdTe was quite enticing. However, recent work suggests that CZTSSe is fundamentally limited by the formation of defects and band tails in the bulk material, and the efficiencies of CZTSSe-based devices have been saturated since 2013.

New materials for the PV market must meet several criteria, including constituent earth abundant elements, outstanding optoelectronic properties, and low propensity to form defects. In this regard, the copper-arsenic-sulfur family of materials is an attractive candidate for PV applications. Cu, As, and S are all earth abundant elements with sufficiently different ionic radii, suggesting high defect formation energies. In addition, previous computational work has suggested that several ternary phases, most notably enargite Cu_3AsS_4 , have appropriate bandgaps, high absorption coefficients, and high predicted efficiencies in a thin-film PV device. The system must be investigated experimentally, with attention not only paid to synthesis and device performance, but also to characteristics that give clues as to whether high efficiencies are actually achievable.

This dissertation studies the Cu-As-S system in the context of thin-film photovoltaics, with an emphasis on Cu_3AsS_4 and detours to related materials when appropriate. The first synthesis of Cu_3AsS_4 thin-films is reported using solution-processed nanoparticles as precursors. Initial device efficiencies reach 0.18%, which is further boosted to 0.35% through optimization of the annealing procedure. Several limitations to the initial approach are identified (most notably the presence of a carbonaceous secondary phase) and addressed through post-processing treatments and ligand exchange. Cu_3AsS_4 is also rigorously characterized using a suite of optoelectronic techniques which demonstrate favorable defect characteristics that motivate continued research. The current limitations to Cu_3AsS_4 performance stem from improper device architecture rather than material properties. Further development of Cu-As-S thin film devices must focus on identifying and fabricating ideal device architectures in parallel with continued improvements to the optoelectronic properties and quality of the Cu_3AsS_4 absorber layers.

This dissertation ultimately demonstrates high promise for Cu_3AsS_4 as a thin-film PV material. It also may serve as an example for other researchers studying new materials, as the examination of fundamental optoelectronic properties early in the material's development phase is key to ensure that limited scientific resources are invested into the compounds with the highest potential impact on society.