

# **Pure sulfide kesterite solar cells with cation substituted absorber and back contact intermediate layer**

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Chalcopyrite Cu(In,Ga)Se<sub>2</sub> (CIGS) and CdTe thin film solar cells have the potential to reduce the cost of the photovoltaic (PV) technology. They showed high power conversion efficiency (PCE) of more than 20% shrinking the gap between them and champion crystalline Si solar cell. Despite of high efficiency and ease of fabrication, application of CdTe PV technology is limited due to toxicity of Cd and scarcity of Te. In contrast, CIGS does not contain toxic elements. However, a high demand for In from flat panel display industry along with its limited availability results in increasingly high cost of In. The commercial success of CIGS solar cells has brought much attention to earth abundant, non-toxic and low cost kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) where In and Ga are replaced with Zn and Sn. The similar electronic and optical properties of these adamantine semiconductor materials enable CZTS solar cells to inherit the device structure of CIGS solar cells. CZTS is an intrinsic p-type semiconductor with a direct bandgap of about 1.5eV and high absorption coefficient of  $>10^4 \text{ cm}^{-1}$  for visible wavelengths. Bandgap of Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> can be tuned from 1eV to 1.5eV by changing S/(S+Se) ratio from 0 to 1 which provides a degree of flexibility in device fabrication with the material.

There is still a large difference in PCE (~12%) between the best pure sulfide chalcopyrite and kesterite solar cells. First, solid state reaction occurs at the back interface between CZTS absorber layer and Mo back contact during high temperature sulfurization. S diffuses into Mo to form resistive MoS<sub>2</sub>. In addition, as a result of the reaction, CZTS may decompose into secondary phases such as ZnS, Cu<sub>2</sub>S and volatile SnS causing void formation. Second, a large open-circuit voltage deficit limits performance of the kesterite solar cells. Similar size of Cu and Zn cations in CZTS facilitates cation disordering and formation of detrimental defects causing charge recombination.

In this thesis, effect of sputter-deposited TaN, ZnS and CuO intermediate layers (IL) on the quality of the back interface of solar cells with pure sulfide kesterite absorber layer was studied in detail. The novel IL were used to slow down the back interface reaction and control crystal quality of kesterite absorber layer. It has been found that interfacial MoS<sub>2</sub> thickness between sputtered Cu-poor CZTS and Mo can be effectively controlled using TaN IL. When 12nm TaN IL is present, no continuous MoS<sub>2</sub> is observed using scanning transmission electron microscopy (STEM) after sulfurization at 600°C for 10 min. Incorporation of 10nm ZnS IL at the interface between solution-processed Cd-substituted CZTS (CZCTS) and Mo enhances CZCTS grain growth and suppresses

void formation. Moreover, deposition of the ZnS IL does not cause increase of MoS<sub>2</sub> thickness. Positive effect of the ZnS IL incorporation was observed for both solution-processed CZCTS and CZTS solar cells prepared by co-sputtering of ZnS, SnS and Cu targets. PCE of solution-processed CZCTS solar cells was enhanced from 9.5% to 10% as a result of 10nm ZnS IL layer insertion. A higher PCE of 10.8% was achieved for solution processed CZCTS solar cells using CuO IL incorporation. Insertion of the optimized 4nm CuO IL resulted in enhancement of short-circuit current density ( $J_{sc}$ ) while open-circuit voltage ( $V_{oc}$ ) and fill factor (FF) were almost constant. Moreover, further increase of CuO IL thickness enables to get as high  $J_{sc}$  as 28.5 mA/cm<sup>2</sup>. To the best of my knowledge, this is the highest reported  $J_{sc}$  for pure sulfide CZCTS solar cells. In addition, increased carrier lifetime in absorber is observed for 32nm CuO IL. It has been found that absorbance is increased with CuO IL. Moreover, CZCTS/CdS devices with CuO IL demonstrate improved stability of PCE.

To address the problem of the absorber layer quality, impact of Mo on sputtered CZTS thin films was studied. Mo was found to be a dopant for CZTS enabling to tune CZTS resistivity in a wide range. Mo shows graded concentration profile in CZTS resulting in internal electric field. In addition, it has been revealed that Mo incorporation enables to enhance absorbance of CZTS thin films while not affecting bandgap of CZTS based on measured external quantum efficiency spectra. Mo incorporation into CZTS results in reduced lattice parameters suggesting Sn substitution. Furthermore, Mo incorporation in CZTS demonstrates a substantial effect on the photovoltaic performance of the solar cells prepared by sputtering of quaternary compound Cu-poor CZTS target. When optimized Mo co-sputtering power is applied, PCE of CZTS solar cell is increased from 1.6% to 5.5%.

In addition, effect of carbon (C) incorporation in sputtered CZTS and Cu doped ZnS (ZnS:Cu) thin films was investigated. It has been found that optimized content of C facilitates growth of CZTS crystallites and reduces void formation. Furthermore, an increase of CZTS lattice parameters is observed suggesting formation of interstitials by incorporated C atoms. As a result of C incorporation, resistivity of CZTS thin films decreases by 1-3 orders of magnitude while measured bandgap is tuned in the ranged from 1.39eV to 1.6eV. Sulfurization of C deposited on co-sputtered ZnS:Cu leads to a blend of doped ZnS and CuS with a wide bandgap, high hole concentration and low resistivity. Moreover, formation of copper sulfide phase is suppressed while formation of ZnS is enhanced with increase of C content in p-type ZnS:Cu thin films resulting in increase of its bandgap from 3.2eV to 3.6eV. Furthermore, the addition of C in sputtered ZnS:Cu thin films enables reduction of tail states through defects passivation.