ABSTRACT

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Degree Received: May 2017
Title: Development of Novel Solution Processing Routes to High Efficient Metal Chalcogenide Thin-Film Solar Cells
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Metal chalcogenide thin films offer a pivotal opportunity to provide low-cost photovoltaic (PV) modules to replace use of conventional energy sources. The thin-film PV technology based on $Cu(In,Ga)Se_2$ (CIGSe) layers has been the focus of extensive investigation due to their direct bandgap, high optical absorption coefficients, high tolerance of defects and impurities, and tunable bandgap. The quality of the CIGSe films strongly depends on the deposition techniques used. Current state-of-art deposition methods for high efficiency CIGSe devices are mainly based on vacuum-based methods such as sputtering or co-evaporation from elemental sources. However, these techniques exhibit limitations during industrial scale-up and cost reduction. In that respect, solution processing and deposition of inorganic semiconductors is often promoted as alternative approaches to reduce capital equipment costs, offer high throughput processing and eventually reduce the PV module prices.

Here, three innovative solution processing methods for the fabrication of CIGSe photovoltaic devices are developed:

1) Mesoparticle ink-based method: $Cu(In,Ga)S_2$ (CIGS) and CIGSe mesoparticle are synthesized for the first time. These mesoparticles show better uniformity, higher crystallinity and less defect compared with the CIGS/CIGSe nanoparticles in literature. $Cu(In,Ga)(S,Se)_2$ (CIGSSe) solar cells based on the mesoparticle inks are fabricated with power conversion efficiencies up to 12.6 %.

2) Molecular precursor solution based method: we demonstrate a versatile monoamine-dithiol mixture which possesses the remarkable ability to rapidly dissolve a variety of metal salts and metal chalcogenides under ambient conditions for the fabrication of device quality CIGSe films. Using the soluble precursors, a CIGSe solar cell with an efficiency of 12.2 % has been fabricated, which is the highest reported value for solar cells using an amine-thiol solvent system. Then a

detailed research of the metal dissolution mechanism in amine-thiol solution is conducted. Metal thiolates, as the reaction products, are separated from the amine-thiol solution and dissolved in other low toxic and weakly coordinating solvents for a novel molecular precursor processing route, which significantly reduces the impurities in the absorber layer and improve the film quality.

3) Particulate-solution hybrid method: a hybrid approach combining the benefits of the molecular precursor solution process with the CIGSe nanocrystals ink process is developed. Here, CIGSe nanoparticle films are found to be able to coarsen into densely packed large grains after being infiltrated with a cation molecular precursor solution. This method solved the problem that CIGSe nanoparticle film cannot coarsen even at high temperature (> 500 ^{o}C), and increases the efficiencies of the nanoparticle ink-based CIGSe solar cells from 0 % to 11.50 %.

All three methods achieved well controlled composition uniformity at mesoscale or molecular level, and have exceeded 11 % solar-power conversion efficiency. These methods enable uniform deposition over large areas and overcome many of the disadvantages of established solution-processing approaches. They are versatile and can be adapted for the fabrication of thin films and semiconductor devices based on other metal chalcogenide materials.