ABSTRACT

Graeser, Brian K. PhD, Purdue University, May 2017. Development of New Materials and processing Techniques for Photovoltaic Devices. Major Professor: Rakesh Agrawal.

Renewable energy sources are vital part of the future. As fossil fuel resources start to dwindle a new source must meet the worlds energy demand. Due to its abundance, solar energy is poised to be this new source. Currently, there are many technologies being investigated. Each of these though has their own draw backs, and none of them have been able to surpass fossil fuels in the current marketplace. Investigating new materials provides new opportunities for a better solar cell. These new materials could be the key to pushing renewable energy ahead of fossil fuels. I have explored two different absorber materials, the first is an alloy of zinc selenide and copper indium selenide (CIZSe). This material represents a new class of materials based on alloying two different materials together. Earlier examples of alloying are replacing one or two elements in a material with other from the same group. This can be used to modify the band gap, but it does not change the crystal structure. CZISe does not have this limitation though. As solar cell absorber materials, alloys of $CuIn(S,Se)_2$ and Zn(S,Se) provide an opportunity to reduce the usage of indium along with the ability to tune the band gap. I have developed a successful synthesis of alloyed $(CuInS_2)_{0.5}(ZnS)_{0.5}$ nanocrystals by a method that solely uses oleylamine as the liquid medium for synthesis. These nanocrystals are used to make inks that are doctor bladed onto substrates. The reactive sintering of a thin film of these nanocrystals via selenization at 500 C results in a uniform composition alloy $(CuIn(S,Se)_2)_{0.5}(Zn(S,Se))_{0.5}$ layer with micron size grains. Due to the large amount of zinc in the film, the sintered grains exhibit the zinc blende (sphalerite) structure instead of the usual chalcopyrite structure of

$CuIn(S,Se)_2$ films. The use of the selenide films as a p-type absorber layer has yielded solar cells with total area power conversion efficiencies as high as 6.7% (7.4% based on active area). These preliminary results are encouraging and indicate that with further optimization this class of materials has promise as the absorber layer in solar cells. The second material is copper selenophosphate (Cu_3PSe_4). This material uses earth abundant cations similar to copper zinc tin selenide. Exploring the group V elements for use in solar cells could prove to be a exiting and promising new area for solar absorber research. There has been some theoretical work done on some of these materials and they are predicted to be quality absorbers. The main issue facing this field has been the lack of good synthesis methods. My research into this area has about that. I have tried both molecular precursor routes as well as nanocrystal methods. These solution based routes provide a scalable synthesis option to the previous methods of making these materials. The nanocrystal route has shown significant progress. I can currently make Cu_3PS_4 nanocrystals, via a simple thermal method. I have expanded beyond just know a single reaction setup that will produce pure phase Cu_3PS_4, to know exactly which conditions direct the synthesis products. The key factor is the state of the phosphorus precursor. The dissolved P_2S_5 leads to the formation of Cu_6PS_5Cl, and the solid P_2S_5 leads to the formation of Cu_3PS_4. Using reaction conditions where the copper and phosphorus source are added together, the Cu_3PS_4 nanocrystals can be formed faster than the dissolution can remove all of the P_2S_5. If the P_2S_5 is dissolved ahead of time, then the reaction will only produce CU_6PS_5Cl. This leaves a very narrow window of conditions that will produce pure phase Cu_3PS_4. The final major development has been the selenization of Cu_3PS_4. A method has been developed where the sulfide nanocrystals can be converted to the selenide phase and achieve significant grain growth. This is the first time this type of procedure has been done with this material. The issue that is holding it back from getting functional photovoltaic deives is the film morphology. The grains produced in this method, do not form a contiguous film. Instead they form isolated grains, that are often elongated. If this issue could be solved, then the first device could be made from this material.