Na-assisted grain growth in CZTS nanoparticle thin films for solar cell applications

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We have studied the effect of Na in Cu2ZnSnS4 nanoparticle thin films [1]. The as-synthesized CZTS nanoparticles were inherently ligand-free [2], which allows us to use of polar solvents, such as water and ethanol. Another advantage of these particles is that the user- and environmentally-friendly NaCl salt can be directly dissolved in controllable amounts. This further circumvents the need for later incorporation of dopants, or a ligand-exchange step to functionalize the surface of the nanoparticles. In addition, the homogeneous distribution of Na in the ink allows uniform grain growth within the deposited absorber layer. By including Na in the nanoparticle ink, micron-sized grains throughout the whole absorber are achieved after annealing in a sulfur atmosphere at 600°C. The absorber layer appeared to be of full density, and no closed porosity could be detected. In addition, the photoluminescence signal increased by a factor of 200 after Na-inclusion.

Without Na, the grains were very difficult to sinter, the film was porous, and the photoluminescence was low. A concentration of Na/(Cu+Zn+Sn)=30% was necessary for the densification of the absorber, which is significantly higher than that used in other Na-doped CZTS systems. The annealed films were found to be of the desired Cu-poor and Zn-rich composition. We also found that a sulfidation temperature above 550°C was required. At 550°C, NaCl-crystals appeared on the surface of the thin films, suggesting an incomplete transformation of Na into the liquid phase Na2Sx-additive during sintering. At this temperature, grain growth was only detected in close proximity to the NaCl regions. It was also observed that the NaCl crystals could be easily removed by a quick water rinse, but that this treatment reduced the photoluminescence signal. This is relevant as it is customary to leave the absorber layer in a water-based solution after annealing before buffer layer deposition.