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Annealing in sulfur of CZTS nanoparticles deposited through doctor blading

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Solar cells made from nanoparticles of copper zinc tin sulfide (CZTS) from solution-processing are expected to be comparatively inexpensive, but their efficiency is still low compared with cells produced by vacuum processing. However, (1) the high carbon content in nanoparticle thin films is one of the main limitations for this approach, and (2) grain boundaries and defects are believed to be a site for recombination that limit the efficiency. Annealing in vacuum and/or nitrogen atmosphere facilitates grain growth and improves the electronic properties. Conventionally selenization shows the best results, however sulfurization has the advantage of being less toxic.

In this work, nanocrystals of CZTS with a targeted Cu-poor/Zn-rich composition are synthesized through a hot-injection method with oleylamine as the solvent. The nanocrystal inks are deposited through doctor blading in octanethiol, and annealed in a vacuum furnace using a graphite box with sulfur. The surface morphology and thus grain growth is studied for various annealing conditions in vacuum at 10^{-5} mbar or up to 10 mbar nitrogen atmosphere and with a varying amount of sulfur content.

The films are characterized in terms of their optical and electronic properties before and after annealing. The effect of S content on grain growth is studied, and the topographic changes (i.e. grain size and morphology) are characterized with bidirectional reflectance distribution function (BRDF) and compared to surface profiling from atomic force microscopy (AFM) and scanning electron microscopy (SEM) images. Raman spectroscopy is used to examine the sulfur distribution between the surface and the bottom of the film. Compositional changes are monitored by energy dispersive X-ray spectroscopy (EDX) and the crystallinity by X-ray diffraction (XRD).

A photovoltaic device of the structure soda lime glass (SLG)/Mo/CZTSSe/CdS/ZnO:Al/Ag has been built, and our preliminary results show a power conversion efficiency of 1.41% for the nanoparticles annealed in selenium.

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