BAPVC Annual Project Report

Project Title: In Situ Characterization of Grain Growth in Thin Film Semiconductors

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Summary:
This project focuses on the development of thin film absorbers from a solution-processed nanocrystal of multicomponent copper chalcogenide-based compound semiconductor such as CIGS, CZTS and CIS. The nanocrystals film can be subsequent transformed into large grain thin film by thermal annealing. The group is deliberately making nanocrystal with hexagonal phase (Wurtzite), which is a metastable structure for these materials with the hope to leverage the transformation to the stable phase will trigger grain growth effectively. Further surface functionalization of these nanocrystal with elements that drive grain growth, like selenium and sodium, thereby result in "in situ selenization" upon annealing. Thin film growth during thermal annealing is studied by In-situ X-ray diffraction, Raman, XPS, TEM and SEM and the resulting microstructures are now being correlated with optoelectronic properties of the materials.

Key Accomplishments:
Over the last two year the group has been developing a versatile colloidal approach to synthesize high quality compound semiconductor nanocrystals [Cu_2ZnSnS_4, $CuInGaS_2$, Cu-In-Zn-S, $CuInS_2$, $Cu_2ZnSn(S_{1-x}Se_x)_4$, etc.] with tight control of shape, size, composition and crystal phase. Specifically, the group has developed a synthesis in which the shape (spherical and rod) and crystal structure of nanocrystals is precisely controlled by reaction conditions – the novelty of this work was the synthetic achievement of hexagonal Wurtzite phase alloyed copper chalcogenide (CIGS and CZTS), which is a metastable structure for these materials. The group has experimentally demonstrated that the use of metastable phase nanocrystal helps in inducing the grain growth under thermal treatment due to metastable to stable conversion. By doing *in-situ* and *ex-situ* XRD studies, this transformation was revealed as being very fast and happening within few minutes of annealing, and thin films of absorber materials with average grain sizes up-to one micron (see Figure) can be achieved not only at low temperature but also without the need of traditional high temperature selenization process. The resulting thin films have been further analyzed with Raman, XPS, PL and SEM to understand the quality of the absorber material. During this study of grain growth using metastable nanocrystals, we have found that we can control more precisely the nucleation and growth regime during annealing by simply using different shapes (rod and sphere) of nanocrystals with similar composition. Further, we have functionalized the surface of our nanocrystals with chalcogenidometallate clusters (ChaMs) consisting of elements that drive grain growth, like selenium, thereby resulting in "*in situ selenization*" upon annealing. By controlling the nanocrystal loading in the ChaMs matrix (Figure), we have achieved not only the polycrystalline thin films with micron size grains but also compositional tunability through ion exchange process of Se with S, which is similar to high temperature selenization process. Resulting absorber material has been characterized with Raman, XRD and PL to confirm the material composition and properties.

Two papers have been published and one more submitted. We expect to publish a complete report about the phase transformation-driven grain growth later this year.

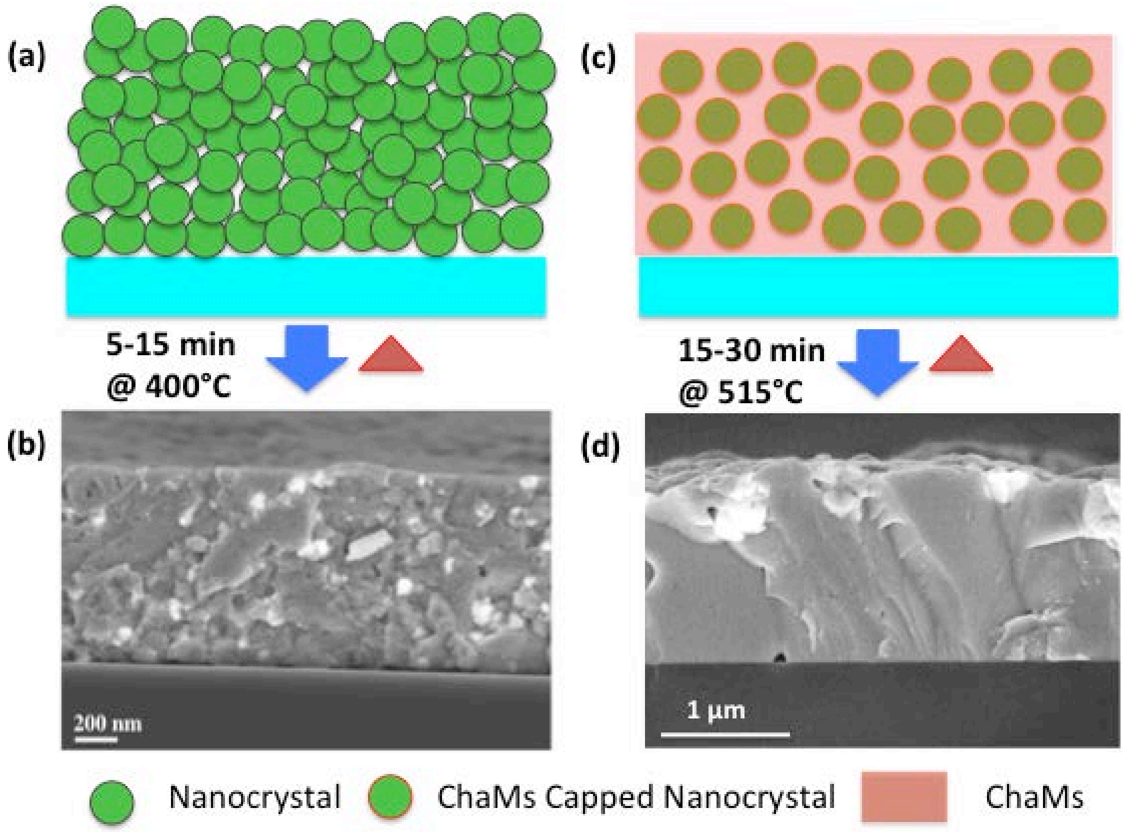

Figure. (a) & (b) Thermal treatment of a nanocrystal film containing metastable nanocrystal results in grain growth. **(c) & (d)** Surface functionalized nanocrystals embedded in a ChaMs matrix consisting of elements that drive grain growth.

Future Work:

In the coming year, we will continue our focus in optimization of film thicknesses with controlled composition and grain growth over device scale area for the fabrication of full PV devices. The optoelectronics properties (hall measurement and PL) of the resulting polycrystalline thin film deposited with and without ChaMs on the substrate will also be investigated. We will further try to introduce other dopants such as antimony in the nanocrystal (during synthesis) or on the surface through ChaMs to understand their effect on the selenization process. This will be studied by using RTP developed by Mike Toney's group at SLAC (BAPVC member) and employing their in-situ x-ray diffraction facility, which will be further accompanied with ex situ SEM analysis and Raman spectroscopy to understand the course of selenization of absorber material.