Atomic layer deposition of multi-component metal sulfides applied to thin film photovoltaics

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Multi-component alloys are a reliable solution to many materials problems. For example, the structural properties of stainless steel, an alloy of Fe, C, Cr and other metals, are vastly superior in nearly every respect compared to the elemental parent compound Fe. For structural materials, and other applications that require large production volumes such as solar cells, earth abundance is a critical factor. Despite the success of $Cu(In,Ga)(S,Se)_2$ (CIGS) as a photovoltaic absorber, the expense and relative scarcity of Ga and In has raised concerns that these elements will prevent deployment at the terawatt (TW) level. There is tremendous current excitement about copper chalcogenides based on the kesterite structure, the prototypical of which is Cu_2ZnSnS_4 (CZTS). CZTS, like CIGS, is much more stable and higher performance than the binary parent compound Cu_2S. CZTS is based on low cost and relatively abundant elements. Devices based on the CZTS platform have reached efficiencies of ~ 10% in the laboratory. There is much promise, but more work is necessary to claim high efficiency in addition to low cost and earth abundance. The power conversion efficiency of the absorber layer is intimately related to its synthetic processing, which currently is not optimized or well understood.

CZTS thin films are currently synthesized by two general approaches, both of which require two-stage processing. In the first stage, a thin film “precursor” is deposited onto the substrate, which is then subjected to a high temperature treatment for grain growth in the second stage. In the first synthesis approach, the precursor has the incorrect metal to sulfur ratio (e.g. metallic), and it is reacted with sulfur in the second stage. The alternative second synthetic approach is to start with a precursor having the correct metal to sulfur ratio, for example $CuZnSnS_4$ nanoparticles or $Cu_2S/SnS_2/ZnS$ thin film stacks. Then the precursor simply needs to be mixed, while preventing decomposition, to form a continuous CZTS film in the second stage. We will focus on the second synthetic approach since it is not complicated by chemical reaction during the second stage.

Atomic layer deposition (ALD) is an ideal method to synthesize the metal sulfide precursor to study solid state mixing and grain growth. Beyond fundamental research, the ability to deposit conformal semiconductor photovoltaic absorber layers is a boon to the nascent nanostructured solar cell community. I will discuss our ALD process for synthesizing metal-sulfide precursor stacks of Cu_2S, SnS_2 and ZnS, which exhibits a rich surface chemistry. One of the attractions of ALD is that it forms smooth films over large areas, and so roughness does not limit the resolution of depth profile measurements by secondary-ion mass spectrometry (SIMS). Thus we can study the evolution of the composition profile to gain fundamental insight into the processes occurring during the high temperature mixing stage. Smooth films of precisely known thickness (exclusively available through ALD) also allow accurate determination of the sputtering rate under carefully controlled conditions in the SIMS apparatus. We propose that the sputtering rate from SIMS depth profiles can be used to determine the surface binding energy of atoms in polycrystalline CZTS thin films, which can then, in principle, be used to calculate the lattice cohesive energy and enthalpy of formation. To our knowledge, these important fundamental parameters have not been determined experimentally for CZTS.