Unveiling the Amine-Thiol Molecular Precursor Chemistry for Fabrication of Semiconducting Materials

by

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Inorganic metal chalcogenide materials are of great importance in the semiconducting field for various electronic applications such as photovoltaics, thermoelectrics, sensors, and many others. Compared to traditional vacuum processing routes, solution processing provides an alternate cost-effective route to synthesize these inorganic materials through its ease of synthesis and device fabrication, higher material utilization, mild processing conditions, and opportunity for roll-to-roll manufacturing. One such versatile solution chemistry involving a mixture of amine and thiol species has evolved in the past few years as a common solvent for various precursor dissolutions including metal salts, metal oxides, elemental metals, and chalcogens.

The amine-thiol solvent system has been used by various researchers for the fabrication of inorganic materials, but without the complete understanding of the chemistry involved in this system, utilizing its full potential, and overcoming any inherent limitations will be difficult. So, to identify the organometallic complexes and their reaction pathways, the precursor dissolutions in amine-thiol solutions, specifically for elemental metals like Cu, In and chalcogens like Se, Te were studied using X-ray absorption, nuclear magnetic resonance, infrared, and Raman spectroscopy along with electrospray ionization mass spectrometry techniques. These analyses suggested the formation of metal thiolate complexes in the solution with the release of hydrogen gas in the case of metal dissolutions confirming irreversibility of the dissolution. Insights gained for chalcogen dissolutions confirmed the formation of different species like monoatomic or polyatomic clusters when different amine-thiol pair is used for dissolution. Results from these analyses also identified the role of each component in the dissolution which allowed for tuning of the solutions by isolating the complexes to reduce their reactivity and corrosivity for commercial applications.

After identifying complexes in metal dissolution for Cu and In metals, the decomposition pathway for these complexes was studied using X-ray diffraction and gas chromatography mass spectrometry techniques which confirmed the formation of phase pure metal chalcogenide material with a release of volatile byproducts like hydrogen sulfide and thiirane. This allowed for the fabrication of impurity-free thin-film Cu(In,Ga)S_2 material for use in photovoltaic applications.

The film fabrication with reduced carbon impurity achieved using this solvent system yielded a preliminary promising efficiency beyond 12% for heavy alkali-free, low bandgap $CuInSe_2$ material. Along with promising devices, by utilizing the understanding of the chalcogen complexation, a new method for $CuInSe_2$ film fabrication was developed with the addition of selenide precursors and elemental selenium which enabled the first-ever fabrication of a solution-processed $CuInSe_2$ thin film with thickness above 2 μm and absence of any secondary fine-grain layer.

Along with thin-film fabrication, a room temperature synthesis route for lead chalcogenide materials (PbS, PbSe, PbTe) with controlled size, shape, crystallinity, and composition of nanoparticle self-assemblies was demonstrated. Micro-assemblies formed via this route, especially the ones with hollow-core morphology were subjected to a solution-based anion and cation exchange to introduced desired foreign elements suitable for improving the thermoelectric properties of the material. Adopting from traditional hot injection and heat up synthesis routes, a versatile synthesis procedure for various binary, ternary, and quaternary metal chalcogenide (sulfide and sulfoselenide) nanoparticles from elemental metals like Cu, Zn, Sn, In, Ga, and Se was developed. This new synthesis avoids the incorporation of impurities like O, Cl, I, Br arising from a traditional metal oxide, halide, acetate, or other similar metal salt precursors giving an opportunity for truly impurity-free colloidal metal chalcogenide nanoparticle synthesis.