

## **Project 14: Novel Homojunction Thin-film Photovoltaic Devices Based on Nanostructured Cu(In,Al)S<sub>2</sub> Materials Synthesized Using an Innovative Colloidal Method**

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### **Introduction**

In the actual energetic and environmental context, in Canada and elsewhere throughout the world, the development of green energy technologies, like solar energy, should be accelerated. Ternary compounds from the I-III-VI<sub>2</sub> family, especially CuInSe<sub>2</sub> and CuInS<sub>2</sub>, have been considered for photovoltaic applications by the scientific community because of their interesting optical properties. CuInS<sub>2</sub> has a favorable direct bandgap energy of 1.5 eV<sup>1</sup> (827 nm), which matches closely the solar spectrum, and an absorption coefficient of 10<sup>5</sup> cm<sup>-1</sup> (at 730-750 nm)<sup>2</sup>, which allows for greater than 99% of the incident photons to be absorbed within the first micron of the material. Therefore, less expensive thin films may be used. Furthermore, CuInS<sub>2</sub> is less toxic than CuInSe<sub>2</sub>. Depending of the Cu/In ratio, it displays a *n*-type (Cu/In < 1) or a *p*-type (Cu/In > 1) semiconductivity. Meese et al. suggested that CuInS<sub>2</sub> has a theoretical conversion efficiency up to 30%,<sup>3</sup> making it an interesting semiconductor for photovoltaic applications. CuInS<sub>2</sub> is mainly used in solid-solid photovoltaic cells, such as Mo|*p*-CuInS<sub>2</sub>|*n*-CdS|ZnO, which provide an efficiency of about 10%.<sup>4,5</sup> Commonly, this type of device can achieve a maximum efficiency of about 20% for laboratory scale cells.<sup>6</sup>

Several synthesis methods of CuInS<sub>2</sub> have been reported, such as RF sputtering,<sup>7</sup> reactive magnetron sputtering,<sup>5</sup> flash evaporation,<sup>8</sup> electrodeposition,<sup>9</sup> single and double-source evaporation,<sup>10,11</sup> chemical spray pyrolysis,<sup>12</sup> molecular beam epitaxy,<sup>13</sup> and heat treatment of Cu-In alloys<sup>14</sup> or of Cu<sub>2</sub>In<sub>2</sub>O<sub>5</sub><sup>15</sup> in H<sub>2</sub>S. Most of these methods yield CuInS<sub>2</sub> with *p*-type semiconductivity. Therefore, the control of stoichiometry is a major difficulty in the synthesis of ternary materials. Recently, a novel (patented) and simple method to synthesize nanocrystalline *p* and *n*-type CuInS<sub>2</sub> particles has been discovered in Prof. Marsan's laboratory<sup>16</sup>. This method is based on the use of a complexing solvent to dissolve the three precursors that are afterwards mixed together in an appropriate order and under certain conditions to obtain the semiconducting crystals. After filtration, a low temperature annealing step is necessary to increase the material crystallinity. This new method is already able to produce particles (dia~20 nm) with a high degree of crystallinity. In order to decrease the content of In in the material (and hence its cost) and to increase the cell efficiency, we propose to prepare *p* and *n*-type Cu(In,Al)S<sub>2</sub> particles of various compositions (Cu/In and In/Al atomic ratios). Indeed, Cu(In,Al)S<sub>2</sub> has been reported to give solar cells more efficient than when CuInS<sub>2</sub> is used (16% vs 12%)<sup>17</sup>. Interestingly, the possibility of preparing Cu(In,Al)S<sub>2</sub> with both conduction types allows us to replace the conventional and toxic CdS *n*-type layer in the cell architecture.

This project aims at developing low-cost, highly efficient and stable thin-film photovoltaic (PV) cells based on the junction between *p* and *n*-type nanostructured Cu(In,Al)S<sub>2</sub> semiconductors synthesized using our colloidal method. This unconventional PV architecture will take advantage of the very interesting possibilities offered by this novel synthetic method. More specifically, the objectives of the research are: (i) modification and optimization of the original synthesis method, optimized to obtain *n*-type Cu(In,Al)S<sub>2</sub> particles, to obtain *p* and *n*-type nanosized

semiconducting Cu(In,Al)S<sub>2</sub> materials with the appropriate chemical, morphological, crystallographical, optical, electrical and charge carrier transport properties, compatible with the establishment of a high quality homojunction; (ii) deposition of Cu(In,Al)S<sub>2</sub> thin films (both *p* and *n*-type) on various substrates, using aerosol jet deposition technique, and optimization of the deposition parameters; (iii) preparation and optimization of the Cu(In,Al)S<sub>2</sub> *p-n* junction (successive *p* and *n* layers); (iv) fabrication, characterization (under dark, light of varying wavelengths and white light conditions) and optimization of PV devices of increasing surface area (1-100 cm<sup>2</sup>); and (v) evaluation of the device stability under white light (AM 1.5) condition at 60°C. It is anticipated that device energy conversion efficiencies above 10% will be reached.

### **Synthesis and characterization of Cu(In,Al)S<sub>2</sub> materials**

In an argon filled glovebox, N-methylimidazole (NMI) solutions of InCl<sub>3</sub>, AlCl<sub>3</sub> and CuCl are prepared and stirred. A Li<sub>2</sub>S suspension is also prepared as described elsewhere.<sup>16</sup> Appropriate volumes of the InCl<sub>3</sub> and AlCl<sub>3</sub> solutions are first added slowly to the Li<sub>2</sub>S suspension followed by several cycles of magnetic stirring and ultrasonication. A given volume of the CuCl solution is then added, producing a suspension of Cu(In,Al)S<sub>2</sub> particles that is heated and cooled to room temperature. The resulting black suspension is then filtered, rinsed and dried under vacuum. The particles are afterwards annealed at 500°C under vacuum (100 mTorr). In this project, *p* and *n*-type Cu(In,Al)S<sub>2</sub> particles of various compositions (Cu/In and In/Al atomic ratios) will be prepared and characterized.

The materials chemical stoichiometry (*bulk* [inductively coupled plasma-atomic emission spectroscopy, ICP-AES, and energy dispersive X-ray, EDX, analyses] and *surface* [X-ray photoelectron spectroscopy, XPS]), crystallographical (phases present [X-ray diffraction, XRD, and Raman spectroscopy] and crystallite size [XRD]) and morphological (particles size [scanning electron microscope, SEM, and high-resolution transmission electron microscopy, HRTEM]) properties will be determined as they influence the cell performance. The bandgap energy of the Cu(In,Al)S<sub>2</sub> materials prepared as thin films will be obtained using UV-visible spectroscopy.

### **Deposition of thin films, and fabrication and characterization of photovoltaic cells**

Since the nanostructured Cu(In,Al)S<sub>2</sub> materials can be deposited from solution, they are very attractive for PV applications (reduction of manufacturing costs). In this project, the *p* and *n*-type semiconductors will be deposited as thin films on various substrates (rigid and flexible), using the unique aerosol jet deposition system available in Prof. Izquierdo's laboratory, and the deposition parameters will be optimized (e.g., deposition rate, film thickness). In the aerosol jet printing method, the solution containing the nanoparticles is atomized to produce droplets on the order of one to two microns in diameter. The atomized droplets are entrained in a gas stream and delivered to print head where a second gas is introduced around the aerosol stream to focus the droplets into a tightly collimated beam and also to eliminate clogging of the nozzle. The combined gas streams exit the print head through a converging nozzle that compresses the aerosol stream to a diameter as small as 10 microns. Patterning is accomplished by translating a computer-controlled platen where the substrate is attached. Materials with viscosities ranging for 1 cP to 1,000 cP have been successfully atomized and deposited using aerosol jet.<sup>18</sup> Aerosol jet deposition apparatus uses lower droplet sizes than inkjet deposition system, leading to more

homogeneous films, and is less sensitive to the materials particle size and viscosity of the particles suspension that may cause problem.<sup>19</sup> The films must be uniform, adherent, crack-free, with a good electrical contact with the substrate.

We will start by depositing  $p$  type or  $n$  type  $\text{Cu}(\text{In},\text{Al})\text{S}_2$  on top of Si substrates with patterned gold electrodes and glass substrates with ITO electrodes in order to start electrical characterization of the deposited films with and without illumination. Afterwards,  $p$ - $n$  junctions will be obtained (and optimized) by depositing a  $p$ - $\text{Cu}(\text{In},\text{Al})\text{S}_2$  layer (or successive layers if it gives a film of higher quality) onto the best flexible substrate on which will be deposited the  $n$ -type layer. After a thermal treatment, the front electrical contact will be established and the cell will be sealed before characterization in the dark (diode behavior) and under illumination (1- light of varying wavelengths to get the cell spectral response and 2- white light from a AM 1.5 solar simulator ( $P_{\text{inc}}=100 \text{ mW cm}^{-2}$ ) to determine the photovoltaic parameters). The relation between the device performance and the properties of the semiconductor films (including the chemical composition of  $p$  and  $n$ -type  $\text{Cu}(\text{In},\text{Al})\text{S}_2$ ) will be studied for a better understanding of the fundamental factors governing the cell performance that will be optimized. The surface area of the best cell will be increased up to  $100 \text{ cm}^2$  and the device will be characterized as above. Finally, the long-term stability of the device will be tested at  $60^\circ\text{C}$  under the same white light conditions.

### **Electrical characterization**

In order to maximize the quality of the  $p$ - $n$  junction, the following characterizations will be done in Prof. Santato's laboratory. First, charge carrier transport measurements will be carried out in a micromanipulated optoelectronic probe station, under inert atmosphere and vacuum conditions. Nanostructured films will be incorporated into conventional three-electrode transistor structures to identify the type of mobile charge carriers (holes vs. electrons) and their mobility<sup>20-23</sup>. These characterizations are of paramount importance as we need to prepare  $p$ - and  $n$ -type materials with appropriate charge carrier mobilities. From the measurement of the transistor current, it will be also possible to give an estimation of the charge carrier density within the films, another very important parameter. To this purpose, unconventional transistors making use of electrolytes as the gating media will be included in the study. In electrolyte-gated transistors, the application of a gate voltage induces the formation of an electrical double layer (EDL) at the electrolyte/semiconductor interface. To briefly illustrate the working principle of such electrolyte-gated transistors, we can consider the concept of EDLs formed at electrode/electrolyte interfaces in electrochemical cells. Here, when an electrical bias is applied between two electrodes immersed into an electrolyte, electrolyte ions move toward electrodes of opposite charge, driven by the electric field to form a charged plane at the electrode, i.e. the Helmholtz plane. The Helmholtz plane and the electrode surface form two parallel oppositely charged layers: this is the EDL. If we replace one of the electrodes with a semiconductor connected to source and drain electrodes, we obtain a field-effect transistor (FET), where the EDL induces an *electrostatic doping* at the interface with the semiconductor. Because of their nanoscale thickness (of the order of a few nm), EDLs are able to accumulate a *high density of charge carriers* upon application of a low gate bias. Electrolyte gating is therefore used to fabricate transistors operating at low voltage (below 1 V). The EDL approach, with electrolytes such as  $\text{LiClO}_4$  solutions or ionic liquids, has allowed the fabrication of low-voltage transistors. Finally, it will be possible to gain insight into the mechanism of charge carrier transport by

measuring the current (*i*) at different temperatures in order to estimate the energy required to activate the charge transport process and (*ii*) considering different interelectrode distances (2  $\mu\text{m}$  to 500  $\mu\text{m}$ ). Besides that, a time of flight (TOF) setup to characterize in "contactless" mode the charge carrier transport properties of the films could be also employed.<sup>24</sup> In this case, mobile charge carriers will be photoproduced in thin films of  $\text{Cu(In,Al)S}_2$ , sandwiched between two electrodes. As the light source, a tunable solid-state pulsed (ns) laser will be used (400 – 2500 nm).

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