

CuInS₂ Solar Cells by Air-Stable Ink Rolling

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Solution-based roll-to-roll deposition techniques are widely considered to be a route to low-cost, high-throughput electronic and energy device fabrication. The ink and the deposition method must be carefully designed to produce high-quality devices, such as solar cells. For solar cells, the deposition must be scalable, and the ink must be tuned to make dense, sufficiently thick layers without pinholes and with minimal residual contamination. Ideally, the solution should be air-stable and environmentally friendly. Various groups have reported the fabrication of photovoltaic devices using inorganic nanocrystal (NC) inks.^{1–3} Wu et al.⁴ made Cu₂S/CdS heterojunction solar cells having a photovoltaic conversion efficiency of 1.6% from nanoparticles and nanorods. Guo et al.^{5,6} demonstrated the fabrication of Cu₂ZnSnS₄ solar cells and large-grained CuInSe₂ using sulfide nanocrystal inks. Li et al.⁷ demonstrated ~4% efficient nanocrystalline CuInS₂ solar cells using an in situ nanocrystal synthesis. NC inks offer the advantage of dispersibility in organic solvents for coating, but their encapsulating organic ligands can leave behind residues that hurt device performance.^{3,8} Furthermore, NC synthesis is often air-sensitive, requiring complicated Schlenk-line techniques. Mitzi et al.⁹ were able to make large-grained Cu(In,Ga)Se₂ with efficiencies of >10% by spin-casting precursor inks based on hydrazine. While this is a very exciting approach, it involves hydrazine, which is toxic and explosive. Other nonvacuum processing routes have also been explored.¹⁰ In this work, we demonstrate a process called air-stable ink rolling (AIR), which includes an easily decomposable vulcanized polymeric ink and a fast rolling process. The ink is made from low-cost commercially available precursors with relatively low toxicity, and the fast rolling process can deposit uniform layers over large areas. Using CuInS₂ as an initial demonstration, we made solar cells with an absorber layer that is flat, contaminant-free, and large-grained. We demonstrate an initial power efficiency of 2.15%. This AIR approach can be generalized for the development of low-cost solar cells of other materials.

The ink for CuInS₂ consists of elemental sulfur, Cu(acac)₂, and In(acac)₃ (acac = acetylacetonate) dissolved in pyridine. In the ink, the acac reacts with sulfur (a reaction known as a “vulcanization” reaction¹¹) to create a rubberlike polymer, providing the viscosity and wetting that allows the ink to be coated onto the substrate uniformly. When In(acac)₃ and sulfur are mixed, the ink quickly undergoes a color transition from clear to deep yellow-orange, suggesting the formation of the polymer. Figure 1a–c provides a summary of our deposition process. A layer of CuInS₂ precursor material is deposited in air by rolling our vulcanized ink onto a molybdenum-coated substrate using a roller bar. The AIR process can be extended to a large-scale roll-to-roll process. The intrinsic roughness of the roller bar allows it to coat in a manner similar to a Mayer rod, leaving a uniform wet film. The resulting film is baked in air on a hot plate at ~370 °C to burn off all the organics,

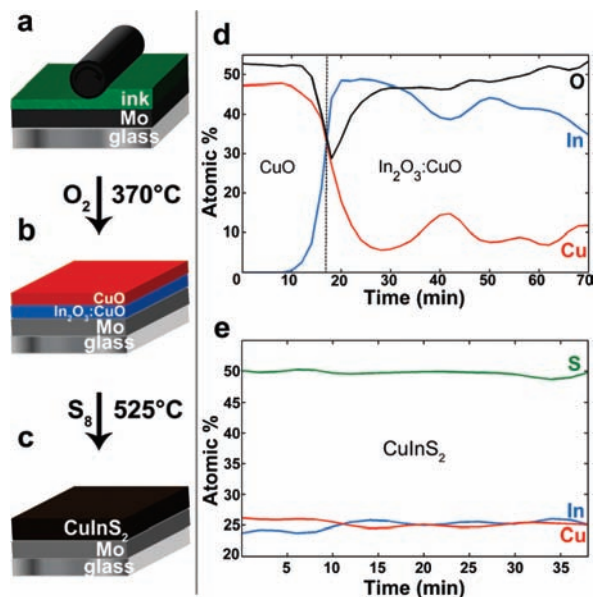


Figure 1. (a) Ink deposition process using a roller bar. (b) Oxide bilayer formation after heating at 370 °C in air. (c) Film after sulfurization in sulfur vapor at 525 °C. (d) AES depth profile of an oxide film showing segregation into a CuO/In₂O₃:CuO bilayer. (e) AES depth profile of the resulting CuInS₂ film after KCN etching.

producing an air-stable Cu–In oxide (Cu–In–O) film that is free of ink residues. This process can produce a ~400 nm thick layer of Cu–In–O (Figure S1 in the Supporting Information) and can be repeated to produce the desired final thickness. The Cu–In–O film is converted to CuInS₂ by sulfurization using elemental sulfur in a bomb at 525 °C.

Efficient CuInS₂ devices must be dense films that have minimal contamination (e.g., from carbon). Furthermore, an ideal absorber would have a columnar grain structure to aid carrier collection. The elemental depth profile (Figure 1d) of our air-heated precursor film (corresponding to the step in Figure 1b) obtained using Auger electron spectroscopy (AES) revealed that the ink decomposed into a bilayer of oxides. The top layer consisted nearly exclusively of CuO, while the bottom layer was a mixture of CuO and In₂O₃. The bilayer structure might result from the higher diffusion rate of Cu than In ions during the oxidation process or the lower decomposition temperature of Cu(acac)₂ in comparison with In(acac)₃. Interestingly, sulfur was not detected and appears to have been completely lost, which suggests the easy decomposition of the vulcanized sulfur polymer. Carbon, which is believed to be a major undesirable impurity in solution-processed solar cells, was not seen after the air-heating process. These data indicate that the decomposition/oxidation products are gaseous and removed completely.¹² After sulfurization using elemental sulfur, we characterized the film again using AES. Figure 1e shows the complete

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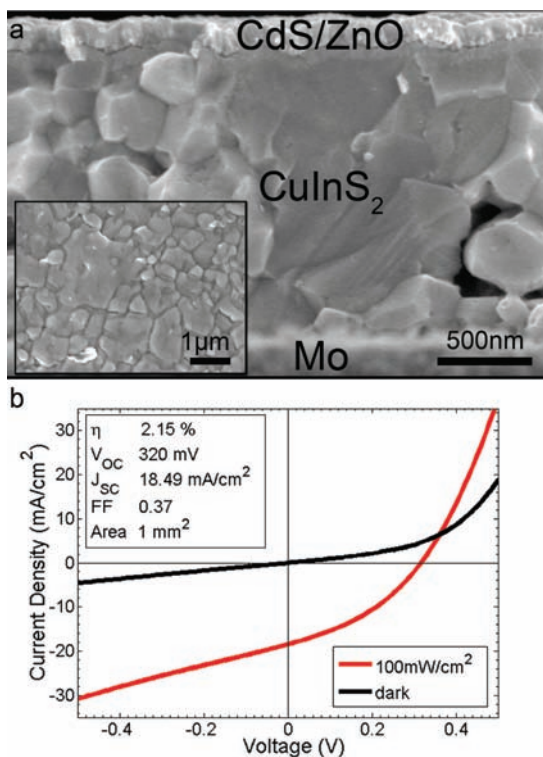


Figure 2. (a) SEM cross section of a solar cell. Inset: top view of the CuInS_2 film. (b) CuInS_2 solar cell characteristics.

conversion of the bilayer oxide film into a uniform and dense layer of CuInS_2 , free of carbon and other impurities. XRD patterns (Figure S2) also confirmed the formation of tetragonal CuInS_2 . Most excitingly, the AIR process with our vulcanized ink was able to produce large-grained CuInS_2 after sulfurization of the oxide (Figure 2a and its inset). Many grains indeed extended across the entire thickness of the film. The intermediate oxide precursors appear to be important for the growth of large grains, as previous attempts to achieve grain growth at high temperature under sulfur atmospheres when starting from nanocrystalline CuInS_2 have generally not been successful.⁶

To fabricate a solar cell device, the CuInS_2 film was etched with 0.5 M KCN for 10 min to remove residual copper sulfide, which is known to be produced easily during CuInS_2 film formation and cause shunting in solar cells. The n-type CdS buffer layer was deposited by chemical bath deposition,¹³ and ZnO was deposited by reactive DC magnetron sputtering. The device was completed by deposition of an indium tin oxide (ITO) top contact. A 1 mm \times 1 mm shadow mask was used to define the device area. Figure 2a shows a scanning electron microscopy (SEM) cross section of a solar cell device, in which different layers of materials can be clearly identified. The CuInS_2 layer was $\sim 1.5 \mu\text{m}$ thick and the CdS/ZnO layer $\sim 0.2 \mu\text{m}$ thick.

The current–voltage measurement for a CuInS_2 solar cell is shown in Figure 2b. The short-circuit current density, J_{sc} , was 18.49 mA/cm^2 , which is comparable to those of high efficiency CuInS_2 solar cells.^{14–16} The power conversion efficiency, η , in this initial

device was 2.15%. The fill factor ($\text{FF} = 0.37$) and open-circuit voltage ($V_{\text{oc}} = 320 \text{ mV}$) were not high, most likely because of the low shunt resistance. We believe that this might be due to film cracking induced by mechanical stresses created during sulfurization, a chemical transformation involving structural and volumetric changes. We are currently investigating the mechanical properties of our film before and after sulfurization in order to increase the shunt resistance, which should significantly increase the V_{oc} , FF, and photovoltaic conversion efficiency. We believe that resolving this issue will allow us to produce CuInS_2 solar cells with much higher efficiencies.

In summary, we have demonstrated an air-stable, easily decomposable, vulcanized ink and its deposition process for producing uniform, dense, contaminant-free, large-grained CuInS_2 absorber layers from low-cost, commercially available precursors. We have shown the ability to make solar cells from these films with a short-circuit current density similar to those of the best CuInS_2 solar cells. A variety of metal acac precursors are commercially available, allowing for the addition of nearly any metal to our ink. The versatility of the AIR process should make it widely applicable to many materials systems for optoelectronic and electronic devices, including solar cells, transparent electrodes, thin-film transistors, and memories.

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Supporting Information Available: SEM image of a Cu–In–O film and XRD patterns for a CuInS_2 film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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