# Using a field-assisted simultaneous synthesis and transfer technique to print CIGS thin-film photovoltaic devices

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ABSTRACT

In recent years, a new generation of solar electric products has emerged from the lab into the global market: thin-film technologies that employ approximately 1% of the active, expensive photovoltaic material used by standard crystalline-silicon cells. Through a combination of cost advantages and new product applications, cadmium telluride (CdTe), amorphous silicon, and copper-indium-gallium-selenide (CIGS) thin-film PV have the potential to foster a paradigm shift toward distributed electricity generation at cost parity with other forms of energy.

CIGS has long been seen as one of the most promising thin-film PV materials. But until recently, the photoactive compound has not had a reliable, rapid manufacturing process that could scale effectively to multi-megawatt-scale volume production and provide significant amounts of electricity at the point of use. This article describes a novel process, known as field-assisted simultaneous synthesis and transfer (FASST) printing, a manufacturing approach that enables the rapid printing of microscale CIGS films with p- and n-type nanodomains that are critical for achieving the highest efficiencies possible.

## The promise of CIGS

More efficient than CdTe, amorphous silicon, and other thin-film materials, CIGS has achieved 20% conversion efficiency in laboratory settings for small-area cells [1] and 13.5% for large-area modules [2]. This performance level pushes CIGS to near parity with traditional crystalline silicon panels, which usually boast panel efficiencies in the 12-18% range.

CIGS thin films have other competitive advantages. The relatively low material usage means that $1 worth of silicon can be replaced with just $0.03 of CIGS materials. The silicon market has been constrained by an imbalance between supply and demand, resulting in manufacturers being tied to a volatile, unpredictable commodity market characterised by wide price fluctuations. CIGS production benefits not only from material advantages, but also from the potential for improving costs throughout the value chain, leveraging manufacturing maturity in related thin-film technologies, such as the electronics and display industries.

Because of its inherent aesthetic versatility, CIGS also offers expanded product innovation choices. While the current solar market has recently been

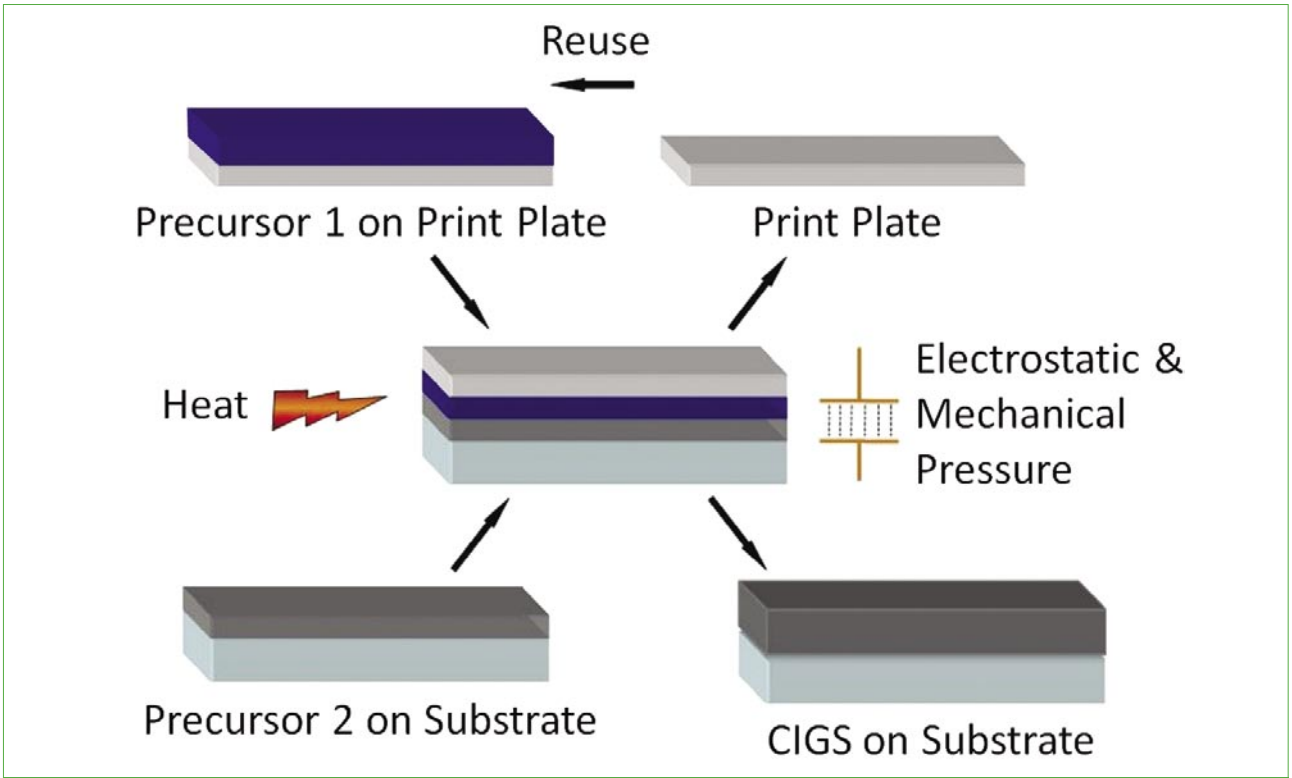


Figure 1. Schematic of the field-assisted simultaneous synthesis and transfer (FASST) process.

underserved with demand outpacing supply, differentiators such as appearance and the ability to adapt products to various market segments will play an increasingly important role as the sector approaches equilibrium. Silicon PV companies such as SunPower have already proven that high-end products with a strong aesthetic advantage can attract significant investment and secure market share at a premium.

CIGS thin-film builds on this idea. The material can be integrated into a wide variety of building and construction materials. For instance, CIGS can offer the appearance of tinted glass on sides of buildings, or of slate on rooftop applications. Semitransmissive modules could serve the dual function of vision glass and electricity generation.

> "The relatively low material usage means that US$1 worth of silicon can be replaced with just US$0.03 of CIGS materials."

Among the TFPV materials, CIGS may be the most promising for cost-effective power generation. With its high conversion efficiency, it has the potential to provide the maximum power per unit area available, and with it, an attractive energy payback time of about 1.5 years, with expected advances leading to a payback time of about a half-year in the near future.

## A novel way to produce CIGS

Depending on the manufacturing technique, CIGS can be processed as monolithically interconnected modules (MIMs). Instead of discrete, individual cells that are strung together, PV modules can take the form of photovoltaic integrated circuits (PVICs), which can simplify the manufacturing process and reduce costs. MIMs consist of a packaged PVIC, in which the thin films are deposited on a substrate and undergo a series of scribe patterning steps that create an integrated circuit of cells already in series. The integration method circumvents the significant cost associated with cell cutting/testing/sorting/assembly used in many other thin-film PV technologies. First Solar has taken a similar approach, which has proven very effective for scalable, high-throughput manufacturing of CdTe thin-film modules. While not all CIGS manufacturing processes can use PVICs, FASST's reactive transfer process capitalises on the advantages of this approach as well as offering rapid deposition over large areas.

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High-performance CIGS is characterised by relatively large grain sizes, an overall copper deficiency compared to the structure of the conventional α-phase copper indium diselenide ($CuInSe_2$), and a composition lying in the equilibrium α+β 2-phase domain [3]. This latter characteristic is behind the intra-absorber junction (IAJ) model that describes the formation within individual grains of α domains that are copper-rich with p-type conductivity and β domains that are copper-poor with n-type conductivity, forming nanoscale p-n junction networks [4]. The n-type networks act as preferential electron pathways, while the p type networks act as preferential hole pathways, allowing positive and negative charges to travel to the contacts in physically separated paths, reducing recombination and improving efficiency.

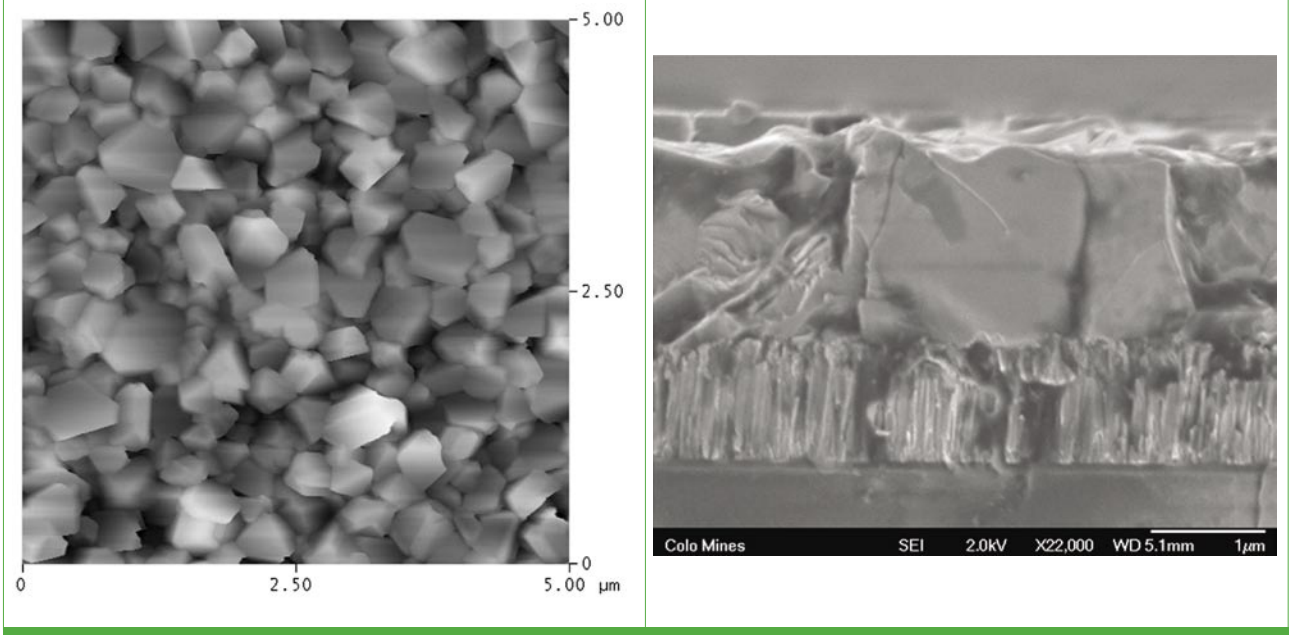


Figure 2. (a) Precursor film and (b) FASST CIGS cross-section.

The most common conventional method used to synthesise high-performance thin-film CIGS devices is a high-temperature, coevaporation method. The multistep deposition sequences developed to achieve this performance involve the topotactic transformation of a fairly large grain precursor into very large grain CIGS, rather than the direct synthesis of CIGS from condensation of elemental vapours as in molecular beam deposition. The FASST process uses this same topotactic transformation.

The process utilises a two-stage reactive transfer printing method relying on chemical reaction between two separate precursor films to form CIGS (see Figure 1). In the first stage, two Cu-In-Ga-Se-based precursor layers, forming the chemical basis of the films, are deposited onto a substrate and print plate, respectively. The two separate precursors provide independently optimized composition, structure, deposition method, and processing conditions for each precursor. Separating the precursors eliminates prereaction prior to the second-stage of the process and facilitates optimized CIGS formation in the second stage. Precursors can also be deposited at a low substrate temperature, which can help lower cost and increase throughput.

In the second stage, these precursors are brought into close contact and rapidly reacted under pressure in the presence of an applied electrostatic field. The method utilises physical mechanisms characteristic of rapid thermal processing (RTP) and anodic wafer bonding (AWB), effectively creating a sealed microreactor that ensures high material utilisation, direct control of reaction pressure, and low thermal budget. The rapid thermal transient provides the similarity between FASST and RTP. By pulse heating the film through the print plate, the overall thermal budget is significantly reduced, allowing the use of low-cost, less thermally stable substrates.

Sufficient mechanical pressure can substantially prevent the loss of selenium vapour from the reaction zone, thereby achieving highly efficient incorporation of the vapour into the composition layer. The use of an electrical bias between the print plate and substrate creates an attractive force that serves to ensure intimate contact between the precursor films on an atomic scale, and can thus be used in conjunction with mechanical pressure to control the total pressure in the reaction zone. This is the area where FASST resembles AWB, a method developed historically to reduce the temperature required to bond two dissimilar materials together.

## Using precursors to synthesise high-quality CIGS films

Large-grain, high-quality CIGS is synthesised from two precursors in

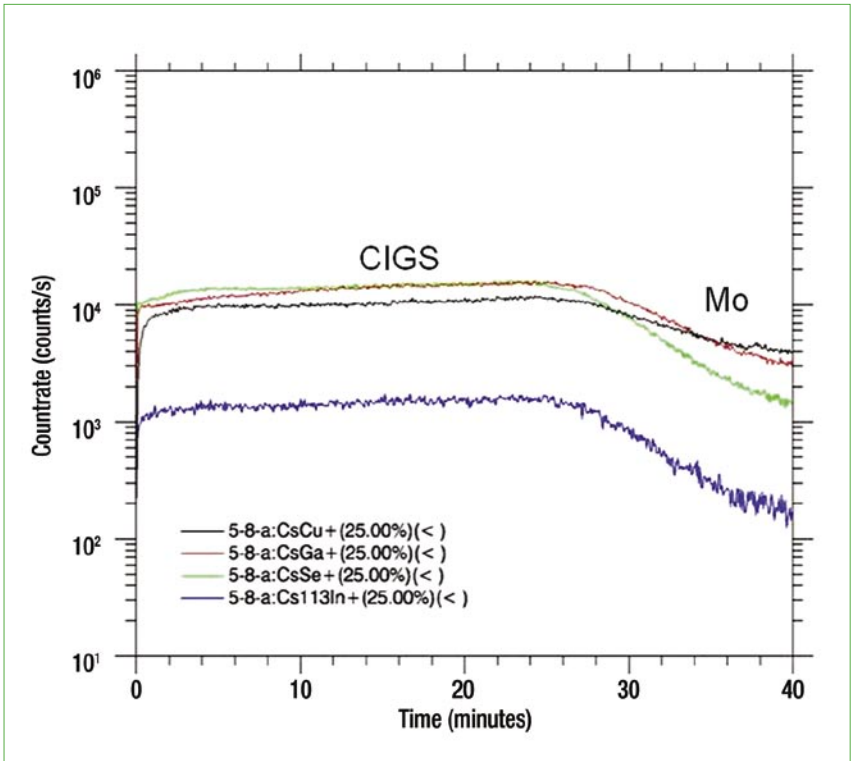


Figure 3. SIMS depth profile of a CIGS film. This film was formed in six minutes by the novel transfer process.

six minutes using the process. Figure 2 depicts a precursor film with grains on the order of a quarter-micron in size and the cross-section of a printed CIGS film with micron-scale grains.

Figure 3 shows a secondary ion mass spectrometry (SIMS) depth profile of a CIGS thin film processed by the synthesis and transfer technique. The precursors are produced by physical vapour deposition (PVD). The uniform elemental distribution indicates a complete reaction of the precursors, and the x-ray diffraction (XRD) analysis shown in Figure 4 confirms the absence of deleterious phases other than CIGS. The XRD peaks are indexed based on a chalcopyrite-type CIGS and molybdenum structure. The processed film has a (220/204) preferred orientation. Evidence indicates that the (220/204) oriented films help junction formation and improve solar cell performance [5].

The rapid processing of the CIGS formation significantly increases the manufacturing throughput. As noted above, this approach results in a much lower thermal budget as compared to the more commonly used coevaporation and two-step selenization processing techniques. The reduced thermal budget, virtual elimination of selenization, and high throughput all contribute to the potential to lower the process cost and improve manufacturability.

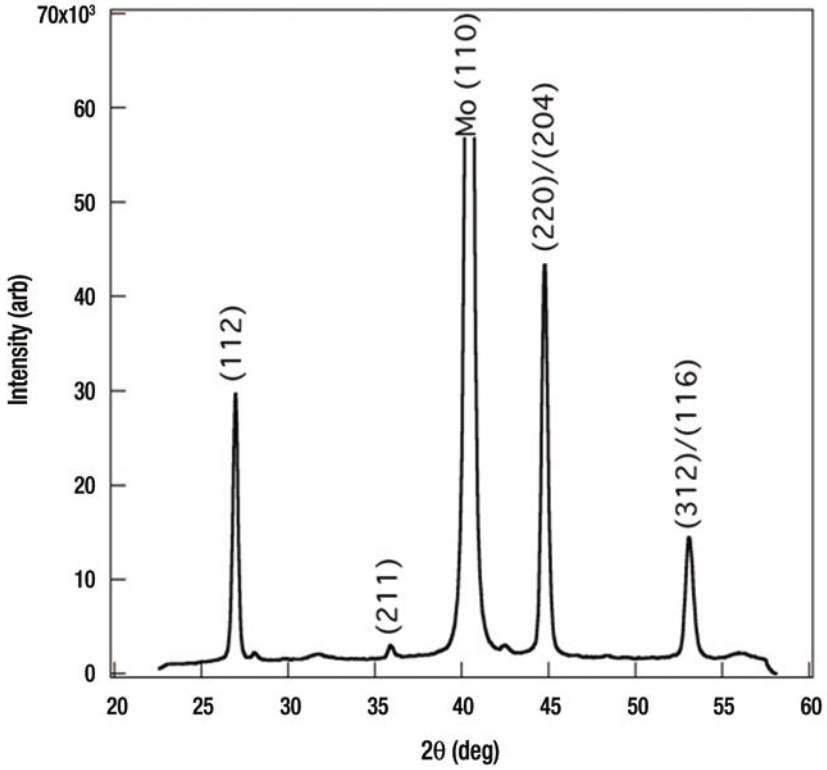


Figure 4. XRD pattern of a CIGS film fabricated by the process.

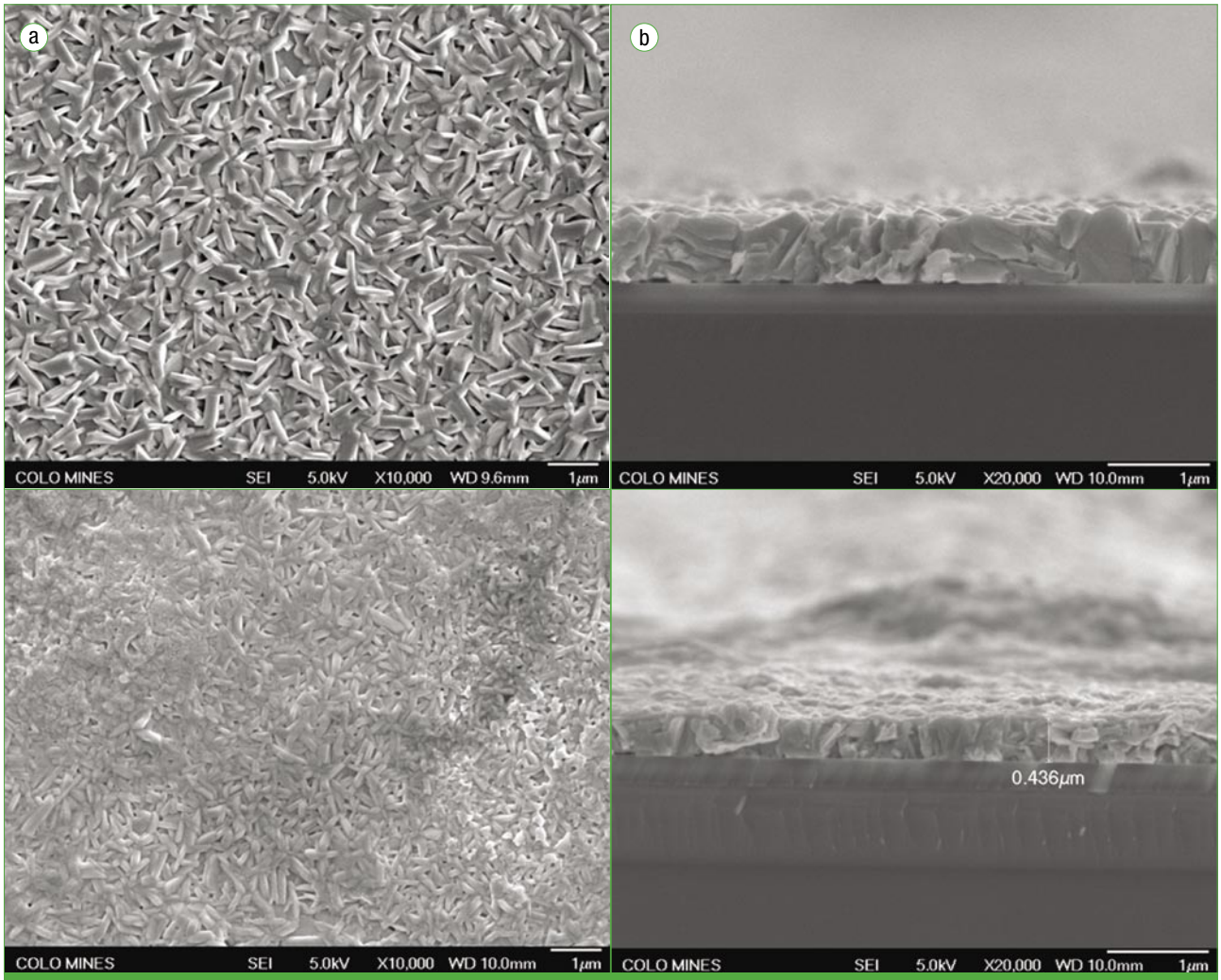


**Figure 5. Top views and cross-sectional SEM views of (a) a PVD-deposited CuSe film, and (b) an atmospherically spray-deposited CuSe film from a solution-based process.**

The opportunity to tailor the two precursors independently permits the use of unconventional, nonvacuum deposition techniques, such as die extrusion coating, ultrasonic atomization spraying, pneumatic atomization spraying, inkjet printing, direct writing, and screen printing. These atmospheric-pressure-based deposition tools can offer enhanced flexibility and open up new avenues for materials processing. They also provide a viable means of introducing nanoparticle technology, metallorganic chemistry, and novel reaction paths to produce CIGS. The low capital equipment cost and high-throughput capabilities associated with atmospheric-pressure processing can reduce manufacturing costs. Since these materials can be deposited at temperatures below 200°C, there is potential for a lower thermal budget [6].

Proprietary inks containing a variety of soluble copper, indium, and gallium multinary selenide materials were developed by HelioVolt and the U.S. National Renewable Energy Laboratory. These inks – so-called metal-organic

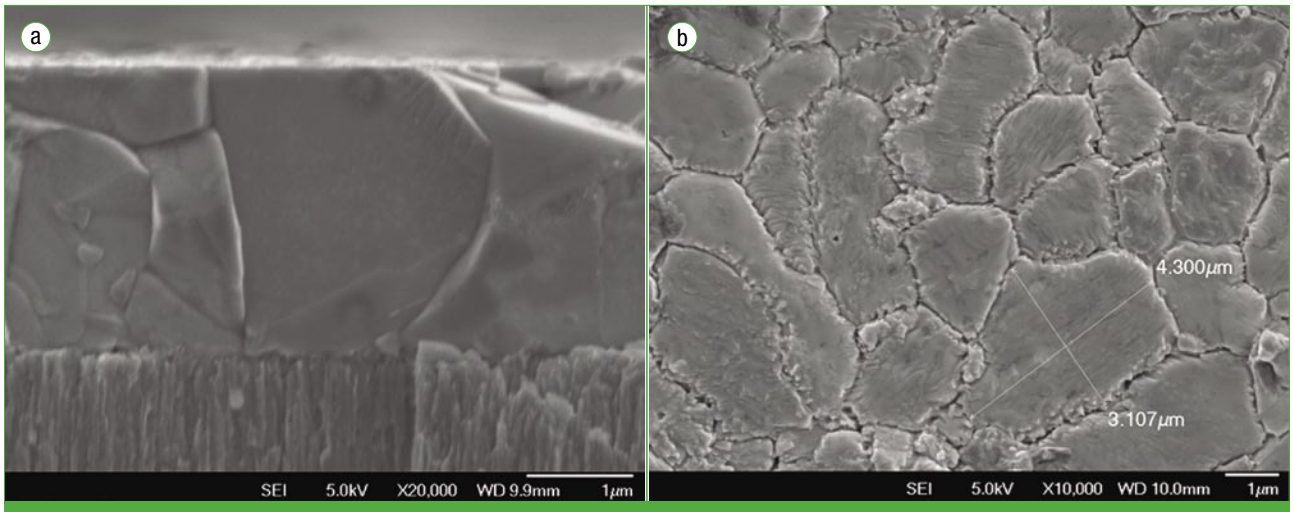


**Figure 6. SEM micrographs of (a) the cross-section and (b) the top view of a CIGS film synthesized using a nonvacuum-deposited precursor.**

decomposition (MOD) precursors – are designed to blend into the desired precursors, which are then used in step one of the FASST process.

For the work described here, the inks were deposited using an ultrasonic spray head fed by a variable-speed liquid pump. A substrate heater mounted on a computer-controlled X-Y motion system allowed for the movement of heated substrates under the sprayed stream. The thickness of the sprayed film was controlled by varying the ink concentration, the flow rate through the sprayer, and the number of coats deposited. Conditions were optimized such that smooth, uniform precursor films were obtained for all of the sprayed inks.

The precursor films were converted to the desired materials through RTP in a controlled atmosphere. The thermal processing conditions were varied systematically to ascertain the effect of conditions on the film compositions and morphologies obtained. The film compositions were characterised by X-ray fluorescence (XRF), crystalline phases were identified using XRD, and film morphology was examined using scanning electron microscopy (SEM).

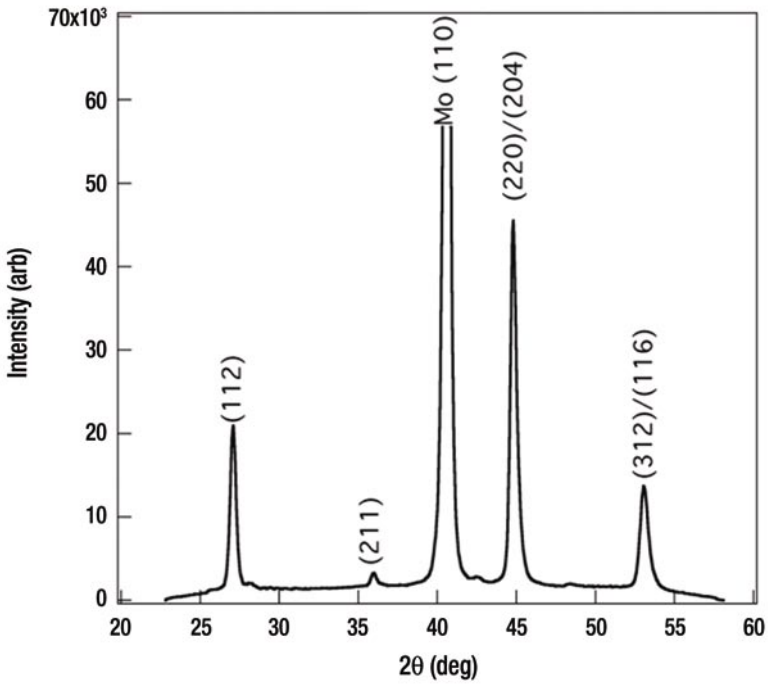


Figure 7. XRD pattern of a CIGS film using a nonvacuum-deposited precursor.

> "Various Cu-Se MOD precursor recipes were also formulated, resulting in tunable phase and stoichiometry in as-deposited films, ranging from phase-pure $CuSe_2$ to $Cu_2Se$."

Binary Cu-Se, In-Se, and Ga-Se materials were developed and then used to produce precursors. Various Cu-Se MOD precursor recipes were also formulated, resulting in tunable phase and stoichiometry in as-deposited films, ranging from phase-pure $CuSe_2$ to $Cu_2Se$. Figure 5 compares the cross-sectional morphology of vapour-deposited CuSe films to that of atmospheric MOD CuSe films. The remarkable similarity between grain size, morphology and density shows the promise of using solution-based precursors as alternatives for vacuum deposition-produced process materials.

A hybrid CIGS can be produced when one precursor is deposited via PVD and the other precursor in ink form via atmospheric-pressure deposition. Figure 6 features cross-sectional and top-view micrographs of such a film, revealing high-quality, large columnar grains up to 4µm in size. The XRD pattern for the sample in Figure 7 shows that the chalcopyrite CIGS phase is clearly identified.

Various In-Se and Ga-Se precursors were developed and used individually and in combination to produce $In_2Se_3$, $Ga_2Se_3$, and $(In,Ga)_2Se_3$ films. These films were reacted with solution-deposited Cu-Se to produce CIGS absorber layers on molybdenum/glass substrates. In another approach, a single-source Cu-In-Ga-Se MOD precursor was developed by mixing the binary inks in the proper ratio, then deposited by ultrasonic spray and thermally processed to directly make CIGS.

An important benefit of FASST is that there is no constraint on the combination or type of precursors that can be brought together. The only requirement is that all of the elements in the correct stoichiometry must be present on the substrate and print plate prior to the process.

The tunability, scalability, high throughput, low thermal budget, and capital equipment cost reduction that atmospheric processing of MOD precursors offers is a promising route to the eventual replacement of vacuum deposition methods for CIGS absorber layer fabrication. From a manufacturing

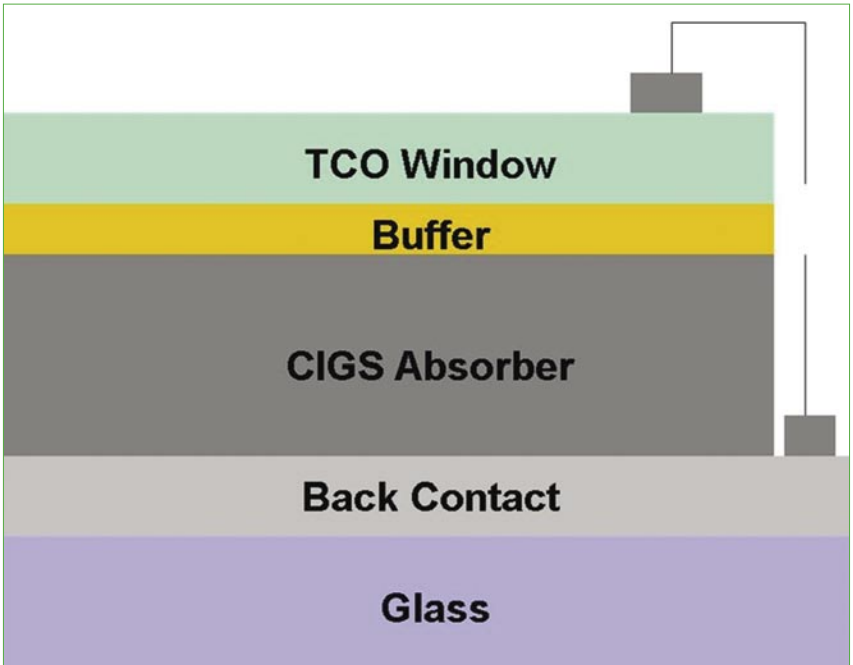


Figure 8. Cross-sectional schematic of a typical CIGS solar cell.

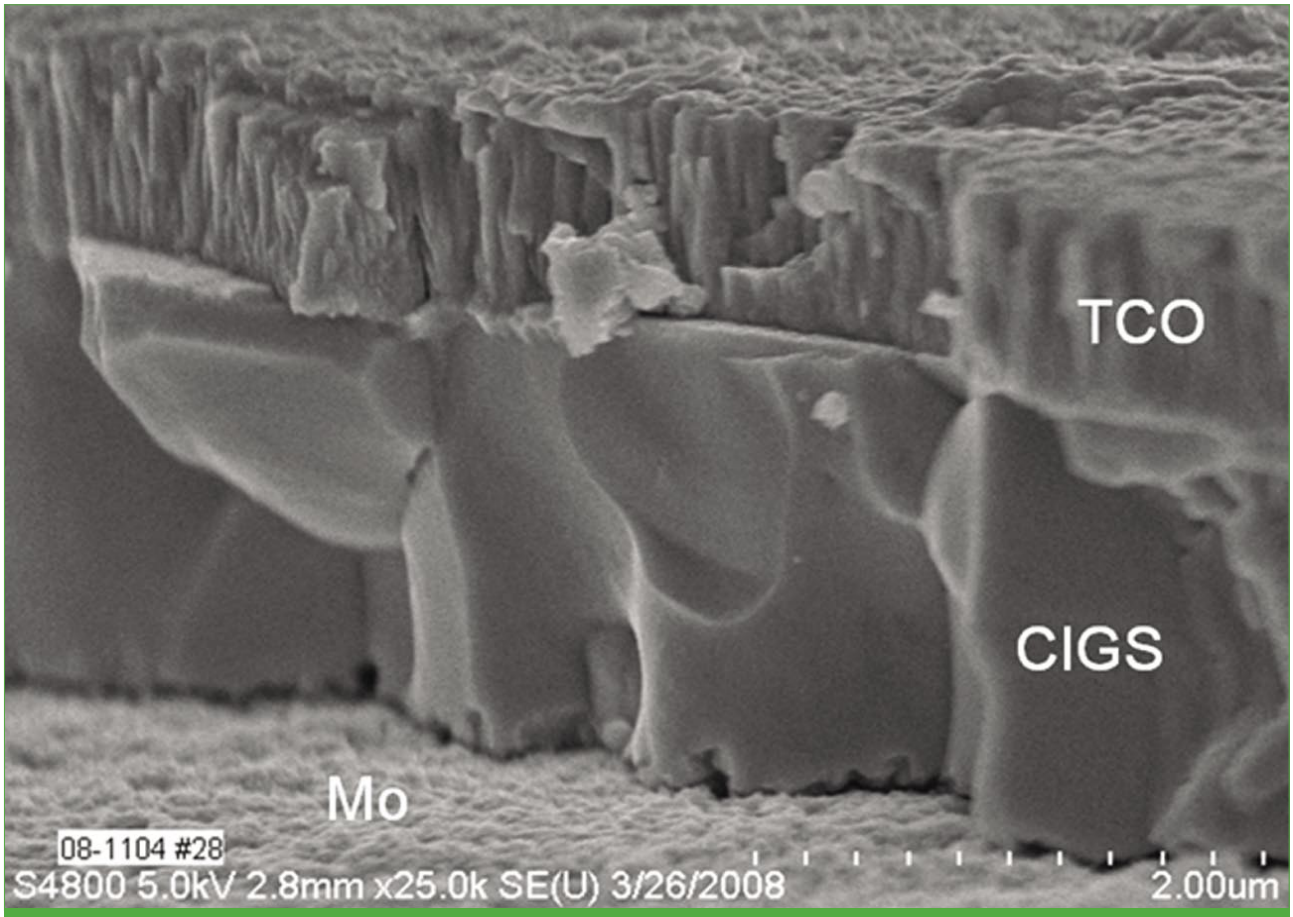


Figure 9. SEM cross-sectional image of a FASST CIGS device.

standpoint, any deposition method, whether it is PVD-based or atmospheric pressure-based, has relative advantages and disadvantages.

While the capital equipment cost for atmospheric-pressure-based systems may be lower than that of corresponding PVD systems, the raw material costs tend to be higher for solution rather than for PVD sources. Therefore, the best choice is ultimately governed by differences in the performance and yield of products manufactured by these two approaches. Because of its better utilisation of materials, atmospheric pressure-based processing offers a compelling CIGS approach, especially once the nanotechnology field matures enough to facilitate the volume availability of low-cost liquid precursors.

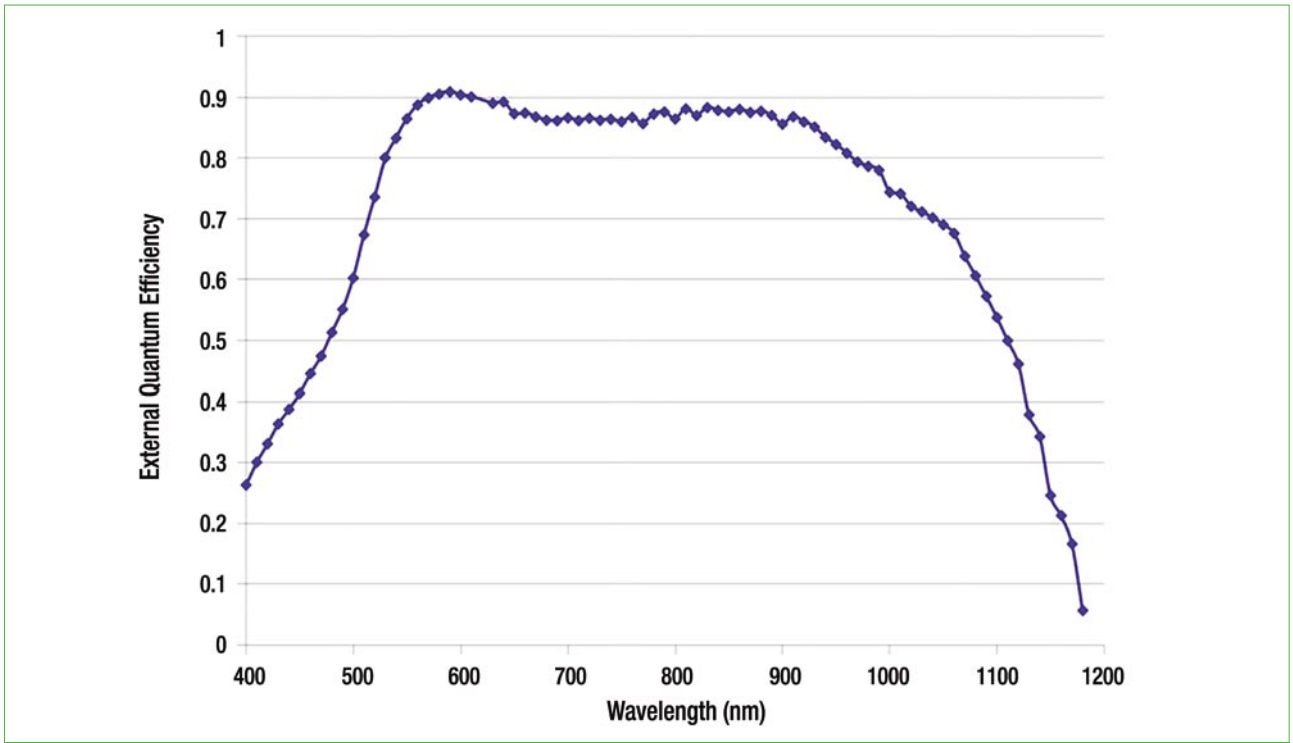


Figure 10. QE curve of a FASST CIGS solar cell.

### Analysing CIGS cells, improving efficiencies

As part of the work described in this article, solar cells with a conventional device structure of glass/Mo/CIGS/buffer/TCO were fabricated. The CIGS absorber layers were formed by the FASST process with PVD-based precursors. Figure 8 shows a cross section of a typical CIGS cell, while Figure 9 depicts a cross section of a representative device. As can be seen, high-quality films with large columnar grains were obtained.

Figure 10 shows the external quantum efficiency (QE) versus wavelength for the device without an antireflective coating (ARC). High QE at wavelengths over 550nm reveals very good carrier collection and good performance of the CIGS layer. A low QE at short wavelengths indicates the need to further optimize window layers.

> "An important benefit of FASST is that there is no constraint on the combination or type of precursors that can be brought together."

Solar cells of better than 12% efficiency have been fabricated using the FASST process. A J-V curve of a 12.2% efficient, AR-coated efficient device (based on tests done at Colorado State University) is illustrated in Figure 11. The composition of the CIGS film in this device, as measured by XRF, is 21.8% Cu, 21.6% In, 6.3% Ga, and 50.4% Se, which gives a Cu ratio (Cu/(In+Ga)) of 0.78 and Ga ratio (Ga/(In+Ga)) of 0.22. When the Cu and Ga ratios are optimized, device efficiency should increase using this process. For instance, an open-circuit voltage of 590mV was obtained by increasing the Ga/(In+Ga) ratio to 0.3. Analysis of the J-V data of the device showed a diode quality factor of about 2, and a high saturation current density, which means that the large recombination at the junction region limits the open circuit voltage and fill factor.

Further analysis of the device was carried out by capacitance-voltage measurement [7]. The results from this analytical method revealed a hole density of $2.5\times10^{16}cm^{-3}$ and a depletion width of ~0.2µm. Figure 12 depicts the carrier concentration as a function of distance from the junction, as derived from the C-V data. The hump in carrier density against distance might be a signature of the measurement responding to deep states near the interface [8,9], and direct measurement of deep-level defects would be needed to verify it. Such states have a detrimental effect on the cell efficiency, because they constitute effective recombination paths for forward current opposing the photogenerated current.

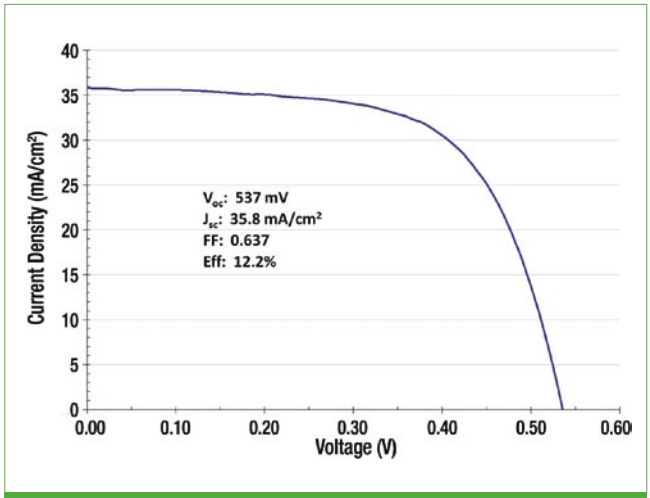


**Figure 11. J-V curve of a FASST CIGS solar cell measured by Colorado State University.**

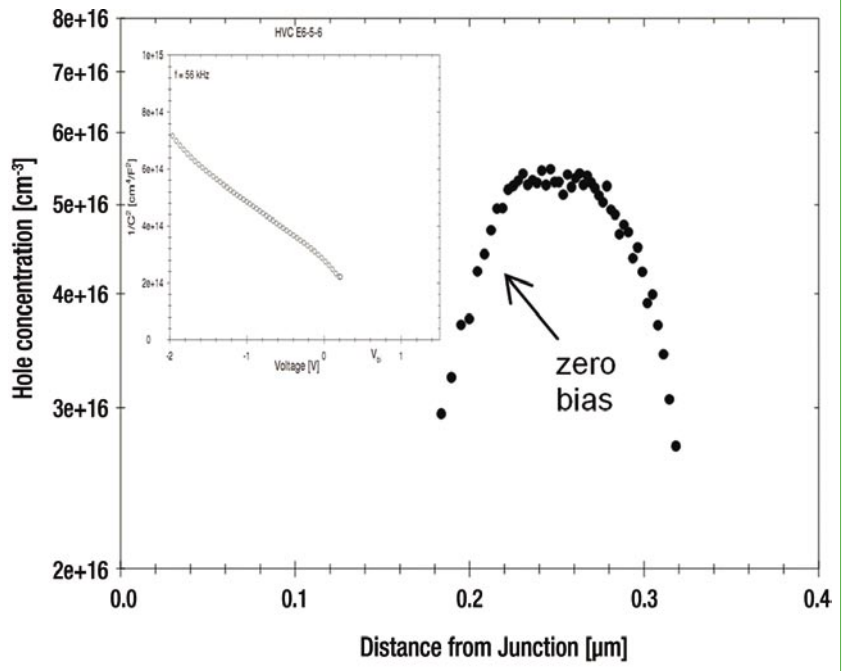


**Figure 12. Carrier density as a function of distance from the junction, as derived from a C-V measurement.University.**

These kinds of forward currents might also result from enhanced tunnelling recombination through these states [10], suggesting that the interface region, including the CIGS surface termination and post-CIGS treatment, require further optimization. Elimination of these states by improving the CIGS surface termination could significantly improve the open-circuit voltage and the fill factor.

## BIPV, solar-powered "skin," and beyond

A novel field-assisted simultaneous synthesis and transfer printing technique, recently deployed in a factory setting, shows great promise for the volume production of high-performance CIGS devices rapidly and at low cost, based on harnessing the key elements required for the creation of high-quality materials. The approach, especially when combined with the use of liquid ink precursors, has the potential to provide a sustainable, long-term technology-based cost advantage and open the doors to further advances in the commercial manufacturing of CIGS thin-film PV.

Since the process is compatible with rigid and flexible glass, metal, alloy, composite, and plastic substrates, it may offer improvements on existing product applications as well as enable many new ones, from traditional glass modules to construction materials that incorporate thin-film PV. True building-integrated PV represents a paradigm shift, paving the way for the construction of buildings with a solar-powered "skin," turning the structure itself into a power plant. Once cost-effective, high-volume manufacturing has been successfully achieved, CIGS-based solar skins could one day become pervasive not only in roofing, curtain walls, and façades, but also in sunshades, skylights, atriums, canopies, and pergolas, with a wide range of form factors, shapes, colours, and transparencies, incorporating dynamic behaviour and innovations in lighting, heating, and cooling.

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