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Atmospheric deposition techniques for photovoltaics

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ABSTRACT
With the never-ending need to reduce production costs, interest in atmospheric deposition techniques is steadily increasing. Even though atmospheric deposition is not new to photovoltaics, and in some cases is actually required to get the best cell performance, many of the fabrication processes for photovoltaic cells are vacuum-based. Due to the diversity in atmospheric deposition techniques available, there are opportunities for applications in thin film and patterned deposition. This paper discusses some of the deposition techniques and their applications, benefits and drawbacks.

Introduction

Solar cell manufacturing involves a myriad of simple and complex thin-film deposition techniques that include sputtering, evaporation, printing and chemical bath. Solid sources such as targets or powders provide the required elements and compounds to form films via the vacuum-based techniques, and there is a broad base of knowledge available for processing materials like ZnO or Mo into the appropriate precursor shapes. Vacuum-based techniques utilizing such precursors have traditionally dominated thin-film production, and steady improvements in material handling and processing conditions have led to dramatic decreases in the cost of photovoltaic-generated electricity to the current lowest prices of US$1.74/Wp for multicrystalline modules and US$1.07/Wp for thin-film modules [1].

"Vacuum-based techniques utilizing such precursors have traditionally dominated thin-film production."

Also key to the vitally important decrease in the price of solar modules has been the more recent integration of solution-based thin-film deposition techniques like screen-printing and electro-deposition. While appropriate chemistries for the inks and baths are not fully established and often take time to develop, many of these liquid precursors are composed of low-cost materials such as water and abundant metal salts. Developing processes like aerosol jet-printing can produce patterns directly, so the inks are used efficiently and little waste is produced. Many of these techniques can also be used to deposit inks at atmospheric pressure – often simply in air, so there is no need for a vacuum chamber and the accompanying infrastructure. There are clearly some attractive aspects of solution-based thin-film deposition techniques.

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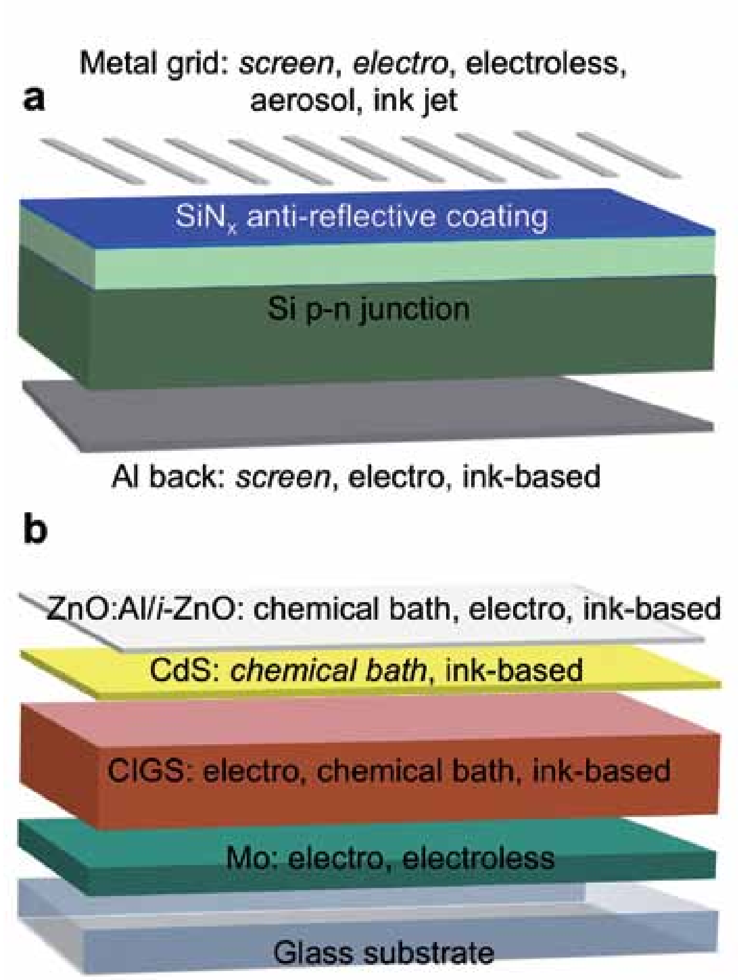

Figure 1. Atmospheric deposition processes that have the potential to contribute to a) a standard Si solar cell, and b) a standard CIGS solar cell. The techniques already utilized in production are indicated by italicized text.

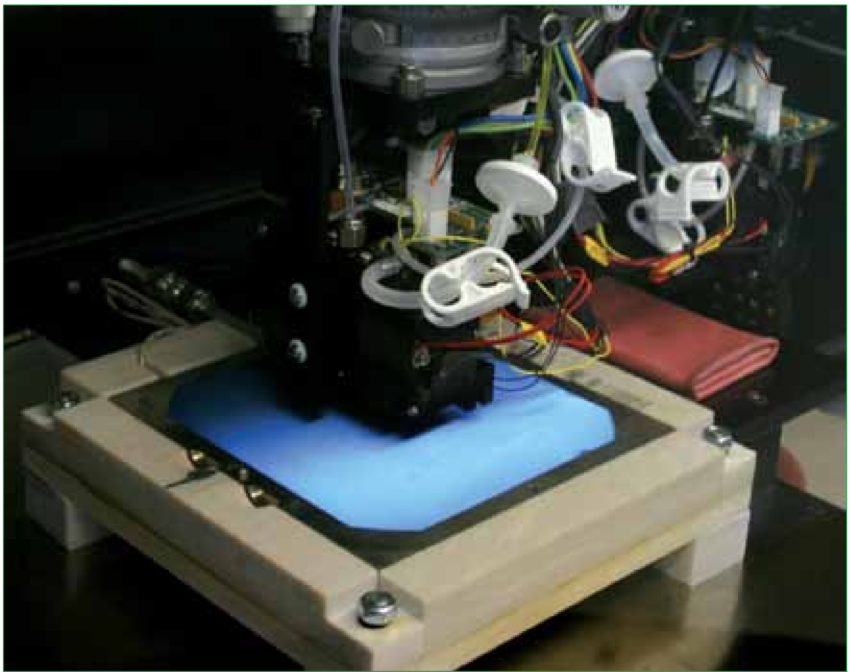

Figure 2. A research multi-material inkjet system with Dimatix Spectra piezo inkjet heads mounted on a universal X-Y platform. This research system is part of the Atmospheric Processing Platform in the Process Development and Integration Laboratory at NREL [5].

We will review the atmospheric processing techniques that are already contributing to photovoltaic module production, along with other promising methods that are under development. These techniques are summarized for wafer Si and thin-film $CuIn_{1-x}Ga_xSe_2$ (CIGS)-based cells in Fig. 1. The basic mechanics of each deposition methodology are described and further illustrated with specific examples and references for those interested in more details.

Direct patterning techniques

Screen-printing

For conventional wafer silicon photovoltaics, the most commonly-used technique to deposit contacts is screen-printing, which utilizes a woven mesh to support a mask with the desired pattern to deposit both of the contacts on the front and the back. The screen is placed in direct contact with the substrate, and paste is extruded through the screen onto the substrate. This process directly exposes the substrate to a force, which can result in breakage of the silicon wafer. Typical line widths that can be obtained are in the 100 to 125µm range; however, recent developments in screens and pastes have enabled line widths as low as 50µm [2]. Overall, screen-printing is a well-established deposition method in the photovoltaics industry. Silver pastes containing glass frit for high-temperature contact formation to silicon have been around since the 1970s. A close alternative to screen-printing is gravure printing in which the paste is transferred using a printing plate.

Screen-printing can also be used for alternatives to the normal front grid contact structures, i.e. interdigitated contacts, although the highest efficiency has been obtained using vacuum-based deposition approaches. Screen-printing is also used to deposit contacts on other types of photovoltaics, where the problem of breakage is limited since the substrate is either rigid, i.e. glass, or flexible, i.e. metal or plastic foil. Alternatively, screen-printing can be used to deposit films with thicknesses of several microns, i.e. CIGS or CdTe absorber layers.

Inkjet and aerosol jet printing

In an effort to reduce the contact grid line width, and therefore the shadow losses, inkjet printing (Fig. 2) and aerosol jetting (Fig. 3) are being developed as non-contact replacement methods for screen-printing. In the case of inkjet printing, small droplets (1-30pL) are created in a controlled fashion within the inkjet nozzle. These droplets can be deposited onto a substrate with great precision and reproducibility. In the case of aerosol jetting, a cloud of small droplets (~1pL) is

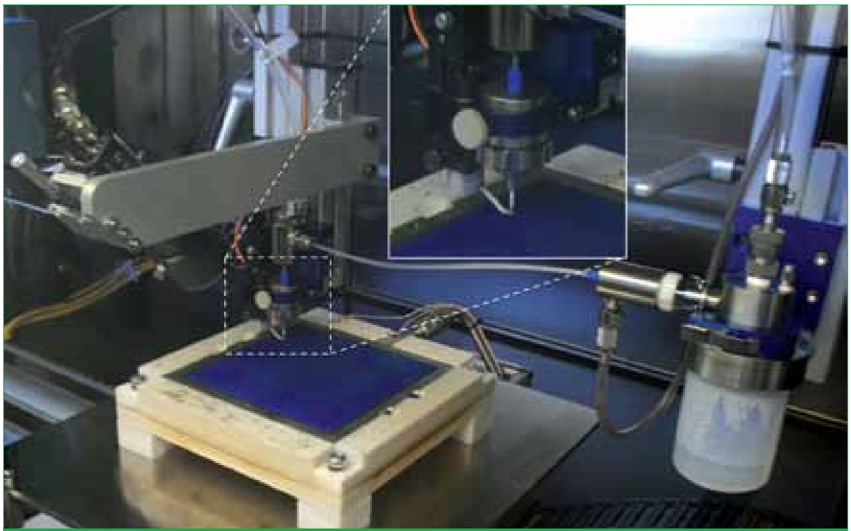

Figure 3. An Optomec research aerosol jet deposition system mounted on a universal X-Y platform. This research system is part of the Atmospheric Processing Platform in the Process Development and Integration Laboratory at NREL [5].

created and then transported to a nozzle via a gas stream. In the nozzle the aerosol is surrounded by a second gas stream, which confines the aerosol so that it can be deposited in a narrow area. Droplet position is random within the deposition area. Inkjet printing can produce metal grid lines with widths of less than 25µm [3], and aerosol jetting can even push below 10µm line widths [4].

Besides the reduced shadow losses of a front metallization grid, benefits of using non-contact printing methods include thinner wafers (in the case of wafer silicon), therefore reducing the material usage. It also enables the development of alternative contact structures, i.e. doped contacts and multi-layer contacts. The printing technologies permit changes to the printed pattern on the fly, which is ideal for prototyping. Multi-material printing systems enable deposition of interdigitated back contacts without the use of lithography. An example of a cell with aerosol-jetted contacts is shown in Fig. 4.

The key to the success of non-contact printing methods in photovoltaics is the development of deposition tools with sufficient throughput and inks that work well with these systems and produce the desired material properties, i.e. conductivity, adhesion, line width, line thickness, contact resistance, etc. Both methods are under development and in their initial production testing phases. Several companies are developing non-contact printing tools for the photovoltaic industry that work at production throughput [6], while smaller tabletop printing systems for initial rapid solar cell application development are also available. Most of the screen-printing paste suppliers and some chemical companies are actively developing non-contact printable inks.

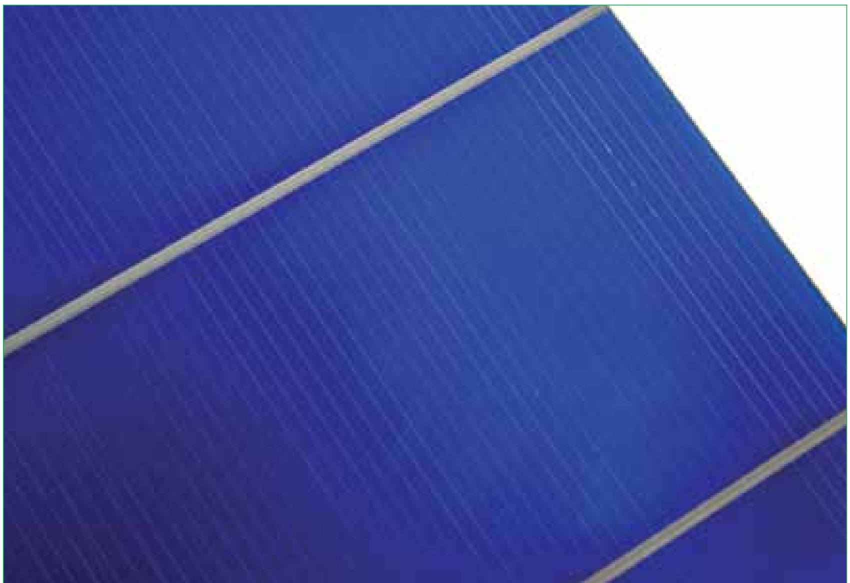

Figure 4. A single crystal silicon wafer with silicon nitride anti-reflection coating and a metallization grid deposited by aerosol jet.

The majority of metallization inks use nanoparticles as a precursor component; however, alternative inks exist that use metal organic decomposition precursors [3]. Non-contact printing methods can also be used for thin-film deposition, but their real strength is in the field of patterned deposits.

Bath-based thin-film deposition techniques

Bath-based deposition techniques require little up-front equipment investment in that they can be carried out in almost any container that will hold liquid. In addition, many useful films and patterns can be deposited from baths that are composed of abundant and low-cost reactants in aqueous solution. Bath-based deposition techniques have broad application, and as a result a dizzying number of variations exist. Here the focus will be on electro-, electroless, and chemical bath deposition to provide an overview of how such techniques are already contributing to photovoltaic cell production and where they may be utilized in the future.

Electro-deposition

In addition to the bath itself, the electro-deposition process requires an external current source [7]. This current is applied to the bath via two electrodes: the negative cathode, where positive cations migrate, and the positive anode, where negative anions collect. The most common use of this technique is to reduce metal cations to metal atoms at the cathode and thus form a coating. This cathode can be anything from a metal film or TCO-coated substrate to printed metal lines. For

Figure 5. A Sono-Tek spray deposition nozzle. This nozzle is part of a research deposition system at NREL.

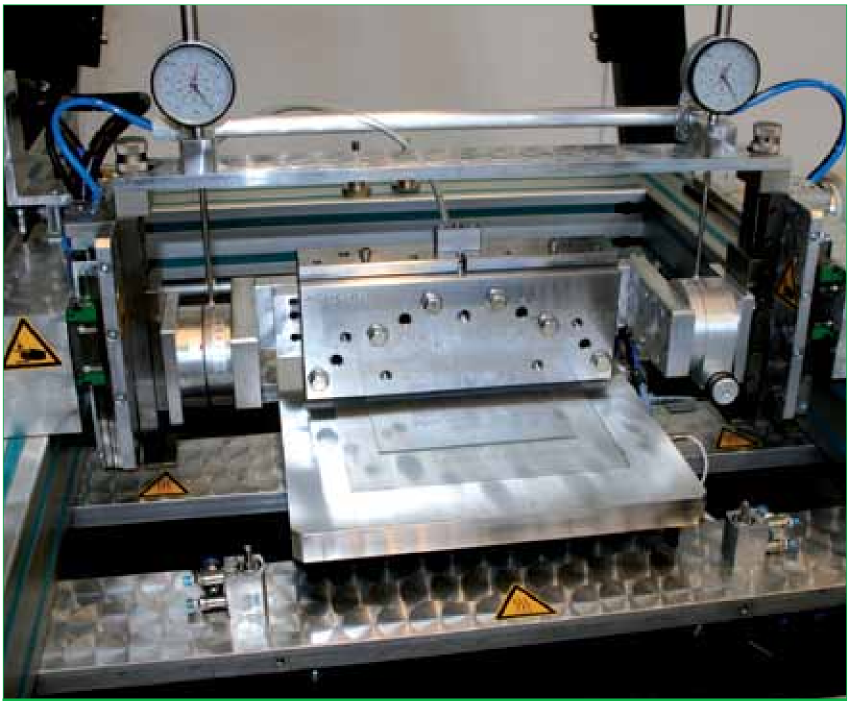

Figure 6. A Coatema easycoater with a 6" slot-die coating blade.

contact formation, electro-deposition can be used in a seed and plate approach to thicken seed lines deposited by a printing technique on a solar cell. While deposition of metals by means of this process is well established, a more recent and innovative application is the deposition of CIGS thin-film absorbers [8].

Electroless deposition

The very name of this approach provides a clear indication of the difference between this technique and its electro-deposition cousin. Instead of electrodes providing external current, chemical reducing agents are added to the bath to provide the driving force to produce individual metal or alloy coatings [7,9]. Not every metal or alloy can be deposited in an electroless fashion because a catalytic surface is required to drive the reduction process, so both the initial surface and the growing film must be able to fill this role. This technique can also be used to thicken previously deposited metal seed lines.

Chemical bath deposition

The compound films produced by chemical bath deposition proceed via a different mechanism than the electron-based electro- and electroless techniques. The final compound should be rather insoluble and also very stable in the typically aqueous bath, and the necessary ions must be generated slowly or the compound will simply precipitate from solution as large-grained powder [10]. The chemistry required to accomplish these stringent goals varies with the desired film, but once it is established the compound may be deposited on metals, plastics or ceramics. CdS is a widely-studied material that can be deposited via chemical bath, a technique that still produces the best quality films for buffers in CIGS solar cells [11]. CIGS layers have also been produced from chemical baths [8], and the deposition of metal oxide insulators and conductors have been widely explored [12].

Ink-based thin-film deposition techniques

Deposition techniques such as screen-printing and non-contact printing can

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be used for the deposition of thin films, but might not be the most cost-effective approach when a uniform coating is required on a large-area substrate. Alternative techniques that also have high material utilization used in production of photovoltaic devices are based on spray deposition and blade coating. Obviously, the main use for these techniques is in the deposition of thin film.

Spray coating

Spray coating is a technique that can be used to deposit homogeneous films on large substrates. During spray deposition, precursor ink is pumped toward the tip of a spray nozzle, where the liquid is agitated (ultrasonically or otherwise), creating a mist of small droplets. A gas flow can be used to carry this mist toward a substrate (Fig. 5). Many different spray nozzle configurations, shapes and sizes are available. Spray deposition is extensively used to deposit fluorine-doped tin oxide (FTO), a TCO commonly used in CdTe photovoltaics. In order to spray deposit FTO, a precursor solution is sprayed onto a hot substrate, and the desired material is acquired by means of pyrolysis on the surface. Due to the high temperature, this method can only be used to deposit a thin film on top of materials that can sustain such aggressive heating, such as glass.

"During spray deposition, precursor ink is pumped toward the tip of a spray nozzle, where the liquid is agitated."

An alternative and less aggressive method using a spray-coating technique is to deposit the inks at a lower substrate temperature, and subsequently use moderate heating to drive off solvent. When using this method, in most cases, a post-deposition processing step will be required to obtain the desired material. If this processing step includes high temperatures, rapid thermal processing (RTP) can be used to keep the exposure time of underlying layers to a minimum. Spray deposition of films other than TCOs for photovoltaics is currently predominantly used on a research level, although it can be readily scaled to production-size substrates and throughput.

Blade coating

Blade-coating techniques come in numerous variations, and slot die coating is one of the most widely used in photovoltaic production. In slot die coating, two metal or plastic plates with controlled spacing are used to create a small bead of liquid at the open end. The slot die is positioned in such a way that the bead touches the substrate surface but the applicator itself does not. The substrate is moved perpendicular to the opening in the slot die. Ink must be pumped through the slot die at a rate equal to the consumption at the substrate in order to get a homogeneous coating (Fig. 6). Slot die coating is extensively used in the field of organic photovoltaics as it allows for the deposition of extremely thin films (~100nm). Slot die coating is very versatile as it can also be used to deposit film with thicknesses of several µm, which makes it suitable for deposition of inorganic thin-film photovoltaics such as CIGS and CdTe. The thickness of the deposited films is controlled by the properties of the ink, i.e., viscosity and wetability, as well as the slot die deposition parameters, i.e., substrate draw speed, slot width, slot-to-substrate distance and angle. As an alternative to slot die coating, knife coating can be used. Knife coating is less suitable for some applications since it is a contact deposition method, whereas slot die coating is a non-contact method.

Spin coating

Like the other ink-based thin-film deposition techniques, spin coating starts with liquid ink containing carefully chosen components. This ink is applied to the substrate, and the substrate is rotated rapidly. Solvent is lost as the ink flows radially outward and thins, which increases the concentration of the remaining solids and the overall viscosity of the ink [13]. Ultimately, the ink viscosity reaches a critical point and the final solid film forms, although in many cases post-deposition heat treatment is required to decompose undesirable components. Spin coating was developed to deposit organic photoresists for patterning electronic components, and it is a favourite technique of the organic photovoltaics research community for depositing conducting or semiconducting polymers. Inorganic material scientists have also developed inks that can be spin coated to deposit high-quality films of materials such as ZnO [14] and CIGS [15]. While this technique is quite versatile and useful for small-scale precursor ink development, it may not be the best choice for the large-scale manufacturing regime where fast processing and high throughput are required.

Conclusions

We have reviewed atmospheric thin-film deposition techniques that are already used in solar cell production, such as screen-printing, electro-deposition, and chemical bath deposition, as well as other techniques that are under development for future use. Many of these methods are simple enough that they can be implemented rapidly with low capital investment, although development of precursor inks is not always as straightforward. An excellent overview of chemical strategies for preparing such solutions for inorganic materials is available in a recent publication [16].

The ultimate goal of any efforts made toward precursor development and thin-film or pattern deposition is to decrease cost, and based on this criterion the atmospheric processing techniques described here are not equivalent. While low up-front equipment costs are attractive, materials utilization over the lifetime of a manufacturing plant will have a more significant impact on the final module cost. Spray and slot die coaters are able to deposit the majority of their inks as blanket-coated films, and the various printing techniques discussed utilize an even greater percentage of the precursor solution to create thin-film patterns. By contrast, bath-based techniques convert a small fraction of the initial solution into thin films or lines.

The photovoltaics community will undoubtedly continue to develop innovative approaches to reducing the cost of solar cells, and atmospheric techniques will play their part along with more traditional vacuum-based thin-film deposition methods. While it cannot be predicted which atmospheric processing techniques will gain wide acceptance within the industry, we are confident that at least some of them will provide stepping-stones toward the goal of grid parity.

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About the Authors

Dr. Heather Platt studied the solution deposition of metal oxide thin films during her Ph.D. work with Prof. Douglas Keszler at Oregon State University. She is now developing inks to deposit metal films and lines on silicon wafers for photovoltaic cells at the National Renewable Energy Laboratory (NREL). She is extensively using direct-write deposition, spray deposition and RTP.

Dr. Maikel van Hest is currently a senior scientist in the process technology and advanced concepts group in the National Center for Photovoltaics at NREL. His principal areas of research and expertise include: solution-processing for silicon and thin-film solar cell application, vacuum deposition and transparent conductive oxides. His current work focuses on the development and basic science of solution-deposited materials (metals, CIGS, CdTe and TCOs) and the development of next-generation process technology for materials and device development (direct write deposition, spray deposition and RTP).

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