Non-vacuum Processing of CIGS Solar Cells

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ABSTRACT

This work is directed at developing low-cost, non-vacuum techniques for fabricating photovoltaic (PV) solar cells based on thin-film $CuIn_{1-x}Ga_xSe_2$ (CIGS). Processes for forming CIGS optical absorber films and metal oxide transparent conducting electrode coatings are under development. The goal is to accelerate the commercialization of thin-film CIGS PV technology by reducing the cost and complexity of fabricating efficient CIGS solar cells. To date CIGS films formed by non-vacuum techniques based on nanoparticle technologies have yielded 11.7% individual cells and 5% monolithic multi-cell submodules.

1. Introduction

Photovoltaic (PV) solar electric technology will be a significant contributor to the Nation's energy supply portfolio only if reliable, efficient PV power products are manufactured in large volumes at low costs. A promising pathway to sharply reducing PV costs is the use of thin film technologies in which thin layers of photoactive materials are deposited on inexpensive large-area substrates. One of the most promising thin-film PV technologies is based on $CuIn_{1-x}Ga_xSe_2$ (CIGS). CIGS films and the thin-film electrodes (e.g. ZnO) needed to construct thin-film PV devices are typically deposited by vacuum-based techniques. While vacuum-based techniques can capture a portion of the materials cost savings inherent in thin-film concepts, a promising pathway to reducing capital intensity and functional complexity so as to reduce costs, increase overall return on investment, and accelerate the transition to large-volume production is the use of non-vacuum techniques for depositing PV thin films.

Unisun has pioneered techniques for preparing high-quality PV thin films by non-vacuum techniques, including techniques based on nanoparticle materials. One of the core concepts is the use of non-vacuum techniques such as spraying and printing to deposit thin layers of sub-micron precursor powders and the use of low-temperature, reactive sintering to convert porous particulate layers into high-quality PV films. The use of multinary particulate precursors simplifies composition control for multi-component materials like CIGS since key components (e.g. Cu, In, Ga, etc.) can be precisely pre-mixed in the precursor particles.

Unisun recently initiated exploration of improved processes for fabricating CIGS solar cells using non-vacuum means. This work is being undertaken with support from the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) under the auspices of the "Photovoltaic Technologies Beyond the Horizon" program. The *Beyond the Horizon* program is aimed at nurturing basic scientific research directed to identifying and developing non-conventional breakthrough solar electric technologies that will be able to compete with other energy technologies used in the world on a large scale. The basic scientific research supported by the program is directed toward the goal of generating inexpensive electricity from sunlight.

Unisun's work under the *Beyond the Horizon* program is aimed at demonstrating a non-vacuum process for fabricating high-efficiency thin-film CIGS solar cells. The goal is to fabricate efficient thin-film PV devices using non-vacuum processing to deposit high-quality thin films of CIGS alloy optical absorber materials and to deposit coatings of optically-transparent, electrically-conducting metal oxide materials useful for forming solar cell electrodes. The objective of the research is to identify, explore, evaluate, and develop non-conventional solar electric technologies capable of making a breakthrough in the production of low cost electricity from sunlight.

2. Experimental Methods

In Unisun's baseline process, CIGS films are formed from particulate precursor materials prepared by an aerosol pyrolysis process. Typical CIGS precursor materials are solid sub-micron spheroids containing Cu, In, Ga and O [1]. Layers of precursor particles are deposited by preparing a slurry, paste or ink of precursor material with suitable solvents and dispersing agents, and spraying or printing 2-4 µm thick layers on Mo-coated soda lime glass. Porous precursor layers are converted into dense CIGS films by reactive sintering at 400-600°C.

Solar cells are formed by overcoating p-type CIGS films with n-type transparent conductors and metal grids. A typical transparent conductor sequence includes 30-50 nm of a "buffer" material (e.g. CdS, In(S,OH), etc.) and 0.2-0.5 µm of a conductive semi-transparent metal oxide (e.g. ZnO:Al, ITO, etc.). Buffer layers are typically deposited by solution deposition techniques, e.g. aqueous autocatalytic reactions that deposit thin conformal coatings on immersed substrates. Metal oxide layers are typically deposited by vacuum deposition techniques, e.g. rf or pulsed dc sputtering from oxide targets. A typical metal grid consists of 1-3 µm of Ni, Al, In, Ag, etc. deposited by vacuum evaporation, sputtering, etc.

Unisun works closely with a range of collaborators. Mo-coated glass is obtained from university and private sector collaborators. CIGS precursor materials, precursor layers and films are processed by Unisun. CdS, ZnO and grids are deposited on Unisun CIGS films by the Institute of Energy Conversion (IEC) at the University of Delaware by solution deposition, rf sputtering, and e-beam evaporation, respectively. In parallel, Unisun is exploring non-vacuum techniques for depositing high-transparency, high-conductance metal oxide films at temperatures compatible with underlying CIGS p-n junctions.

3. Experimental Results

Layers of particles have been deposited by spraying and printing techniques. Spraying techniques yield a wide range of layer characteristics depending on the specific spraying parameters chosen [3]. Pneumatic spraying can yield 1-5 μm thick precursor particulate layers that are adherent (i.e. the particulate layer adheres to the Mo) and coherent (i.e. the particles in a layer cohere to one another) with average particle packing densities of 15 to 35 % depending on spray parameters. Layers can be sprayed with uniform matte appearance indicative of a microscopically planar morphology. Surface morphology, deposition rate, and materials use efficiency vary with spray parameters. In general with pneumatic spraying layer planarity and materials use efficiency are inversely related. Materials use efficiencies of ca. 95% have been demonstrated; typical efficiencies are lower.

Industrial printing is a workable alternative to spraying. Printing processes can be used to deposit thin layers of particulate suspensions (e.g. inks) on large areas. While the screen printing processes often used to deposit grids on crystalline silicon solar cells are ill-suited to making the thin (e.g. 1-2 μm), large-area (e.g. 0.5-2 m^2) uniform layers desirable for thin-film PV, other printing techniques are capable of printing uniform thin layers on large areas. A wide range of printing technologies has been developed for specific applications. For rigid nonporous substrates (e.g. glass), doctor blading, wire-wrapped rods and flexographic printing are promising options. Doctor blading and wire-wrapped rods are common techniques for depositing controlled thicknesses (e.g. of commercial paints) on modest areas (e.g. 100 – 1000 cm^2). Flexographic printing (i.e. transfer printing from a inked compressible plate, similar in many respects to a rubber stamp) using highly fluid inks is well-suited to high-speed printing, e.g. for high-volume production of printed labels. Unisun aims to deposit layers with ± 10% short-range thickness variation and 40% apparent packing with greater than 85% materials use efficiency.

Particle-based technologies can also be used to deposit films of transparent, conducting metal oxides. Metal oxide nanoparticles have been used to deposit particulate coatings, but it is difficult to obtain low sheet resistances using nanoparticulate material.. Even when using high-conductivity particles like ITO, layers of particulate materials generally exhibit poor electrical transport between adjacent particles.

Unisun has prepared sub-micron metal oxide materials (e.g. Zn:Al oxide powders) suitable for use as precursors for electrode films. Layers of particles can be deposited by spraying or printing; and can be densified into high-conductance films by reactive annealing. The challenge is to achieve good optical transmission and lateral electrical conductance at temperatures that an underlying CIGS junction will tolerate.

Cell efficiencies of 11.7% and multi-cell module efficiencies above 5% have been confirmed by NREL for ZnO/CdS/CIGS/Mo cells incorporating particle-based, CIGS films [4].

At present, cell efficiencies appear to be limited by the quality of the CIGS film itself. Quantum efficiency measurements without light bias show a monotonic reduction of photocarrier collection efficiency at longer wavelengths, indicative of poor minority carrier diffusion. Quantum efficiency measurements with light bias show a wavelength-independent, voltage-dependent photocarrier collection, suggestive of recombination losses near the CIGS surface. High-frequency capacitance measurements suggest that hole densities are relatively high (e.g. ca. 10^{17} cm^{-3}) in the CIGS film and upwards of 10^{18} cm^{-3} near the CIGS surface. Cross-sectional scanning electron micrographs show reasonably dense CIGS films, but grain size varies considerably, e.g. 0.25 – 1 μm. These results suggest that cell efficiency improvements will accrue from improvements in CIGS film defect density, mass density, and grain size.

5. Conclusions

This project aims to demonstrate the feasibility of using particulate precursor materials in a simple, easily scalable, non-vacuum process for depositing CIGS films for large-area, low-cost PV modules. The process promises to halve the cost of a CIS film for a thin-film solar module, to increase the ROI for thin-film PV, and to significantly accelerate the large-scale commercialization of CIGS PV technology.

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