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HIGH-PERFORMANCE THIN-FILM PHOTOVOLTAICS USING LOW-COST PROCESS TECHNOLOGY

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ABSTRACT

$CuIn_xGa_{1-x}Se_2$ (CIGS) based photovoltaic (PV) thin films can deliver sunlight-to-electricity conversion performance superior to that of CdTe or silicon based thin films, and can exceed the energy delivery of crystalline silicon PV under real-world operating conditions. However, the functional and operational complexity of using high-vacuum processes to deposit CIGS thin films results in yield and throughput limitations that tend to negate any manufacturing cost advantage over CdTe and crystalline silicon cells. In this paper, we report on progress made at Nanosolar in developing CIGS process technology capable of realizing the economics of high-throughput, high-yield processing in the form of (non-vacuum) printing of nanoparticles onto low-cost substrates and converting these layers into high-quality electronic films using rapid thermal processing (RTP) techniques. Solar cell efficiencies of 14% have been confirmed by NREL.

1. INTRODUCTION

CIGS based PV thin films can deliver sunlight-to-electricity conversion efficiencies of 19.5% [1], which is superior to micromorph and amorphous silicon as well as CdTe based thin films. In addition, CIGS thin films tend to deliver real-world kWh performance superior to that of crystalline silicon [2] and CIGS exhibits outstanding long-term stability and durability when properly packaged [2-4].

CIGS based thin films resulting in high efficiencies have been grown by various methods, showing that efficiency is not intrinsic to the growth method. However, the functional and operational complexity of high-vacuum processes conventionally used to deposit CIGS films (sputtering, co-evaporation), while successful in the laboratory on small-scale cells, faces known CIGS-stoichiometric and other uniformity issues that manifest as yield challenges in commercial manufacturing in a way that tends to negate any potential cost advantage [5].

In this paper, we report on progress made at Nanosolar in developing process technology that circumvents the throughput and reproducibility limitations of high-vacuum based deposition techniques by coating a homogeneously mixed ink of nanoparticles with industrial wet coating techniques. This approach combines the built-in reproducibility from composition-controlled nanoparticle materials, high materials utilization typical of industrial wet coating, and distinctly superior production throughput of non-vacuum processing. Materials use efficiencies above 90% have been achieved in addition to coating speeds more than ten times faster than possible with high-vacuum based deposition techniques, which also suffers from substantially more expensive and functionally and operationally more complex equipment.

The CIGS roll-printing technology developed by Nanosolar combines high-speed, high-yield, non-vacuum, wet coating of nanoparticles onto low cost per unit area of metal foil substrates with rapid thermal processing (RTP) techniques for converting these particle layers into high-quality electronic films (as well as similar innovations for cost reduction on the electrodes, etc. not discussed here).

Earlier work on particle-based CIGS PV primarily focused on films on rigid substrates processed using long heating cycles [6-8]. The combination of fast non-vacuum deposition using low-cost equipment followed by fast heating techniques is recognized by experts as a promising marriage to considerable price reduction [2]. In addition, Nanosolar's equipment and processes are designed to allow for easy in-line process control to maximize yield and throughput.

Nanosolar's rapid thermal processing of nanoparticle-based coatings resulted in solar-cell efficiencies confirmed by the National Renewable Energy Laboratory (NREL) to be 14.5%, which amounts to a world record for any printable solar cell.

In this paper, the impact of sodium on gallium grading of CIGS, the impact of substrate on film morphology, and the nature of nanoparticle precursors that enable fast one-step film conversion will be discussed.

2. EXPERIMENTAL

The inks containing the precursor nanoparticles were deposited by typical wet coating techniques onto thoroughly cleaned rigid and flexible substrates coated with a back electrode.

Porous as-coated layers were converted into dense PV-quality films using RTP techniques. CIS and CIGS films were grown in a bench-scale modified Jipelec JetFirst 150 system where the parts are placed into a graphite box where a spring-loaded backside thermocouple accurately measures the temperature of the graphite box.

The dynamic SIMS depth-profiling measurements were performed on a Cameca 5f magnetic sector SIMS apparatus where sputtering and analysis were performed with a 150 nA 5.5 keV Cs^+ primary beam. No electronic gun for charge compensation was used.

The secondary ions used were Na (m/z = 22.99), Ga+Cs (m/z = 201.83), Cu+Cs (m/z = 197.84), and In+Cs (m/z = 247.81).

CIGS samples with a flat compositional depth-profile with composition measured by atomic absorption (AA) were used to convert secondary ion counts into Ga/(In+Ga) atomic ratios. AA measurements were performed on a Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer. Thickness measurements required to convert sputter time into thickness were performed with both cross-sectional SEM measurements and a Dektak IIA Stylus Profilometer.
Spectrally resolved photocurrents and external quantum efficiency maps were measured with monochromatic light with a spot-size of ~0.5mm (~0.1mW/cm^2) calibrated against a Hamamatsu Si photodiode with known spectral response. Maps are acquired by moving the solar cell on an x-y stage in steps of 0.25mm.

3. RESULTS AND DISCUSSION

In the following, we discuss the impact of the substrate on the absorber growth, the impact of sodium on the absorber growth, the nature of nanoparticle precursors that enable a fast one-step semiconductor processing, and NREL-certified solar cell efficiencies obtained using nanoparticle precursors.

3.1 Impact of Substrate on Absorber Growth

As is generally seen with most CIGS film formation processes, CIGS film characteristics are affected by the specifics of the underlying layers and substrates.

With similar electrode coatings, films formed on soda-lime glass substrates present a more faceted surface as a result of a smaller grain structure at the surface of the film than do films formed on metal foils.

CIGS films on metal foil turn out to be more planar as a result of a larger grain size at the surface of the film (see Fig. 1). Films with through-film grain sizes comparable to the 1-2 μm film thickness can be achieved on both glass and foil (not shown).

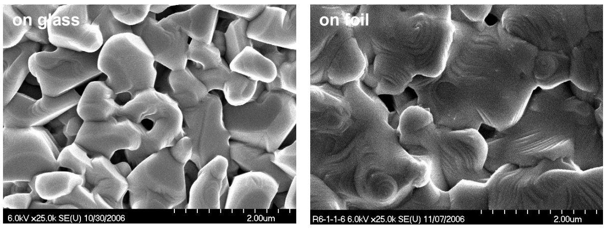

Fig. 1 SEM images of CIGS film on glass (left) and on foil (right).

The choice of substrate also affects the compositional gradients in the resulting CIGS films. For example, otherwise similar processing of CIGS on glass and foil substrates can result in different gallium concentration profiles as evidenced by differences in x-ray diffraction where CIGS films on glass substrates have higher near-surface gallium concentrations than do CIGS films on foils (see Fig. 2). SIMS depth profiles support the XRD results (not shown).

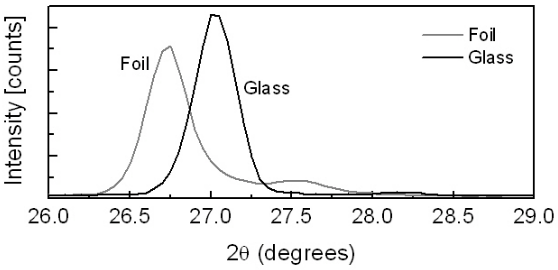

Fig. 2 Low-angle (3°) grazing incidence x-ray diffraction spectra for CIGS films on glass and on foil.

3.2 Impact of Sodium on Absorber Growth

Gallium profiles are correlated with sodium content; films in which sodium concentrations are higher show increased near-surface gallium and sodium concentrations (see Fig. 3).

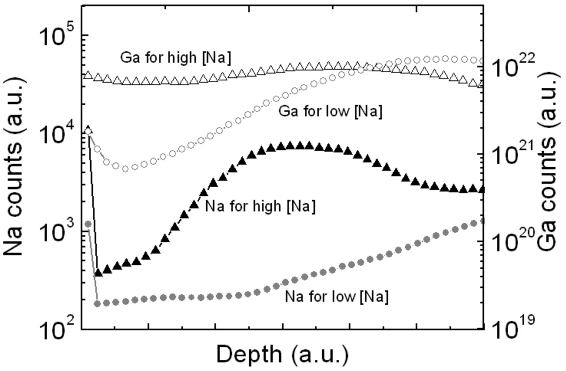

Fig. 3 SIMS depth profiles showing Ga (open symbols) and Na counts (solid symbols) in CIGS films.

Co-evaporated CIGS thin films made by NREL and the Institute of Energy Conversion (IEC), both depth-profiled on the same instrument as the samples made by Nanosolar, are added for comparison (see Fig. 4).

As absorber growth conditions are further refined one can reasonably aim to achieve homogeneous compositions or to approximate the “saddle” profile used in the co-evaporated CIGS cells with record high efficiencies.

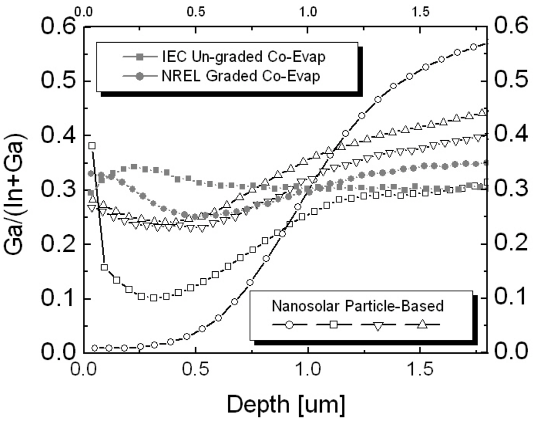

Fig. 4 SIMS derived Ga/(In+Ga) depth profiles of CIGS films formed by Nanosolar particle-based processes, by NREL co-evaporation processes with an intentional Ga gradient, and by IEC co-evaporation processes with no intentional Ga gradient.

3.3 Growth of CIS from Nanoparticles

In earlier work, non-vacuum CIGS films have been created using partially or fully oxidized particles. The disadvantage of such pioneering research work [7] is that it either requires two heating steps, one of oxide reduction to a metallic alloy film followed by a second heating step of selenization, or a slow one-step process with highly toxic H_2Se.

The use of selenides as CIGS-film precursor particles has the potential for a fast one-step process. But earlier work growing CI(G)S from selenides either used high-melting CIS or CIGS precursor particles which fail to result in a thin, uniform, dense absorber film of large-grained CI(G)S [6,8].

Various other related approaches have been investigated and only resulted in limited success [9].

Copper selenide (Cu-Se) with a Se-to-Cu ratio larger than for $Cu_{2-x}Se$ melts at temperatures typically used to grow high-quality CIGS films. Starting from Cu-Se nanoparticles, therefore, should aid the growth of dense films. When starting from an ink containing Cu-Se and indium selenide (In-Se) nanoparticles dense large-grained thin CIS films can be grown with RTP techniques (see Fig. 5), supporting the liquid-assisted growth mechanism for nanoparticle derived films. XRD measurements show single-phase CIS (not shown).

This Nanosolar-patented work is the first time that high-quality (uniform, dense, large-grained) thin PV films were grown with one fast heating step, directly based on selenide particles.

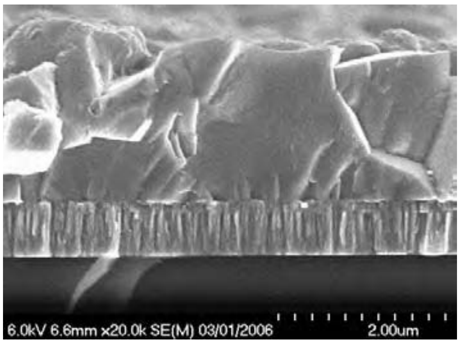

Fig. 5 SEM image of CIS film grown from (non-oxide, non-metallic) nanoparticles.

3.4 Solar Cells

Using low-cost, high-throughput, nanoparticle-ink based methods, cells have been fabricated on foils with efficiencies sufficient for fabricating multi-cell modules that can compete on a total-area basis directly with the high-volume sector of today’s silicon PV market.

Solar cells have been fabricated by depositing layers as typically used in CIGS thin-film laboratories, being a stack of CdS/i-ZnO/ZnO:Al with grids of Ni/Al, and without an anti-reflective coating.

Cell current-voltage behavior is typical of CIGS cells with photovoltage and photocurrent density largely determined by the bandgap profile. Open circuit voltages of 430-630mV, photocurrents of 30-37mA/cm^2, and fill factors of 65-72 are measured for printed nanoparticle cells using Nanosolar technology.

External Quantum efficiencies (EQE) are reasonably flat for printed-CIGS cells and show buffer layer absorption at short wavelengths, variations in long-wavelength band-edges consistent with bandgaps estimated from compositional data, and a slight decrease in EQE with wavelength related to photocarrier diffusion and collection. EQE uniformity on small test cells is excellent. See Figure 6.

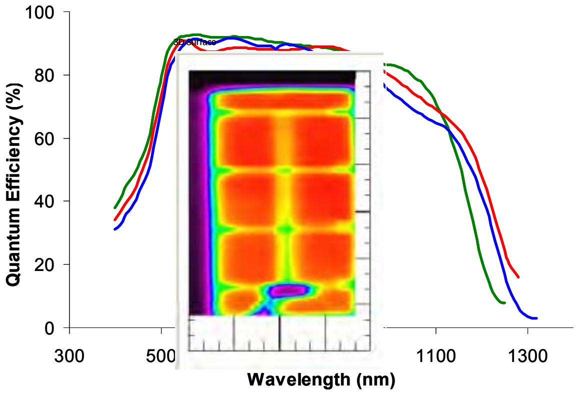

Fig. 6 EQE for representative CIGS solar cells; insert shows EQE uniformity for a gridded CIGS cell measured at 600 nm.

NREL measured one of Nanosolar's cells on glass at about 14% on a total-area basis, equivalent to about 14.5% on an active-area basis after correcting for shadowing by the grid (V_{oc} = 599mV, J_{sc} = 32.2mA/cm^2, FF = 72.3).

To our knowledge, this is the highest efficiency yet reported for any printed solar cell of any kind and any CIGS cells fabricated using non-vacuum methods in particular.

4.0 CONCLUSIONS

Nanosolar is developing nanoparticle-printing based CIGS technology with built-in stoichiometric reproducibility (superior commercial yield performance), near-perfect materials utilization (low materials cost), and orders of magnitude higher throughput per capital equipment investment. Combined with a similar level of innovation for substrate, electrode, and system-integration cost reductions (not described here), high W/m^2 performance can be combined with radically low \$/m^2 area cost to achieve distinctly superior PV cost efficiency.

The world-record performance results presented here demonstrate that, with innovation in science and nanomaterials, low-cost processes can yield solar cells whose film quality is as good as that obtainable with far more expensive high-vacuum based deposition techniques.

A clear correlation between Ga and Na depth profiles in CIGS films grown from nanoparticles has been shown. In addition, it has been shown that dense large-grained absorbers with varying Ga depth profiles can be obtained from nanoparticles.

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