Semiconductor Nanocrystal Inks for Printed Photovoltaics

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Abstract:

Copper indium gallium diselenide (CIGS) is an effective light-absorbing material for photovoltaic devices (PVs). Commercially fabricated CIGS films are vapor-deposited. A different approach to CIGS film deposition that is potentially much cheaper is to formulate nanocrystal-based inks that can be coated onto the substrate under ambient conditions, thus alleviating the need for vacuum or high temperature processing. Such an approach could greatly reduce the processing complexity and cost of CIGS deposition. Recently, we demonstrated 3.1% power conversion efficiency under AM 1.5 illumination from spray-deposited CIGS nanocrystal-based PVs. The nanocrystal films in those devices were deposited manually from a spray gun; thus, leading to variations in film thickness and uniformity across the entire substrate that gave significant differences in device performance. To better control the uniformity and thickness of the nanocrystal films, we have developed an automated deposition process that is described here. The focus of this research project was to understand how the deposition parameters, including tip-sample distance, ink formulation, raster rate and flow rate influenced the morphology and thickness of the films.

Introduction:

The changeover from the manual spray deposition to the automated process required an identification of how the deposition parameters impacted the film morphology and thickness. The key parameters were the tip-to-substrate distance, spray pressure, dispersion concentration, flow rate, and spray gun angle to the substrate. The dimensionless parameters involved in the spray process, including the Reynolds (Re), Weber (We), and Ohnesorge (Oh) numbers were calculated and correlated with the film morphology.

The Reynolds number characterizes the flow regime of the carrier gas and solvent in stream. It was found that laminar flow was desired in which the droplets are carried in the stream. The Weber number provides insight about how stable the suspension droplet was in the carrier gas. Under conditions of high We (i.e., We > 10) the stream would disintegrate, leading to poor deposition morphology. Therefore, We < 1 were found to provide uniform micro-droplets that settled on the substrate and quickly dried, leaving the most uniform film. The Ohnesorge number of the process revealed how individual droplets impacted the substrate.

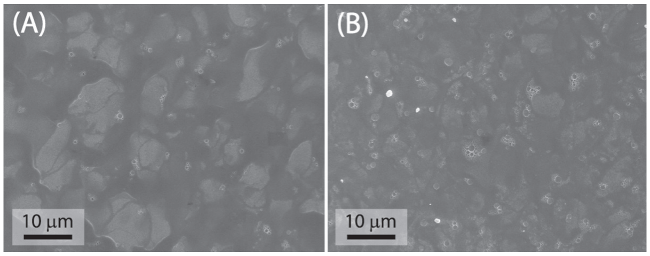

Figure 1: SEM image of (A) manually sprayed and (B) auto-sprayed CIGS nanoparticles on Au back contact.

Figure 1 shows scanning electron microscopy (SEM) images of a nanocrystal layer that was manually spray-deposited, compared to a layer deposited using the automated spray process. The optimal deposition conditions for a uniform 200-300 nm thick film were a nanocrystal dispersion concentration of 20 mg/ml in toluene, a 10.2 cm distance from the nozzle to the substrate, and a gauge pressure between $3.45 \times 10^5 - 3.79 \times 10^5$ Pa (50~55 Psi). The most uniform films were obtained by spraying several coats with a 180 degree rotation of the substrate between each one coat.

Controlling Deposition Morphology:

The nanocrystal layer morphology and thickness of manually-deposited films could be reproduced using the automated spray deposition process. Devices fabricated with nanocrystal layers deposited with the automated spray process were also found to have similar power conversion efficiencies as those made with manually deposited films.

Over the course of understanding how to control the nanocrystal film morphology, it became apparent that there could be an opportunity to control and exploit the roughness of the films to obtain higher device efficiency. In some cases, the deposition gave corrugated films with raised features that could perhaps be utilized to improve the interfacial contact area between junctions in the device. Therefore, an effort was made to very precisely understand the role of the spray deposition parameters on the film morphology.

The separation between the spray head and the substrate was found to be the most influential parameter on the film morphology. A series of depositions were carried out by varying the tip-to-sample distance. When the separation was less than 2.5 cm, the nanocrystal film exhibited a "mud-slide" consistency, indicating that the spray had not disintegrated into individual droplets.

Separations of 2.5-4.5 cm led to stripe like features. Under these conditions, the stream had become unstable, but had not reached a stage with well-defined droplets. For separations between 5.1 and 8.2 cm, the spray was in the droplet regime, and at distances greater than 8.2 cm, there was evidence of solvent, as the particles appeared to reach the substrate as dried aggregates.

Figure 2 illustrates the regimes in the stream and the transitions between each stage. Such changes are well understood in terms of the dimensionless numbers that govern the deposition.

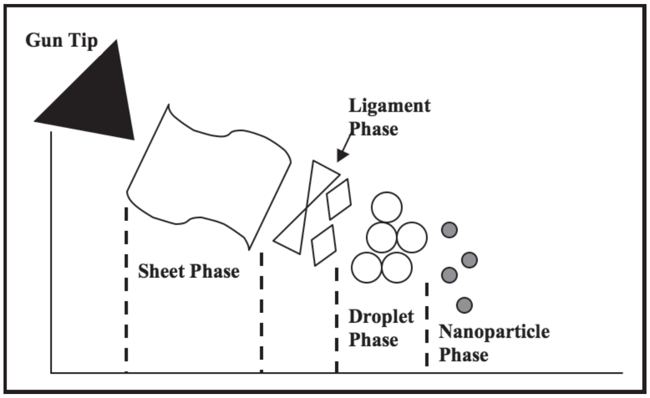

Figure 2: The regimes in the stream and the transitions between each stage.

Results:

The transition from turbulent to laminar flow occurs at Re = 1. At large Reynolds numbers greater than 100, the nanocrystal film had a "mudslide"-looking morphology. The film morphology became much more uniform as the Re decreased. The critical value of We of 0.01 was found to be necessary for droplet formation and deposition from the spray. Higher values of We resulted in sheet-like deposition that had the "mudslide" appearance, similar to the films obtained at high Re. Low values of We produced scattered clusters of nanoparticles on the substrate, which gave rough non-uniform films. When operated at low values of Oh, droplets bounced off the substrate and did not absorb.

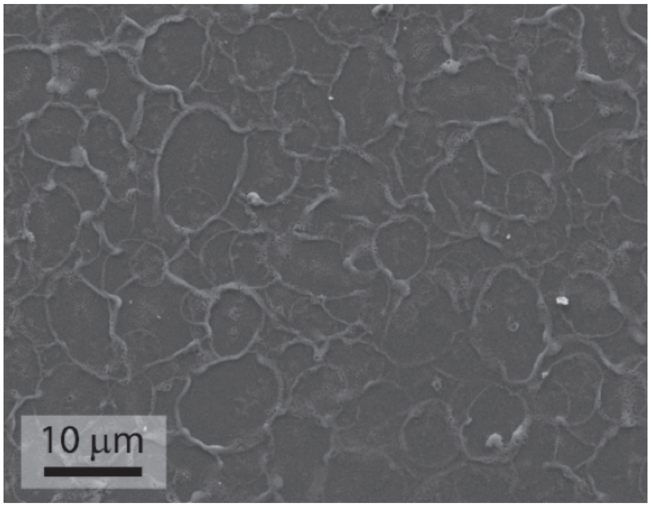

Figure 3: SEM image of structured film enabled through automatic spray deposition.

At high Oh, each droplet impinged onto the substrate and left a circular splash effect. The solvent then dried from this droplet to leave a characteristic "coffee-ring" effect, as shown in Figure 3.

A critical value of Oh = 0.05 is believed to be the point where a single droplet absorbs evenly on the substrate without any distortion.

Future Work:

It may be possible to improve device performance by increasing the interfacial contact area at the p-n junction in a device without increasing the average nanocrystal film thickness by depositing featured—not planar—films of nanocrystals. Although many rather exotic methods are being explored to create such heterojunctions, like nanopillar arrays for example, the spray deposition process may have the ability to create textured surfaces in a single deposition step, which could potentially improve device efficiency compared to devices made with uniform, flat nanocrystal films. The appropriate deposition conditions were identified in the automated spray process to deposit such structured films across large-area substrates, as shown in Figure 3. This may now facilitate studies of how featured electrodes might impact device efficiency.

References:

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