

Continuous Microreactor-Assisted Solution Deposition for Scalable Production of CdS Films

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Solution deposition offers an attractive, low temperature option in the cost effective production of thin film solar cells. Continuous microreactor-assisted solution deposition (MASD) was used to produce nanocrystalline cadmium sulfide (CdS) films on fluorine doped tin oxide (FTO) coated glass substrates with excellent uniformity. We report a novel liquid coating technique using a ceramic rod to efficiently and uniformly apply reactive solution to large substrates (152 mm \times 152 mm). This technique represents an inexpensive approach to utilize the MASD on the substrate for uniform growth of CdS films. Nano-crystalline CdS films have been produced from liquid phase at ~90°C, with average thicknesses of 70 nm to 230 nm and with a 5 to 12% thickness variation. The CdS films produced were characterized by UV-Vis spectroscopy, transmission electron microscopy, and X-Ray diffraction to demonstrate their suitability to thin-film solar technology.

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Cadmium Sulfide (CdS) thin films are commonly used as heterojunction partners in cadmium telluride (CdTe) and copper indium gallium di-selenide (CIGS) thin-film solar cells.^{1–3} Thin CdS films are used to maximize the amount of light absorbed in the active area of the solar cells⁴ while still thick enough to minimize shunting.⁵ Chopra et al.¹ and Mitzi et al.⁶ in their reviews on thin film solar cells have emphasized the necessity of low-cost manufacturing techniques for CdTe and CIGS thin film solar cells. Solution deposition techniques offer a promising economical pathway for cost effective PV manufacturing.

Among the solution based deposition techniques, electrodeposition⁷⁻¹¹ and chemical surface deposition^{12,13} exhibit substantial potential for facile integration with large scale production. In the case of screen printing, it is challenging to produce films less than 10 μ m thick,¹⁴ a full two orders of magnitude too high for solar PV-relevant CdS films. In addition, there is a cost burden because of the substantial heat-treatment required to produce high quality films.¹⁵ Doctor blading can only be used for solution chemistries that do not aggregate or crystallize at high concentration.¹⁶ Spray pyrolysis has been reported in the literature,¹⁷ however it necessitates higher deposition temperature (>400°C). Chemical bath deposition (CBD) is an extensively investigated solution-based method for generating CdS films.^{18–23} Although, CBD has been implemented for large scale manufacturing,⁷ lower material utilization and significant waste generation continue to be issues.

Continuous solution deposition process offers advantages over several shortcomings of the CBD process. The success of integrating continuous solution deposition into industrial scale production is largely dependent on the choice of coating technique. There is a need in thin film coatings industry for simple and cost effective processes that can be used in non-ideal environments and involving aggressive chemicals, high temperature, and challenging reaction chemistries. The requirement is to create a thin layer of aqueous reactive solution on the substrate without long upstream hold-up time. These long hold-up times will cause the solution to age, leading to undesirable precipitation reactions.^{12,24} The reaction mixture for CdS production is time sensitive, with longer times favoring homogenous formation of undesired particles that will aggregate, create poor films, cause equipment fouling, and reduce overall material yield.

Groups led by Chang^{25–27} and Baxter^{28,29} have demonstrated the incorporation of microchannel devices in a continuous process of

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solution deposition for semiconductor films. These researchers have shown that using microreactor technology has enabled enhanced control on process parameters for challenging reaction chemistries commonly involved in generating semiconductor films. Based on a similar framework, Paul et al.³⁰ have developed a deflected plate flow cell method for coating CdS films by microreactor-assisted solution deposition (MASD) process. Although, this approach was capable of producing uniform CdS films on 150 mm substrate, it is not suitable for conveyorized reel-to-reel manufacturing.

The work described here adapts the MASD for deposition of CdS films and demonstrates a route to process scale-up. MASD facilitates precise control of solution temperature and residence time prior to application. The objective of this paper is to demonstrate a near room temperature continuous-flow deposition process capable of depositing CdS films with high film uniformity operating under atmospheric pressures. The rod coater developed during this study is simple and cost effective to implement, in comparison to other thin film deposition techniques. It requires no hold-up time and facilitates precise control of solution temperature and residence time prior to application. We report a scalable deposition unit that shows a pathway to larger scale manufacturing.

Methods and Materials

Description of experimental process characteristics.— Positive displacement pumps (Acuflow Series III) were used to pump each stream of reagents at a constant flow rate. All chemical reagents used were of ACS grade (>99% purity). Cadmium chloride provided the cadmium source, and thiourea provided the sulfur source. Stream A consisted of cadmium chloride (0.004 M), ammonium chloride (0.04 M), and ammonium hydroxide (0.04 M) in water. Stream B consisted of thiourea (0.08 M) in water. Special care should be taken in the handling of cadmium-containing solutions, including personal protective equipment, adequate ventilation, and proper disposal of waste. The reagent reservoirs were placed on analytical balances (Ohaus) and the changes in the mass were recorded throughout the duration of the test. The reagents from the two streams were mixed in a T-mixer (Idex, Inc.) before entering the heat exchanger. Thermocouples at the inlet and outlet of the heat exchanger recorded the temperature of the fluid. Commercial soda lime glass (Pilkington TEC-15) with a transparent conducting oxide (TCO) layer was employed as the substrate for film deposition. The TCO layer consisted of fluorine-doped tin oxide (FTO). A LabView (National Instruments) program was

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Figure 1. Schematic of pilot deposition unit for CdS thin films. Prepared substrate travels on heated boat from left to right through (a) substrate preheat (b) liquid deposition (c) rinse.

developed for data acquisition and control of temperatures, flow, and substrate positioning over time.

Deposition unit – Process sequence.— The scalable deposition unit is representative of the potential industrial form of the deposition setup with several process steps for CdS deposition described below and shown in Figure 1. The main steps of the deposition process included substrate preheating, dispensing reagents, dwell time, and rinsing which were employed in series.

Preheating.— The CdS reagents were heated to the desired solution temperature of ~90°C using the microchannel heat exchanger described previously.²⁴ A linear stage (Techno, Inc) equipped with a platform and location controller was employed for moving the substrate between process sequences. A custom-designed boat intended for substrate heating and excess reactant solution collection was fixed to the platform. The boat housed a silicone heating pad (203 mm \times 203 mm, 10 W/in², Omega) which was sandwiched between two

metal plates. The cleaned substrate was then placed on the metal plate, where it received heat transferred from the silicone heating pad. The silicone pad was controlled manually by a variable voltage source. Four ceramic infrared heaters (152 mm \times 51 mm, Tempco, Inc., 425 W each) were mounted above the travel path to maintain a constant substrate temperature during transit. A programmable controller (Phoenix, Inc.) was used to precisely control the speed and position of the stage on the linear slide. A previously optimized program for the linear slide was chosen depending on the feed flow rate and the deposition time used for a specific test.

Reagent dispensing .- A drip and spread mechanism as shown in Figure 2 was used for evenly coating the glass with reactive solution to grow uniform CdS films.³¹ At an optimized flow rate of ~45 mL/min, the pre-heated CdS reagents were pumped through a customized manifold onto the pre-heated FTO coated glass substrate. A ceramic rod (Superior Technical Ceramics, ~5 mm diameter and ~230 mm long) was utilized to spread the droplets of reactant solution into a thin layer. The ceramic rod was composed of hydrophilic alumina, which assisted in spreading the liquid into a thin layer on the hydrophilic FTO surface. The ceramic rod was anchored into the deposition unit by a custom designed fixture which enabled precise height adjustment of the rod from the FTO substrate. A prescribed gap of ~ 0.5 mm between the ceramic rod and the glass substrate provided lateral wicking action to uniformly coat the dripping pre-heated CdS solution on the substrate as it moved beneath the rod. The gap between the substrate and the ceramic rod is sufficient to maintain a liquid meniscus between the hydrophilic material and the substrate. A secondary result of the rod movement is to siphon off excess reagents. The combination of rod and glass hydrophilicity and the size of the gap between the two were crucial in providing adequate wicking action to spread the fluid across the entire substrate width. This mechanism can easily be scaled to any substrate size by appropriately designing the length of the ceramic rod.

Dwell time and rinsing.— Once coated with reactant solution, the substrate was held at constant temperature (usually the same temperature as for deposition) while the CdS film grew from the reagents in the liquid. Multiple passes of dispensing and dwell time were required to avoid substrate dry-out and achieve the required thickness of CdS film. At the end of each experiment, the CdS film deposited on the glass substrate was rinsed with de-ionized water. A uniform, continuous, and particle-free CdS film was thus obtained and no further processing was required. One of the significant features of this process is that any thickness can be easily obtained with appropriate optimization of deposition time.

A typical deposition involved the following steps. A constant solution residence time of 15 seconds was used in the heat exchanger for



Figure 2. A schematic illustration for developing a thin liquid layer using the ceramic rod. Initial imperfect liquid deposition on substrate is adjusted by the wicking action of the rod/glass interface as the rod passes above the glass surface.

all experiments. The 15-second residence time was chosen based on our previous parametric study.²⁴ The heat exchanger was pre-heated while circulating water and the FTO glass substrate was simultaneously heated to deposition temperature ($\sim 90^{\circ}$ C). The program for the linear slide was then activated, upon which the substrate was positioned exactly below the outlet of the heat exchanger. At the appropriate time, valves were switched from water to reagents for the pumps to begin feeding reagent mixtures A and B. The two reagent streams then flowed through the micro-mixer and entered the heat exchanger. The mixed fluid entering the heat exchanger assembly was rapidly heated to the reaction temperature in approximately one second, followed by the additional 14-second residence time period. Upon exiting the heat exchanger, the CdS reagent solution was distributed on the edge of the glass substrate, forming an initial puddle. The linear slide then traveled at an optimized speed of ~1250 mm/min, bringing the heated substrate under the rod and spreading the reactant fluid into a thin layer on the surface of the FTO glass.

The CdS reagents that continuously dripped on the FTO glass substrate were spread into a thin film by the ceramic rod while the linear slide moved back and forth to cover the entire area of the glass for the specified time. The thickness of the CdS film can be easily controlled by varying the dwell time which is essentially the number of multiple passes the linear slide traveled during the entire run. The CdS film formed on the substrate was rinsed with de-ionized water to remove any particulates and by-products. The films produced were analyzed as-deposited, without any post-annealing.

Characterization of CdS film.— The combination of inherently rough substrate, large sample area, and the need for rapid, nondestructive characterization of many samples required that we utilize a high-throughput thickness characterization method. Thin film thickness characterization techniques such as profilometry, SEM, ellipsometry, and AFM are inadequate for this task due to various limitations in throughput or performance with this film/substrate system. As a result, we developed a rapid, repeatable, and non-destructive thickness measurement technique based on UV-vis spectroscopy (Ocean Optics USB2000). Transmittance and reflectance were recorded at a constant wavelength of 500 nm at 36 different positions on each 152-mm sample. The UV-vis spectroscopy technique was calibrated to TEM-validated calibration samples, as previously described.²⁴

The optical bandgap (Eg) was determined from the formula,

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$
[1]

where hv is the incident photon energy, A is a constant and the exponent "n" is an index value used to describe the direct bandgap $(n = \frac{1}{2})$.

For morphological and structural characterization, the original 152-mm CdS/FTO sample was diced into 25.4-mm coupons. Focusedion-beam milling (FIB) (FEI Quanta 3D SEM/FIB) was used for sample preparation for cross-sectional characterization by TEM (Philips CM-12). Carbon and platinum layers were deposited on top of the CdS layer to reduce surface charge accumulation and to introduce a surface protection layer during the FIB milling process. The crystalline structure was studied using grazing-incidence X-ray diffraction (Bruker, D8 Discover). All measurements were performed at room temperature for various CdS film thicknesses obtained at different deposition times. A Cu-K α ($\lambda = 1.54$ Å) radiation with an incident angle of 0.5° was used for all scans.

Results and Discussion

The film thickness average and standard deviation for each tested condition is summarized in Table I. Three deposition times of 2.6, 6.3 and 9 mins were investigated. The results reported represent the average of three replicates at the same condition. After glass precleaning and system start-up, the 152-mm substrates were coated with a thin film of CdS having thickness ranging from 72 nm to 234 nm using process times of 2.6 min to 9.0 min. The entire surface of the glass was coated with CdS to the desired thickness with excellent uniformity and continuity. Figure 3 shows the thickness of the CdS film sample developed at a 2.6-min deposition time on a 152-mm



Figure 3. CdS coating profile on 152 mm \times 152 mm FTO glass, produced with a deposition time of 2.6 min. Insert image illustrates the thickness profile for the center region (102 mm \times 102 mm) of the sample. The scale bar represents thickness in nanometer.

Table I. Summary of CdS film thickness and uniformity for the various experimental conditions tested, including the entire 152-mm substrate and the 102-mm central portion.

Size of Glass				
substrate	$152 \text{ mm} \times 152 \text{ mm}$		$101.6 \text{ mm} \times 101.6 \text{ mm}$	
Deposition	Thickness	Uniformity	Thickness	Uniformity
Time (min)	(nm)	(%)	(nm)	(%)
2.6	72.5 ± 3.9	~5.3	74.6 ± 1.8	~ 2.4
6.3	94.7 ± 5.1	\sim 5.3	97.4 ± 4.1	~ 4.2
9.0	233.9 ± 29.2	~ 12.4	256.6 ± 12.2	~ 4.7

FTO glass substrate, as recreated from 36 data points measured on the surface. The inset image of Figure 3 represents the thickness for the central 102-mm area of the sample excluding the border of the substrate where most of the thickness deviation occurs. A picture of CdS film deposited by MASD is shown in Figure 4.

The 2.6-min deposition exhibits an average thickness of 72.5 ± 3.9 nm, or a 5.4% thickness deviation over the entire surface. For the 102-mm central area, the average thickness is 74.6 ± 1.8 nm, representing a 2.4% thickness deviation. It can be observed from Table I that CdS films with thickness varying from 72 nm to 230 can be easily, rapidly and continuously produced with excellent uniformity by varying the deposition time. The thickness of the CdS film at the corners of the substrate tends to be lower than for the rest of the substrate. We attribute this to reduced substrate temperature along the edges, which is normally about 3°C lower than the center of the substrate. It is known that temperature plays a key role in the growth rate of the CdS layer.^{24,32} The substrate is heated by a resistance heater from the bottom and IR lamps from above, but due to non-uniformities in air movement inside the hood used for development, the edges tend to be slightly cooler. In production, additional humidity and air temperature controls could easily be implemented to mitigate the edge cooling seen in this laboratory setup.

The grazing-incidence X-ray diffraction pattern of a typical CdS film deposited by MASD on FTO coated glass substrate is shown in Figure 5. The as-deposited CdS film exhibits diffraction patterns typical of standard CdS (JCPDS-75081) with a preferred orientation of a cubic crystalline <111>. It can also be observed that the diffraction pattern of the FTO matches closely with the standard (JCPDS-411445), as expected. The TEM cross-sectional image of the CdS/FTO sample shown in Figure 6 clearly shows the CdS conformally coated



Figure 5. Grazing incidence X-ray diffraction patterns. Comparison of MASD-deposited CdS/FTO and FTO only, with JCPDS data for SnO2 and cubic CdS.

on the undulating pattern of the underlying FTO. Previously reported high-resolution TEM of our CdS/FTO films showed the CdS to be nano-crystalline and conformally coated to the crystalline FTO layer.²⁴

The plot of square of absorption coefficient vs. bandgap is shown in Figure 7. A sample CdS film with ~ 100 nm thickness was used for estimating optical bandgap, found at the intersection of the linear portion of the curve with the x-axis (0.0 eV/cm²). The bandgap estimated for the MASD-produced CdS is ~ 2.39 eV and is consistent with the values reported in the literature.



Figure 4. A picture of CdS film deposited by MASD on 152 mm \times 152 mm (6 in \times 6 in) FTO glass substrate (scale bars are in inches).



Figure 6. TEM cross-section image of the CdS/FTO sample coated by MASD, indicating the FTO and CdS layers as well as the carbon and platinum layers utilized for FIB and TEM.



Figure 7. Band gap estimation for a MASD produced CdS film.

Conclusions

A deposition unit has been developed for CdS deposition on a FTO coated glass substrate ($152 \text{ mm} \times 152 \text{ mm}$) using the continuous MASD process. The deposition unit developed in this study demonstrates the fundamental production-level operations required for a continuous, conveyorized production line. This study has demonstrated a novel coating technique that uses a ceramic rod for CdS deposition process with capabilities to easily develop CdS films ranging from small thickness of 70 nm to thicker films of 230 nm with excellent uniformity. The structural properties and the optical bandgap of the CdS films developed exhibit the properties necessary to be integrated in a thin film solar cell.

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