A Uniform Residence Time Flow Cell for the Microreactor-Assisted Solution Deposition of CdS on an FTO-Glass Substrate
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ABSTRACT: Photovoltaic cells have long been a desirable alternative to the consumption of fossil fuels, but current manufacturing practices suffer from poor energy efficiency, large carbon footprints, low material utilization, and high processing temperatures. A critical step in production of thin film CdTe and CuInSe₂ solar cells is the chemical bath deposition of a CdS thin film to serve as a “buffer layer” between the optically absorbent layer and the transparent conducting oxide. In prior work, functional CdS films were demonstrated at low temperature using a continuous flow, microreactor-assisted deposition process showing good selectivity of heterogeneous surface reactions over homogeneous bulk precipitation. In this paper, we develop a flow cell for implementing a uniform CdS film over a 152 mm substrate. Analytical models are coupled with computational fluid dynamic simulations to design a flow cell with more uniform flow fields. Experimental results demonstrate a 12% coefficient of variance for a 21.5 nm thick film.

INTRODUCTION
Cadmium sulfide (CdS) is often used to form the junction of a heterojunction thin film photovoltaic (PV) cell.1,2 It serves to form the p–n junction and extend the distance photocarriers can travel before recombination can occur and to reduce reflection in the absorber layer of the cell.3 Methods that have been explored for CdS deposition include vapor phase techniques, such as physical and chemical vapor phase deposition (PVD and CVD) and liquid phase processes, such as chemical bath deposition (CBD), electrochemical deposition, and successive ionic layer adsorption reactions. Of these methods, CBD is typically valued as the industry standard due to its relative ease of implementation, low temperatures (<100 °C), atmospheric pressures, and consequent low expense for covering large surface areas.

The typical CBD process utilizes a large volume of reaction fluid that is not in intimate contact with the substrate surface, leading to a high volume-to-surface area ratio. This arrangement provides conditions for spatially uniform film growth rates across the substrate area but also results in low yields of cadmium conversion to the final film due to precipitation of CdS in the bulk solution. The unwanted precipitates and byproducts can settle on the film, interrupting the coherency of the film. Additionally, the reagent concentrations decrease over time in a static bath, causing the reaction conditions and growth rate to vary in a temporal manner.

Microreactor-assisted solution deposition (MASD) is the coupling of microreactor technology with continuous flow deposition to resolve the temporal evolution of reaction chemistry. Under continuous flow conditions, byproducts and precipitates can be swept through the reaction chamber and reaction conditions can be kept constant and optimized with respect to time.4 It has been shown that microreactors can improve material yield and decrease solvent usage in comparison to typical CBD reactor conditions.5–7 Prior work showed results from a continuous flow microreactor using mL/h flow rates to increase the efficiency and conversion of [Zn²⁺] to ZnO nanowires.8,9 This occurs due to the greatly reduced diffusion times experienced in submillimeter diameter channels. Interference pattern measurements showed spatial variation in the ZnO nanowire length due to faster growth near the inlet of the reaction chamber and slower growth near the end as the bulk fluid neared depletion of active species. In addition, a distinct parabolic growth rate pattern can be seen as the fluid traveled faster down the axial center regions in comparison to the outer edges of the reactor. They also inverted the positioning of their flow cell, placing the substrate on the top surface to allow precipitating species to settle away from the growing ZnO wires.

In this paper, we report the development of a high flow rate continuous flow MASD reactor to deposit CdS films over large substrates that compensates for lateral flow variation across a single high-aspect-ratio flow cell. Although much prior work has
been performed to control flow maldistribution across an array of parallel channels, little work has been performed to address flow uniformity across a single high-aspect-ratio channel. Chung et al.\textsuperscript{10} designed inlet ports with sizable preresorvoir chambers that showed good lateral flow uniformity across a submillimeter cell culture cultivation chamber. However, this approach suffered from increased dead zone regions in the reservoir chamber. An alternative design by Hung et al.\textsuperscript{11} effectively split a single inlet into multiple perfusion channels arranged in a semicircular pattern. The total surface area of each perfusion channel was designed to be much smaller than the original inlet port area. The increase in pressure drop across each perfusion channel was designed to regulate flow between channels.

The approach taken in this paper is to manipulate the cross-sectional area of the reaction chamber in a manner to compensate for the variation in travel length based on flow streamlines. This is done by increasing the resistance to flow near the axial center region of the flow cell by deflecting the upper surface into the reaction chamber, thus reducing the channel height in that region.

\section*{FLOW CELL DESIGN}

The design of a solution flow cell for depositing thin films with uniform thicknesses requires control of deposition both in the breadth and in the length of the flow cell. The flow cell consists of an inlet header, a deposition region, and an outlet header. In this work, triangular inlet and outlet headers were used to connect the inlet and outlet to the deposition region. The size of the inlet header was minimized to eliminate dead volume prior to deposition while efforts were made to minimize backpressure in the outlet header by reducing the angle of convergence. Consequently, the outlet header was found to be larger than the inlet header.

The rationale for the design of the deposition region was as follows. Assuming uniform temperatures within the flow cell, control over film thickness along the axial length of the deposition region has to do mainly with avoiding depletion of reactants by balancing reagent concentration and residence time within the deposition region. Assuming that reagent concentrations are uniform within the flow, control over film thickness uniformity in the breadth of the deposition region has to do mainly with a uniform velocity profile across the breadth of the region. The velocity profile not only affects the residence time of reagents across the deposition region but also determines the thickness of the fluid boundary layer through which reactants diffuse.

Many researchers have looked at ways to distribute or otherwise control flow velocity across headers and microchannels.\textsuperscript{12–16} In the deposition region, we applied the approach taken by Pan et al.\textsuperscript{17} to optimize the inlet and outlet header design for a microchannel array to minimize the variation of flow distribution across the array by modeling the array as a complex system of flow resistances arranged in series and parallel. For analysis purposes, the flow cell deposition region of the flow cell, consisting of a single high-aspect-ratio flow channel (0.8 mm deep \times 152 mm wide), was represented as an array of imaginary parallel channels. The pathway and length of each of these imaginary channels were determined by flow streamlines generated using tracer particles within computational fluid dynamics (CFD; Fluent, version 6.3, using GAMBIT as meshing tool) simulations, as shown in Figure 1.

As a first approximation, assuming equivalent pressure drop and velocity within each channel, the relationship between

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Computer-simulated streamline pathways generated by releasing and tracing point particles from the flow cell inlet to outlet (half model shown).}
\end{figure}

channels reduces to a ratio of the pathway length to the square of the hydraulic diameter. To simplify the analysis, each imaginary channel was assumed to have a constant submillimeter width. Using channel lengths represented by the streamlines in Figure 1, hydraulic diameters were calculated for each streamline, leading to an initial cross-sectional profile for the flow cell. A cartoon of a deflected channel profile in the deposition region of the flow cell is shown in Figure 2.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Cartoon of a deflected cross-sectional channel profile showing the need to change the hydraulic diameter as a function of breadth to achieve equivalent velocities or residence time within each individual channel.}
\end{figure}

\section*{COMPUTATIONAL FLUID DYNAMIC SIMULATIONS}

To refine the cross-sectional channel profile of the flow cell, CFD simulations were used to evaluate the effect of the channel profile on flow front development and flow distribution within the deposition region. Flow cell cross sections were constructed in SolidWorks 2010. The baseline case to which all deflected-plate results were compared was the condition of two perfectly parallel plates set 800 \mu m apart. The flow chamber geometry was imported into Fluent, and a three-dimensional CFD analysis was performed. Two-dimensional triangular meshes were generated on the base surface, and the channel depth was partitioned into 10 segments, resulting in 1,763,700 total elements. The boundary conditions for the simulation consisted of no-slip conditions at the flow cell walls and atmospheric pressure at the outlet. Water with a density and viscosity of 9.98 \times 10^3 kg/m^3 and one cP, respectively, was used as the fluid. While the properties of water do not precisely match those of the precursor solution, it was expected that water would closely simulate the flow behavior of the precursor solution. An inlet velocity of 0.089 m/s was calculated from an inlet area of 5.85 mm^2 and a volumetric flow of 31 mL/min. Laminar flow conditions were used at the inlet with a Re of 1,211. Residual values for mass and momentum at convergence were below 1 \times 10^{-5} g and 1 \times 10^{-4} g m/s, respectively (Figure 3).

Flow uniformity was evaluated by tracking the flow front across the flow cell. Fluent was used to simulate the pulse injection of 100 point particles and track their position over the progress of time. Flow front
The flow cell (Figure 10). The goal of the finite element analyses (FEAs) was to determine the position of point forces needed to closely match deflected channel profiles of promise. For FEA, material properties of the flow cell were input into the Cosmos model and forces were applied at various positions along the central axis and elsewhere. Resultant channel profiles were evaluated in CFD until channel profiles providing the best constant velocity profile within the deposition region of the flow cell were identified. The simulated flow front response for the final deflected profile is shown in Figures 6 and 7. The final deflected-plate profile required roughly 200 μm of deflection along the centerline of flow cell. The final channel profile used in CFD and per the experimental setup is compared in Figure 15 below.

## EXPERIMENTAL APPROACH

A schematic of the final flow cell experimental setup is shown in Figure 8. Reagents were fed into a microchannel T-mixer using positive displacement pumps (Acuflow Series III). This mixed stream was then fed into a heat exchanger to bring the reactants to temperature and hold for a specific induction time before being introduced into the CdS film deposition flow cell. The flow cell accommodated a glass substrate and contained an integrated heating system to maintain a uniform substrate temperature throughout the fluid residence time. Excess reagents and byproducts were collected into a waste container beyond the flow cell outlet. A LabVIEW program was used for system control and for data acquisition during the experiments. A more detailed description of the test setup surrounding the flow cell is provided elsewhere.\

The flow cell assembly developed for deposition of CdS is shown schematically in Figure 9. It consists of a five-layer stack beginning with a 376 × 256 × 6.4 mm thick 6061 T651 aluminum (Al) base plate on which is placed an equally sized 3 mm thick FTO-coated glass substrate. Kapton tape was used to mask the glass for 152 mm deposition. A thin layer of thermal adhesive was applied between the based plate and glass substrates to aid in heat transfer and temperature control. The geometry of the reaction chamber is then defined by a double stack of 800 μm thick highly compressible closed cell silicone foam (Bisco HT-800). The upper surface of the reaction chamber consists of a 3.18 mm thick polycarbonate (PC) sheet with inlet and outlet ports. This was topped by a secondary 12.7 mm top PC plate fitted with complementary...
inlet and outlet ports. Seals between plates were made using silicone gasket o-rings. Eleven set screws were placed into this upper plate at the locations shown in Figure 9. Eighteen threaded posts (6.4 mm diameter, 38.1 mm length) were mounted along the perimeter of the aluminum base and topped with nuts and washers to provide a compressive sealing force between each layer. To restrict the amount of compression in the silicone foam, stainless steel shims (800 $\mu$m thick) were cut into patterns to reside just outside the silicone foam layer and act as "hard stops" for compression. Six thermocouples were inserted through the edge of the flow cell and compressed between the two silicone foam gaskets, allowing the tips to protrude into the flow chamber (Figure 10).

Additional silicone vacuum grease was applied to all layer interfaces to aid in sealing potential leaks once pressurized.

**Dye Test.** The use of injected dyes for flow visualization is well-known. In this investigation, a dye test was run to verify flow uniformity and the integrity of fluidic seals prior to running reactants for CdS deposition. The flow chamber was filled with deionized water at room temperature at 31 mL/min. The supply stream was then switched to a solution of black dye. Video cameras were used to record and measure the progression of dye as it crossed the front, middle, and back planes of the substrate region.

**Deposition Tests.** A 152 $\times$ 152 mm commercial soda lime glass substrate (Pilkington TEC-15) with a fluorine-doped tin oxide (FTO) layer was assembled within the flow cell reactor. The flow cell was then fixed to a 9 in. $\times$ 9 in.Wenescot hot plate (1100 W) and positioned vertically to remove any bubbles that were introduced during priming.

To deposit the films, the reaction chamber was first circulated with room-temperature deionized water and allowed to reach a steady temperature of 83 °C before switching to reagents. One percent by volume of Triton X-100 surfactant was added to the deionized water to

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**Figure 5.** Standard deviations of flow front for baseline parallel-plate channel profile at a depth of 800 $\mu$m for front plane = 7.7 mm; middle plane = 18.5 mm; and back plane = 25.5 mm (shows half of flow field from center axis).

**Figure 6.** Flow front progression for deflected-plate channel profiles roughly 600 $\mu$m high along the flow cell centerline and 800 $\mu$m high along the edge of the flow cell. Flow distribution for tracer particles when they reach the (a) front plane, (b) middle plane, and (c) back plane.
help remove bubbles entrained during priming. Reagents were premixed within two vials marked A and B, with A containing 0.004 M CdCl₂, 0.41 M NH₂OH, and 0.04 NH₄Cl, and B containing 0.04 M thiourea. Equal flow rates (15.5 mL/min) of reagents were supplied to the micromixer before entering the thermally insulated microchannel heat exchanger. The temperature in the heat exchanger was monitored. Induction time after heating was 1 min. The overall deposition time was 5 min, after which all heaters were turned off and the reagent supply was switched off.

Figure 7. Standard deviations of flow fronts for deflected-plate channel profiles roughly 600 μm high along the flow cell centerline and 800 μm high along the edge of the flow cell for front plane = 5.0 mm; middle plane = 4.9 mm; and back plane = 10.0 mm (shows half of flow field from center axis).

Figure 8. Test stand schematic for 152 × 152 mm CdS deposition. Data acquisition and control system are not shown.

Figure 9. Flow cell assembly.

Figure 10. Thermocouple and deflection screw positions.

The temperature in the heat exchanger was monitored. Induction time after heating was 1 min. The overall deposition time was 5 min, after which all heaters were turned off and the reagent supply was switched off.
back to deionized water. The system was allowed to flush until the preheater temperature reduced to <40 °C, at which time the pumps were turned off and the flow cell chamber was drained through the inlet connector. The top cover of the flow cell was then removed, and the substrate was rinsed again with deionized water to wash away any noncohesive particulates.

**Film Thickness Measurement.** Film thickness and uniformity were measured by exploiting the optical properties of CdS at a wavelength of 500 nm. The relationship of film thickness \( t \) and transmission \( T \) can be expressed as

\[
T = e^{-\alpha t}
\]

where the absorption coefficient \( \alpha = 143005.31 \text{ cm}^{-1} \) was calculated by averaging the values obtained from eq 1. Various CdS films were deposited, as explained elsewhere, and used for calibration of the measurement technique. Film thickness \( t \) was determined by cross-sectional imaging the films using a focus-ion-beam (FIB) lift-out process and measuring the cross-sectional thickness of the film using transmission electron microscopy (TEM). Figure 11 shows one of the TEM cross sections at 125 000×, including the entire CdS/FTO structure. The CdS layer is between the FTO film and a carbon film. The carbon and platinum layers on top of the CdS layer were added to prevent surface charge accumulation and to introduce a protection layer during the focused-ion-beam (FIB) milling process. This micrograph shows that the FTO layer on the substrate is rough and the CdS layer on top is conformal.

**RESULTS AND DISCUSSION**

**Dye Tests.** The CFD models for the flow cell were found to be capable of predicting results similar to observations seen in the physical dye tests at 31 mL/min (Figure 13). The distinctive parabolic flow profile is apparent under parallel-plate (PP) conditions, whereas a more uniform profile is seen under deflected-plate (DP) conditions. Statistical comparison of the baseline PP and the DP flow cells is shown in Table 1.

Results show that the DP method significantly reduced dispersion in the flow front at the front, middle, and back plane of the substrate. CFD results typically underpredicted the flow front dispersion by an average 18.5%, which shows good agreement with the experimental data. This underprediction may be an artifact of axial diffusion, which was not adequately accounted for within the model. For both flow cells, the standard deviation of the axial position steadily increased as each successive plane was crossed. For the parallel-plate flow cell, the standard deviation almost tripled during both CFD modeling and the dye test. For the deflected-plate flow cell, the standard deviation is...
Table 1. Comparison of Flow Front Uniformity Measured by the Standard Deviation of the Axial Position of Tracer Particles (CFD) and Dye (Experimental) as a Percentage of the Substrate Size (152 mm)a

<table>
<thead>
<tr>
<th></th>
<th>front (57.5 mm)b</th>
<th>middle (143.1 mm)b</th>
<th>back (228.6 mm)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>no deflection (CFD)</td>
<td>5.16%</td>
<td>12.33%</td>
<td>16.97%</td>
</tr>
<tr>
<td>no deflection (dye)</td>
<td>7.63%</td>
<td>11.63%</td>
<td>22.16%</td>
</tr>
<tr>
<td>change</td>
<td>2.47%</td>
<td>−0.70%</td>
<td>5.19%</td>
</tr>
<tr>
<td>% error</td>
<td>32.37%</td>
<td>−6.02%</td>
<td>23.43%</td>
</tr>
<tr>
<td>200 μm deflect (CFD)</td>
<td>3.36%</td>
<td>3.25%</td>
<td>6.65%</td>
</tr>
<tr>
<td>200 μm deflect (dye)</td>
<td>3.88%</td>
<td>4.83%</td>
<td>7.83%</td>
</tr>
<tr>
<td>change</td>
<td>0.52%</td>
<td>1.58%</td>
<td>1.18%</td>
</tr>
<tr>
<td>% error</td>
<td>13.44%</td>
<td>32.74%</td>
<td>15.11%</td>
</tr>
</tbody>
</table>

aStandard deviation [% of substrate size (152 mm)]. bAxial distance from inlet.

Deposition Tests. For the final set of deposited films, characterization involved dividing the substrate into regions and labeling the regions by column and row for consistent comparison. Figure 14 shows an example labeling scheme used for recording data consisting of nine cells each having nine subcells (three rows and three columns). Initially, a total of 45 data points were collected to evaluate the uniformity of the coating consisting of data for the four corner subcells and one center subcell for each cell. For each film, additional analysis was performed to determine what resolution of data points was needed to adequately characterize the film. In general, it was determined that $6 \times 6$ data points significantly changed the film uniformity compared to the 45 data points, whereas $8 \times 8$ data points and beyond did not significantly change the film uniformity. Figure 15 shows the final film morphologies as measured using the UV–vis spectroscopic method.

Results suggest that the velocity distribution had a direct impact on the uniformity of the final CdS film. The overall average thickness and standard deviation measured were 25.9 ± 13.5 nm and 21.5 ± 2.6 nm for the PP and DP conditions, respectively. The overall thickness of the final film in the DP experiment showed a greater than 5X reduction in the variability of the film thickness. For PP conditions, it is visually apparent that film growth is thicker in the middle and thinner along the outside of the flow cell. This follows the intuition that the final film would grow more rapidly in the faster flowing center regions where the convective boundary layer is thinner. This is also a region where reactants are replenished at a much faster rate. This increase in deposition rate may also explain why the film produced in the PP flow cell is thicker on average than the film produced in the DP flow cell. Alternatively, differences in average thickness also could be due to the shorter residence time for reactants in the DP flow cell caused by the higher velocities due to the smaller channel cross section. The actual cross section shown in Figure 16 below shows an axial flow cell channel height of around 400 μm on average. As a rough analysis, assuming that the DP deflection is triangular, the deflection cuts off about one-quarter of the channel cross section, suggesting a decrease in residence time of 25%. The average thickness of the film consistently one-third to one-half the level of dispersion in the parallel-plate flow cell. An increase in standard deviation on the back plane of the deflected-plate flow cell was seen both in CFD (see Figure 7, right) and experimentally (dye). This may be due to over-restriction of the axial channel height toward the back plane, suggesting that additional optimization of the flow profile is possible.
produced in the DP flow cell is about 83% of the average thickness of the film produced in the PP flow cell. Consequently, a 25% change in residence time could easily explain this difference in film thickness, assuming a linear impact on growth rate with residence time.

Of interest in the DP film is the dip in the film thickness toward the back center of the film, which likely caused a considerable amount of the variability in that film. The CFD results for the DP flow cell in Figures 6 and 7 show that the flow distribution is significantly worse for the back plane of the plate. This is largely due to the fact that FEA results and the experimental setup were not able to closely match the desired constant velocity cross sections adjacent to this region. This is demonstrated in Figure 16, which shows a comparison of the CFD and measured channel cross sections within the deflected-plate flow cell. It is likely that discrepancies in back row dimensions between the experimental and the ideal constant velocity flow cell designs led to higher (double) flow profile deviations for the back row of the flow cell, as shown in Table 1. The suppression of flow in the back center of the flow cell led to a thinner film in that region. This suggests the importance of maintaining a constant velocity through the deposition region of the flow cell. This issue could be ameliorated through the use of a different technique to implement the deflected cross section. One such technique could be to machine the deflected profile into the upper plate rather than to use plate mechanics.

Adding to this problem is the fact that, in Figure 15 (right), the back row of measurements all show lower thicknesses. This suggests that the deposition rate is slower toward the back of the flow cell. Possible reasons for this could be a higher concentration of byproducts impeding mass transfer of reactants or simply depletion of reactants. Of further interest toward the back of the substrate is the fact that the edges of the film are thinning before the center axis of the film. The flow path along the side of the flow cell is longer than the flow path down the axis of the flow cell. This could be further evidence for the depletion of reactants.

**CONCLUSIONS**

In this paper, a 152 × 152 mm deflected-plate flow cell for the microreactor-assisted solution deposition (MASD) of CdS was developed that increased film thickness uniformity by over 5 times for continuous flow deposited films. Final film thicknesses of 21.54 ± 2.64 nm were achieved. This level of film uniformity compares favorably with prior continuous flow cell microreactors for solution deposition showing over 5x variation in chemical product (nanowire) dimensions over a 30 mm dimension.8 This...
improvement was achieved by addressing the problems of flow distribution within the high-aspect-ratio flow cell through deflection of the top plate. It is expected that this technique could open the use of MASD as a technique to produce large area films using short-life intermediate chemistries. As a solution deposition method, MASD holds the potential to deposit films at lower temperatures than traditional PVD and CVD methods without the need for vacuum. To further improve film uniformity for films deposited in the MASD flow cell, greater precision is needed in creating the deflection profile of the flow cell, and efforts are needed to manage the depletion of reactants in the axial direction.

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**Notes**
The authors declare no competing financial interest.

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