Combinatorial Chemical Bath Deposition of CdS Contacts for Chalcogenide Photovoltaics

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ABSTRACT: Contact layers play an important role in thin film solar cells, but new material development and optimization of its thickness is usually a long and tedious process. A high-throughput experimental approach has been used to accelerate the rate of research in photovoltaic (PV) light absorbers and transparent conductive electrodes, however the combinatorial research on contact layers is less common. Here, we report on the chemical bath deposition (CBD) of CdS thin films by combinatorial dip coating technique and apply these contact layers to Cu(In,Ga)Se2 (CIGSe) and Cu2ZnSnSe4 (CZTSe) light absorbers in PV devices. Combinatorial thickness steps of CdS thin films were achieved by removal of the substrate from the chemical bath, at regular intervals of time, and in equal distance increments. The trends in the photoconversion efficiency and in the spectral response of the PV devices as a function of thickness of CdS contacts were explained with the help of optical and morphological characterization of the CdS thin films. The maximum PV efficiency achieved for the combinatorial dip-coating CBD was similar to that for the PV devices processed using conventional CBD. The results of this study lead to the conclusion that combinatorial dip-coating can be used to accelerate the optimization of PV device performance of CdS and other candidate contact layers for a wide range of emerging absorbers.

KEYWORDS: buffer layer, CIGSe, CZTSe, current–voltage characteristics, external quantum efficiency, solar cells

INTRODUCTION

Thin-film chalcogenide solar cells based on CdTe, Cu(In,Ga)-Se2 (CIGSe), and Cu2ZnSnSe4 (CZTSe) have many attractive features, such as high efficiencies, low materials utilization, and potential for low overall cost, as compared to other photovoltaic technologies.1–4 Among numerous layers of thin film solar cells (absorbers, contacts, electrodes, etc.),5 the choice and the thickness contact layer (usually 50 nm thick CdS films) plays a vital role in p–n heterojunction formation, and hence extraction of photogenerated electric charge carriers.5,6 CdS buffer layer can be prepared by various techniques, such as chemical bath deposition (CBD), sputtering, coevaporation, atomic layer deposition (ALD), ionic layer gas atomic reaction (ILGAR), etc.6 Among these techniques, the highest photo conversion efficiency (PCE) of the chalcogenide solar cells (22.3% for CIGSe,5 22.1% for CdTe,5 and 12.6% for CZTSe8) has been achieved by preparation of buffer layer through CBD.

The high-throughput combinatorial experimental approach is a rapid and efficient method for discovery and optimization of new materials for a wide range of applications.8,10 This approach consists of deposition of sample libraries with varying composition, temperature, or thickness,9–16 followed by spatially resolved measurements of the relevant properties.11–16

The combinatorial approach has been implemented for pharmaceutical, electronic, magnetic, optical, and energy-related materials,9,12 as well as in photovoltaics (PV) for earth-abundant nontoxic absorbers14,15 and transparent conductive electrodes.16 Recently, we demonstrated development of alternative contact layers for thin film solar cells using combinatorial reactive sputtering17 that lends itself easily to high-throughput experimental approach. However, combinatorial studies of conventional solution-processed contact layers, such as CdS prepared by CBD, have not been reported, except in the context of the nanocrystal applications of this important material.18,19

One possible approach to combinatorial solution processing is the dip-coating technique. Dip-coating is a thin film deposition process that relies on immersing and extracting a substrate (in this case, soda lime glass) from a vessel containing the precursor liquid (here, chemical bath of CdS precursors). In the past, combinatorial dip-coating with a continuous gradient
in the film thickness of several polymers and oxides has been demonstrated\(^{20,21}\) and applied.\(^{20,21}\) Similarly, combinatorial synthesis of the inorganic sulfide buffer layers prepared by chemical bath deposition should be possible by dip coating, allowing for parallel screening of many thicknesses in a single experiment.

In this Research Article, we present a combinatorial study of thickness of the CdS contact layers synthesized by chemical bath deposition for chalcogenide thin film solar cell applications. First, we describe the combinatorial dip-coating process for creating discrete thickness steps of CdS films across the substrate. Next, properties of the chemical bath deposited CdS layers prepared by combinatorial and standard processes are compared. Finally, the photovoltaic device with combinatorially processed CdS layers are described. This combinatorial dip-coating approach should be applicable to other PV absorber- and contact materials, and other thin film technologies where thickness is an important parameter.

**RESULTS AND DISCUSSION**

**Combinatorial Experiments with CdS Thin Films and PV Devices.** The step changes in thickness of CdS film were achieved with the help of the combinatorial dip coating process, schematically demonstrated in Figure 1a (see Figures S1 and S2 for more details). The dip coater was programmed in such a way that the 50 × 50 mm soda lime glass (SLG) substrate was first immersed into a bath in the reaction beaker with constant high speed, and then removed with the same speed at constant intervals of time (every 5 min), in approximately 10 mm distance increments, to achieve the desired thickness profile with the thickness steps (Figure 1b). After four such steps, the resulting CdS sample library was placed in deionized water and subjected to 30 s ultrasonication to remove the loosely attached CdS particles, and then dried with N\(_2\) gas. Similarly, CdS films were grown on CIGSe and CZTSe absorber layers, and processed into combinatorial libraries of PV devices, as schematically illustrated in Figure 1b.

Note that this hybrid CBD/dip-coating process differs from the conventional dip coating (Figure 1a) and from conventional CBD. In the conventional dip-coating process, the deposition is controlled by the speed of the liquid meniscus at the interface with air. Here, the deposition mechanism is more similar to that in CBD, in that CdS continuously deposits onto the substrate as long as it still in the bath. Therefore, extraction of the substrate stops deposition on the part that is in the air, but continuous deposition on the still submerged part, leading to steps in the resulting film thickness (Figure 1b). This is different than the conventional CBD, where the entire substrate is submerged for the whole deposition time, and hence no thickness steps are achieved.

Also, note that, here, we chose to use the combinatorial dip coating process in step mode to obtain the sample statistics needed for unambiguous interpretation of the PV device efficiency results, and comparison with the conventional CdS CBD process. However, the more traditional continuous gradient mode of combinatorial experiments can also be used for the combinatorial CBD, and this gradient can be much higher than for the continuous-spread combinatorial sputtering approaches (usually a factor of ~2\(\times\) in thickness).\(^{17}\) More CBD
methods details, as well as characterization information, are described in the Experimental Procedures section.

To test the combinatorially deposited CdS thin films, they were integrated in the thin film photovoltaic (PV) devices with CIGSe and CZTSe chalcogenide absorbers synthesized as reported earlier.22,23 The absorber synthesis (Figure 2a) was followed by chemical bath deposition of CdS buffer layers via combinatorial dip-coating process (Figure 2b). Subsequently the front transparent conductive bilayer of ZnO/Al:ZnO was grown by RF sputtering at ambient temperature. Then, the front electrode pads (Al/Ni) were deposited by electron beam evaporation (Figure 2c). Finally, the individual PV devices were grown by mechanical scribing, and tested for energy conversion efficiency ($J-V$) and external quantum efficiency (EQE). For comparative studies, similar photovoltaic devices were also fabricated with CdS contact layer prepared by a conventional chemical bath deposition (CBD),24 without the combinatorial thickness steps.

**CdS Thin Film Material Properties.** The morphology of the CdS thin films prepared by CBD process using combinatorial dip-coating on glass substrates is shown in Figure 3, in comparison with standard CBD process. At the initial stage of growth, the film is nonconformally deposited on the glass (Figure 3a, 5 min). As time progresses, CdS particles start to cover the substrate uniformly (Figure 3b, 10 min), but some small voids are present in the film even for later times (Figure 3c, 15 min). It appears that the CdS film deposited by the standard CBD process (Figure 3d) is denser than the combinatorially processed film (Figure 3c), which likely has to do with lower nucleation and growth barriers. The mechanistic origin behind this difference is presently unclear, but it might be related to the orientation of the substrate during the deposition (horizontal in standard CBD, vertical in combinatorial CBD). Also, it is noted that this difference in morphology of CdS films on glass substrate may not necessarily be the same for the deposition on the chalcogenide absorbers.

The transmittance spectra of CdS layers deposited on SLG substrate via both combinatorial dip-coating (different times) and standard chemical bath deposition (CBD) technique are shown in Figure 4a. The transmittance of CdS film decreases with the increase in CdS deposition time, and the most likely reason for this change is the stronger light absorption in thicker films.25,26 However, we also observed that the transmittance of the combinatorial CBD film is slightly lower in the long-wavelength region than that of the standard CBD film for the same deposition time (15 min), which may be related to the differences in light scattering due to different film morphologies (Figure 3).

To support our conclusions about the change in the optical transmittance of CdS thin films with changing deposition time, the thickness of CdS film processed through both conventional and dip-coating CBD techniques was measured and is shown in Figure 4b (see also Table S1). It was not possible to measure the thickness of CdS film at 5 min deposition time due to the rough morphology at the initial growth stages of film. The variation of CdS thickness with deposition time clearly indicates the linear increase. A slight spatial variation in thickness is observed near the gradient steps of combinatorial processed CdS film, evidenced by the changes in color in Figure 2b. The most likely explanation is the fluctuations of the liquid level in the chemical bath because of stirring and different deposition dynamics at the liquid/atmosphere interface.

Figure 3. SEM images of CdS film prepared by combinatorial dip-coating chemical bath deposition (CBD) after (a) 5, (b) 10, (c) 15 min of deposition. Panel d shows the results of the conventional CBD of CdS film after 15 min, without combinatorial dip coating.

Figure 4. (a) Optical properties (transmittance) of CdS films prepared by combinatorial and conventional CBD and (b) variation of the CdS thickness with deposition time measured by X-ray fluorescence (XRF) and profilometry techniques.

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CIGSe and CZTSe Photovoltaic Device Performance.
The CdS films grown by both combinatorial and regular CBD processes were used as contact layers in CIGSe and CZTSe solar cells. From the $J-V$ curves (Figure 5), it appears that for the CIGSe PV devices, the biggest change with changing CdS thickness is in short circuit current, whereas for the CZTSe the short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), and fill factor (FF) are all changing (also see Tables S2 and S3). However, for both CIGS and CZTS the device performance parameters increase with increasing deposition time up to certain point (15 min), and then these parameters decrease with increase in deposition time (Figure S3). This non-monotonic trend derived from the combinatorial experiments is in good agreement with literature results 27–30 that used traditional experimentation approaches. Overall, the efficiency of the devices fabricated with combinatorially deposited CdS buffer layer is slightly (~10% relative) lower than that for the CdS contacts deposited using the conventional CBD technique.

Discussion of Materials and Devices. The results of our work demonstrate that the combinatorial dip-coating is a rapid approach to find the optimal thickness of the CdS films prepared by chemical bath deposition. However, one disadvantage of this method compared to the conventional CBD is the somewhat unfavorable morphology of the films (Figure 3). To address the morphology difference of the films prepared by combinatorial CBD compared to that of the standard CBD process (Figure 3), the nucleation and growth process can be improved by changing the chemical bath conditions and initial precursor’s concentration.31–35 It should also be possible to tune the morphology of the CdS film grown thin films by optimizing the dip coating parameters, such as withdrawal speed, solvent evaporation rate, and viscosity of solution of the bath.20,21

Figure 5. Current–voltage ($J-V$) curves of (a) CZTSe and (b) CIGSe solar cells with CdS contact layers of different thicknesses prepared by combinatorial dip-coating CBD process. Black lines correspond to the standard CBD process.

Figure 6. External quantum efficiency (EQE) spectra of (a) CZTSe, (b) CIGSe solar cells with CdS buffer layers deposited by combinatorial dip-coating CBD process. The black lines correspond to PV devices with CdS contact layers prepared by conventional CBD process.
We also note that the dip-coating method described here with the substrates being pulled out from the solution is only one possible implementation of the combinatorial approach to solution processing of thin films. Alternatively, the substrates can be lowered into the solution, which would also result in the thickness steps or gradient; however the disadvantage of this lowering method is that the particles start to form in the solution in addition to the film surface, so the resulting coating may be less conformal. Another geometrical implementation of the combinatorial approach to chemical bath deposition or other solution processing would be to place the substrate in the bath with either a tap at its bottom or a fluid pump connected to the bath. Both of these methods would allow changing the level of the fluid in the bath as a function of time, thereby achieving the thickness variation across the sample without moving it.

The combinatorial dip-coating approach to contact layers for thin film solar cells, described here for the case of the most commonly used CdS buffer with expected results, may be extended to alternative window layer materials that can be processed using chemical bath deposition. For CIGSe and CZTSe solar cells, some of the CBD examples include ZnS, ZnSe, SnO₂, ZnS, SnO₂, ZnS materials, as well as Zn(O,S), (Cd,Zn)₅, In(OH,S)₅ and related alloys. Currently most of these alternative contact materials lead to solar cell performance lower than the state of the art CIGSe and CZTSe with CdS buffer layers, which in part may be due to their nonoptimal thicknesses. Optimization of the thickness for these alternative contact materials using the combinatorial dip-coating approach to chemical bath deposition may address this problem and improve the efficiency of the thin film chalcopyrite photovoltaic devices.

Beyond the well-studied CIGSe and CZTSe absorbers presented here, the combinatorial approach to chemical bath deposition can be used to quickly determine the optimal thickness of contacts for other emerging absorber materials. For example, it has been shown that changing the contact material from CdS to Zn(O,S) in SnS-based thin film solar cells leads to significant improvement of their performance. The need for alternative contact layer development has also been shown for the CuSbS₂ emerging thin film photovoltaic absorber and similar may hold true for the CuSbSe₂ analog. On the basis of the electronic structure, we also expect that the alternative contact layers would be required to further improve performance of the Sb₃Q₃ (Q = S, Se) solar cells, where TiO₂ and CdS are currently used as contacts.

### EXPERIMENTAL PROCEDURES

The CdS combinatorial thin films libraries were grown by chemical bath deposition (CBD) on SLG substrate for physical properties measurements, and on CIGSe and CZTSe for PV device performance characterization (see Supporting Information for more details). After the deposition, the CdS thin films on the SLG substrate were subjected to physical properties measurements. Optical properties of the CdS films were measured using UV–vis–NIR Spectrometer (Agilent technologies) in the wavelength range from 300 to 1100 nm. Surface morphology of as prepared CdS films on SLG substrate was studied using field emission scanning electron microscope (FEG-SEM, JSM-7600F). The thickness of CdS film was measured by X-ray fluorescence (XRF, Helmut Fischer GMBH) and a surface profilometer (VEECO Dektak 8). The current density–voltage (J–V) characteristics of the combinatorial PV device libraries were tested using a Keithley 2420 source meter (Keithley Instruments, Inc.) under AM1.5G simulated solar irradiation (1000 W/cm²), as a function of position on the library (see Supporting Information for more details). For selected samples on the combinatorial PV device libraries, the external quantum efficiency of CIGSe and CZTSe solar cells was recorded in the range from 300–1200 and 300–1500 nm, respectively, using Bentham PVE300 instrument.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscombsci.6b00074.

Methods detailing CdS CBD process and PV device characterization; tables summarizing CdS film thickness and PV device performance; figures showing pictures of the combinatorial dip-coating CBD set up and providing the flowchart for the deposition process; graphs quantifying the JV and EQE changes as a function of CdS thickness (PDF)

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**Notes**

The authors declare no competing financial interest.

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