

# Surfactant-Assisted Growth of CdS Thin Films for Photovoltaic Applications

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# Surfactant-Assisted Growth of CdS Thin Films for Photovoltaic Applications

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## ABSTRACT

A common non-ionic surfactant, Triton X-100, was used to modify the chemical bath deposition (CBD) of CdS "buffer" layers on Cu(In,Ga)Se<sub>2</sub> (CIGS) thin films. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) data demonstrate that films produced with the surfactant have about the same levels of impurities as films grown without it. For thin, ~130 Å CdS layers and relative to devices made without the surfactant, average absolute cell efficiencies were increased from 10.5% to 14.8%, or by a relative 41%. Visual inspection of the CdS depositions reveals one possible mechanism of the surfactant's effects: bubbles that form and adhere to the CIGS surface during the CBD reaction are almost completely eliminated with the addition of the TX-100. Thus, pinholes and thin areas in the CdS layers caused by poor wetting of the substrate surface are sharply reduced, leading to large increases in the open circuit voltage in devices produced with the surfactant.

## 1. Objectives

The objective of this work was to capitalize on a serendipitous observation that occurred during the course of another investigation into the surface chemistry occurring on CIGS during CBD of CdS. Observed was the formation of stationary bubbles on CIGS surfaces during CBD of CdS. That combined with the knowledge that the CBD process beneficially changes the composition, work function, and valence band position of as-grown absorbers, resulted in the hypothesis that the addition of a surfactant to the standard CBD might increase the uniformity of thin CdS layers and might therefore increase the performance of solar cells made with such thin CdS layers. Performance increases both in terms of cell efficiencies and reliability that can be brought about by process changes easy to implement in current manufacturing procedures are in line with the goals of the SETP Multi-Year Technical Plan.

## 2. Technical Approach

Central to the technical approach to this work has been the construction and use of a unique cluster tool that consists of interconnected, capital-intensive analysis instrumentation and deposition equipment. The tool, which allows study of surface and interface properties of PV-relevant materials by XPS, AES, mass spectrometry, and *in-situ* growth represents a contribution to PV research that without Federal support would not be available to the PV community.

In the results reported here and in greater detail elsewhere<sup>1,2</sup>, CIGS films were first grown by the "3-

stage" process and transported through air into the N<sub>2</sub>-purged glove box portion of the cluster tool. Thin CdS films were grown on these absorbers by CBD with and without surfactant addition. Thin (~130 Å) CdS films were used to purposely enter the regime where device performance begins to suffer as a result of the buffer layer being too thin. The effect of the surfactant addition upon the CdS deposition rate was checked to ensure that comparisons between devices were for devices with buffer layers of similar thicknesses. Chemical and electronic properties of the CdS layers were studied with the surface sensitive spectroscopies ultraviolet photoelectron spectroscopy (UPS), XPS, and AES. The ultra-high vacuum sample transfer portion of the cluster tool allowed the study of as-grown surfaces without exposure to air.

## 3. Results and Accomplishments

The effects of surfactant addition on bubble formation during the CBD of CdS on CIGS were dramatic and easily observed by eye.<sup>2</sup> These effects are even more pronounced using highly corrugated hydrophobic substrates such as pictured in Fig. 1.

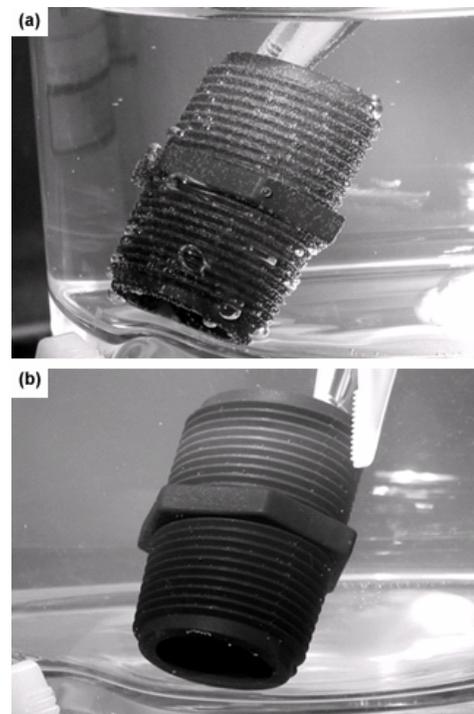


Fig. 1. CdS CBD on hydrophobic substrates without (a) and with (b) surfactant.

Figure 1 is a photograph 300 s into a CdS deposition on a black polypropylene nipple commonly used for plumbing. This test substrate was chosen for its

hydrophobicity, roughness, and visual contrast with lighter-appearing bubbles. As can be observed, surfactant addition to the standard NREL CdS deposition process sharply reduces the formation of adherent bubbles. Uniform and pinhole-free CdS films are deposited on hydrophobic substrates with the surfactant-modified process, whereas the standard CBD process results in films with poor coverage and pinholes that are obvious to the unaided eye (not shown).

AES and XPS data demonstrate that CdS films produced with the surfactant have the same chemical makeup as those produced without.<sup>1</sup> He I UPS data as in Figure 2 show that the two types of films also have the same work function and valence band position with respect to the Fermi energy.

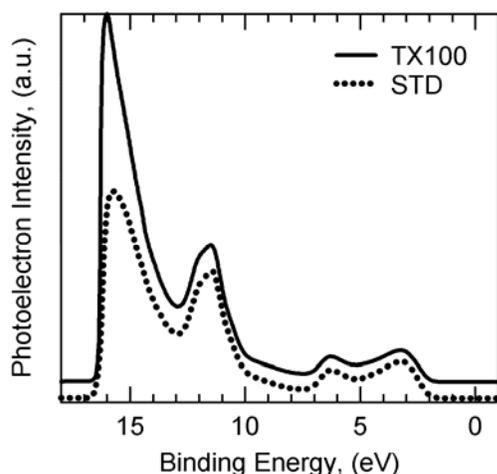


Fig. 2. UPS spectra showing work function and valence band maximum of surfactant (solid line) and standard (dotted line) CBD CdS.

In Figure 2, the work function is given by the difference between the secondary electron cutoff (~16.5 eV) and the energy of the incident light (21.218 eV). For the standard CdS films this found to be  $4.88 \pm 0.05$  eV, and for the surfactant-grown films this was  $4.87 \pm 0.05$  eV. The valence band maxima with respect to the Fermi energy (0 eV binding energy) of films grown by the standard and surfactant-modified processes were  $1.97 \pm 0.05$  eV and  $1.99 \pm 0.05$  eV, respectively.

CIGS-based solar cells were produced using ~130 Å of standard and surfactant-grown CdS and sputtered ZnO window layers, and subsequently tested. Previous device results obtained in this project<sup>2</sup> were for CdS buffer layers that were even thinner (~70 Å). Table I shows the results for the 130 Å CdS films on the same CIGS absorber. It is apparent that use of the surfactant results in a large, ~40% relative increase in the average cell efficiency compared to devices made with the standard CBD process.

Table 1 shows that most of the improvement that results with the surfactant-modified process is in the

Voc as one would expect from a higher quality, pinhole-free, and more uniform buffer layer.

Table 1. Device results for standard (cells 1-6) and surfactant (shaded cells 7-12) CBD processes.

Cell	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF (%)	Eff. (%)
1	0.481	-30.63	68.35	10.07
2	0.482	-31.28	68.43	10.31
3	0.488	-30.57	69.32	10.33
4	0.487	-30.86	67.10	10.08
5	0.495	-31.51	69.77	10.89
6	0.529	-31.00	70.47	11.55
<b>Avg.</b>	<b>0.494</b>	<b>-30.98</b>	<b>68.91</b>	<b>10.54</b>
7	0.685	-29.68	75.18	15.28
8	0.686	-30.33	75.85	15.78
9	0.679	-32.18	73.84	16.14
10	0.663	-32.29	73.49	15.73
11	0.604	-31.92	71.56	13.81
12	0.544	-31.82	70.54	12.22
<b>Avg.</b>	<b>0.644</b>	<b>-31.37</b>	<b>73.41</b>	<b>14.82</b>

#### 4. Conclusions

A common non-ionic surfactant has been shown to substantially improve the performance of CIGS-based solar cells when used in the chemical bath deposition of the n-type CdS buffer layer. XPS, UPS, and AES data demonstrate that the surfactant-modified CBD process produces films with the same chemical and electronic properties as the standard CBD process. Given these facts and that visual inspection of the depositions reveals that the surfactant substantially reduces the formation of adherent bubbles on absorbers, we conclude that performance increases with the surfactant are due to more uniform and pinhole-free buffer layers. Further work will include additional device characterization (LBIC, EL), reliability testing, and testing of suitability of this process for CdTe-based solar cells.

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- <sup>1</sup>C. L. Perkins, F.S. Hasoon, to be published.
- <sup>2</sup>C. L. Perkins, F.S. Hasoon, H.A. Al-Thani, S.E. Asher, and P. Sheldon, Proceedings of the 31st IEEE Photovoltaics Specialists Conference, Lake Buena Vista, FL (2005).

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