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Vapor $CdCl_2$–Optimization and Screening Experiments for an All Dry Chloride Treatment of CdS/CdTe Solar Cells

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ABSTRACT: A dry vapor treatment of $CdCl_2$ is being developed as an alternative approach to the conventional solution $CdCl_2$ treatment of CdS/CdTe devices. In this alternative process, the CdS/CdTe substrates are vapor treated in a close-spaced sublimation configuration. A 16-run Plackett-Burman screening experiment identified source temperature, substrate temperature, and treatment time as being the most significant parameters in the process. Subsequently, a 20-run Central Composite Design showed that a source temperature of 380–390°C, a temperature gradient (ΔT) of 5°C, and a time of 10 minutes provides the most process tolerant combination, yielding a total-area efficiency of 12.6%. A strong interaction between ΔT and treatment time was also identified. The model indicated that for a small ΔT, device performance improved with decreasing time, whereas at larger values of ΔT, performance increased with increasing time.

INTRODUCTION

Polycrystalline thin film CdTe solar cells have yielded efficiencies as high as 15.8% (1). Treatment with $CdCl_2$ is necessary to reach these high performances. The presence of chorine improves device efficiencies by passivating recombination sites on grain boundaries (2), promoting recrystallization and grain growth (2), and directly affecting the defect chemistry of the CdS or CdTe (3). Complications associated with chlorine treatment include introduction of strain at the CdS/CdTe interface (4), which can cause adhesion problems and compensation of p-type doping at the CdTe/backcontact interface (5).

Various approaches to $CdCl_2$ treatment exist. Those that are more amenable to manufacturing include CSS (close-spaced sublimation) $CdCl_2$ (6) and vapor $CdCl_2$ transport (7). CSS $CdCl_2$ processing has raised the efficiency level of non-$CdCl_2$ processed devices from 9% to 13–14%. Vapor treatment (relative to solution treatment) reduces processing time by combining the $CdCl_2$ exposure and annealing into one step. It improves reproducibility and controllability and eliminates a liquid waste

stream associated with the solution method. A more subtle reason for interest in dry processing is that chlorine residues may be more easily removed from CdTe surfaces prior to backcontacting than similar residues associated with solution-based processes (8). This may be important toward developing an all-dry backcontacting procedure (9).

In this paper, we report on a process optimization study of the vapor $CdCl_2$ process in the CSS configuration. To do this, a statistical approach was applied. Initially, 11 factors affiliated with the vapor treatment were identified. These factors were examined in a two level, 16-run Plackett-Burman screening experiment, and the three most significant factors were subsequently optimized in a five level, 20-run Central Composite Design (CCD).

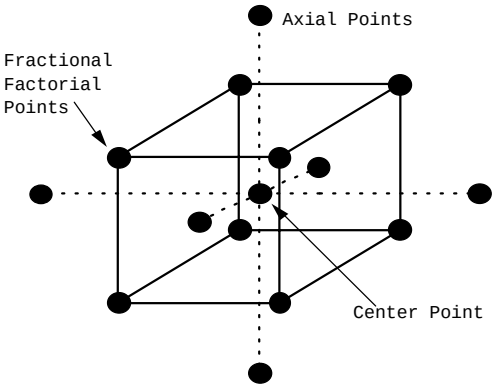

FIGURE 1. Central Composite Design

The CCD design was chosen because it is the most efficient second order modeling design for quantitative factors, and it gives more flexibility in the resolution selection (10). Also, it greatly reduces the number of required experimental points relative to a full factorial design. As illustrated in Figure 1, the experimental points of the CCD were taken from the corners (fractional factorial points), replicated center points, and axial points.

EXPERIMENT AND DISCUSSION OF RESULTS

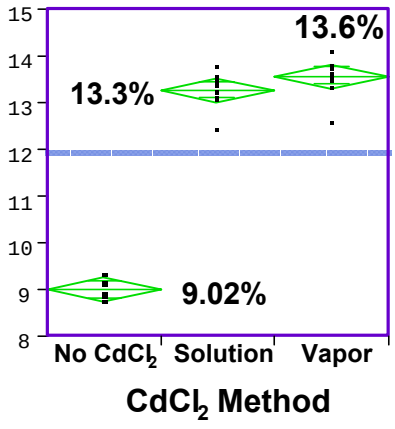

FIGURE 2. Statistical comparison of $CdCl_2$ methods

Processing conditions prior to the vapor $CdCl_2$ treatment were held constant. First, a SnO_2 bilayer was grown on Corning 7059 glass by chemical vapor deposition of tetra-methyl-tin. Next, the CdS layer was grown by chemical bath deposition. The CdTe deposition was performed using a CSS thermal etch process originally developed to minimize possible transparent conducting oxide (TCO) decomposition effects (11). This process was recently used to produce an NREL-confirmed 15.4% total-area device. After CdTe deposition, the vapor chloride treatment is performed by heating the described structure in a CSS configuration over

TABLE 1. List of the factors and the levels at which they are examined

Factors	Level (-1)	Level (+1)
(1) Source temperature (°C) [T(src)]	370	400
(2) Substrate temperature (°C) [T(sub)]	T(source) - 30	T(source) - 0
(3) Pressure (torr)	10	550
(4) Ambient (%O_2:He)	0	50
(5) Time (minutes)	3	10
(6) Spacer distance (mm)	1	5
(7) Nature of the cooling process	natural	programmed
(8) Ramp up time (min.) from 200°C to T(sub)	3	6
(9) Source material density	porous	dense
(10) Subject the source to a humid environment	no	yes
(11) Pre-anneal (10 minutes, 200°C)	no	yes

a 1 mm $CdCl_2$ source plate. Devices were then completed using our standard backcontact procedure consisting of a water rinse, a nitric-phosphoric acid etch, application and He annealing of a Cu-doped HgTe powder with a carbon dag paste, and application and air annealing of a silver paste.

The $CdCl_2$ vapor process is being investigated as a viable alternative to the solution $CdCl_2$ process. In preparing for this optimization study, we assessed the capability of the vapor process by performing a study to gauge the statistical differences in the vapor treated, solution treated, and no $CdCl_2$ cases. Figure 2 (on the previous page) summarizes the results of this experiment. The solid line near the center represents the average percent efficiency for the total set of devices. The diamonds define the confidence interval for each process. Figure 2 shows that the vapor process is comparable to solution processing in terms of device performance.

First, a 16-run Plackett-Burman screening experiment was designed to study 11 factors associated with the $CdCl_2$ vapor process. They are listed in Table 1 along with the two levels, (+) and (-), at which they were examined. Four response variables derived from device current-voltage measurements (V_{oc}, J_{sc}, fill factor, and efficiency) were used to determine the magnitude of the effect of each factor. For the effect to be

TABLE 2. Factors and their corresponding effect ranked in descending order

V_{oc}	*Effect*	J_{sc}	*Effect*	*% FF*	*Effect*	*% η*	*Effect*
T(src)	0.059875	T(src)	0.912625	T(src)	4.690125	T(src)	2.137875
T(sub)	0.033375	PreAnnea l	0.523625	T(sub)	2.598125	T(sub)	1.010125
Time	0.030375	Time	0.410375	Time	1.522125	Time	0.877125
PreAnneal	0.012125	Cool	0.409875	Ambient	1.484125	PreAnneal	0.679125
Ramp	0.012125	Humidity	0.184375	PreAnneal	1.415875	Humidity	0.487375
Ambient	0.011375	Ramp	0.170125	Humidity	1.322875	Ambient	0.422625
Humidity	0.011125	T(sub)	0.122125	Source	1.092875	Cool	0.313625
Spacer	0.005625	Source	0.105625	Cool	0.549125	Source	0.265875
Press	0.002875	Ambient	0.056375	Press	0.540625	Press	0.115625
Cool	0.001375	Press	0.053875	Ramp	0.137375	Ramp	0.111625
Source	0.000625	Spacer	0.001875	Spacer	0.058125	Spacer	0.056625

The minimum significant factor effect for the responses were calculated to be
V_{oc} [MIN] = 0.011335, J_{sc} [MIN] = 0.545786, % FF [MIN] = 0.808039, % η [MIN] = 0.376187.

TABLE 3: Top three factors and the levels at which they are evaluated

	-α	*-1*	*0*	*+1*	*+α*
Source Temperature (°C)	370	378	390	402	410
ΔT [T(src) – T(sub)]	10	8	5	2	0
Time (minutes)	5	7	10	13	15

significant, its magnitude had to be greater than its minimum significant factor effect, [MIN]. [MIN] was established by using a t-test at the 90% confidence level. Table 2 ranks each factor by the magnitude of its effect.

The bold lines in Table 2 brackets the variables into regions of very significant, slightly significant, or insignificant. For each response, the source temperature was a very significant factor. The top three significant factors were source temperature, substrate temperature, and time. Notably, the pressure and spacer distance were not significant effects in this process.

The three significant factors were then evaluated at five different levels (Table 3) in a Central Composite Design. The design required 20 experimental runs, including 8 factorial points, 6 axial points, and 6 replications at the center point. The range selected for each factor was determined based on the results of the screening experiment and previous experience with the vapor process. We adjusted the range of operation to limit adhesion problems. Consequently, device performance was slightly lower. Also, from the screening experiment, it was found that a smaller ΔT [T(src)–T(sub)] yielded a better performance, thus the maximum ΔT used was 10°C.

The statistical analysis package, JMP IN (12), was used to fit collected data and compare them to model predictions. Unfortunately, the data did not fit well with the model. R^2 values obtained for each response was well below the perfect fit (R^2 = 1.0). We attribute this to the non-normal skew introduced by catastrophic adhesion failures sometimes encountered at high $CdCl_2$ exposures. From the 40 devices fabricated, 20% delaminated.

Figure 3 illustrates process responses as a function of the factors. The responses shown (J_{sc} = 22.02 mA/cm^2, V_{oc} = 0.821 mV, fill factor = 69.67%, and efficiency = 12.59%) correspond to a predicted stable operating region where T(src) = 390°C, ΔT = 5°C, and t = 10 minutes. The small slopes in the graphs of ΔT and treatment

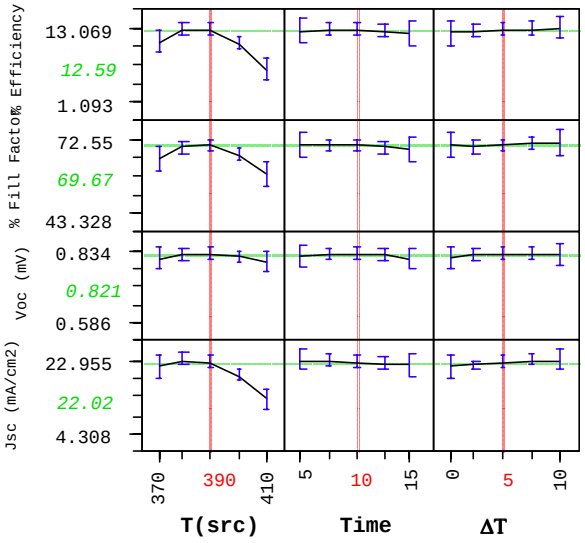

FIGURE 3. Prediction profiles for the stable operating region. Italicized numbers are the responses for the stable region.

time indicate that the process is insensitive to these factors, under these conditions. However, the process is very sensitive to T(src). Since ΔT is a function of T(src), a complex relationship was observed between the two. This relationship is depicted in the contour plots of Figure 4.

Each of the four columns of Figure 4 correspond to a response variable. The contour lines predict better device performance when using shorter treatment times and lower source temperatures when ΔT = 0 (the top row). Interestingly, longer treatment times and higher source temperatures are preferred when ΔT = 12.5 (the bottom row). At the middle row, where ΔT = 5, regions with smaller gradients in the response contours are displayed. Again, this is the operating region where few or no fluctuations in device response are predicted.

Note that the contour lines that predict maximum performance lie outside the magnitude of the responses observed in the experimental data. The model suggests that better performances can be attained, but in process space that is less tolerant of deviations. Further assessment of the suggested conditions will be necessary in a future study.

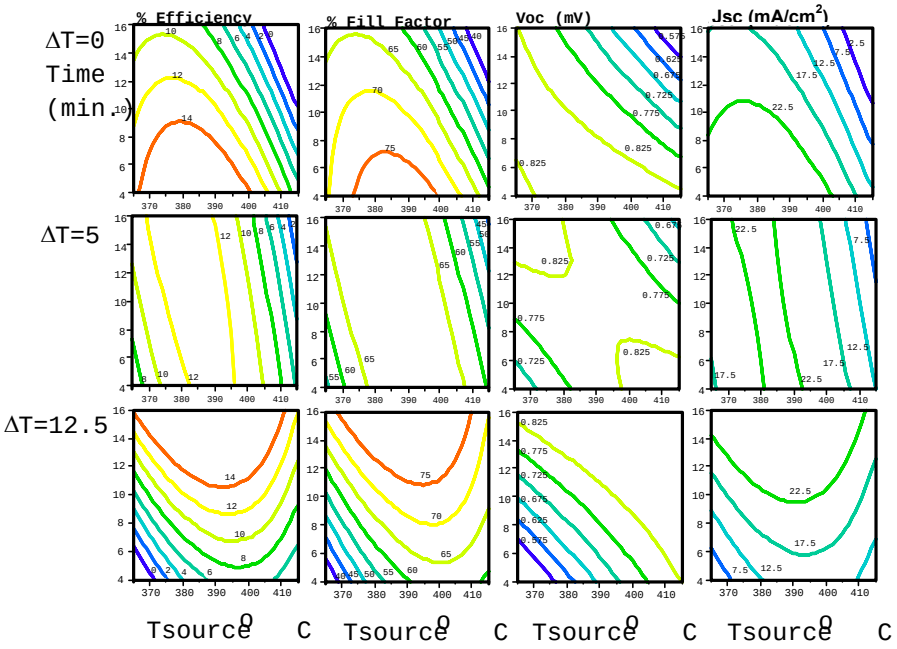

FIGURE 4. Contour plots showing time and temperature interactions at different ΔT settings

SUMMARY

In this study, a screening experiment was used to identify T(src), T(sub), and time as the most significant variables in a CSS $CdCl_2$ vapor process. The three variables were then integrated into a Central Composite Design (Box-Wilson) for an optimization study. From this design, we were able to identify a process tolerant combination of T(src) = 390°C, T(sub) = 385°C, and time = 10 minutes. A very interesting interaction between ΔT and treatment time was also identified. The model suggests that either a combination of short times with a low T(src) and a small ΔT, or a combination of long times with a high T(src) and a large ΔT, should be investigated to optimize performance.

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