

THESIS

IMPROVING THIN-FILM POLYCRYSTALLINE CDSETE/CDTE SOLAR CELL EFFICIENCIES THROUGH STATISTICAL DESIGN OF EXPERIMENTS

Submitted by

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ABSTRACT

IMPROVING THIN-FILM POLYCRYSTALLINE CDSETE/CDTE SOLAR CELL EFFICIENCIES THROUGH STATISTICAL DESIGN OF EXPERIMENTS

In recent decades, cadmium telluride (CdTe) solar photovoltaic (PV) technology has become increasingly popular to meet global energy demands. Its high throughput industrial fabrication methods, low material usage, recyclability, longevity, and theoretical maximum efficiency have led to its widespread integration in the PV sector. Most of the CdTe PV research reported in literature utilizes one-factor-at-a-time (OFAT) experiments. This work leverages statistical design of experiments (DOE) and statistical analysis of data to study the relationships between multiple processing factors and solar cell performance metrics.

OFAT only indicates the primary effect of the chosen variable, whereas DOE determines the primary effect as well as the interaction effects. DOE determines both critical and insignificant factors, whereas OFAT assumes everything is a critical factor. DOE also requires fewer experiments, has more sophisticated predictive capabilities, and streamlines process optimization in comparison to OFAT. Since DOE is most effective with large data sets, the unique high throughput capability of the Advanced Research Deposition System (ARDS) at Colorado State University makes our lab a perfect candidate to utilize DOE for CdTe solar cell research.

In this study, DOE and statistical analysis were used to investigate copper (Cu) doping, electrode painting, absorber deposition rate and temperature, p-doping of $\text{CdSe}_{0.4}\text{Te}_{0.6}$ (CST40) through arsenic (As) incorporation and tellurium (Te) overpressure, and oxide deposition at the back of the cell. Multiple linear regression (MLR) and analysis of variance (ANOVA) were conducted on all DOE's. An improved process was identified for the baseline high efficiency Cu-doped solar cells in which total process time was reduced by 33%. A thick $6\mu\text{m}$ structure of 18.5%+ efficiency was developed following statistical model suggestions. A standard procedure for electrode paint-

ing was developed. As a result of DOE, several 19%+ cells were fabricated achieving the highest efficiency of 19.44%. The best performing As doped CST40 graded CdTe cells of 18.5%+ were also fabricated using these methods. Carrier concentration versus voltage plots indicated successful p-doping of CST40 with As. Annealing the absorber with cadmium arsenide (Cd_3As_2) and depositing tellurium oxide (TeO_x) at the back of the cell improved performance, yielding 80%+ fill factors. Decreasing thickness of CdTe behind CST40:As increased short-circuit current density to 30 mA/cm²+. Lastly, thinner absorbers yielded higher performance when backed with NiO:Cu.

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I cannot express enough gratitude to my family for their continued love, support, and motivation throughout my journey in higher education. They fostered my passion for science and engineering and continually ensure a healthy balance in my life. My father Scott A. Lustig and mother Melora K. Lustig instilled within me a steadfast work ethic and encouraged my obsessions in education and in personal endeavors. I owe my success to them. My sister Emma M. Lustig has always lent her advice in important life decisions, I owe my mental sanity to her. Lastly, I would

like to thank my grandparents and extended family for always believing in my abilities and their continued support in my journey.

DEDICATION

I dedicate this work to my parents who have inspired an endless pursuit of knowledge within me.

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Chapter 1

Introduction

1.1 CdTe PV in the scope of World Energy Demand

From 1971-2019, worldwide annual energy consumption increased 136% in a linear fashion, shown in Figure 1.1, and is predicted to follow the same trajectory in the coming decades [1]. Nearly 20% of worldwide energy usage in 2019 was for electricity, and 2.9% of that electricity came from solar photovoltaics (PV) [1] [2], shown in Figure 1.2.

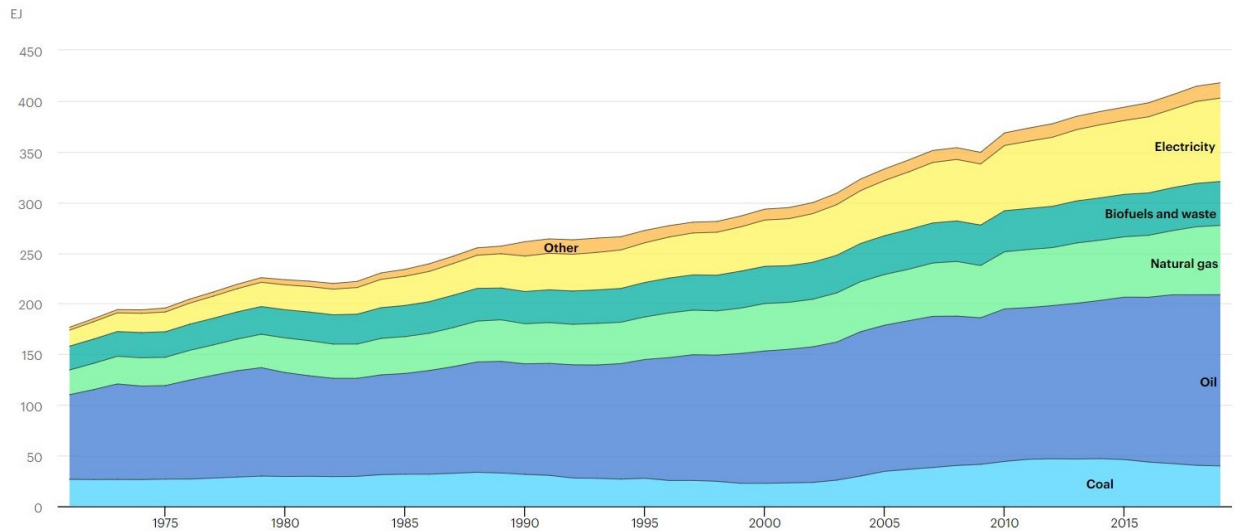


Figure 1.1: World annual total energy consumption by source, 1971-2019.

Between 1998 and 2015, the cumulative photovoltaics (PV) installation capacity has grown between 20% and 72% annually, with a compound growth rate of about 40%. This makes PV the fastest growing renewable energy technology [3]. Within the PV sector, thin-film technologies comprise around 5% of the total market, with cadmium-telluride (CdTe) photovoltaics securing the majority of the thin-film market [4] [5] shown in Figure 1.3. CdTe PV has reached commercial production upwards of 10 GW, and have demonstrated lower unsubsidized levelized cost of electricity (LCOE) than conventional silicon PV, seen in Figure 1.4. Power conversion efficiencies

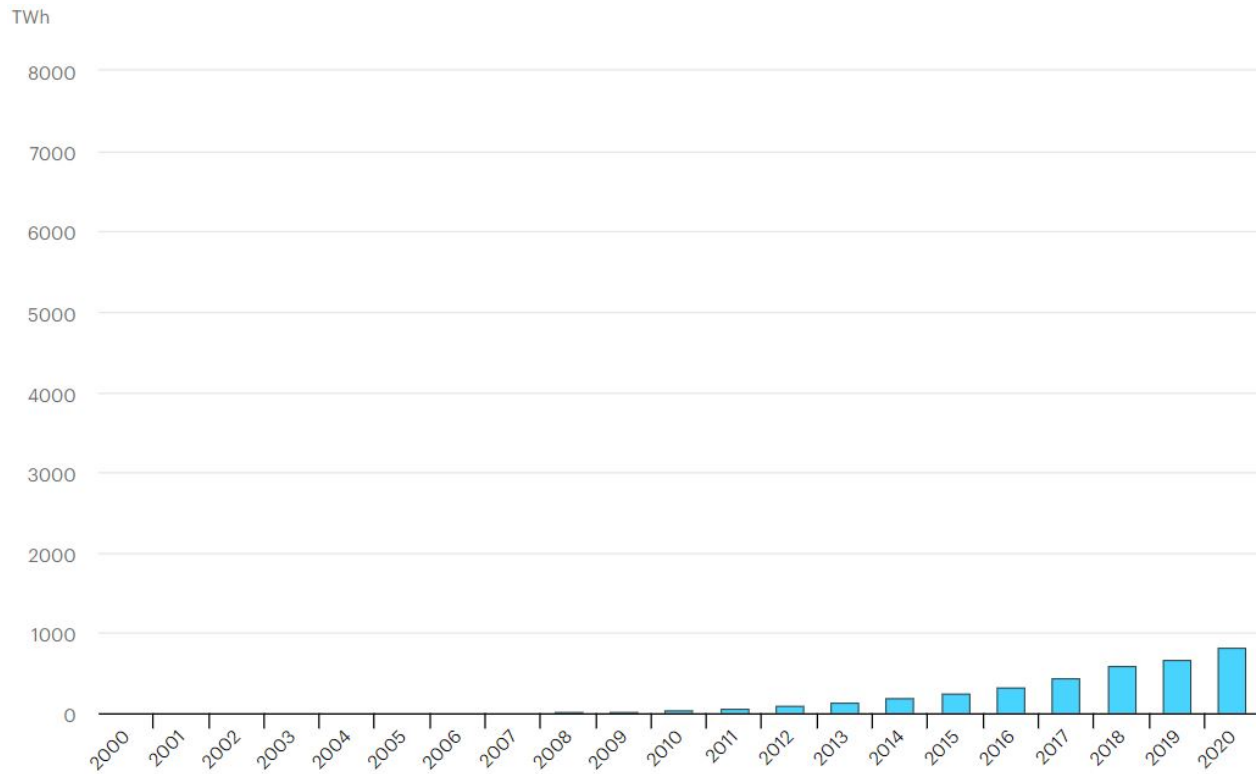


Figure 1.2: World annual total solar PV power generation, 2000-2019.

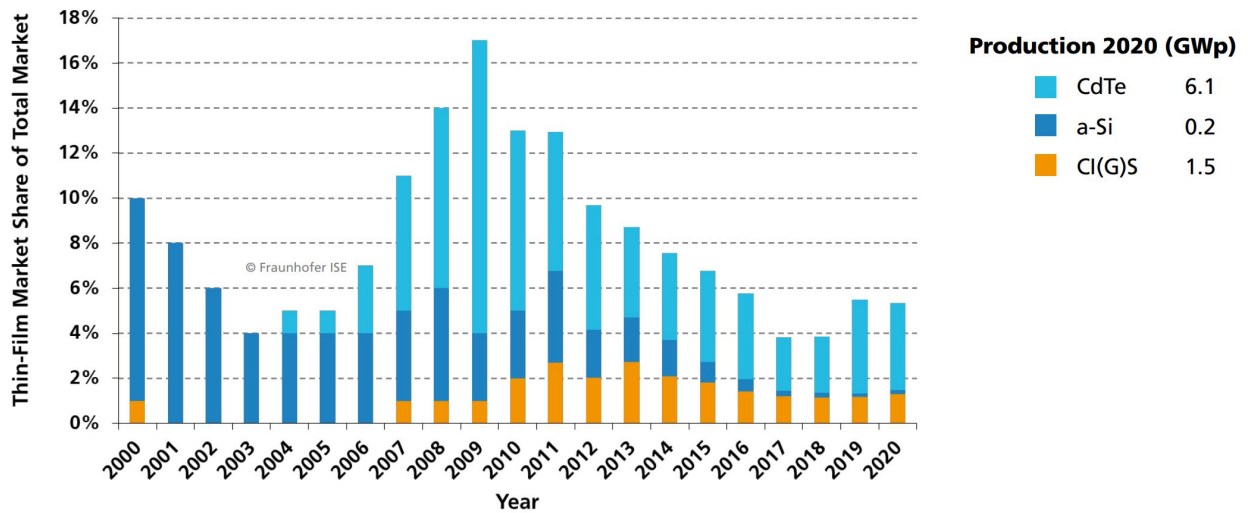


Figure 1.3: Market share of thin-film PV technologies.

have been steadily climbing, as shown in Figure 1.5, with a record CdTe module efficiency of 19% and record CdTe cell efficiency of 22.1% [5], indicating an increasing market presence in years to come.

Levelized Cost of Energy Comparison—Unsubsidized Analysis

Selected renewable energy generation technologies are cost-competitive with conventional generation technologies under certain circumstances

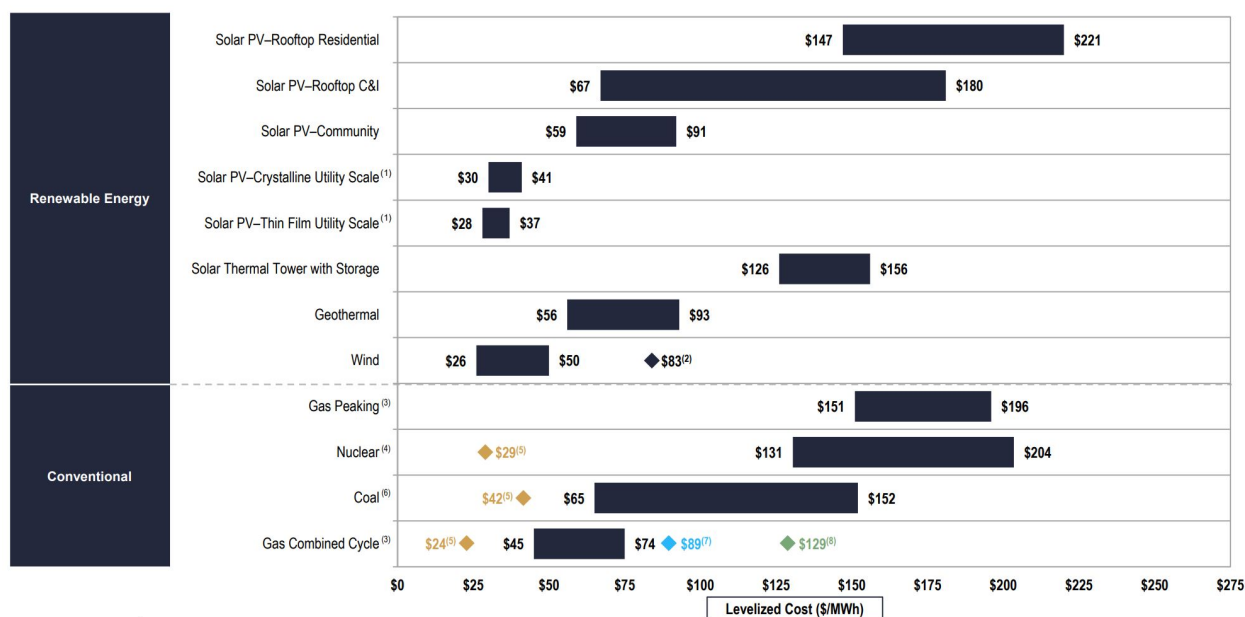


Figure 1.4: Levelized cost of energy comparison between select renewable and conventional energy sources. Solar PV-Crystalline Utility Scale refers primarily to Si PV, and Solar PV-Thin Film Utility Scale refers primarily to CdTe PV.

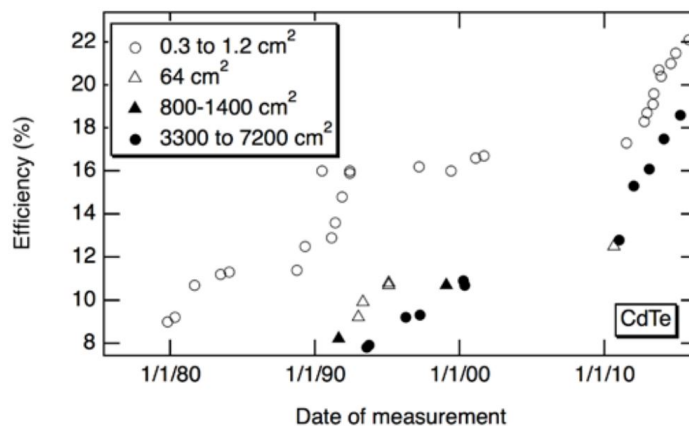


Figure 1.5: Historical record CdTe cells of various sizes.

1.2 Advantages of CdTe PV

The top two most popular PV technologies are crystalline silicon (c-Si) at 95% market share and thin-film CdTe at 4% market share [4]. A comparison of the two technologies is shown in Table 1.1.

Table 1.1: Comparison of CdTe versus Si PV technologies.

	CdTe	c-Si
Material Sourcing	Utilizes mining by-products through transparent and traceable sources	Potentially unethical mining operations strictly for PV module production
Manufacturing	4.5 hours, 50% less air pollution	3 days, more air pollution
Material Usage	~3 micrometers thick	~300 micrometers thick
Operation	2.5X lower carbon footprint, 3X lower water footprint, 2X faster energy payback time	Less environmentally responsible
Material Recovering	90% of original materials recycled at end of lifetime	Only about 10% are recycled
High Temperature Performance	Lower temperature coefficient, better performance in hot environments	Higher temperature coefficient, reduced performance in hot environments
Longevity	0.3% power output annual degradation rate	0.55% power output annual degradation rate
Low-Light Capability	Greater power generation under overcast conditions and diffused light	Struggles to maintain performance under diffused light

1.3 Potential of Solar PV

Compared to all available sources of energy, the solar radiation that reaches the earth's surface significantly exceeds all other energy sources combined [6]. A visual representation of the available energy is shown in Figure 1.6.

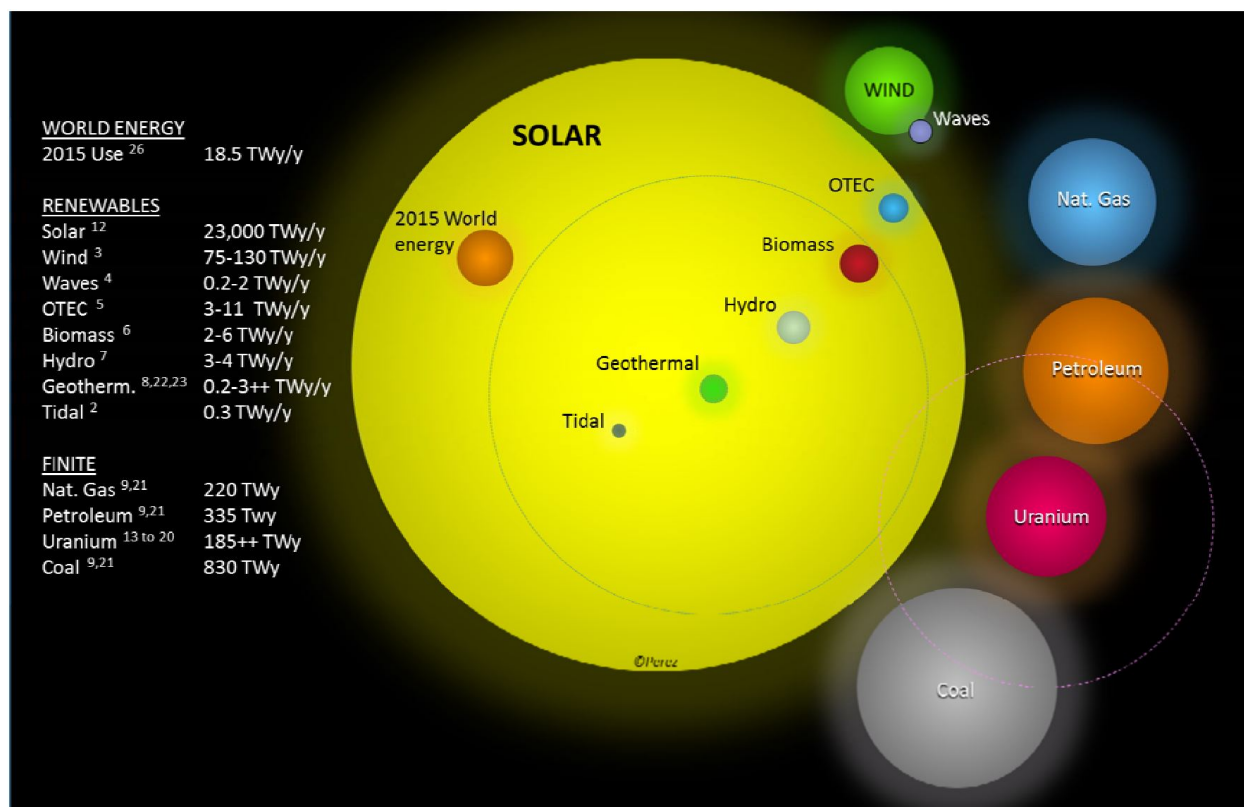


Figure 1.6: Estimated finite and renewable planetary energy reserves.

Figure 1.6 shows that solar energy is more than capable of meeting world energy requirements. Rough calculations reveal that a solar array the area of Spain (191,817 sq. mi.) would be enough to meet all the world's energy needs [7]. Comparing that to the available uninhabited land of the Sahara Desert of 3,500,000 sq. mi., that area is quite small. The incredible potential of solar energy is what makes it a frontrunner in the decarbonization of society.

1.4 CdTe PV Research at Colorado State University

Since the early 1990's, Dr. Walajabad S. Sampath and Dr. James R. Sites have led CdTe PV research at CSU. Their PV lab has been at the forefront of the technology since then. From improving the cadmium sulfide (CdS) window layer by adding oxygen to the film, to pioneering a high-transmission $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ (MZO) window layer, to alloying CdTe with selenium (Se) for higher electrical current collection, and creating a consistent ohmic back contact and simple painted electrode, the research at CSU has always been world class. The CSU record cell efficiency is 20.14%, one of the highest in academia and near the world record cell of 22.1% made by First Solar.

In this work, statistical design of experiments was implemented to explore the effect of a variety of process parameters. Industry has widely adopted statistical process control and design of experiments due to the detailed information it provides and cost effectiveness. Fewer experiments are required than with typical single factor variation experiments, interactions between variables are calculated, and more accurate predictions can be made. Conducting such experiments on high-performing CdTe-based solar cell structures led to increased efficiencies, new processing conditions, and deeper understanding of the solar cell function.

1.5 Operating Principles

The majority of this section can be found on pveducation.org [8]. Beginning from the most basic level, every atom is comprised of three subatomic particles — positively charged protons, equally negatively charged electrons, and a neutrally charged neutrons. The simplest atom is hy-

drogen, which has one proton and one electron. All other elements have more than one proton, neutron, and electron in their typical state. The nucleus is the center of the atom (protons and neutrons) and the electrons orbit the nucleus at varying distances (energy levels) depending on the element. When the atoms are bonded together through charge interactions between the protons and electrons, they form a bulk material. Every bulk material has an electron energy range called the valence band (E_V) in which electrons typically reside, and similarly a conduction band (E_C) that is typically void of electrons. The energy levels in between the high energy edge of the E_V and the low energy edge of the E_C is called the band gap (E_G), in which electrons have a very low chance of residing. With this in mind, there are three classifications of materials — electrical insulators, conductors, and semiconductors. Insulators have a large E_G , typically larger than 9 electron-volts (eV: a unit of energy equal to the work done on an electron in accelerating it through a potential difference of one volt). The energy required to move an electron from the E_V to the E_C is too large in any circumstance, thus the material does not conduct electricity. A conductor has a E_C that overlaps its E_V (zero E_G), thus any amount of energy (applied voltage) allows the electrons to move freely in the material, conducting electricity. In between these two classifications is the semiconductor. The E_G is small enough (usually around 1 eV) that if an electron receives enough energy, it will jump up into the conduction band and become conductive. In its ground state with no supplied energy (at absolute zero, 0 Kelvin), it is not conductive. The illustration in Figure 1.7 shows this concept.

Semiconductor materials are what absorb sunlight and convert it to electricity in solar cells. Given the proper semiconductor, the incident light is enough energy to bump the electrons into the E_C . Correspondingly, there is an absence of an electron remaining in the E_V , which can be conceptualized as a positive charge called a "hole." It is referred to as an electron-hole (e-h) pair that is generated when an electron moves from E_V to E_C , and they are both collectively referred to as charge carriers.

When a semiconductor has more electrons than holes, it is negatively charged and is called n-type. If it has more holes than electrons, it is positively charged and is called p-type. The hole or

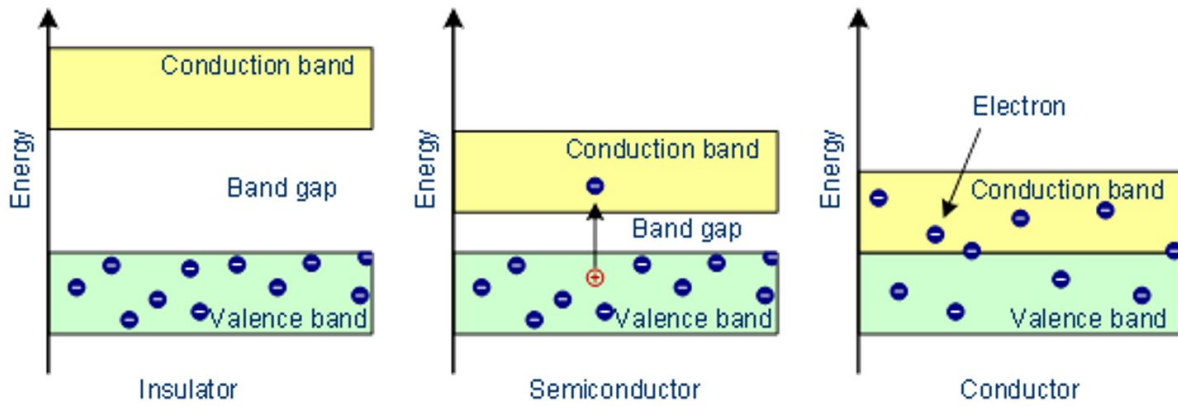


Figure 1.7: Visual representation of insulator, semiconductor, and conductor and their corresponding E_V 's, E_C 's, and E_G 's.

electron leaves behind its nucleus, which is in a fixed position and is ionized (positive in n-type, and negative in p-type). When an n-type semiconductor and a p-type semiconductor come in contact with each other, they form a p-n junction. The electrons from the n-type side diffuse over to the p-type side in an attempt to neutralize, and correspondingly the holes from the p-type side diffuse to the n-type side. The remaining ion cores set up an electric field in the direction from n-type to p-type. At or near the junction, there is a neutral region called the depletion width, as it is depleted of net charge. In a solar cell, when connected to a load, the e-h pair is separated by an incoming photon of sufficient energy, the electron is extracted from the front n-type side and travels through the load to the back p-type side of the cell where it recombines with the hole, completing the circuit and providing useful electrical power. The power conversion efficiency is defined as the quotient of power out and power in, which is synonymous to the useful electrical power generated by the solar cell divided by the power entering the area of the solar cell in the form of electromagnetic radiation (photons).

In the CSU 20.14% cell, the p-n junction is not simply two materials. There is a n^+ (highly n-type) transparent fluorine-doped tin oxide layer deposited on glass, followed by an n-type transparent window layer of MZO, followed by the thickest layer ($3.5 \mu\text{m}$) p-type semiconductor absorber layer of $\text{CdSe}_{0.4}\text{Te}_{0.6}$ (CST40) diffused into CdTe, which is then backed by a p^+ layer of tellurium

(Te), completing the p-n structure. There is a cadmium chloride (CdCl_2) treatment after absorber deposition to passivate the grain boundaries and layer interfaces, meaning there are significantly fewer recombination sites allowing the electrons to reach the front of the cell and the holes to reach the back of the cell [9]. The Cu doping after the CdCl_2 treatment creates an ohmic back contact so the holes can reach the Te layer and be extracted through the electrode. This completes the structure of the CSU baseline solar cell, shown in Figure 1.8.

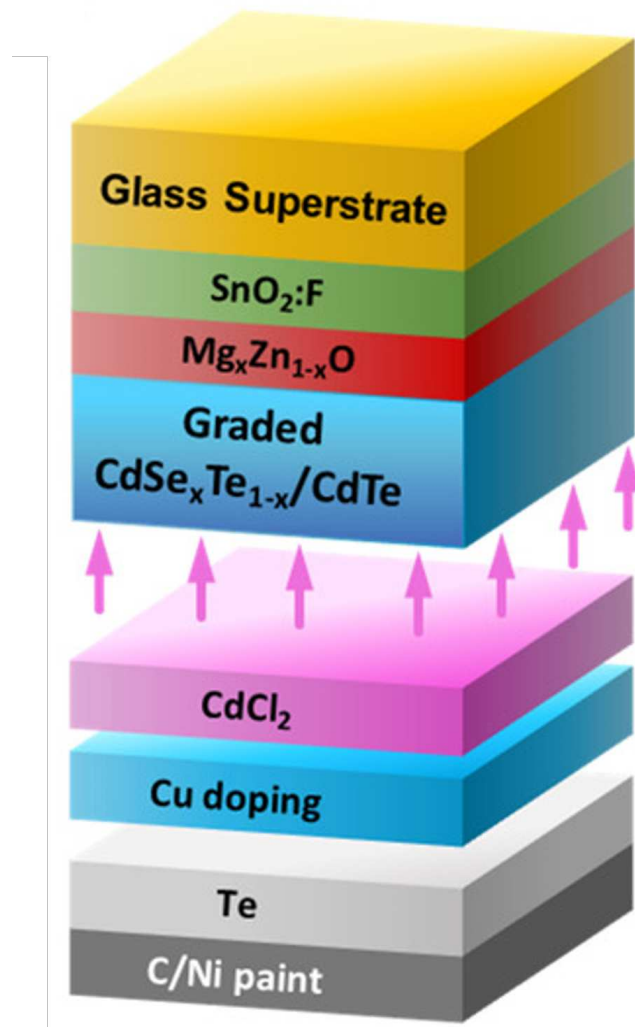


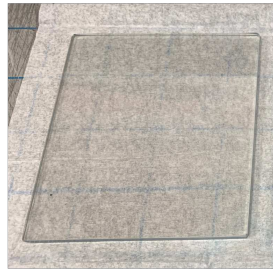
Figure 1.8: Baseline solar cell structure, not to scale.

Chapter 2

Experimental Methods

2.1 Solar Cell Fabrication

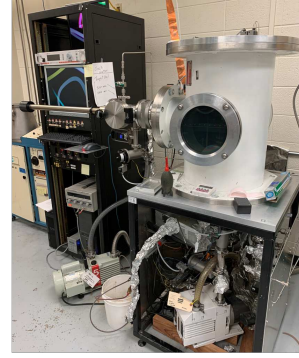
In the CSU lab, the first step in solar cell fabrication is to wash the superstrate glass. Pilkington manufactures the TEC10 soda-lime glass with the n^+ layer of fluorine-doped tin oxide ($\text{SnO}_2\text{:F}$) already deposited. The glass is washed with ultrasonic cleaners and Micro-90 detergent to remove contaminants and a slow drying process is used that prevents visible streaking on the surfaces. This ensures highest light transmission through the glass and promotes strong film adhesion. Next, the 100 nm MZO layer is deposited using radio frequency (RF) sputtering. The process is carried out at 5 mTorr with 97% Ar mixed with 3% O_2 , sputtering at 140 W and a superstrate-to-target distance of 15 cm and no preheating or temperature control. Next, the absorber is deposited via CSS in the Advanced Research Deposition System (ARDS) at 40 mTorr with 98% N_2 mixed with 2% O_2 processing gases. The CdCl_2 treatment also takes place in the ARDS under the same conditions. Swanson et al, have provided a detailed account of the deposition system and process [10]. Following the absorber deposition, the film is doped with Cu. The Cu doping process is carried out at 70 mTorr in N_2 in a similar CSS system as ARDS, including a superstrate preheat station with both heaters at 330°C , then a CuCl sublimation station with bottom heater at 190°C and top heater at 175°C , and lastly an anneal station with both heaters at 200°C . The Te back contact layer of 30 nm is deposited via evaporation at room temperature below 10^{-4} Torr with no active processing gas, thickness determined with a quartz crystal monitor. The electrode is comprised of two spray-painted layers of C and Ni. At this point, the cell is complete but the area is too large and the n-type side of the cell is not easily contacted for measurements. 25 square cells of 0.64 cm^2 are delineated by bead blasting over a mask, followed by indium soldering to the front contact for more consistent measurements. The entire process diagram is shown in Figure 2.1.



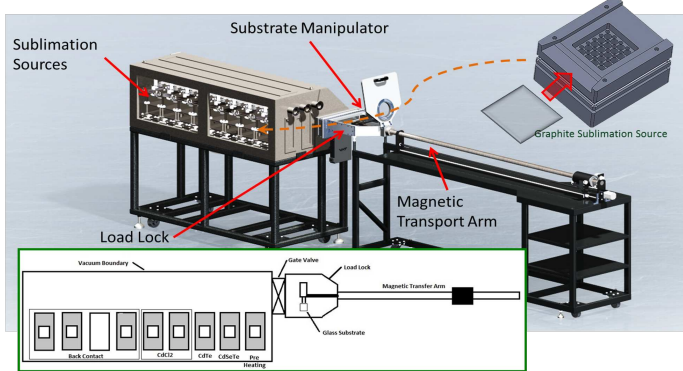
1. Pilkington TEC10 Glass



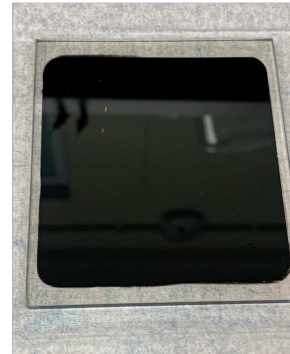
2. Ultrasonic cleaning



3. RF sputtering MZO



4. Absorber deposition and CdCl_2 treatment in ARDS



5. Film after ARDS processes



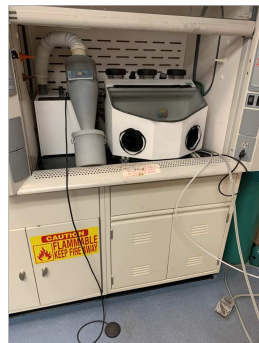
6. Cu treatment



7. Evaporation of Te or RF sputtering oxide back contact



8. Painting electrode



9. Delineation of 25 cells



10. Solder indium and process complete

Figure 2.1: Solar cell fabrication flow chart showing all deposition systems and the film throughout the process.

2.2 Measurements and Characterization

2.2.1 Profilometry

After absorber deposition, the film is scribed in a central location to approximate the thickness of the film across the superstrate. A profilometer is used to determine the step size (total thickness) of the film using a fine-point stylus that contacts the surface. The force from the stylus is measured and converted to deflection in the Z direction (vertically) which is printed to a strip of grid paper. The resulting profile shows a step down when the stylus moved from the film surface to the scribed part of the film, and a step up when the stylus moved from the scribed part of the film to the surface. The steps are visually measured on the grid and the approximate film thickness is recorded.

2.2.2 J-V

Current-voltage (J-V) measurements are recorded for all cells. There are three metrics that determine the efficiency of the cell, open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill-factor (FF). These are measured by applying a voltage to the cell under a standard illumination spectrum created by a solar simulator. This spectrum of light is nearly identical to that which radiates from the sun and travels through 1.5X the thickness of the earth's atmosphere, universally referred to as AM1.5, which is 1000 W/m^2 . The applied voltage is swept from -0.8 V to 1.2 V in 0.025 V increments. At each voltage, the current (I) is recorded and then divided by the cell area to obtain the current density (J, mA/cm^2). The zero-voltage current is J_{sc} , the zero-current voltage is V_{oc} , and the FF is the quotient of the maximum power and product of J_{sc} and V_{oc} . The efficiency is calculated as the quotient of the maximum power and the incident power on the cell. For the standard CSU cell, there is 0.064 W incident on the cell. These four performance parameters are most commonly analyzed.

2.2.3 C-V

Capacitance-voltage (C-V) measurements record the capacitance of the cell from -1 V to 0.8 V in 0.02 V increments. Assuming that there is only one p-n junction, the cell acts as a parallel

plate capacitor, and the species of the charge carrier is known in the depletion width, the C-V data can be converted to carrier concentration versus distance from the junction. This conversion helps visualize the carrier density profile and determine if the diode is of good quality and expected doping is present.

2.2.4 PL

Photoluminescence (PL) measures the radiative recombination from the film. A 532 nm green laser separates charge carriers, which then recombine emitting photons corresponding to the energy difference between where the electron resided and the E_V . The detector determines the energy of the luminescent photon, which is then converted to wavelength and is counted by the software. Over a sampling period, typically 1.5 seconds, the sum of the luminescent photons is shown versus their wavelength. High-performing films typically exhibit one prominent peak at around 890 nm with very few counts outside of the 780-1050 nm range. This is characteristic of recombination around 1.4 eV E_G , corresponding to CST material. Occasionally a double peak is observed, indicating poor intermixing between the CST and CdTe during processing, usually a precursor to poor cell performance. Sometimes there are significant counts at longer wavelengths, indicating recombination from potential defect states closer to the E_V rather than band to band recombination, also typical of poor performing cells.

2.2.5 SEM

Scanning electron microscopy (SEM) is an imaging technique that can give up to 100,000X magnification. It is typically used to visually inspect layer thicknesses, grain sizes, surface roughness, and film quality.

2.2.6 EDS

Energy dispersive spectroscopy (EDS) is typically coupled with SEM and identifies the elements present in the film as well as their locations. When used in conjunction with the previously mentioned characterization methods, advanced understanding of cell function can be achieved.

2.3 Design of Experiments

2.3.1 Benefits of DOE

The majority of the discoveries in this work were directly or indirectly resultant of using statistically designed experiments. The common term for this method of experimentation is design of experiments (DOE) and it has gained considerable popularity since its inception in the 1920's [11]. In primary school, we are taught the basic scientific method which involves developing a hypothesis followed by an experiment in which one variable is changed and all others are held constant. The hypothesis is then accepted or rejected based on the results. This is referred to as one-factor-at-a-time (OFAT) experimentation. This is an effective experimental method if there is only one influential factor on the response. However, if there are many influential factors as with the majority of modern technical optimization problems, OFAT can be misleading due to its sequential nature. For example, assume there are two factors, X and Y, and two levels, 1 and 2, that are to be investigated. A visual representation of such an experiment is shown in Figure 2.2. If condition 1,1 (X=1,Y=1) is tested first and then 1,2, the conclusion would be that factor Y had minimal effect. If 2,2 was then tested, the conclusion would be that factor X has significant effect on the response and factor Y is insignificant. However, if the order of experiments was 1,1, then 2,1, then 2,2, the conclusion would be that factor X has small effect on the response, and factor Y has a more significant effect. This example shows how OFAT can be misleading depending on the order of experimentation. In DOE, these conditions are simultaneously tested, thus the individual effects of X and Y can be analyzed as well as the interaction effect between X and Y, which is indicated by the red arrow in Figure 2.2. This vertical line shows the distance between the connecting diagonals, visually representing the interaction between the two factors. The interaction effect cannot be seen in OFAT, but in DOE it is seen and quantified, one of the primary benefits of this method of experimentation. DOE is quicker than OFAT as multiple factors can be changed simultaneously versus the sequential nature of OFAT. DOE is also more likely to converge upon optimal conditions due to the intricate information obtained from the experiments, whereas OFAT may miss the optimum entirely. DOE also enables for creation of advanced statistical models and

prediction expressions in which the response for untested conditions can be accurately estimated. OFAT has limited primitive forecasting capabilities. These advantages of DOE led to widespread implementation in industry as refining of processes is quicker and cheaper than OFAT.

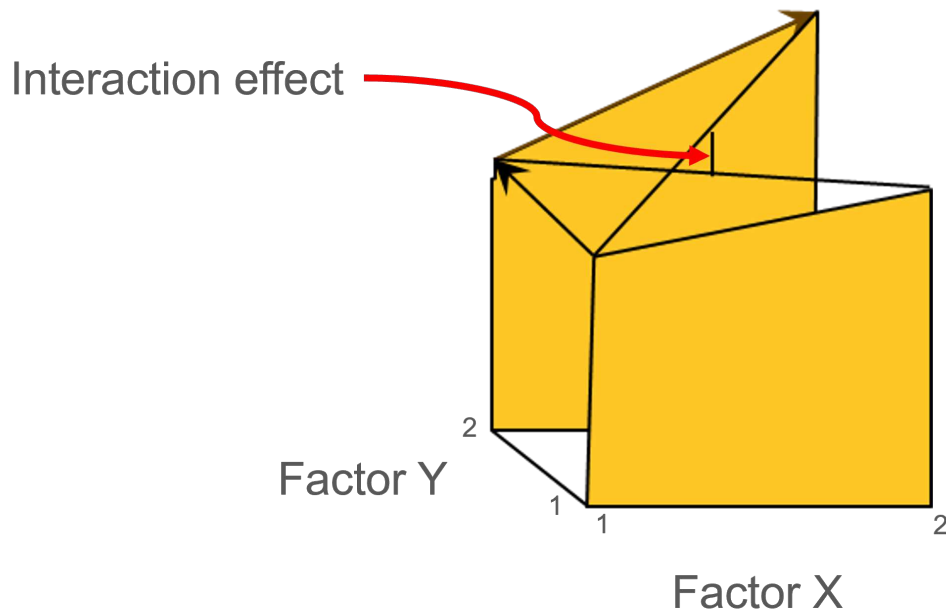


Figure 2.2: Visual representation of a 2-level 2-factor experiment and its response.

Though industry has adopted DOE, it is rarely seen in CdTe PV research literature. To most effectively use DOE, a large data set is required for an accurate statistical model, meaning there must be an ability to generate a high volume of data. Most research-scale CdTe solar cell fabrication is too slow to generate enough data. However, the ARDS at CSU is unique in its high throughput capability, making the CSU PV lab a perfect candidate to implement DOE.

2.3.2 Selecting Factors and Levels

To maximize the effectiveness of DOE, appropriate factors and levels must be chosen. Typically, the experimenter is familiar with the process under investigation and has an intuition of what factors to choose. For instance, assume the experimenter is interested in what affects an individual's alertness throughout the day. From experience and intuition, the experimenter chooses the

factors to be duration of previous night of sleep, caffeine consumption, and interest in the daily activity. These factors are more reasonable to investigate than something else like the duration of your neighbor's work commute or how many tomatoes were recently sold at your local grocery store. If nothing is known about the process or conditions, then many factors should be varied in preliminary experiments before implementing DOE. Once there is something that shows promise, DOE should be used to optimize the response. Choosing the levels of each factor is equally important. There should be a significant enough difference in the levels that there will likely be an effect, but not so extreme that the response goes to zero or infinity. In the case of alertness throughout the day, the levels of caffeine intake should not be 50 mg and 55 mg, because the effect would likely not be noticeable. Levels of 0 mg and 2000 mg should also not be used because the subject may endure cardiac arrest with 2000 mg of caffeine intake. Given the circumstances of the experiment, reasonable levels should be chosen, like 0 mg and 100 mg of caffeine.

2.3.3 Statistical Analysis

Once the experiment is designed and the data collected, the statistical analysis is conducted. The analyses in this study were conducted with the statistical software JMP. The primary statistical analysis used to create a model includes multiple linear regression (MLR) and analysis of variance (ANOVA).

MLR uses several explanatory variables to predict the outcome of a response variable. It models the linear relationship between the factors and responses. The assumptions for MLR are that there is a linear relationship between the factors and responses, the factors are not highly correlated with each other, and the residuals are normally distributed with a mean of zero and a finite variance. An output of the model is a coefficient of determination (R^2) value, which is always between 0 and 1, indicating how much of the variation in response can be explained by the factors. An R^2 value of 0 would mean that the response cannot be predicted by the factors, and $R^2=1$ means the response can be predicted without error by the factors [12]. Another outcome is the root mean squared error (RMSE), which is a quantification of the difference between the fitted line and the actual data

points. A lower RMSE is better, which means the actual data is closer to the fitted linear model, giving a more accurate prediction capability. The P-value is also given in MLR, which indicates the likelihood of the response variance occurring due to random sampling. This is part of a hypothesis test, where the null hypothesis is the scenario in which the factor has no effect on the response, and the alternative hypothesis is the scenario in which the factor does have an effect on the response. A universally accepted critical P-value is 0.05, above which we fail to reject the null hypothesis and below which the null hypothesis is rejected and the alternative hypothesis is accepted. Thus, a $P\text{-value} < 0.05$ indicates that the effect is statistically significant. There is a P-value generated for the whole MLR as well as for each individual factor, thus relative significance between factors can be determined. From the P-value, a 95% confidence interval (CI) can be defined. The CI indicates the range of predicted values that are 95% likely to occur. If there are 100 data points in the model, 5 of them would be on or outside the 95% CI. This is a useful metric for predicting responses with the fitted model. Lastly, the T-value is an output of MLR. It is a metric comparing the means of populations, which has a variable critical value depending on the degrees of freedom of the model and the desired cutoff value. If the T-value is greater than the critical T-value, the null hypothesis can be rejected and it can be said that the means of the populations are significantly different.

ANOVA is another method of analyzing the model's ability to explain the variance in the response. A result of ANOVA is the F-value, which indicates if the variance between the means of the populations is significantly different. Similar to P-value, there is a critical F-value which changes based on the degrees of freedom of the model and the desired cutoff value (again, typically 0.05). If the F-value is greater than the critical F-value and the P-value is less than the cutoff value, then the null hypothesis can be safely rejected. ANOVA is a holistic approach and only determines the joint effect of all the variables. Individual factors must be tested separately.

The combination of ANOVA and MLR gives intricate insight to the effects of each factor and their interactions, and provides prediction expressions for untested conditions. The factors are also ranked by significance, guiding future experiments towards quicker optimization. In this work, the factors examined with DOE were absorber deposition rate and temperature, p-doping of CST40

through As incorporation or , CdCl_2 treatment, Cu doping, and electrode painting. Through experience and intuition, it was determined that each of these had a potentially significant impact on the cell performance. Other exploratory experiments were conducted outside of DOE with the aim of discovering a promising structure to be optimized with DOE. The exploratory experiments investigated a sputtered electrode in comparison to the typical painted electrode, As doping location within the film, and oxides replacing Cu and/or As doping altogether.

Chapter 3

Historical Analysis

3.1 Preliminary Analysis

3.1.1 Methods

The J-V data for all cells fabricated in the lab is stored in one large database, however most experiments analyze only a couple runs simultaneously. There had never been an examination of the macroscopic trends over a long time period. At the beginning of this study, several baseline structure cells (as shown in Figure 1.8) fabricated over the span of a few years were hand selected for analysis. The analysis assumed that the number of vacuum breaks during absorber deposition, processing gas, glass type, CST composition (CST20 versus CST40), and double CdCl_2 had minimal impact on the performances and were considered to be insignificant. The significant factors were assumed to be absorber deposition time was analyzed, as the deposition temperatures were similar for all the superstrates. Contour plots were made in which performance parameters were shown on the abscissa and ordinate, and a colorbar was determined by the total absorber deposition time.

3.1.2 Results

Something in common with the high performing cells was a short deposition time, indicated by the darker blue regions. The converse was not necessarily true. Thin film theory states that slower deposition rates lead to larger grains and higher quality films. The conclusion from these contour plots opposes that theory, but has possible explanations. There could be contamination and impurities that are introduced to the film during deposition, and the benefit of slower deposition is outweighed by the contamination that is introduced over the long deposition time. Therefore, a shorter deposition time would reduce grain size but decrease impurities, yielding better performances. There is also a possibility that these randomly selected samples were not representative

of the entire population of cell data and are showing a false trend. The contour plots are shown in Figure 3.1.

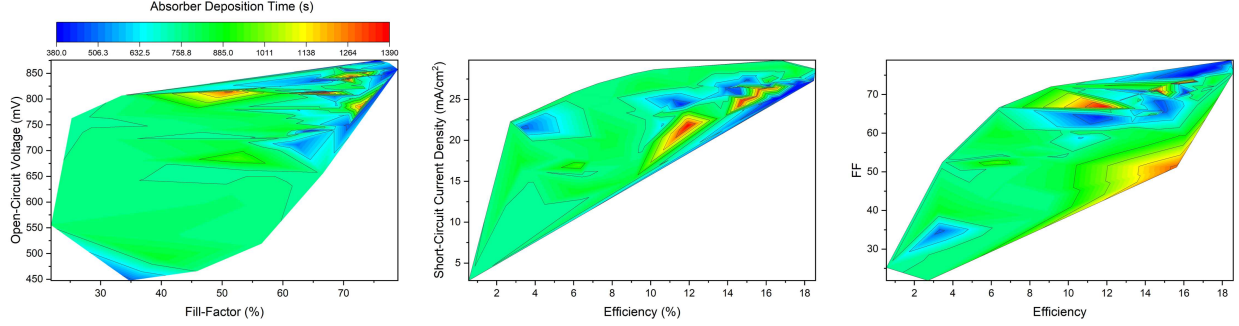


Figure 3.1: Contour plots of several baseline structure cell performances.

3.2 Expanding the Data Set

3.2.1 Methods

To eliminate the possibility that the data was poorly selected, more cell data was randomly selected and added to the analysis. Due to the high volume of data, a Python code (located in Appendix A.1) was written to fetch J-V data from the database automatically. Furthermore, the MZO deposition time and CdCl_2 treatment time were also considered in the study to account for all the primary processing steps. The outliers with respect to efficiency were omitted from the analysis to best eliminate any lurking variables, or factors that are unknown and undocumented. Density dot plots were created using Origin Pro software to show the dwell times for each process that led to the highest performing cells. Furthermore, the effects of glass type and process gas were analyzed using box plots.

3.2.2 Results

The density dot plots showed that the highest density (indicated by red color) of high performing cells corresponded to shorter dwell times in each process. The best efficiencies most often

came from ~1100 seconds of MZO deposition, 540°C preheat, 190 seconds of CST, 300 seconds of CdTe, and 900 seconds of CdCl₂. Higher V_{oc} 's corresponded with shorter CST time, longer CdTe time, and longer MZO time. This is logical because CST is a lower band gap material than CdTe, and a thicker buffer layer would increase resistivity at the front leading to higher V_{oc} 's but sacrificing J_{sc} . Conversely, higher J_{sc} 's were associated with longer CST time, shorter CdTe time, and shorter MZO time. The longer CdCl₂ times also gave higher J_{sc} 's due to better passivation. In regards to FF, the higher densities of higher FF's were associated with longer CdTe time, longer CdCl₂ time, and shorter CST time, indicating that the more p-type CdTe at the back and better passivation lead to a higher quality diode. The density dot plots are shown in Figures 3.2 - 3.5.

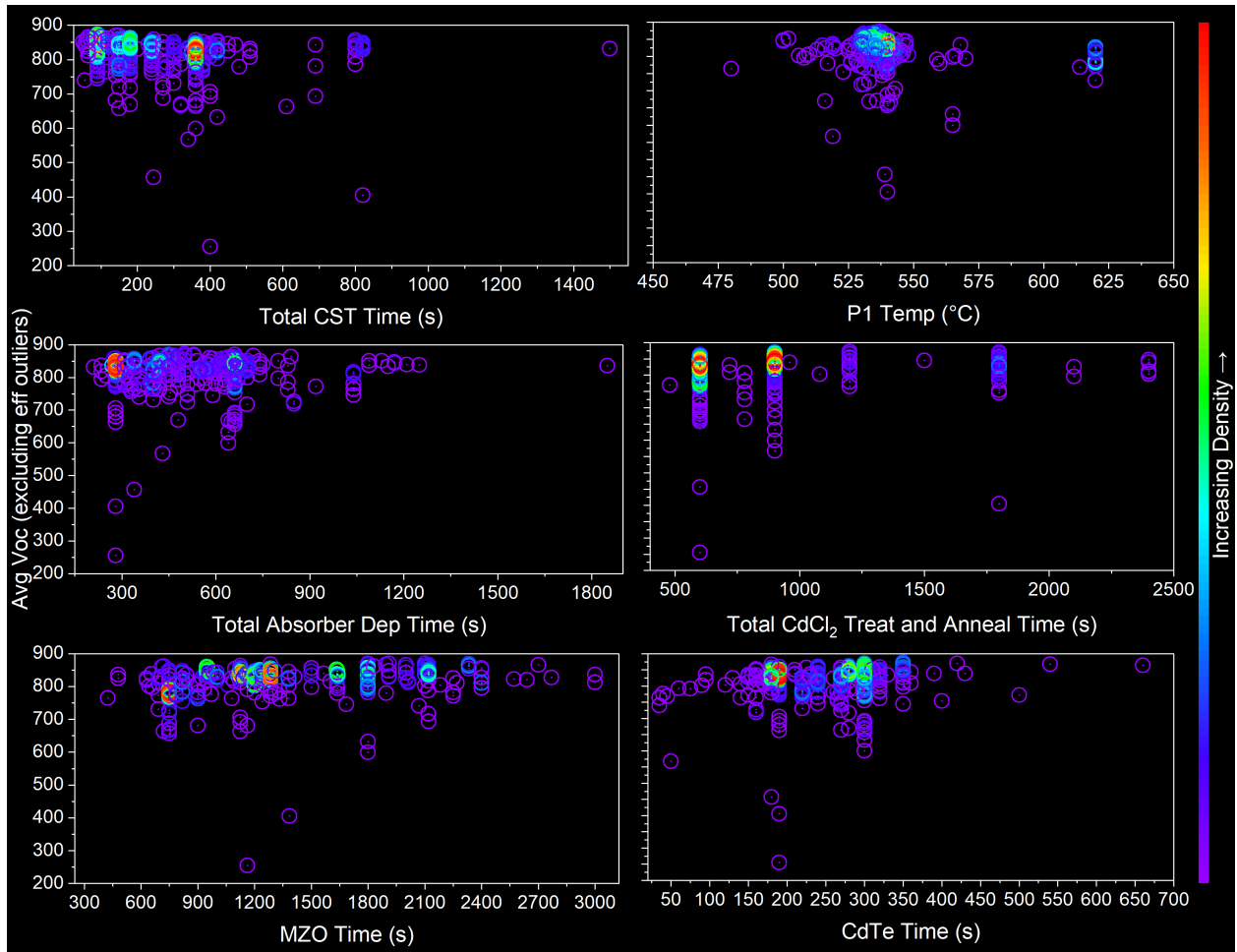


Figure 3.2: Density dot plots of many baseline structure cell V_{oc} 's.

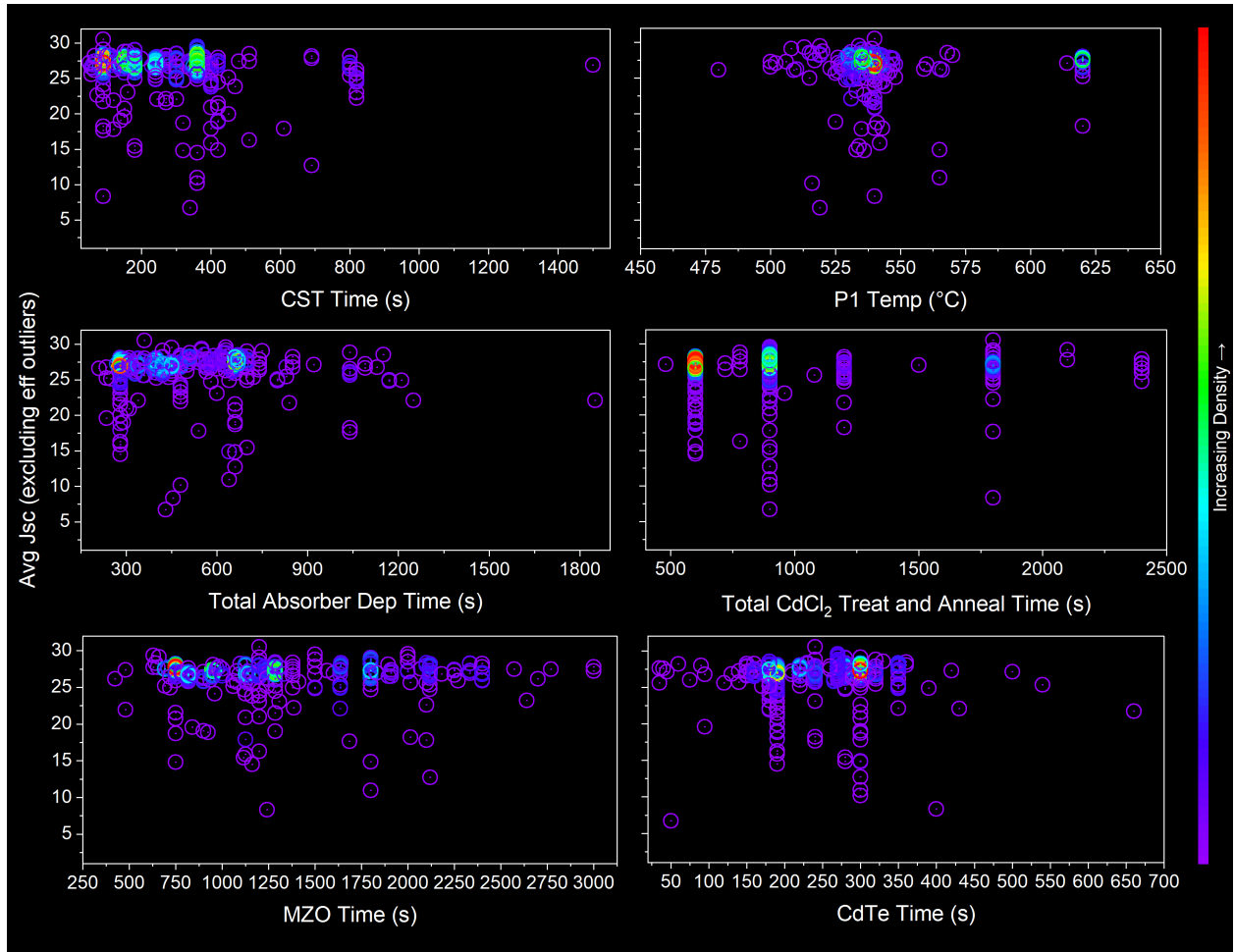


Figure 3.3: Density dot plots of many baseline structure cell J_{sc} 's.

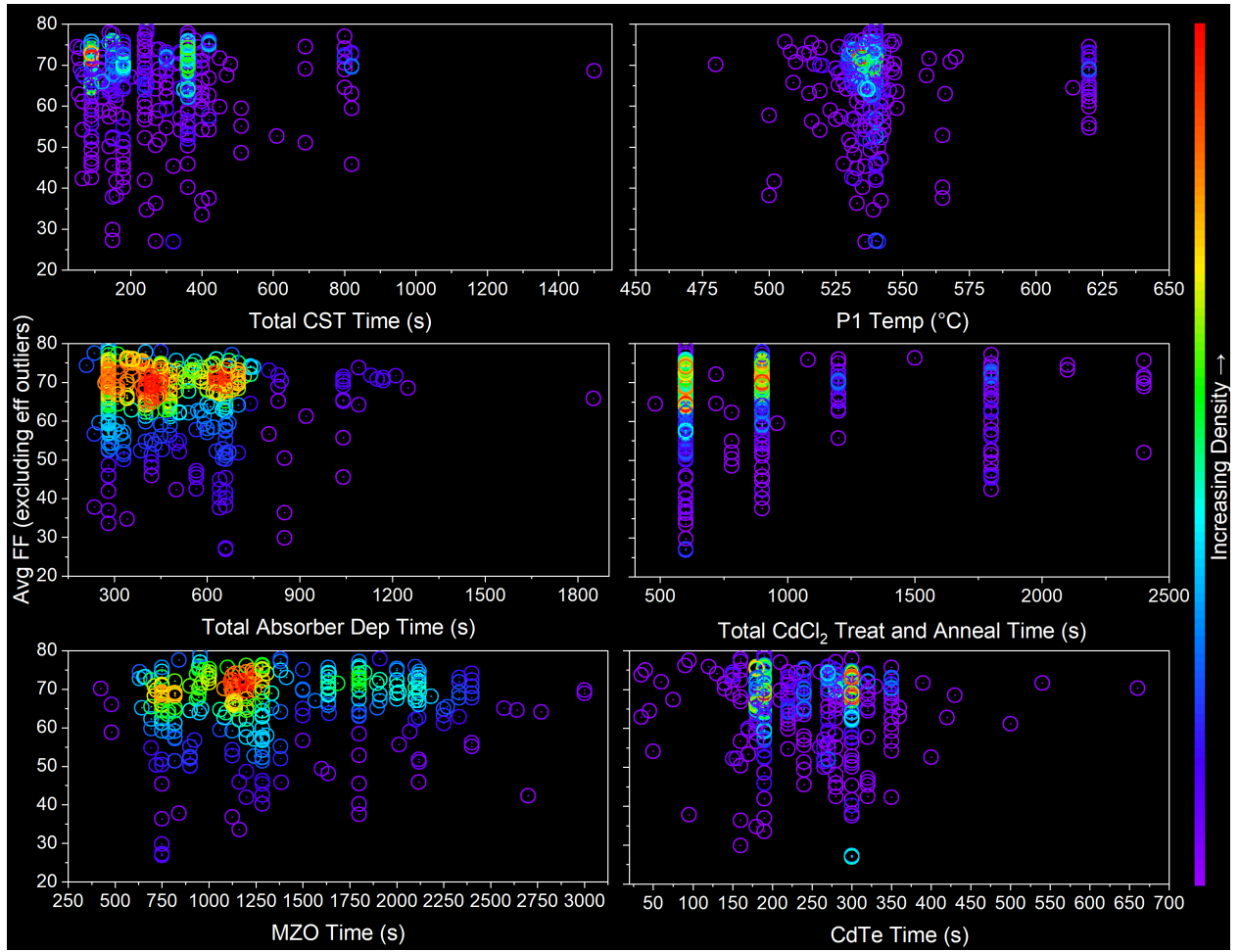


Figure 3.4: Density dot plots of many baseline structure cell FF's.

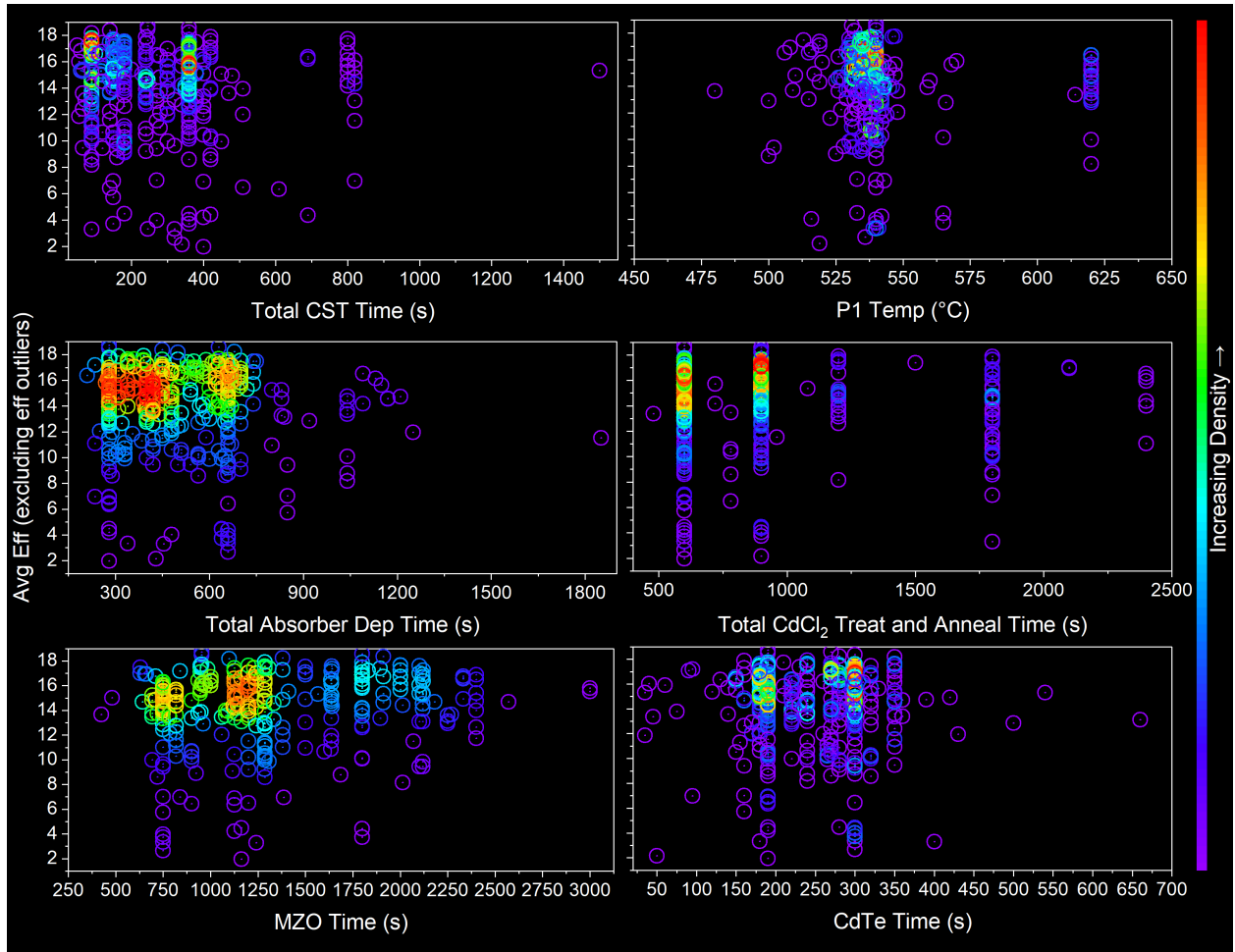


Figure 3.5: Density dot plots of many baseline structure cell efficiencies.

The assumption that glass type and process gas have no impact on performance was also challenged in this study. Figure 3.6 shows that the variance of the process gas distributions is similar, which is also true for the glass type distributions. A perfectly matching variance would be indicated by parallel black lines connecting the tops and bottoms of the boxes, and it can be seen that they are reasonably close to parallel. The mean (red line) increases slightly by processing in 2% O₂ (referred to as mixed gas), and the mean also increases when using First Solar (FSLR) glass instead of TEC10. Though these data sets include other variables and the process gas and glass type are not the sole independent variables, it could be concluded that the processing gas and glass type do have an impact on the cell efficiency.

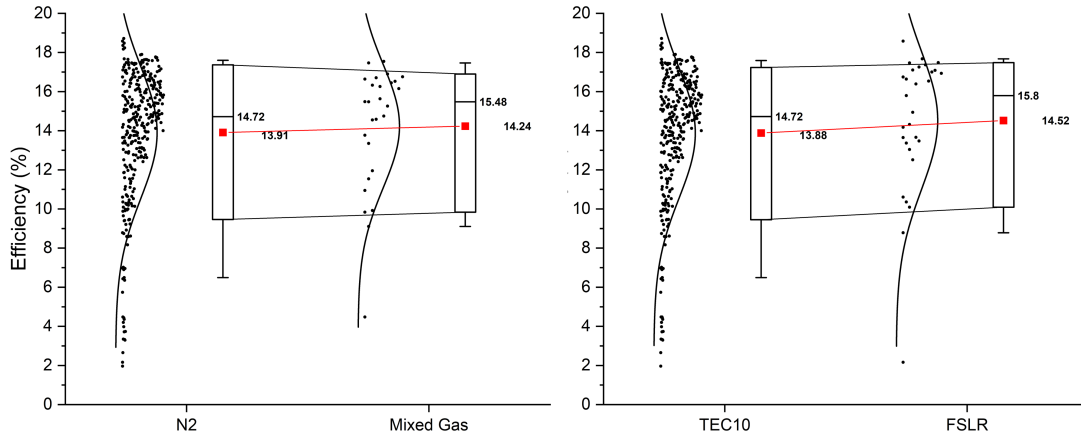


Figure 3.6: Box plots showing the effect of process gas and glass type on cell efficiency.

3.3 Refining the Statistical Model

3.3.1 Methods

There are many conclusions that can be drawn from the previous results in Figures 3.2 - 3.5, however most findings are not quantified and there is minimal direction in what processing parameters to attempt next. To maintain the wide perspective of the study, quantify the discoveries, and

develop a direction for future processing parameters to attempt, MLR and ANOVA analyses were implemented on the data set using JMP software. For all MLR and ANOVA models in this and following experiments, a linear trend was ensured for all residual normal quantile plots, satisfying the assumption of normal distribution of residuals. The mean of residuals was also confirmed to be reasonably close to zero, again satisfying an assumption of the analysis. Any outlying data points from each superstrate were excluded from the analysis to avoid skewing of data. For each model, only the most significant conclusions are discussed as there is a surplus of information and some is redundant or insignificant. Lastly, the response variables were always V_{oc} , J_{sc} , and FF, excluding efficiency due to its collinearity with the other performance metrics. The data set was refined to approximately 500 cells to homogenize the processing conditions, including only cells fabricated with no vacuum break, single $CdCl_2$, N_2 processing gas, CST40 (excluded CST20 cells) backed by CdTe, and deposited on TEC10 glass. The only differences in processing were ARDS preheat temperature, CST40 deposition time, CdTe deposition time, and $CdCl_2$ treatment time. A model was fit to the data considering those four factors and their two-way interactions. Using the prediction capability of the model, a verification superstrate was then fabricated to validate the model.

3.3.2 Results

The V_{oc} model fit had the highest R^2 value out of the responses, indicating that it is the easiest to predict compared to the other two. $R^2=0.81$ essentially means that the factors can explain 82% of the variance in the V_{oc} data points. The R^2 value of FF and J_{sc} were 0.48 and 0.19, respectively. This means that the factors (time spent in preheat, CST40, CdTe, and $CdCl_2$) are best at predicting V_{oc} , then FF, then J_{sc} . All have a P-value<0.05, thus all factors have a statistically significant effect on the performance metrics. The RMSE values are all relatively small. Since they are on different scales, it is useful to compare the rough percentage errors of the three responses. For V_{oc} , it would be around $8/844=0.09\%$, for J_{sc} $.4/28=1.4\%$, and for FF $1.8/73.5=2.4\%$. Thus, it can be said that V_{oc} has the highest confidence, corresponding to a narrow 95% CI shown in light pink shading in Figure 3.7, followed by J_{sc} and then FF.

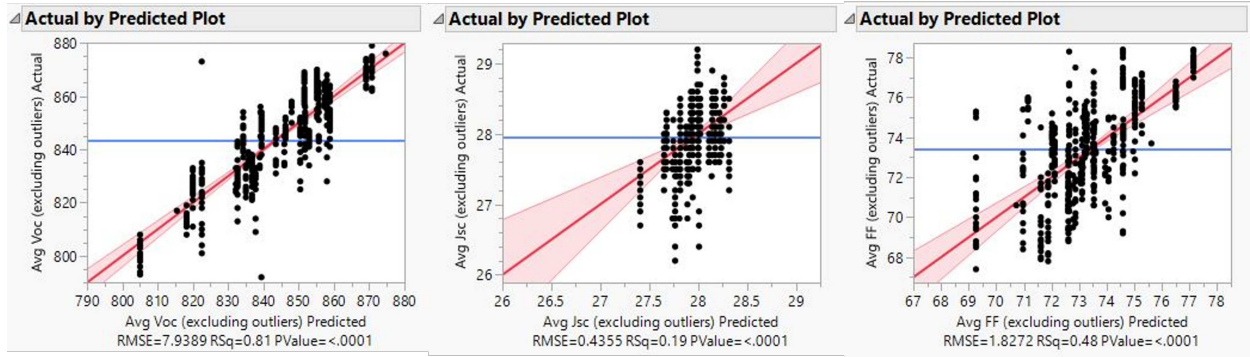


Figure 3.7: Actual (black dots) versus predicted (red line) plots for V_{oc} , J_{sc} , and FF showing the 95% confidence interval (light pink shaded area), grand mean (blue line), RMSE, R^2 , and P-value.

After observing a reasonable model fit for the data, the effect summary was studied. Figure 3.8 shows that CdTe time is the most significant factor with over 5 times greater contribution to the model than the next most significant factor, CST40 time, followed by CdCl₂ time. The interaction factor between preheat temperature and CST40 time is more significant than the preheat temperature itself. This is also true for the interaction between preheat and CdTe. A potential explanation for why these interactions are more significant than the preheat itself is because CST40 is the first deposition after preheat. If the preheat is cooler, the nucleation rate would be higher and the thickness would be slightly greater due to the greater temperature difference of superstrate and source material. This would affect grain size and film quality. After exiting the CST40 source, the superstrate moves to CdTe source. If the preheat was cooler, it is possible that the superstrate is cooler throughout the whole process, even when entering the CdTe source. Thus, the film could be affected in the same manner as described with CST40. These factor interactions would have remained unknown or at least not quantified if OFAT analysis was used instead of MLR and ANOVA. All factors were statistically significant due to all P-values<0.05.

It was informative to observe the low R^2 values present in the case of J_{sc} and FF. This means that there are other factors that are not considered in this model that have much greater influence on those performance metrics. The unexplained variance could have been because the data was collected over a long time period, therefore the deposition systems could have been in slightly different states. For instance, the source material could have been depleted to a lower level for some

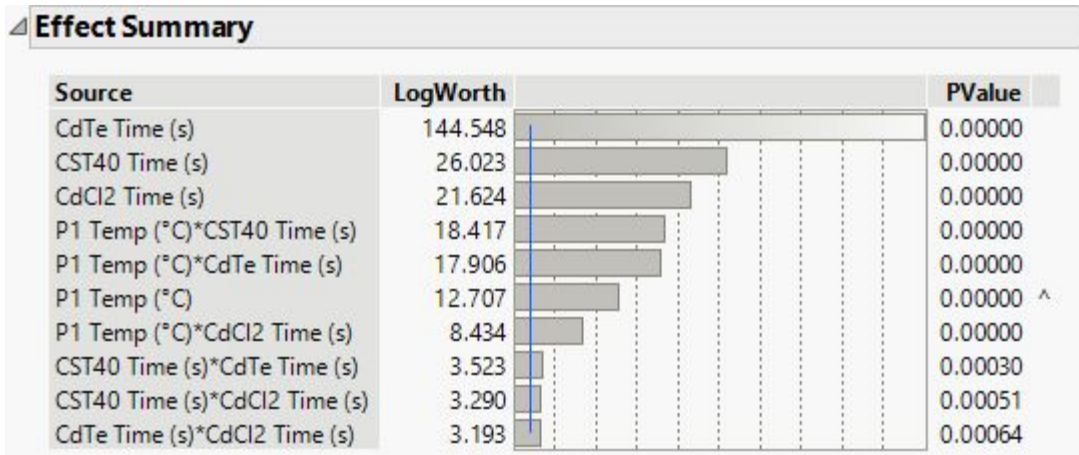


Figure 3.8: Summary of the model fit, showing each factor's contribution to the model and its P-value, ranked by significance. The blue line shows the P-value threshold, and an asterisk denotes an interaction between factors.

cells, whereas others have fresh material. The base pressure could have been different between cells, the heaters could have new thermocouples, the superstrate alignment could have been slightly different, the pumping rate could have been different, and the list goes on. These are the lurking variables mentioned earlier, as they are not controlled or known and hide in the background. To remedy this issue, all possible variables would need to be recorded and controlled or, the easier and more resource efficient option, is to analyze data from only one run or neighboring runs. The lurking variables are more likely to have remained constant over a shorter time frame and thus the model fit would be better. The other explanation for the poor R^2 values in this experiment would be that the data processing recording was poor. If the experimenter processed a superstrate in a particular manner but recorded it in the run log incorrectly, that data would lead the model in a bad direction. Lastly, other processing parameters that were thought to be consistent may have had significant variability, such as the Cu treatment, back contact layer, or painted electrode. That was partially the motivation for the next experiments that will be discussed.

Using the model from this analysis, the prediction profiler function in JMP was used to find the optimal conditions. Since there is a quantified effect of all factors and their two-way interactions, there is an equation for all performance metrics V_{oc} , J_{sc} , and FF. The goal is to maximize all three simultaneously, thus the prediction profiler uses the three equations to find the optimal conditions.

The recommendation from the model was to preheat to 530°C, deposit 150 seconds of CST40 then 420 seconds of CdTe, and then CdCl₂ treat the absorber for 600 seconds. This was an abnormally long CdTe deposition and a shorter CdCl₂ treatment, and the resultant film was 6 µm thick, 1.5X the usual highest performing thickness. The 95% CI for the prediction was range of efficiency of 18.74-22.88%, and the actual efficiency measurement of the best cell was 18.63%. Though the actual efficiency was slightly lower than the lower bound of the CI, it was a reasonable agreement given that the model assumes a linear relationship and it does not consider material limitations. To improve this, a larger data set would be beneficial in predicting efficiencies within the model bounds, and potentially a nonlinear model would be more accurate although it would be more complicated to analyze. This type of cell structure would not have been attempted if it wasn't for the model recommendation, therefore it was a successful experiment.

As concluded from this study, all future statistical analyses were performed on data collected within one experiment to best eliminate lurking variables. Though statistical models predict more accurately with a larger data set to analyze, there is a limit for the systems at CSU. To obtain a large data set without having significant effect from lurking variables, the optimal model would be created with data collected between tool maintenances approximately every two weeks, which would amount to around 10 experiments. That is the ideal situation, however there are other practical considerations. Due to the fact that many scientists in the lab run the systems every week and could potentially change the condition of the tool between experiments, all future statistical analyses are performed on data collected within one experiment. This should give the most accurate models while keeping the influence of lurking variables at a minimum.

Chapter 4

Investigation of the Copper Doping Process

4.1 Copper Doping DOE

4.1.1 Methods

Due to the poor R^2 value for J_{sc} and FF in the historical analysis, the Cu doping process was investigated next. Over the previous 4 years, the baseline Cu doping processing conditions have not been changed or explored significantly. Observations from earlier superstrates showed that small changes in the Cu doping process can have significant effects. Furthermore, the temperatures of doping have been chosen specifically as to not resublime any of the film off and to provide enough thermal energy to sublime the copper chloride ($CuCl$) from the source material and diffuse into the film. Thus, the dwell times for each process were investigated and the temperatures remained constant. There are three steps to the Cu doping process — preheat at $330^{\circ}C$, $CuCl$ treatment at $190^{\circ}C$ bottom heater and $175^{\circ}C$ top heater, and anneal at $200^{\circ}C$. To perform a proper DOE, a full factorial experiment was designed. Each of the three factors was given two levels, so there were $2^3=8$ superstrates in the experiment. The levels chosen were the typical baseline dwell times because it is known that good cells have come from that process. The second levels were half the dwell times for each step. The experimental conditions are shown in Table 4.1, in randomized order as is standard for DOE. Following the DOE, two superstrates were fabricated to validate the model predictions in the region of highest confidence and extrapolating the model outside its bounds to a higher performance.

Table 4.1: Copper Doping Variations

Sample	Preheat (s)	CuCl (s)	Anneal (s)	Pattern
1	60	280	280	– + –
2	60	280	560	– + +
3*	120	280	560	+ + +
4	120	140	280	+ – –
5	60	140	560	– – +
6	60	140	280	– – –
7	120	280	280	+ + –
8	120	140	560	+ – +

*Typical CuCl treatment.

4.1.2 Results

The JV data for all eight superstrates is shown in Figure 4.1, organized by Cu treatment pattern. Two 19.19% cells came from different treatments, the – – + and + + – patterns. However, the mean of – – + was higher and the variance was lower than + + –, thus the best superstrate was – – +. The worst superstrate was – + – with a highest cell efficiency of 13.3%.

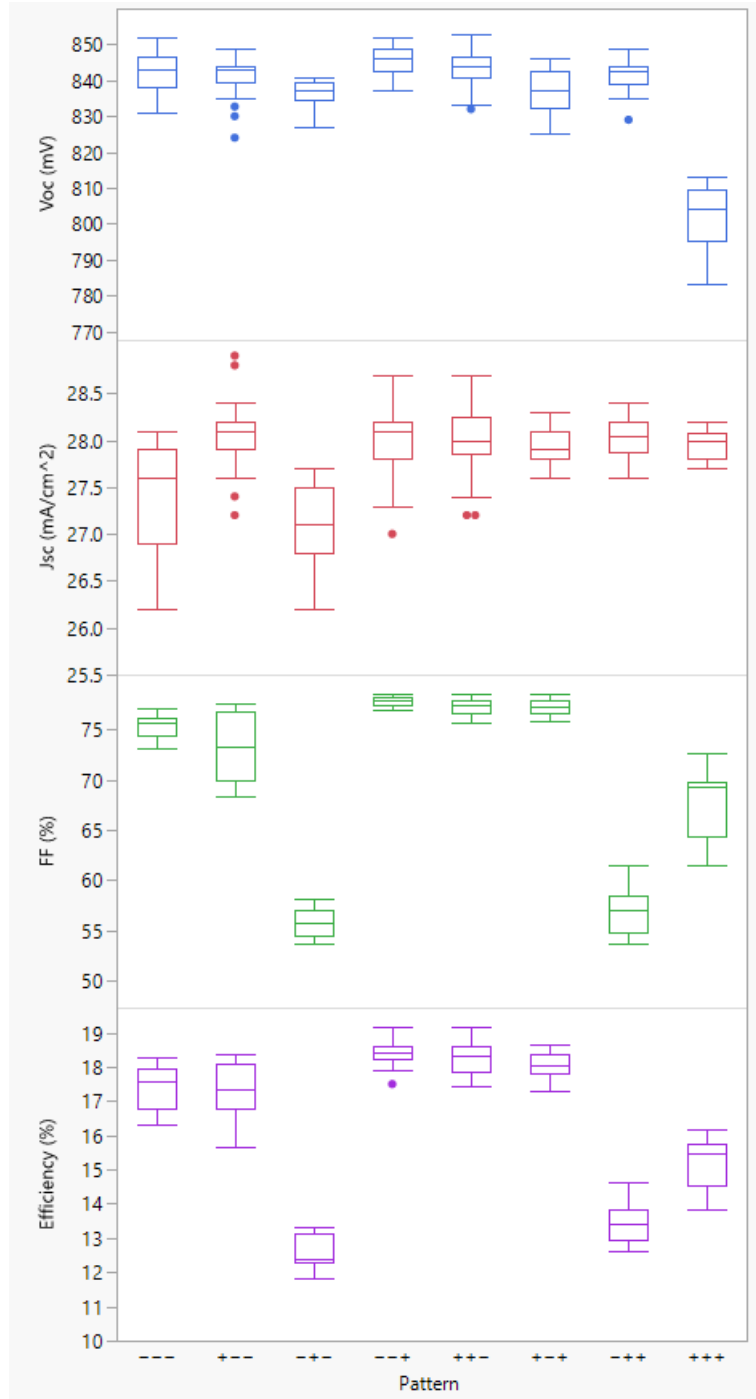


Figure 4.1: Performance box plots for all eight superstrates showing median, 25th and 75th percentiles, and outliers (dots).

In the JMP analysis, 31 out of 200 data points were omitted due to being outside the normal residual distribution. The remaining 169 data points comprise the analysis. The effect summary

(Figure 4.2) shows that all factors and their two-way interactions are statistically significant, as their P-values are all less than 0.05. The implications of these results is that all factors and their interactions are non-negligible and cannot be excluded from the model. The CuCl dwell time has the greatest overall impact on all the performance metrics, while anneal time has the least impact. The interaction between preheat and CuCl is the second most influential factor, which would not have been seen without DOE.

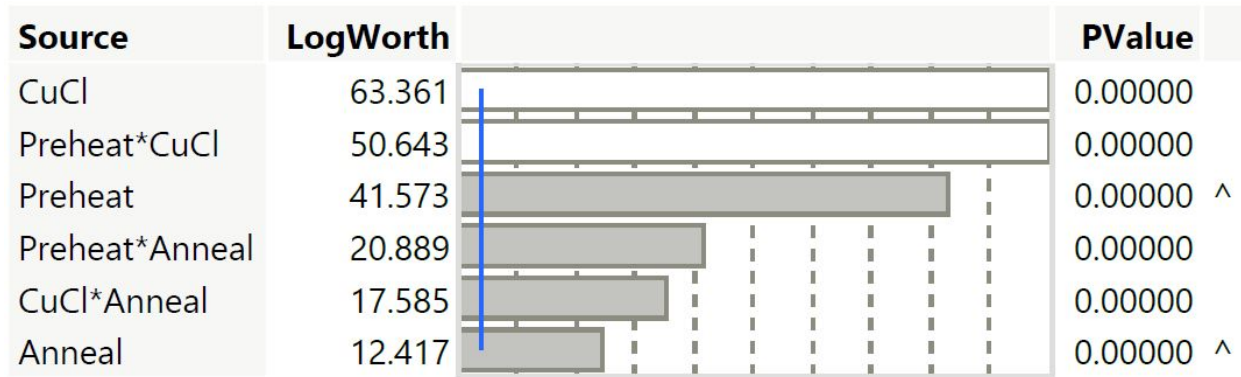


Figure 4.2: Effect summary for the copper doping experiment showing relative significance of each process dwell time.

The R^2 value for the V_{oc} fit was 0.69. This is a good R^2 value and indicates the model can be trusted. For J_{sc} , the R^2 value is 0.43, which shows that more than half of the causes of the variance are not considered in this experiment. For FF, the R^2 value is 0.92, which is an excellent fit and can be used for accurate predictions of FF within the tested range. All RMSE's are relatively small, summarized in Figure 4.3.

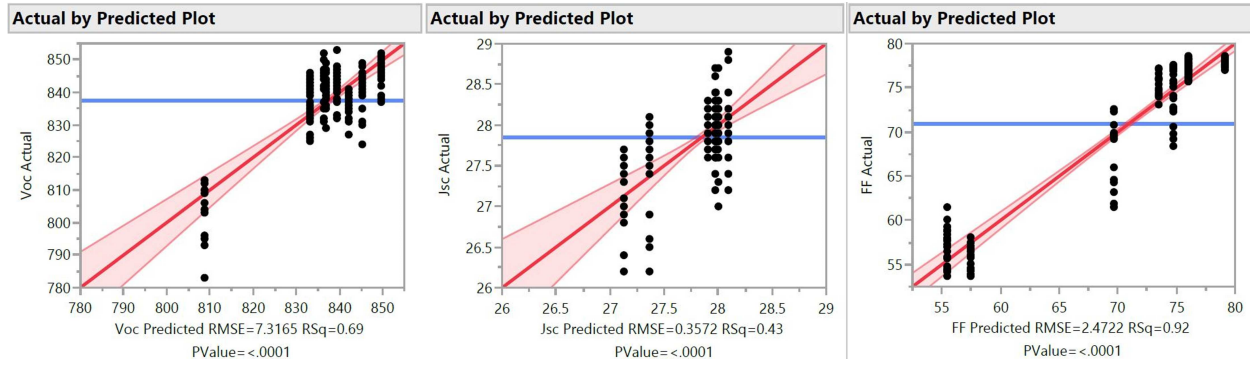


Figure 4.3: Actual versus predicted plots for the copper doping experiment.

The highest performing superstrate was fabricated using a Cu treatment of 60 seconds preheat, 140 seconds CuCl, and 560 seconds anneal. Another nearly equivalent superstrate underwent 120 seconds preheat, 280 seconds CuCl, and 280 seconds anneal. These similar performances could imply that the Cu is doping the film similarly. One explanation for this is with shorter preheat, the film enters the CuCl source at a lower temperature, thus creating a larger difference in temperature between the material source and the film, resulting in faster deposition of CuCl. Therefore, it only requires 140 seconds of CuCl to deposit Cu on and in the film. The longer anneal time drives the Cu deeper into the film into the most beneficial doping profile, and best performance is achieved. Similarly, the longer preheat means the film enters the CuCl source at a higher temperature, leading to smaller temperature difference and less deposition. Thus, it requires a longer time in the CuCl source to deposit enough on and in the film. While in the CuCl source for a longer time, it is simultaneously annealing the Cu into the film. Thus, it requires less anneal time to drive the Cu into the film to the most beneficial doping profile. This is one explanation of how two different processing conditions can yield similar performance. The dependencies of the processing steps on each other are captured in the effect summary where the preheat and CuCl interaction factor is the second most influential, as well as the other statistically significant interactions.

Using JMP's built-in prediction profiler, it is possible to predict performance metrics given certain Cu processing conditions. The predicted performance metrics at the center of the 95% CI for the highest performing cell were 850 mV V_{oc} , 79.1% FF, and 28.00 mA/cm² J_{sc} , yielding an

efficiency of 18.82%. This superstrate, an identical duplicate of the best superstrate, was fabricated 46 days later. In addition, the model was extrapolated out and a superstrate with Cu treatment of 30 seconds preheat, 70 seconds CuCl, and 560 seconds anneal was fabricated. The actual and predicted performance metrics of both are shown in Table 4.2.

Table 4.2: Copper Doping Model Validation

Sample	V_{oc}(mV)	J_{sc}(mA/cm²)	FF(%)	Efficiency(%)
Predicted performance within bounds	850	28.00	79.1	18.82
Actual performance within bounds	854	27.6	77.1	18.17
Predicted performance extrapolated	861	28.09	96.8	23.41
Actual performance extrapolated	846	25.35	73.5	15.79

The V_{oc} of the duplicate was higher than the model predicted, however the J_{sc} and FF were lower which lead to a slightly lower efficiency than predicted. However, 18.17% and 18.82% are reasonably similar to each other. The lower values of the 95% confidence interval from the model prediction yield an 18.45% efficient cell, thus the experimental cell is part of the 5% outside the confidence interval. The extrapolated superstrate was simply to test to what extreme the model was accurate, and it proved to be worse in every performance metric. It is clear a linear model may not be sufficient for the behaviors that are seen in the cells, and that more conditions should be tested to obtain a more reliable model. Extrapolations should not be trusted outside the experimental area until the model is trained with more data.

4.2 Painted Electrode DOE

4.2.1 Methods

The painted back electrode was investigated due to the highly variable and undefined nature of the process. It was known that a poorly painted electrode significantly reduces the performance of the cell, so the electrode must be painted properly. However, there was no defined proper painting procedure, thus the motivation for the study. The electrode contains a layer of C paint followed by a layer of Ni paint. The factors investigated were the thicknesses of both layers as well as the spray

distance in a 2-level 3-factor DOE. The thicknesses were visually determined by approximating pinhole density and light transmission through the paint, as the purpose of the painted electrode is to be quick and using no measurement devices. The low thickness included many pinholes and higher light transmission, and the higher thickness was defined as very few if any pinholes, and no light transmission through the paint. This corresponds to about 2 coats for thin and about 4 coats for thick. The spray gun pressure was 70 PSI, and the spray pattern was a vertical line of a height slightly greater than that of the superstrate. A short spray distance was defined as about 3 inches and the long spray distance was defined as about 8 inches. The distances were not precisely controlled as it is a human-oriented process and each operator will hold the gun at slightly different distances. There are more controlled methods of producing an electrode such as sputtering metal, but that takes a much longer time and is impractical for experiments with more than 4 superstrates. The experimental details are summarized in Table 4.3

Table 4.3: Painted Electrode Variations

Sample	C Thickness	Ni Thickness	Spray Distance	Pattern
1	Low	High	Low	– + –
2	Low	High	High	– + +
3	High	High	High	+ + +
4	High	Low	Low	+ – –
5	Low	Low	High	– – +
6	Low	Low	Low	– – –
7	High	High	Low	+ + –
8	High	Low	High	+ – +

4.2.2 Results

The spray distance was the most influential factor, followed by C thickness and then the interaction between spray distance and C thickness. The interaction between spray distance and Ni thickness was not statistically significant and was omitted from the model. The effect summary is shown in Figure 4.4.

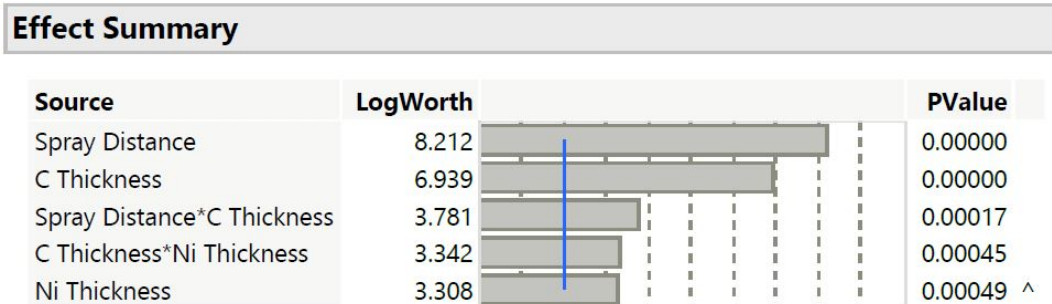


Figure 4.4: Effect summary for the painted electrode experiment.

There were many important trends observed from this experiment. According to the least squares means plots, thick Ni paint led to ~20-30 mV higher V_{oc} and ~1 mA/cm² higher J_{sc} . A low spray distance led to ~2-7% higher FF, and its interaction with C thickness shows that a low spray distance allows for more leniency of C thickness when concerned with FF. Thick C led to ~2-7% higher FF and ~3mA/cm² higher J_{sc} . The plots associated with these results are shown in Figure 4.5.

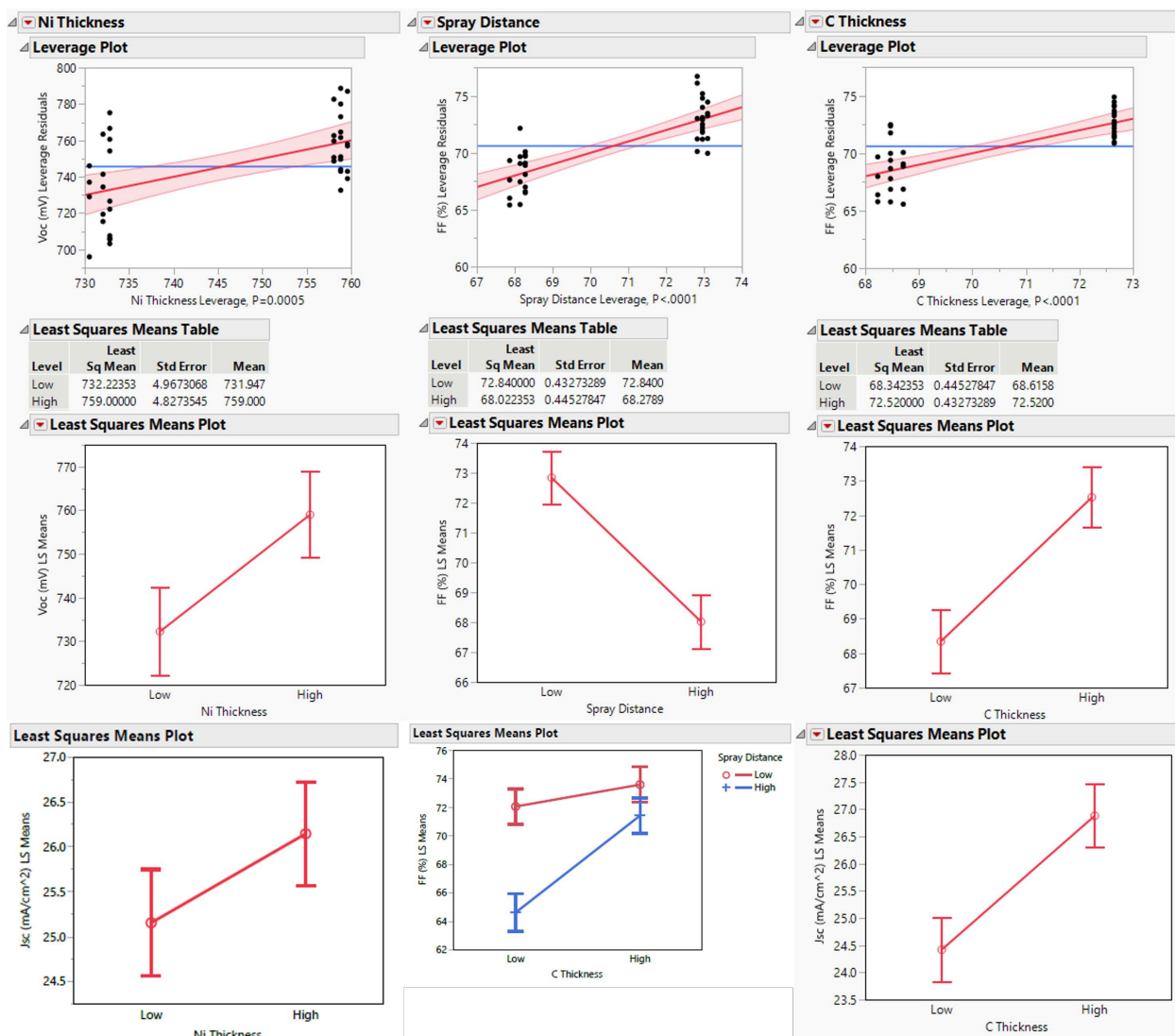


Figure 4.5: Most significant model fit plots and least squares means plots from the painted electrode experiment.

As a result of the model, the prediction profiler recommended to paint thicker C and Ni at a lower spray distance. Two superstrates were fabricated to validate the prediction, both sprayed at low distance and one with 4 coats of each paint and one with 8 coats of each paint. These results are shown in Table 4.4.

The actual performance was considerably lower in all aspects than the predicted performance, similar to the validation superstrate from the Cu experiment. This again illustrates how the models cannot be carelessly extrapolated beyond their confident bounds. If this were done in an industry

Table 4.4: Painted Electrode Model Validation Superstrates

Sample	V_{oc}(mV)	J_{sc}(mA/cm²)	FF(%)	Efficiency(%)
Baseline Electrode	854	27.6	77.1	18.17
2X Thickness Electrode	847	27.3	70.1	16.20

scenario, there could have been significant time, money, and effort invested in the creation of the extrapolated superstrate, and the expected results were not at all reached. This emphasizes the importance of choosing appropriate levels to test for each factor.

4.3 Sputtered Electrode

4.3.1 Methods

The painted electrode is a quick and functional process for research purposes, however in commercial PV modules, a sputtered electrode is used instead. From previous experiments, it has been seen that paint degrades quicker than a sputtered electrode, and may be limiting the ultimate performance of the cell. The sputtering process is more controlled than the painting process, which is a benefit. The only disadvantages of a sputtered electrode is that it is easy to damage during measurement compared to the painted electrode, and the process requires more time. Three superstrates were fabricated with a typical painted C-Ni electrode, a sputtered chromium (Cr) electrode, and a sputtered aluminum-chromium (Al-Cr) bilayer electrode. Each sputtered layer was around 500 nm thick. The J-V data was recorded when the cells were first fabricated, and then again after two weeks of storage in air.

4.3.2 Results

The painted C-Ni electrode was the highest performing, followed by sputtered Cr and then sputtered Al-Cr. Though there were better performing cells from the Al-Cr compared to Cr, the variance was much higher in Al-Cr and the median for Cr was higher, thus Cr is a better choice than Al-Cr. The box plots are shown in Figure 4.6.

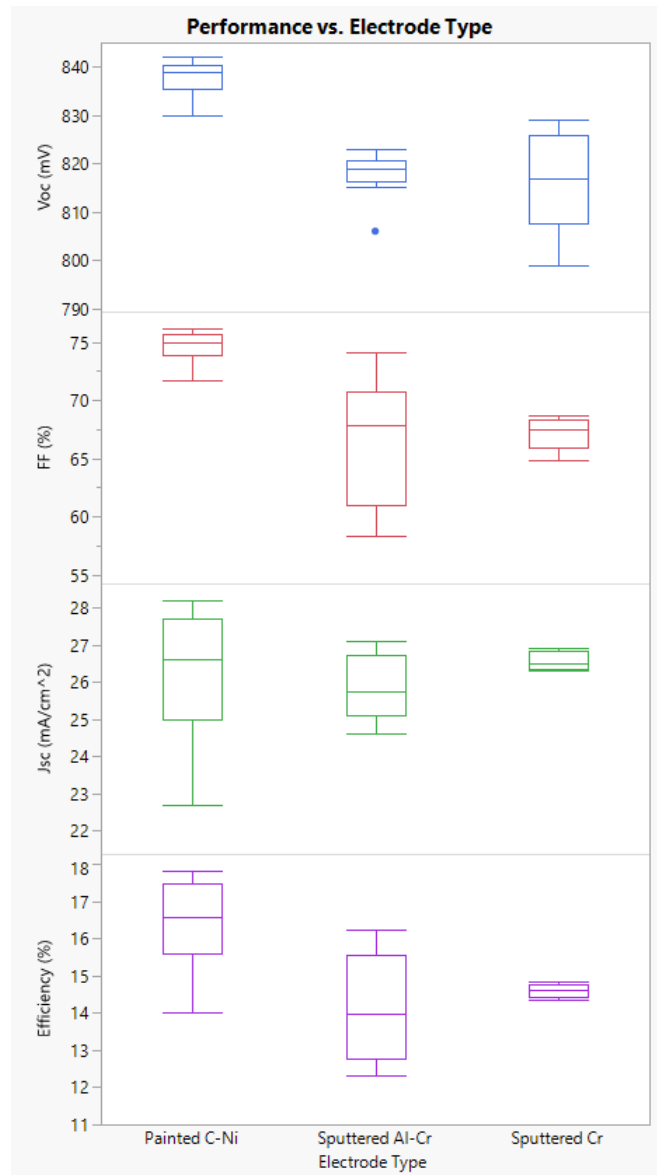


Figure 4.6: Box plots for the electrode experiment.

A t-test was performed on the painted and Cr distributions, and the results show that the means of the distributions are significantly different from each other. The mean efficiency for painted and Cr electrodes were 16.4% and 14.6%, respectively. Therefore, the painted electrode was best for this cell structure. The t-test is shown in Figure 4.7.

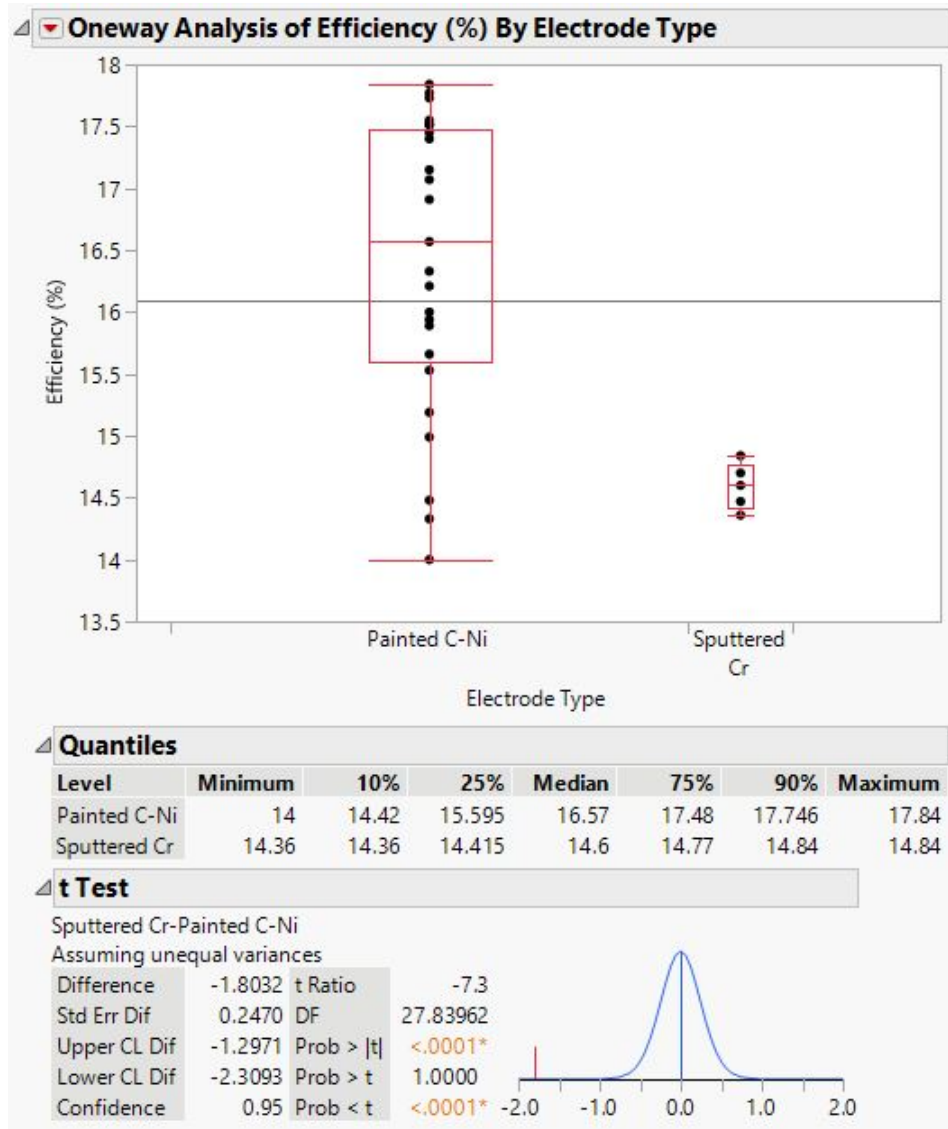


Figure 4.7: T-test for the electrode experiment. Box size is representative of sample size that comprises each distribution.

The J-V measurements were recorded again two weeks later for the painted C-Ni and sputtered Cr electrodes. The same 3 cells from each superstrate were analyzed for longevity. Over the span

of 14 days in air storage, the painted electrode lost ~0.5% efficiency on average and the sputtered Cr increased ~0.1% on average. This could be due to the paint being slightly porous and allowing humidity to reach the film, and the sputtered Cr kept the film isolated from humidity. The sputtered Cr electrode could have oxidized as well changing the band alignment and electric field effect on the diode, potentially explaining the increase in J_{sc} and efficiency over time. The box plots are shown in Figure 4.8.

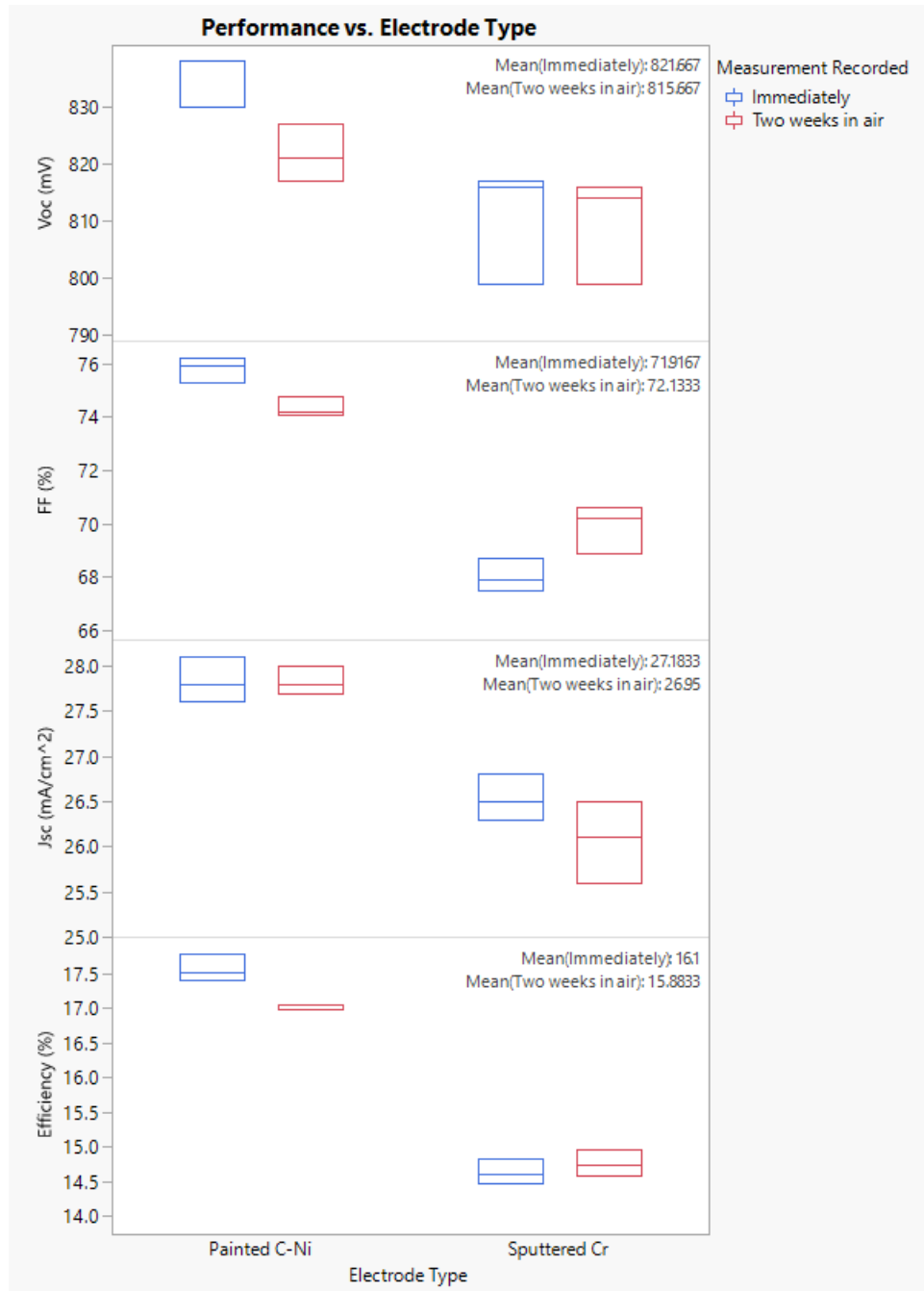


Figure 4.8: Longevity test for the electrode experiment. Remeasured indicates measurement after 14 days in air storage.

Based on cell performance, the painted electrode should continue to be used for research purposes. Based on the longevity and control over the sputtering process, the painted electrode should be replaced. Different metals and thicknesses should be further explored in future experiments to

achieve similar performances as the painted electrode while maintaining the longevity advantage of a sputtered electrode. The longevity is an issue for research cells that require performance certification as the process of packing, shipping, and measuring the cell at the certification facility takes several days. With a sputtered electrode, the certified performance of the cell would likely be higher than that with a painted electrode by the time it is measured. Potentially a thicker sputtered electrode would remedy the fragility issue, or using a less destructive probe during J-V measurements. In the future, the sputtering tool should be upgraded by including a high vacuum valve over the diffusion pump and a load lock to reduce process time. This way, the sputtering process would be comparable in process time to painting while improving the longevity and potentially the performance after some more optimization with DOE.

4.4 Absorber Temperature DOE

4.4.1 Methods

There has been literature published showing the significance of superstrate temperature throughout processing conditions [13] [14] [15]. Voids within the film reduce the performance and can be prevented by maintaining proper superstrate temperature throughout the process. The typical absorber deposition temperatures are 575°C bottom and 420°C top for CST40 and 555°C bottom and 500°C top for CdTe. These temperatures have given the highest performing cells, but potentially there are voids that could be eliminated within the film. Thus, all the heaters temperatures were increased 50°C to explore this area. This experiment was compounded with Cu doping as well, creating a 2-level 2-factor DOE, to explore if there are any interactions between absorber temperature and Cu treatment. The Cu doping parameters were the — — + pattern from the previous Cu DOE, denoted as "best." The second level was the model extrapolation Cu conditions, 30 seconds preheat, 70 seconds CuCl, and 560 seconds anneal, denoted as "extreme." The experimental details are shown in Table 4.5.

Table 4.5: Absorber Temperature and Copper Doping Variations

Sample	Absorber Temperature	Cu Treatment	Pattern
1	High	Best	++
2	High	Extreme	+-
3	Low	Best	--+
4	Low	Extreme	---

4.4.2 Results

The effect summary shows that the Cu treatment is much more influential than the absorber deposition temperature, however both are statistically significant. The interaction between the two was not statistically significant and was eliminated from the model. The summary is shown in Figure 4.9.



Figure 4.9: Effect summary for the temperature and Cu doping experiment.

For J_{sc} and V_{oc} , deposition temperature has a statistically significant effect, albeit nearly negligible. The deposition temperature does not have an impact on the FF. The extreme Cu treatment reduced V_{oc} by ~6 mV, FF by ~4.5%, and J_{sc} by ~3 mA/cm². Again, this suggests to use caution when extrapolating the model. An interesting visual to see that there are no interactions between the two factors is seen in Figure 4.10. Whether the deposition temperature is high or low, the Cu

treatment boosts the V_{oc} ~6 mV, indicating no interaction. The response surface is an especially effective tool for large data sets as many conditions can be compared simultaneously.

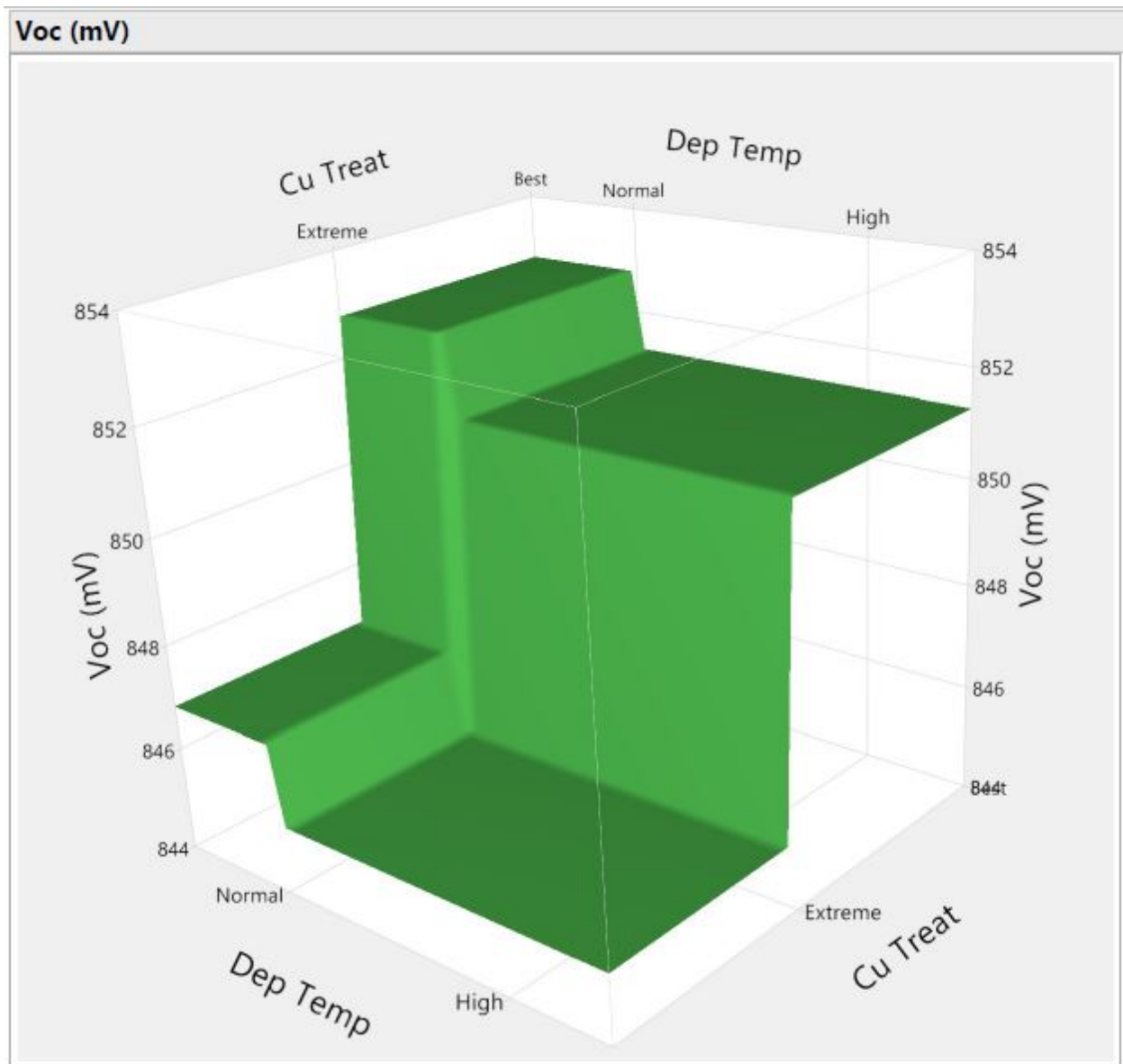


Figure 4.10: V_{oc} response surface for the temperature and Cu doping experiment.

The carrier concentration versus depletion width measurements in conjunction with the box plots for the four superstrates are shown in Figure 4.11. The higher performing cells exhibit a narrower depletion width shifted towards the front of the absorber, which was a universal observation

from the cells in this study. The effects on depletion width were caused by the Cu treatment rather than the absorber deposition temperature.

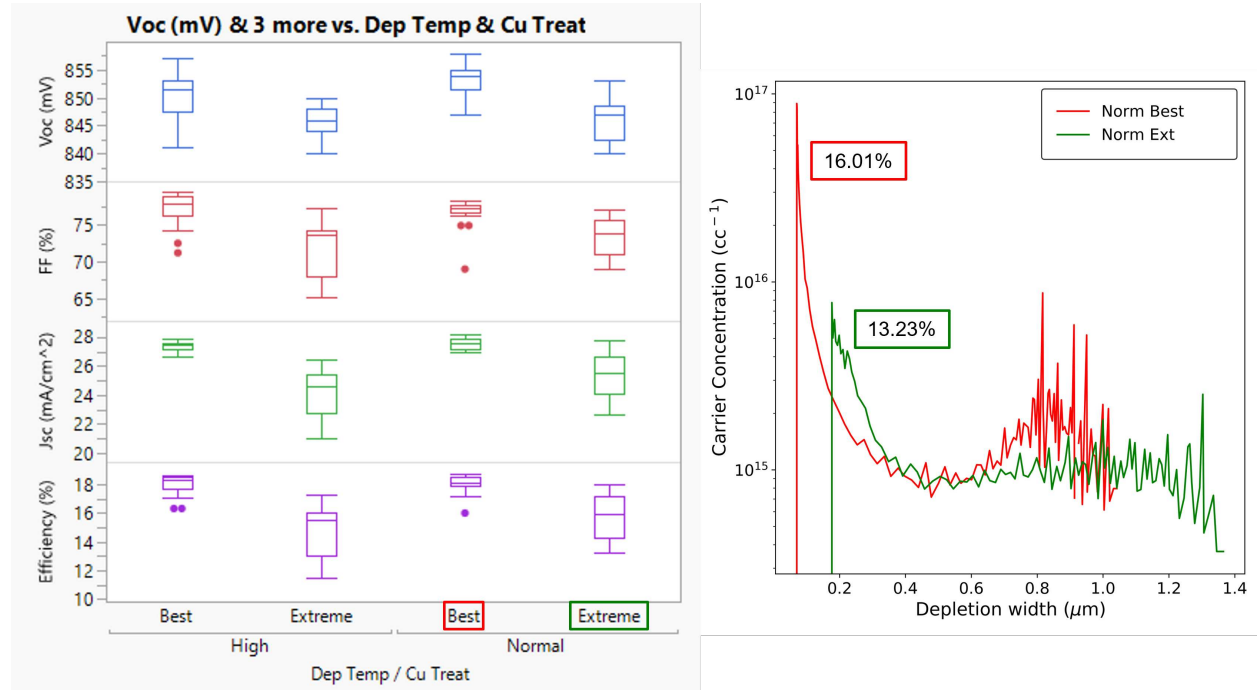


Figure 4.11: Carrier concentration versus depletion width measurements and box plots for the temperature and Cu doping experiment. Red and green boxes correspond in the two plots.

Furthermore, increasing the deposition temperature also increased the deposition rate ~600%. This in conjunction with the best Cu process reduced the overall fabrication time by 33% while maintaining comparable efficiencies. In an industry setting, this would be an incredible discovery as it would lead to higher throughput and reduced cost.

4.5 Tellurium Overpressure DOE

4.5.1 Methods

Recent measurements of CSU solar cells from the National Renewable Energy Laboratory indicate that the first 300 nm of the CST40 layer in the baseline structure is n-type. This may potentially be beneficial, but the intent is that the absorber is p-type. If the front of the CST40

is made more p-type, the p-n junction may become stronger and create a higher quality diode, boosting efficiencies. Since Se has the highest vapor pressure of the elements in CST40, it may not stick in the film as desired, creating Se vacancies and effectively making the material more n-type. In an attempt to fill the Se vacancies, Te was co-sublimated at a higher temperature during CST40 deposition, increasing its vapor pressure, thus referred to as Te overpressure (OP). In two DOE's, preheat temperature, Te OP, CST40 thickness, and CdTe thickness were investigated. All of these structures had 100 nm 11% MZO followed by 4 μm thick absorber with the specified CST40 thickness and the remaining thickness was CdTe. All have the + + + copper treatment as this experiment was conducted prior to finding the – – + optimum. All have 30 nm Te back contact and standard standard The experimental details for the first and second DOE are shown below in Table 4.6 and Table 4.7 respectively. A Te OP of 100°C is considered to have negligible effect.

Table 4.6: Te OP Experiment 1

Sample	Te OP (°C)	CST40 Thickness (μm)
1	100	0.5
2	100	1.5
3	312	0.5
4	350	1.5
5	312	1.5
6	350	0.5

Table 4.7: Te OP Experiment 2

Sample	Te OP (°C)	Preheat (°C)	CST40 Thickness (μm)	Pattern
1	372	550	0.6	+ + -
2	372	530	3.0	+ - +
3	350	530	0.6	- - -
4	350	550	0.6	- + -
5	350	530	3.0	- - +
6	372	530	0.6	+ - -
7	372	550	3.0	+ + +
8	350	550	3.0	- + +

4.5.2 Results

Though neither experiment produced any cells above 12% efficiency, there were some interesting observations and trends. The first Te OP DOE box plots shown in Figure 4.12 show that increasing Te OP increases V_{oc} , and increasing CST thickness increases V_{oc} as well. It appears that the differences in efficiency are primarily due to the differences in V_{oc} , but the details are investigated later in the statistical analysis.

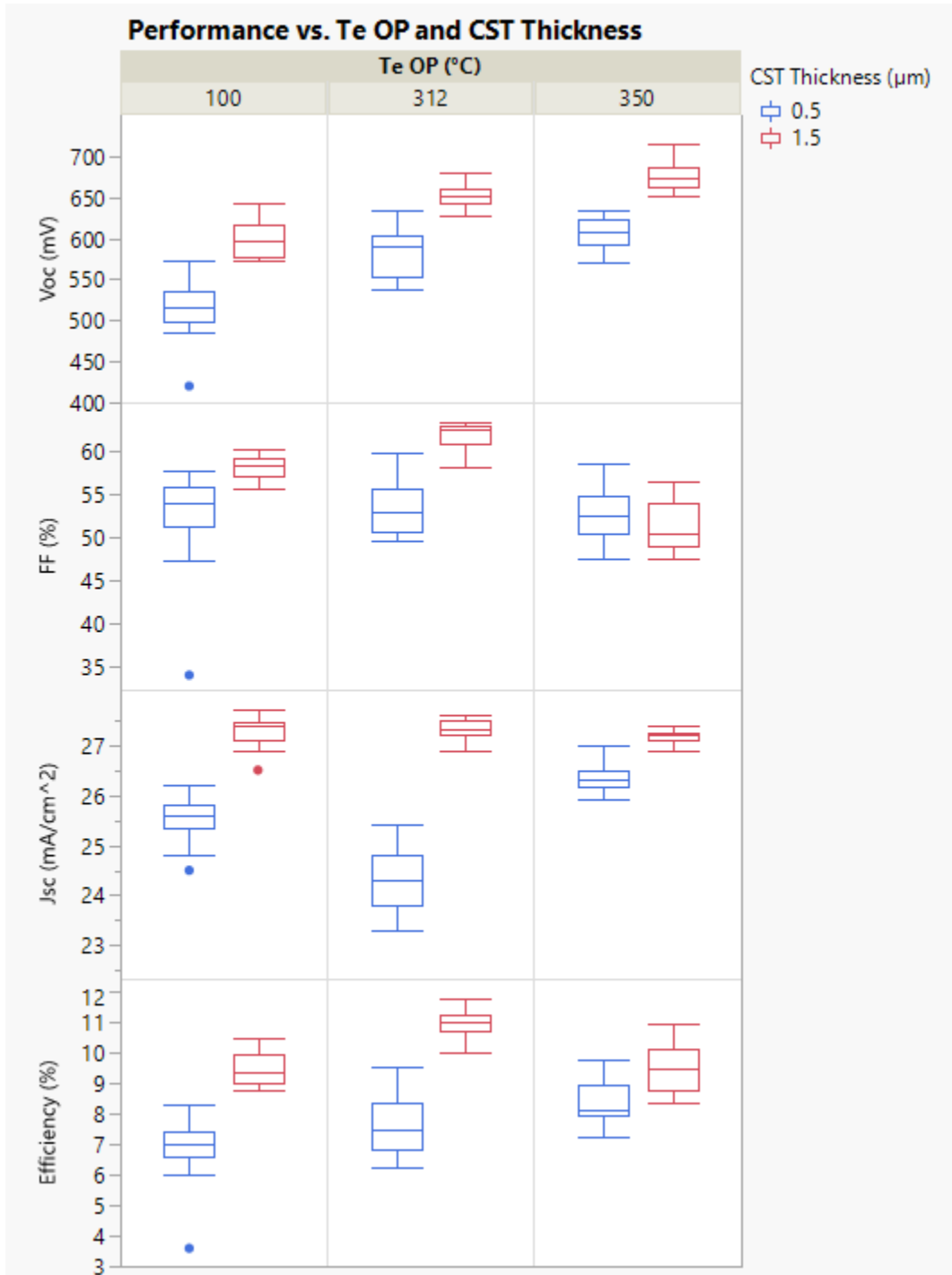


Figure 4.12: Box plots from the first Te OP experiment.

It is difficult to make conclusions upon first glance of the second Te OP DOE box plots shown in Figure 4.13. The best cells came from all high levels of preheat, Te OP, and CST40 thickness,

however the worst cells came from high preheat and lower Te OP. The details are further investigate in the statistical analysis.

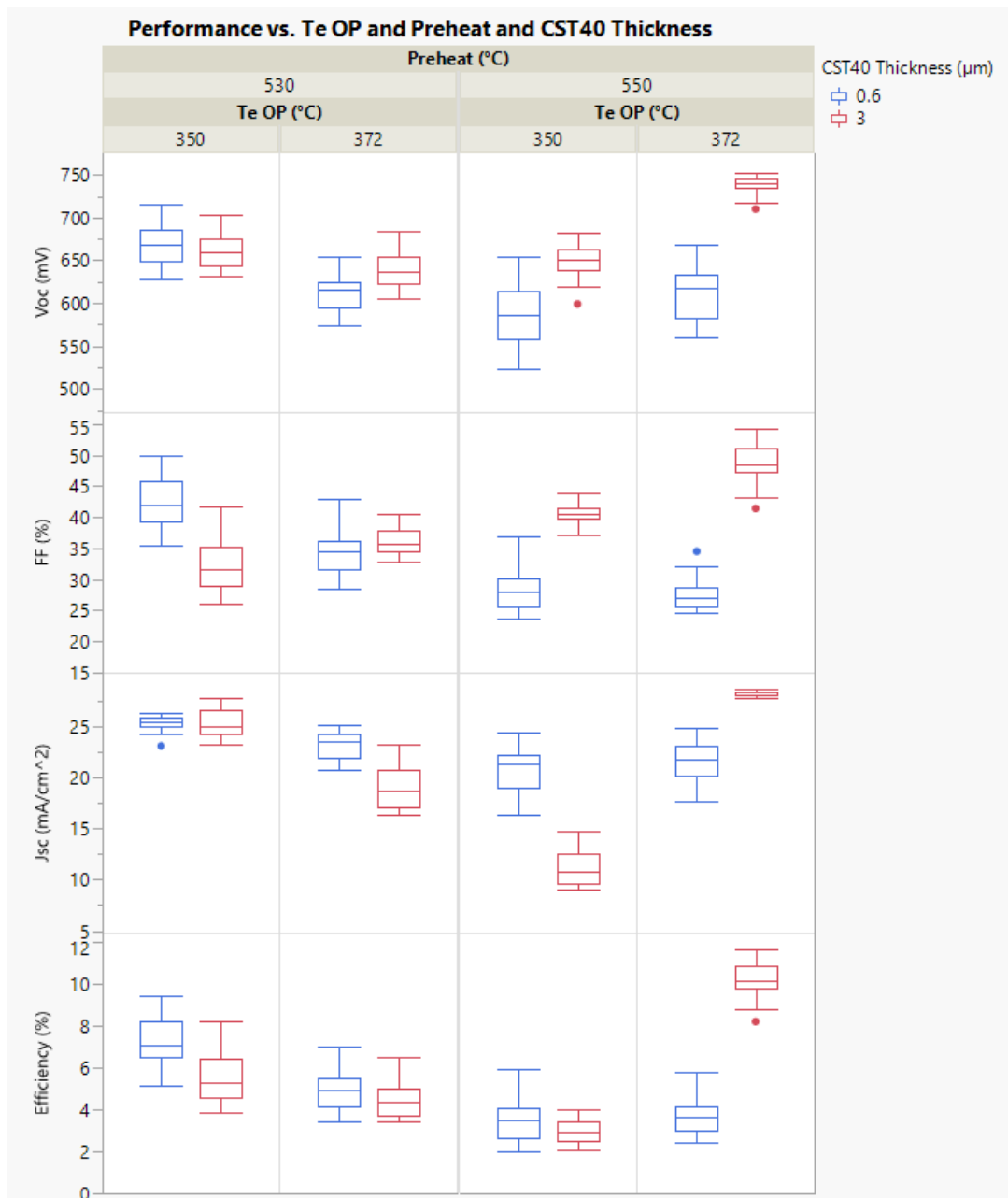


Figure 4.13: Box plots from the second Te OP experiment.

The first Te OP DOE statistical analysis showed that the interaction factor between Te OP and CST40 thickness was insignificant, and was therefore excluded from the MLR and ANOVA

analyses. The resulting model fit showed that the most influential factor is CST40 thickness and then Te OP, however they were nearly equal. The model summary is shown in Figure 4.14.

Source	LogWorth	PValue
CST Thickness (μm)	42.365	0.00000
Te OP ($^{\circ}\text{C}$)	41.085	0.00000

Figure 4.14: Effect summary from the first Te OP experiment.

The CST40 thickness was statistically significant in predicting all three performance metrics, but the Te OP was only statistically significant in predicting the V_{oc} . The model fit for V_{oc} , FF, and J_{sc} are shown in Figure 4.15, Figure 4.16, and Figure 4.17, respectively.

Summary of Fit

RSquare	0.837121
RSquare Adj	0.834905
Root Mean Square Error	22.80757
Mean of Response	605.32
Observations (or Sum Wgts)	150

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	393005.40	196503	377.7552
Error	147	76467.24	520	Prob > F
C. Total	149	469472.64		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	449.52189	5.985989	75.10	<.0001*
Te OP (°C)	0.3244545	0.01693	19.16	<.0001*
CST Thickness (µm)	73.386667	3.724461	19.70	<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Te OP (°C)	1	1	191045.29	367.2639	<.0001*
CST Thickness (µm)	1	1	201960.11	388.2464	<.0001*

Figure 4.15: Summary of model parameters and V_{oc} fit from the first Te OP experiment.

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	52.301574	1.100526	47.52	<.0001*
Te OP (°C)	-0.005938	0.003113	-1.91	0.0584
CST Thickness (μm)	4.16	0.684743	6.08	<.0001*

Figure 4.16: FF fit from the first Te OP experiment.

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	24.489375	0.182777	133.99	<.0001*
Te OP (°C)	-0.00005	0.000517	-0.10	0.9230
CST Thickness (μm)	1.8493333	0.113723	16.26	<.0001*

Figure 4.17: J_{sc} fit from the first Te OP experiment.

A possible explanation for these results is that the Te OP is behaving as expected and occupying the Se voids, however this makes the ternary alloy more like CdTe in the sense that it is increasing the band gap of the material, leading to higher V_{oc} . Assuming that the Se content remains the same as in CST40 with no Te OP, this would maintain the J_{sc} . Further characterization would be required to confirm or deny this theory. The important conclusion from this experiment is that higher Te OP led to higher efficiencies, thus justifying the higher Te OP temperatures in the second DOE.

The best cells in the second Te OP DOE were fabricated using the + + + conditions, shown in Figure 4.13. The MLR and ANOVA analysis showed that all factors and their interactions were significant in the model fit summary, shown in Figure 4.18. The preheat and CST40 thickness interaction factor was the most significant, followed by the preheat and Te OP interaction factor. This was an interesting observation, as typically one of the primary effects is the most significant. This may highlight the importance of grain size and nucleation rate as the superstrate enters the CST40 source.

The V_{oc} fit parameters show that preheat has no statistically significant effect on V_{oc} , which is logical as there is no change in the cell structure during preheat. This is shown in Figure 4.19.

Source	LogWorth	PValue
Preheat (°C)*CST40 Thickness (μm)	54.696	0.00000
Te OP (°C)*Preheat (°C)	35.190	0.00000
CST40 Thickness (μm)	34.653	0.00000 ^
Te OP (°C)*CST40 Thickness (μm)	21.725	0.00000
Preheat (°C)	9.263	0.00000 ^
Te OP (°C)	7.291	0.00000 ^

Figure 4.18: Effect summary from the second Te OP experiment.

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	443.92957	104.9747	4.23	<.0001*
Te OP (°C)	0.4077135	0.151001	2.70	0.0076*
Preheat (°C)	0.0304369	0.166118	0.18	0.8548
CST40 Thickness (μm)	21.346359	1.384316	15.42	<.0001*
(Te OP (°C)-361)*(Preheat (°C)-539.899)	0.2199747	0.015102	14.57	<.0001*
(Te OP (°C)-361)*(CST40 Thickness (μm)-1.81212)	0.9153624	0.125847	7.27	<.0001*
(Preheat (°C)-539.899)*(CST40 Thickness (μm)-1.81212)	1.8407292	0.138439	13.30	<.0001*

Figure 4.19: V_{oc} fit from the second Te OP experiment.

Preheat also has no direct effect on FF according to the analysis, and Te OP follows the same conclusion. However, Te OP does have an effect on FF in the interaction factors, although it is of less magnitude than those associated with CST40 thickness. These model fit parameters for FF are shown in Figure 4.20.

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	12.318382	14.65652	0.84	0.4017
Te OP (°C)	0.0394399	0.021083	1.87	0.0629
Preheat (°C)	0.0095287	0.023193	0.41	0.6817
CST40 Thickness (μm)	2.5580938	0.193278	13.24	<.0001*
(Te OP (°C)-361)*(Preheat (°C)-539.899)	0.0131584	0.002108	6.24	<.0001*
(Te OP (°C)-361)*(CST40 Thickness (μm)-1.81212)	0.195271	0.017571	11.11	<.0001*
(Preheat (°C)-539.899)*(CST40 Thickness (μm)-1.81212)	0.4336059	0.019329	22.43	<.0001*

Figure 4.20: FF fit from the second Te OP experiment.

Five of the six factors had statistically significant influence on J_{sc} , the sixth being the interaction factor between preheat and CST40 thickness. This could potentially highlight how grain size and

nucleation rate does not have much influence on J_{sc} , but further characterization would be required to verify that hypothesis. The factor with greatest magnitude of effect was CST40 thickness as shown in the parameter estimates in Figure 4.21.

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	59.093149	13.58673	4.35	<.0001*
Te OP (°C)	0.1108815	0.019544	5.67	<.0001*
Preheat (°C)	-0.140629	0.0215	-6.54	<.0001*
CST40 Thickness (μm)	-0.753926	0.17917	-4.21	<.0001*
(Te OP (°C)-361)*(Preheat (°C)-539.899)	0.0304907	0.001955	15.60	<.0001*
(Te OP (°C)-361)*(CST40 Thickness (μm)-1.81212)	0.1094713	0.016288	6.72	<.0001*
(Preheat (°C)-539.899)*(CST40 Thickness (μm)-1.81212)	0.0165243	0.017918	0.92	0.3576

Figure 4.21: J_{sc} fit from the second Te OP experiment.

These two experiments indicated that higher Te OP, higher CST40 thickness, and higher preheat yield higher performing cells. Future experiments should focus on replicating similar results at the higher efficiencies that are comparable with the baseline Cu-doped structure.

4.6 High Efficiency Baseline Cells

Using the guidance of the previously discussed experiments, a high-performing cell of 19.44% was fabricated. This is the second highest in lab history, and one of the highest in published literature. Its performance metrics and representative J-V curve are shown in Figure 4.22. The absorber deposition times, Cu treatment, and electrode were all directly influenced by the results in the previous experiments. This cell was 500 nm CST40, 3.5 μm CdTe, and 900 seconds CdCl₂ on 100 nm 8% MZO sputtered at 180 W, and processed in mixed gas as described in the Solar Cell Fabrication section. The Cu treatment was 60 seconds preheat, 280 seconds CuCl, and 560 seconds anneal. The typical 30 nm Te back contact was deposited, and then thick C and Ni paint sprayed at a close distance.

This structure was imaged via SEM and EDS, shown in Figure 4.23. The images show a strong signal of Cd and Te within the absorber, as expected from literature. The characteristic Se gradient

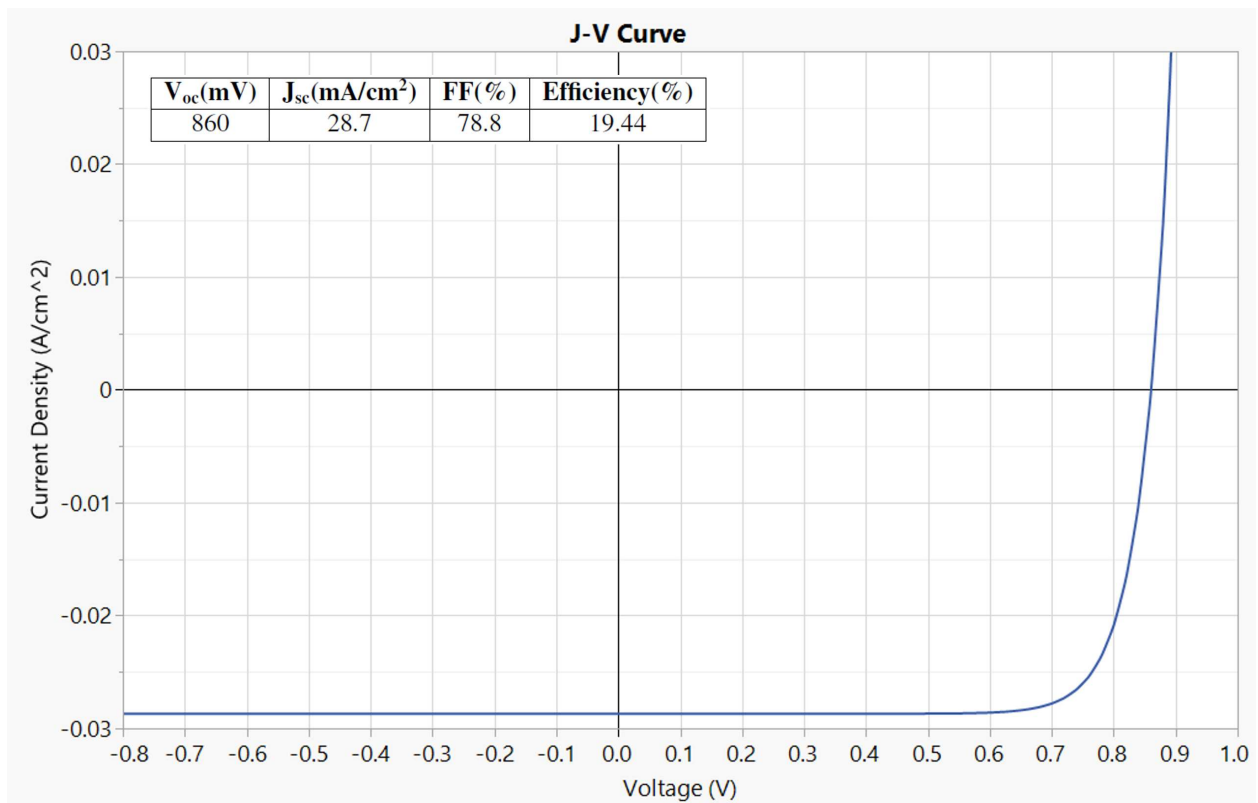


Figure 4.22: Performance metrics and representative J-V curve for high performing copper-doped solar cell.

is also seen through the first $\sim 1.5\ \mu\text{m}$ as expected. Zn and O are confined to the MZO layer as expected. Sn and O are shown in the FTO layer and Si and O are shown in the glass, which are all expected and reinforce the characteristics reported in literature of other high performing cells.

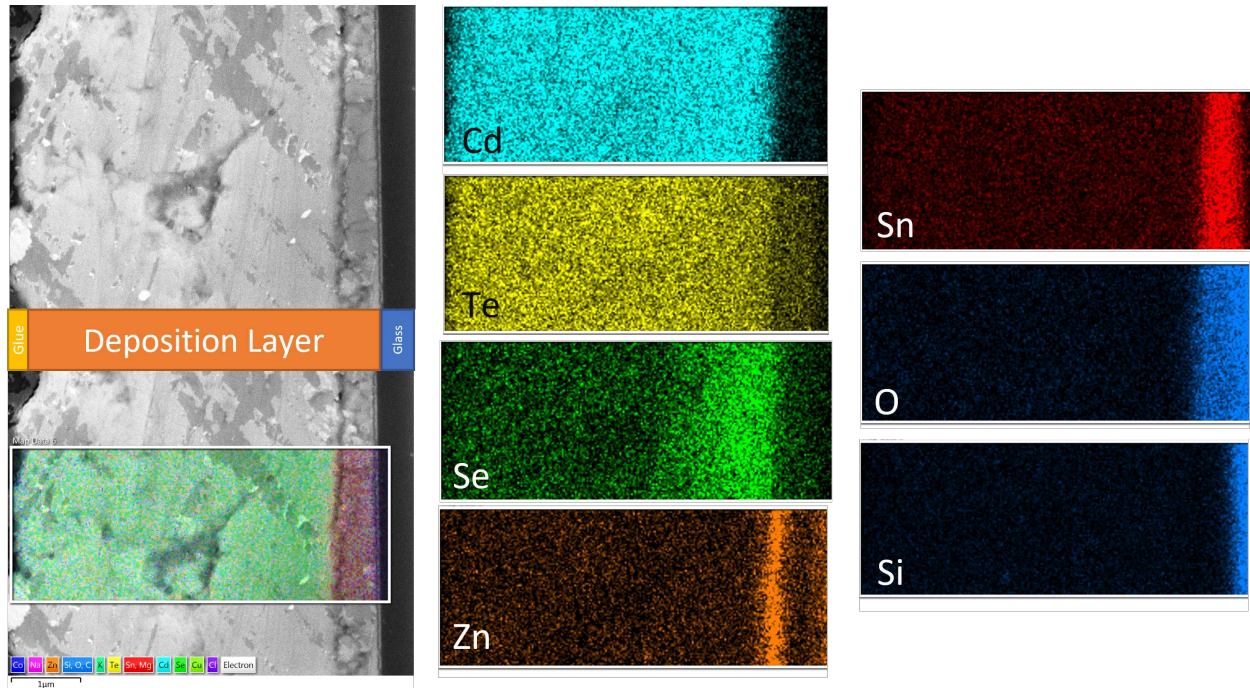


Figure 4.23: SEM image of the high-performing baseline structure without overlay (top left) and with elemental mapping overlay (bottom left). EDS elemental distributions are shown in the colored plots (right).

Chapter 5

Investigation of the Arsenic Doping Process

5.1 Location of As in the Absorber

5.1.1 Methods

It is known that the primary cause of degradation in Cu-doped PV modules is the Cu diffusing towards the front of the absorber. One solution that has been implemented on a large industrial scale by First Solar is replacing Cu with As. The As atoms are larger and have lower diffusivity while still increasing the carrier concentration as Cu does. Ultimately, this gives modules a longer lifetime in the field. To achieve this, Washington State University has made an As-doped CST40 material (CST40:As) with varying As concentrations. Over the past 4 years, cells with the CST40:As material have typically reached maximum efficiencies of ~10% in the CSU lab, however they show promise for improvement [16]. In recent preliminary experiments with the material, the efficiencies have been significantly increased. Initially, 1 nm of CST40:As was added to the Cu-doped CST20 baseline structure (same as previously described, only CST20 material instead of CST40. The tool had issues with the CST40 source at the time, hence using CST20.) in different locations within the CST20 layer to ensure the material wasn't entirely defective. The Cu was not removed from the process due to its consistency over the years, and it was the logical next small step to simply add As and leave everything else unchanged. This experiment included 4 superstrates, the CST20 baseline, the CST20 baseline with CST40:As between CST20 and CdTe, the CST20 baseline with CST40:As sandwiched in the middle of the CST20 layer, and the CST20 baseline with CST40:As at the front.

5.1.2 Results

CST40:As at the front of the absorber achieved the highest efficiencies; most importantly it was better than the baseline structure. A t-test was performed to confirm that the mean efficiency was statistically greater than the other structures. The box plots are shown in Figure 5.1.

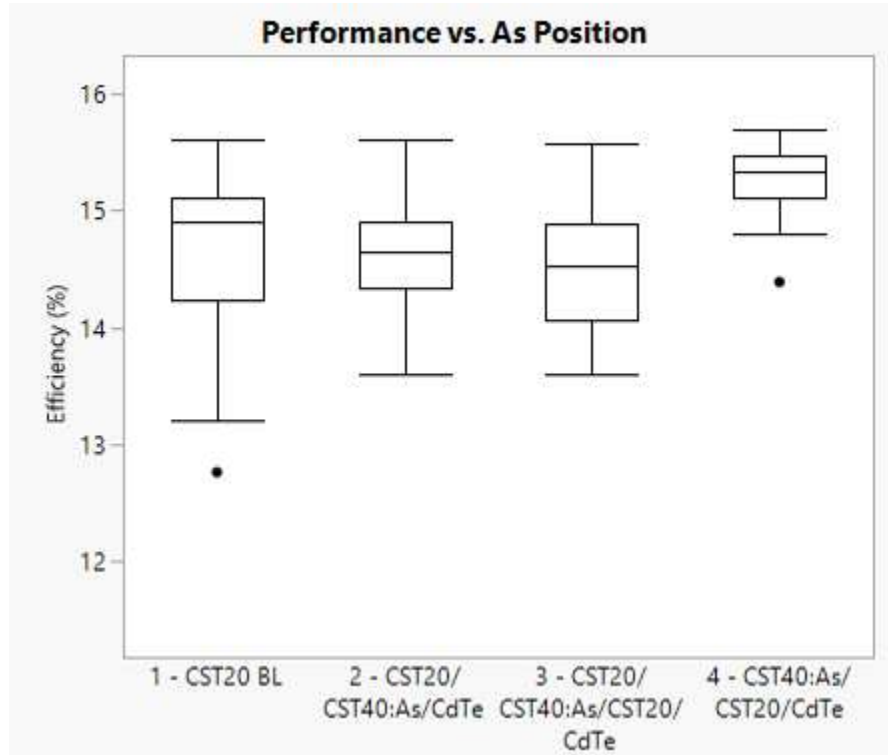


Figure 5.1: Efficiency box plots for the As doping position experiment.

These results indicated that CST40:As material was likely functioning as intended, increasing the carrier concentration in the front of the absorber.

5.2 CST40:As Thickness

5.2.1 Methods

The next logical progression of As incorporation in the CST layer was to increase the CST40:As layer thickness, aiming to further increase carrier concentration, making the front more p-type. An experiment of 5 superstrates was designed, where the total thickness of the CST40:As/CST20 lay-

ers remained 500 nm in attempt to maintain the diffused Se profile seen in the typical baseline. The CST40:As thickness at the front was swept from 0 nm (baseline) to 1 nm, 100 nm, 250 nm, and lastly 400 nm. An exploratory superstrate of 500 nm CST40 backed by 5.5 μm CST40:As followed by a Cd_3As_2 anneal was also fabricated and characterized with C-V.

5.2.2 Results

A distinct upward trend in V_{oc} was observed as CST40:As thickness was increased, from ~755 mV to ~810 mV, a 55 mV increase, similar to other As-doping experiments in literature [17]. Paired t-tests showed that each of these increases is statistically significant, refer to connecting letters report in Figure 5.2.

Connecting Letters Report		
Level		Mean
400nm CST40:As	A	808.60000
250nm CST40:As	B	799.80000
100nm CST40:As	C	789.96000
1nm CST40:As	D	778.08000
0nm CST40:As	E	754.08333
Levels not connected by same letter are significantly different.		

Figure 5.2: Connecting letters report for V_{oc} in CST40:As thickness sweep.

ANOVA analysis also confirms the increase in V_{oc} is significant, shown in the summary in Figure 5.3.

This was promising as one of the primary project objectives for the lab is to reach 950 mV V_{oc} . Since these were CST20 baselines and on a different MZO target, there was a potential repetition of the trend at higher V_{oc} 's in coming experiments from the typical 850 mV to 905 mV. The box plots for V_{oc} are shown in Figure 5.4.

The exploratory superstrate of 500 nm CST40 backed by 5.5 μm CST40:As followed by a Cd_3As_2 anneal yielded nearly dead cells. However, the carrier concentration versus depletion width plots indicated a very high carrier concentration with a narrow depletion width, a characteristic of high performing cells. A potential explanation for this is that As diffuses into the CST40 and

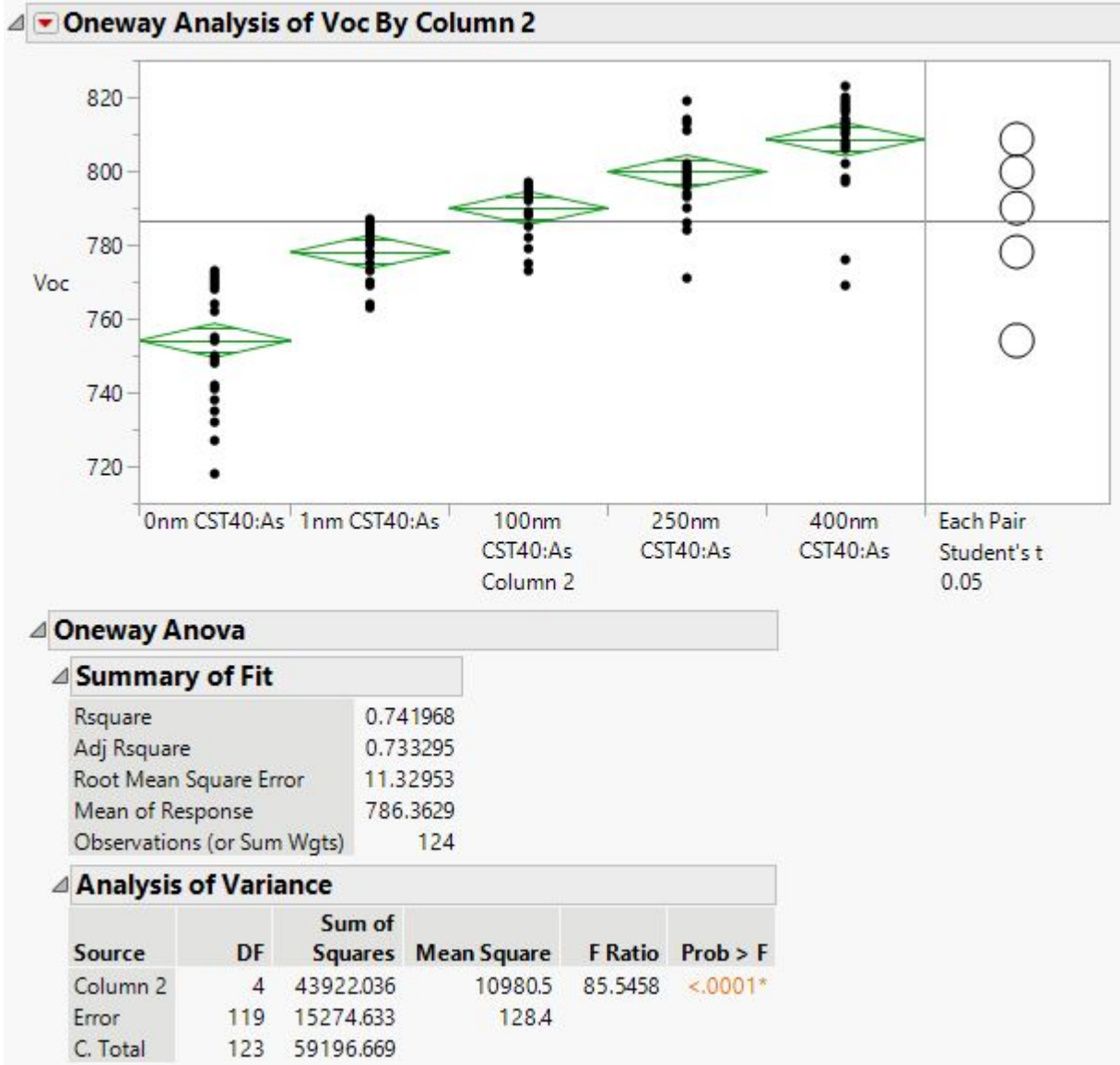


Figure 5.3: ANOVA summary for V_{oc} in CST40:As thickness sweep.

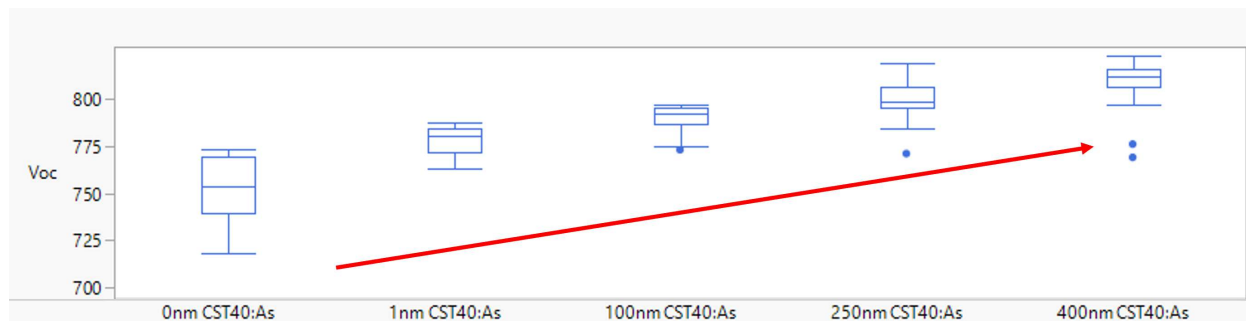


Figure 5.4: V_{oc} box plots for the As doping thickness experiment.

is activated properly, thus showing the high carrier concentrations, but the remaining CST40:As is not properly activated and reduces the performance drastically. The comparison of an undoped baseline and this exploratory structure carrier concentration versus depletion width plots are shown in Figure 5.5.

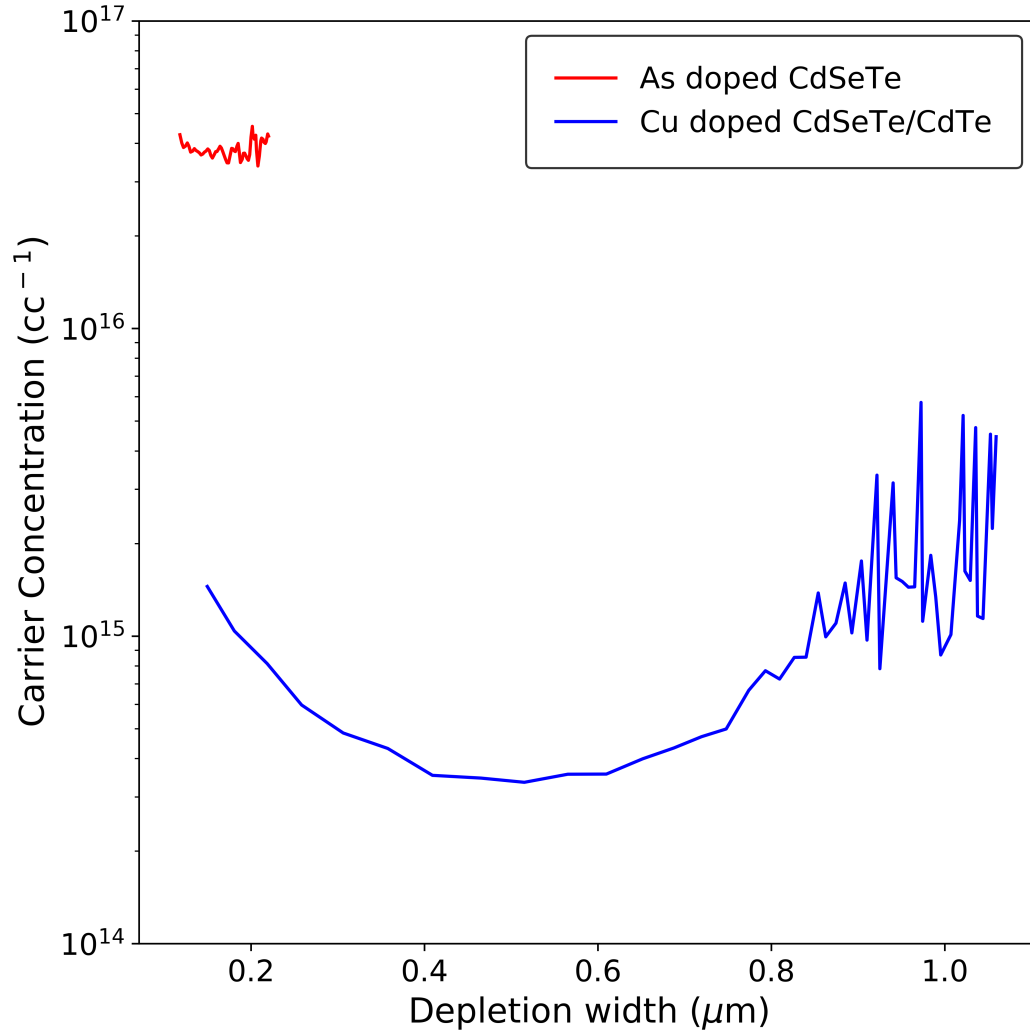


Figure 5.5: Carrier concentration versus depletion width plot comparing an undoped CST40 baseline structure (blue) and exploratory CST40/CST40:As structure (red).

5.3 High Efficiency CST40:As Cells

5.3.1 Methods

The V_{oc} trend from the previous experiment suggested further increasing CST40:As thickness and correspondingly decreasing CST20 thickness. Also, a more reliable MZO target was installed for the next superstrates. Thus, the experiment consisted of three superstrates of structures $0.5\text{ }\mu\text{m}$ CST40:As/ $3.5\text{ }\mu\text{m}$ CdTe and $1.5\text{ }\mu\text{m}$ CST40:As/ $2.5\text{ }\mu\text{m}$ CdTe, holding all other baseline processing conditions the same, and a CST40 baseline for comparison.

5.3.2 Results

The trend of increasing V_{oc} with increasing CST40:As thickness did not hold. Though the V_{oc} 's were the highest seen thus far, the thicker CST40:As gave around 12 mV less V_{oc} . It also had around 3% less FF, but 0.7 mA/cm^2 better J_{sc} , likely due to higher Se content, thus a lower band gap and more low energy photons absorbed. Overall, the deficit in V_{oc} and FF led to around 0.5% less efficient cells for the thicker CST40:As cells. The mean efficiencies of these distributions is significantly different as indicated by t-test shown in Figure 5.6.

There is likely an optimum thickness of CST40:As that should be explored with DOE in the future. The box plots for these two superstrates are shown in Figure 5.7.

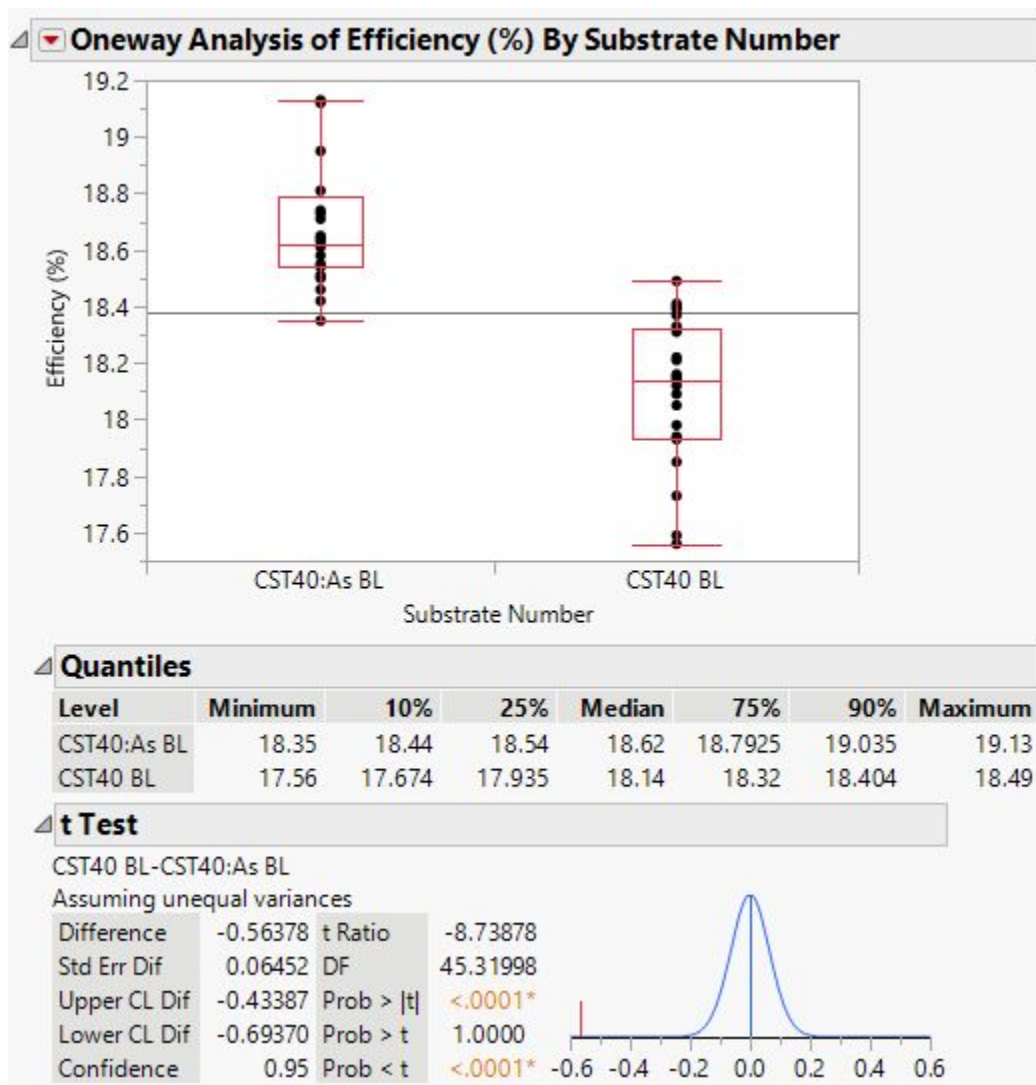


Figure 5.6: T-test comparing the CST40 BL and the CST40:As BL.

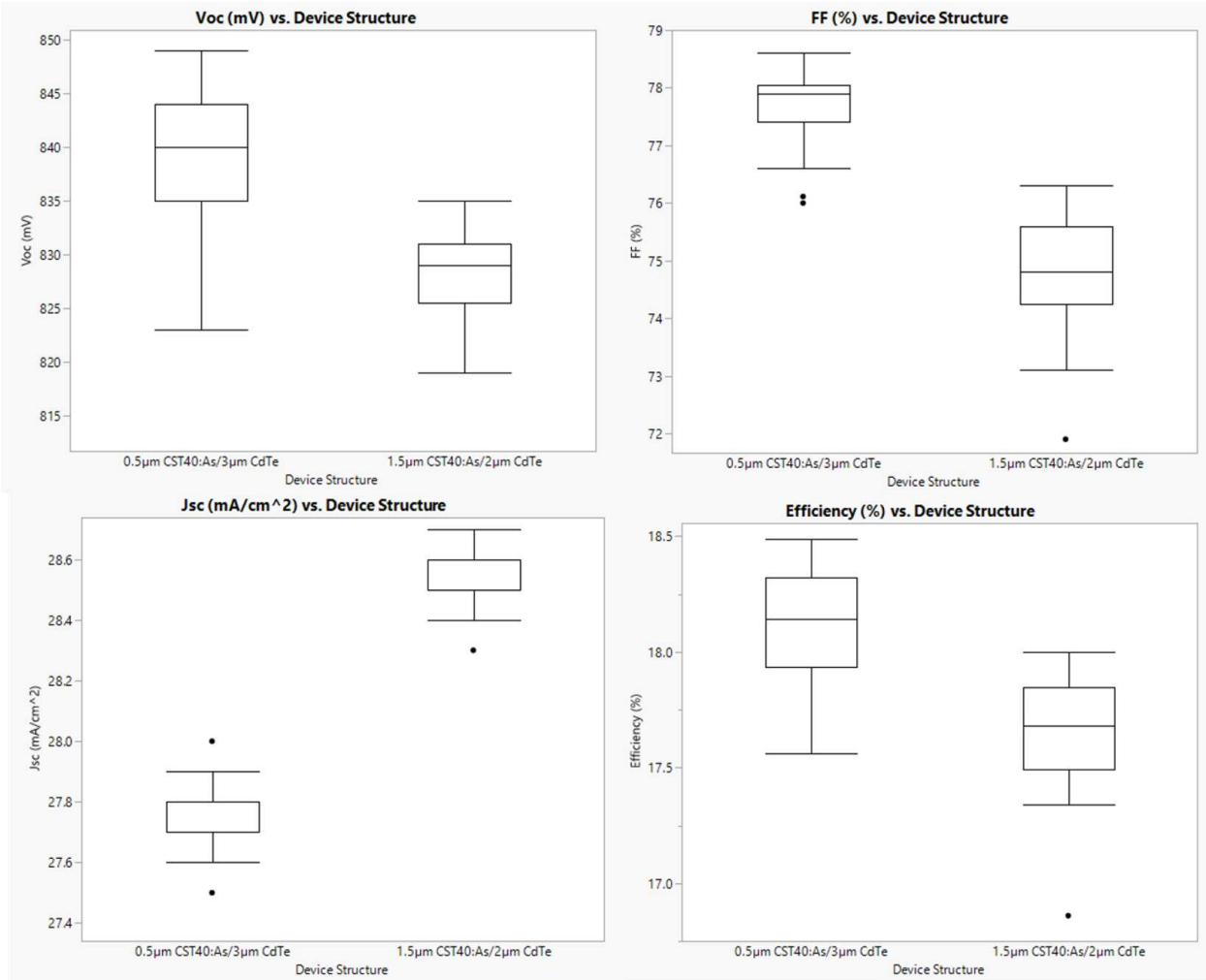


Figure 5.7: V_{oc} box plots for the As doping thickness experiment.

The carrier concentration versus depletion width for these two superstrates (Figure 5.8) shows a general trend of higher carrier concentration and narrower depletion width with increasing thickness of CST40:As. This result confirms that the front of the absorber is effectively p-doped with As.

In comparison to the typical baseline structure, the As baseline structure is nearly equivalent. Though the V_{oc} is slightly lower in the As baseline, the FF is higher, agreeing with results reported in literature [17]. The J_{sc} is slightly lower in the As baseline, indicating a potential Se deficiency compared to the CST40 baseline. Both superstrates produced 18%+ efficiencies, and these are the highest performing CST40:As cells to date. The box plots are shown in Figure 5.9.

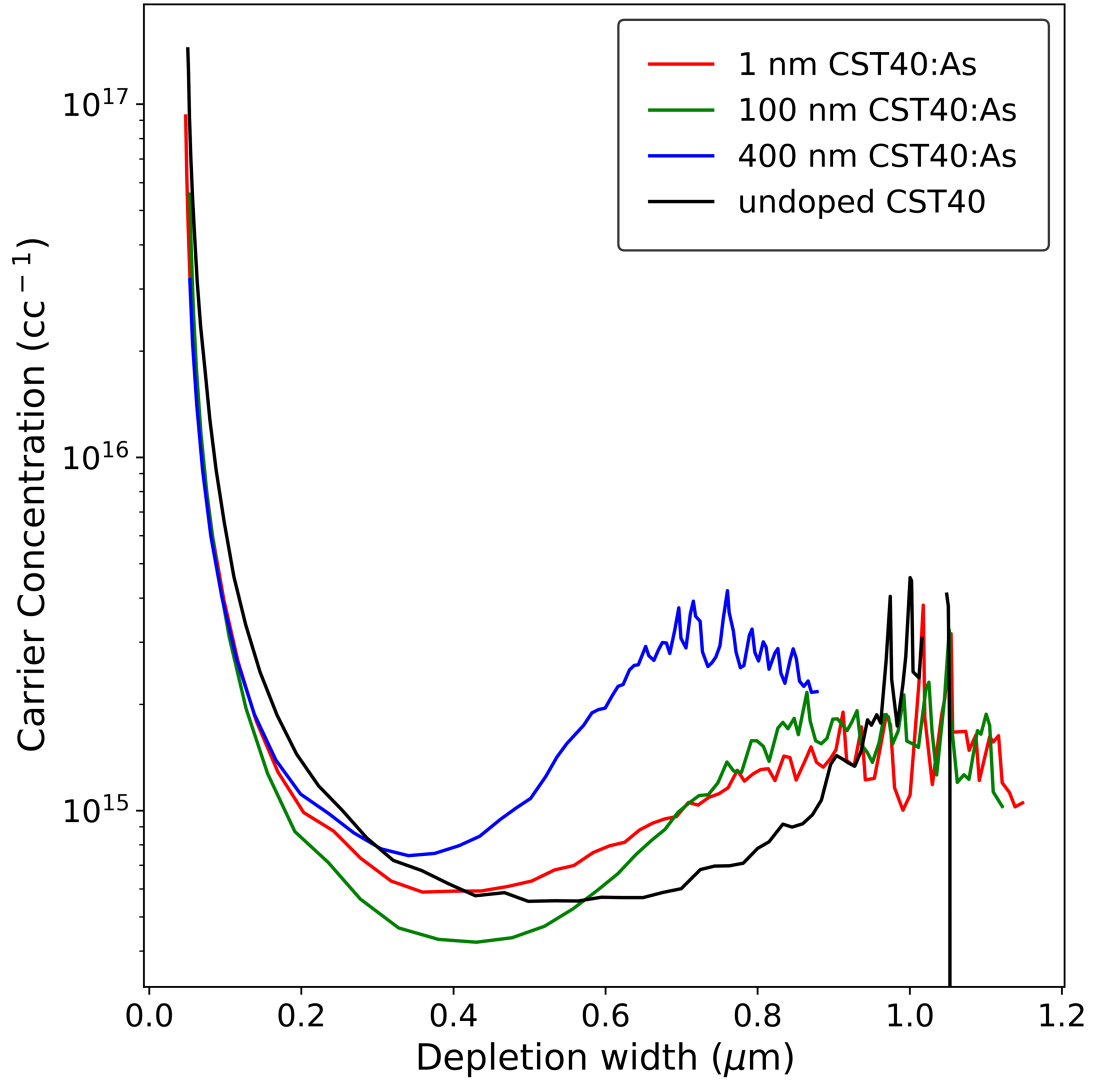


Figure 5.8: Carrier concentration versus depletion width plots for the As doping thickness experiment.

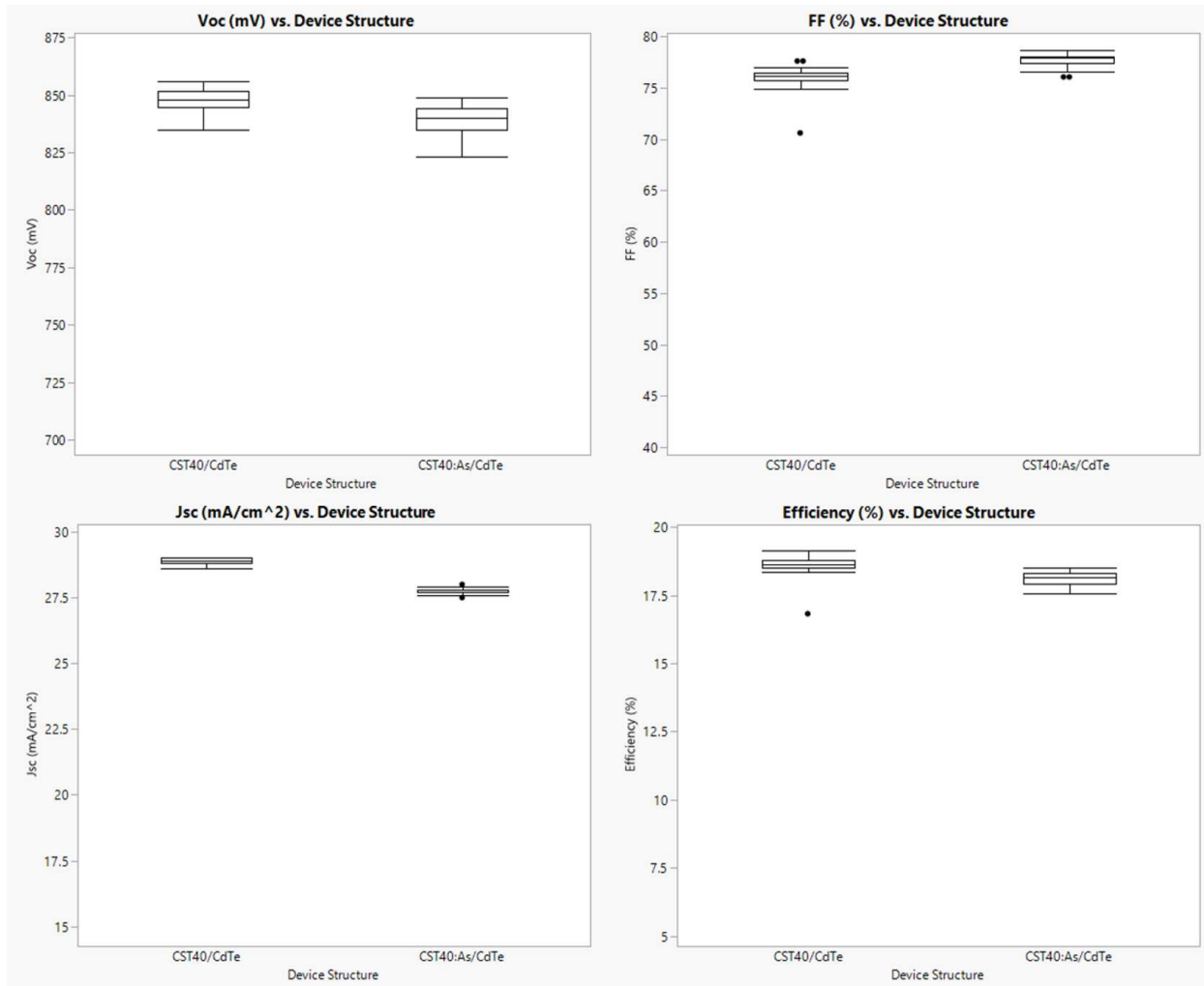


Figure 5.9: Performance box plots for the As doping thickness experiment.

Another piece of evidence explaining the lower J_{sc} in the As baseline is the PL plots. The As baseline had a PL peak farther to the left, shorter wavelength and higher energy, than the typical baseline. This implies that the e-h pair is recombining from a larger band gap in the As baseline. CdTe has a band gap of 1.5 eV, and Se alloying reduces the band gap to around 1.4 eV in CST40. Therefore, a likely explanation of the lower J_{sc} is lower Se content in the As baseline film. The PL measurements are shown in Figure 5.10. Cross-sectional SEM and EDS would be the final evidence needed to solidify this conclusion.

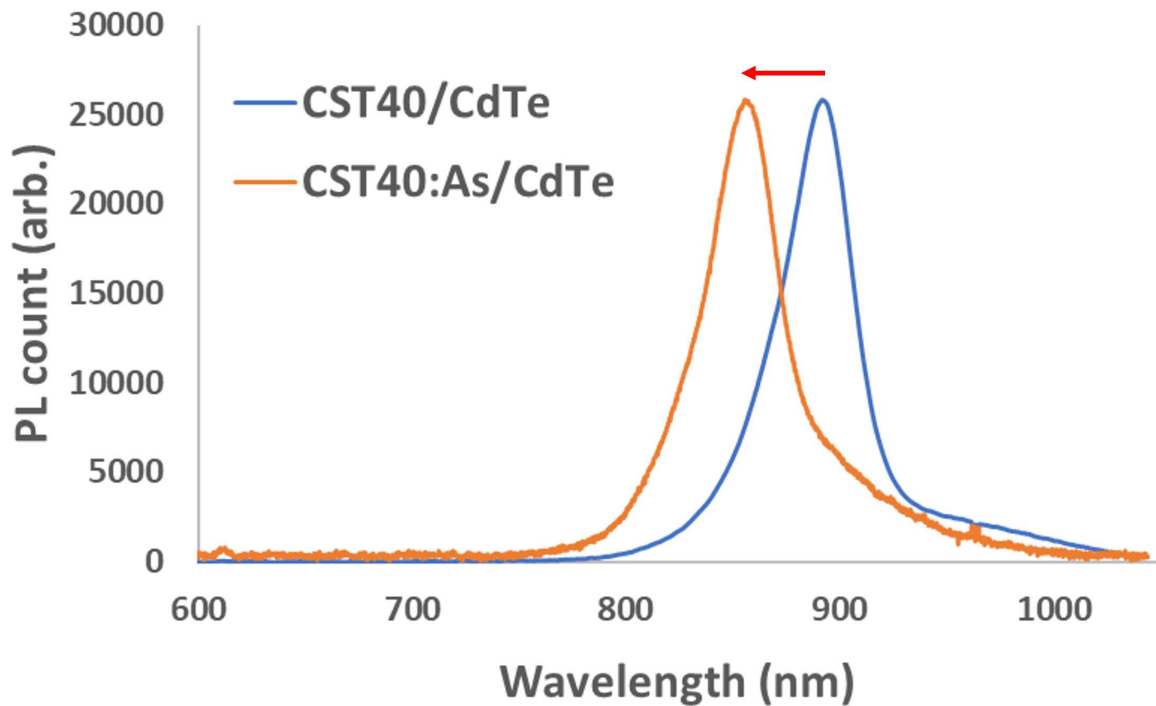


Figure 5.10: PL measurements for As baseline and typical baseline cells.

5.4 CST40:As/CdTe Ratios DOE

5.4.1 Methods

CST40 cell structures not backed by CdTe have been difficult and inconsistent to extract current. However, the bulk material shows high carrier lifetimes (the duration the e-h pair remains

separated before recombining) an order of magnitude higher than that of CdTe. The high lifetime increases the likelihood of extracting the e-h pair before they recombine, thus increasing the efficiency of the cell. One theory explaining why CST40 makes inconsistent cells is that there is a Se loss at the back surface due to resublimation as Se has the highest vapor pressure among Cd, Te, and Se. A Se loss at the back surface would bend the E_V and E_C downward, hindering hole extraction. In an attempt to maintain the V_{oc} in Se alloyed CdTe and increase the J_{sc} , a thinner layer of CdTe was deposited at the back in an effort to diffuse Se almost all the way through the CdTe layer. Furthermore, the optimal CST40:As thickness could be between the previously attempted thicknesses of 0.5 μm and 1.5 μm , thus a thickness of 1 μm was fabricated. The rationale for these two superstrates led to a 2-level 2-factor DOE to further explore the effects of CST40:As thickness, CdTe thickness, and their interactions. The experimental details are summarized in Table 5.1. Some of these cells were also imaged with SEM and EDS.

Table 5.1: CST40:As and CdTe Thickness Variations

Sample	CST40:As Thickness (μm)	CdTe Thickness (μm)	Pattern
1	3	3	++
2	3	1	+-
3	1	3	-+
4	1	1	--

5.4.2 Results

From glancing at the box plots, it can be seen that the CST:As thickness has more influence over V_{oc} and J_{sc} than the CdTe thickness. Also, thicker CdTe leads to slightly better V_{oc} than thin CdTe. A more detailed discussion of the individual effects comes later in this section. The 1 μm CST40:As/1 μm CdTe superstrate yielded the highest J_{sc} values seen in lab history at 30 mA/cm^2 . The box plots, J-V curves, and best cell performance metrics are shown in Figure 5.11, Figure 5.12, and Table 5.2, respectively.

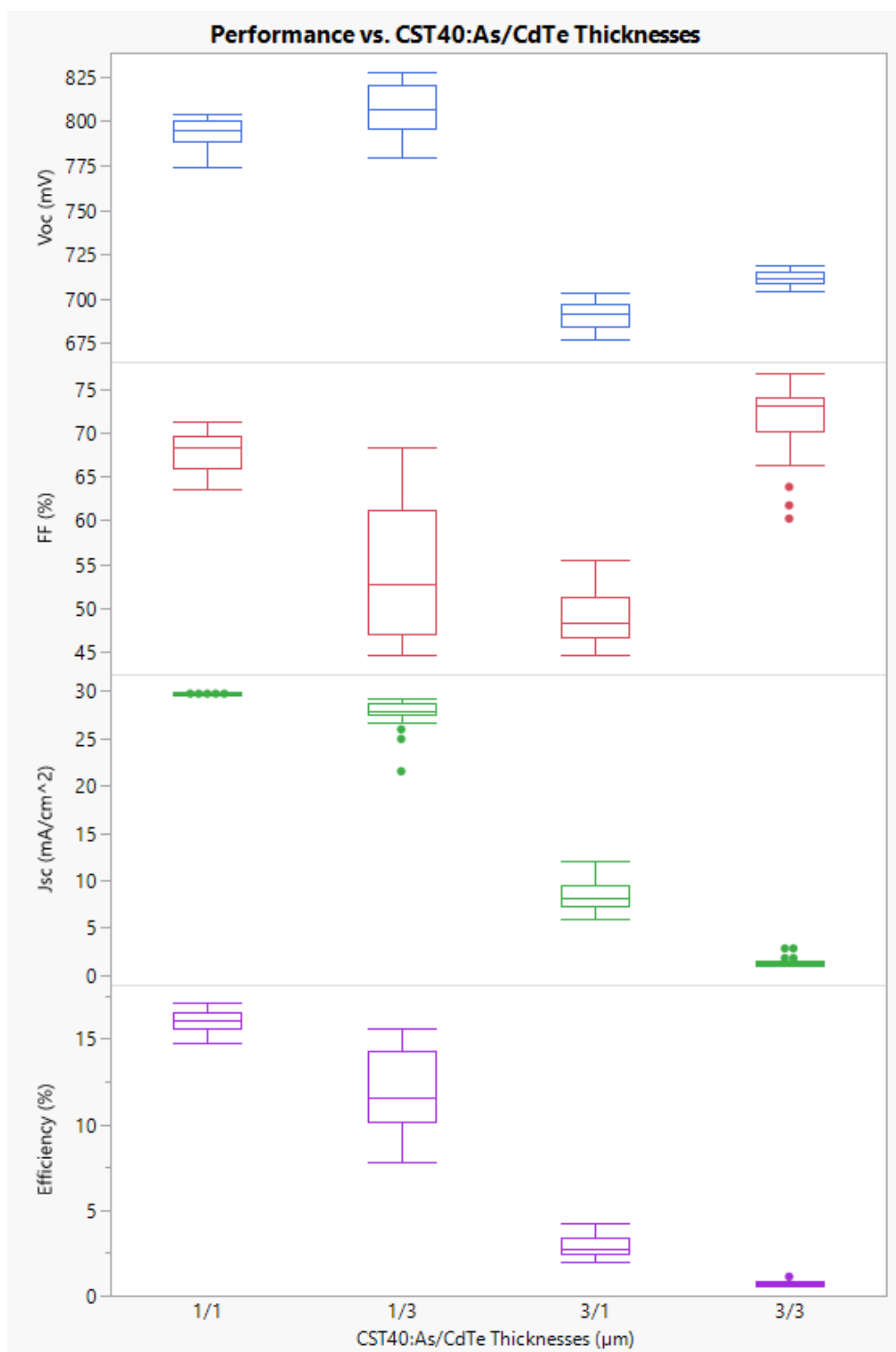


Figure 5.11: Performance box plots from CST40:As/CdTe ratio experiment.

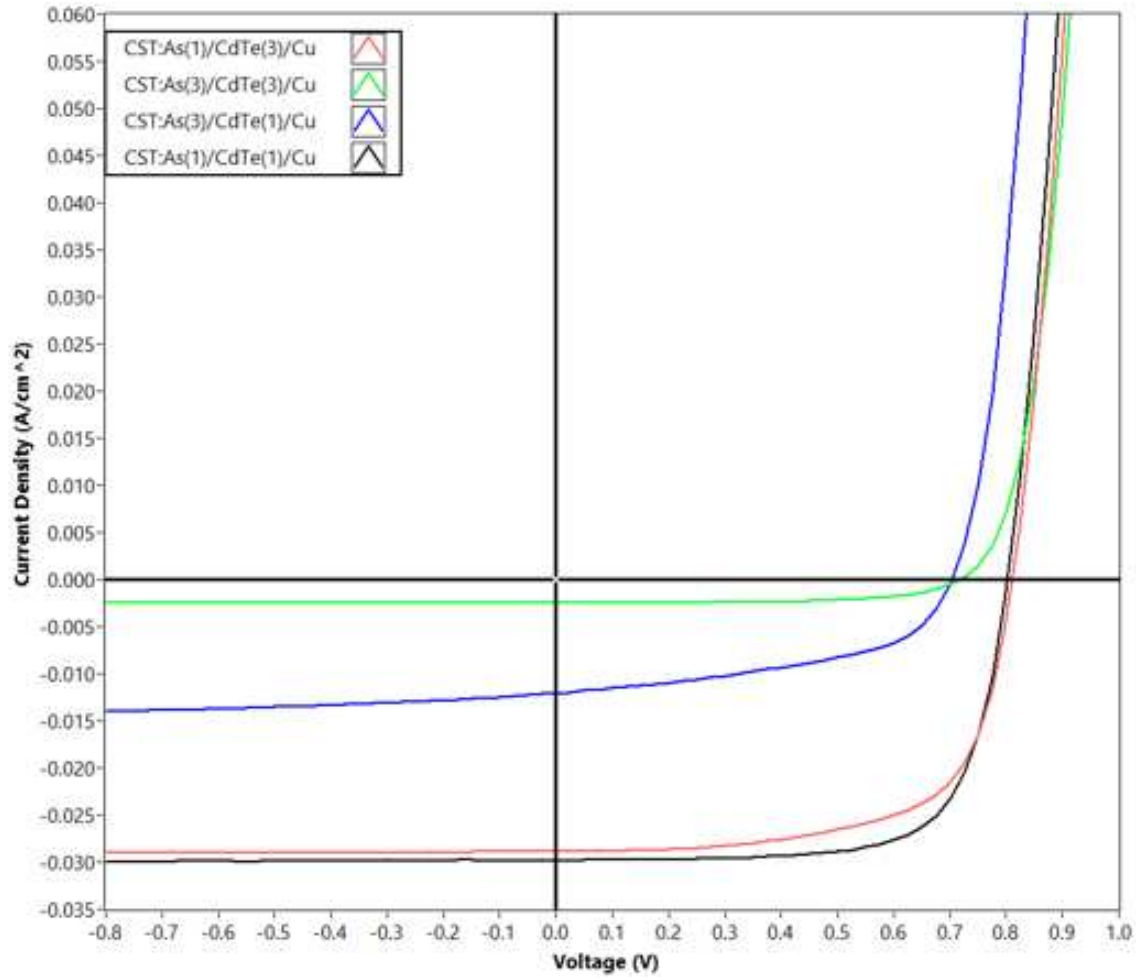


Figure 5.12: J-V curves from best cells in the CST40:As/CdTe ratio experiment.

Table 5.2: Best Cell Performances from CST40:As/CdTe ratio experiment

Sample	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF(%)	Efficiency(%)
CST:As(1)/CdTe(3)/Cu	812	28.9	65.9	15.47
CST:As(3)/CdTe(3)/Cu	718	2.5	61.7	1.11
CST:As(3)/CdTe(1)/Cu	703	12.1	49.6	4.21
CST:As(1)/CdTe(1)/Cu	804	29.8	71.2	17.07

The carrier concentration versus depletion width plots are relatively similar, but some conclusions can be made. The smoothest curves both had 1 μm CST40:As and high J_{sc} , the symmetry of the depletion width is also better, and the trough is closer to the front of the absorber. All superstrates had similar carrier concentrations at the belly of the depletion width, there is not a clear trend for that. The carrier concentration versus depletion width plots are shown in Figure 5.14.

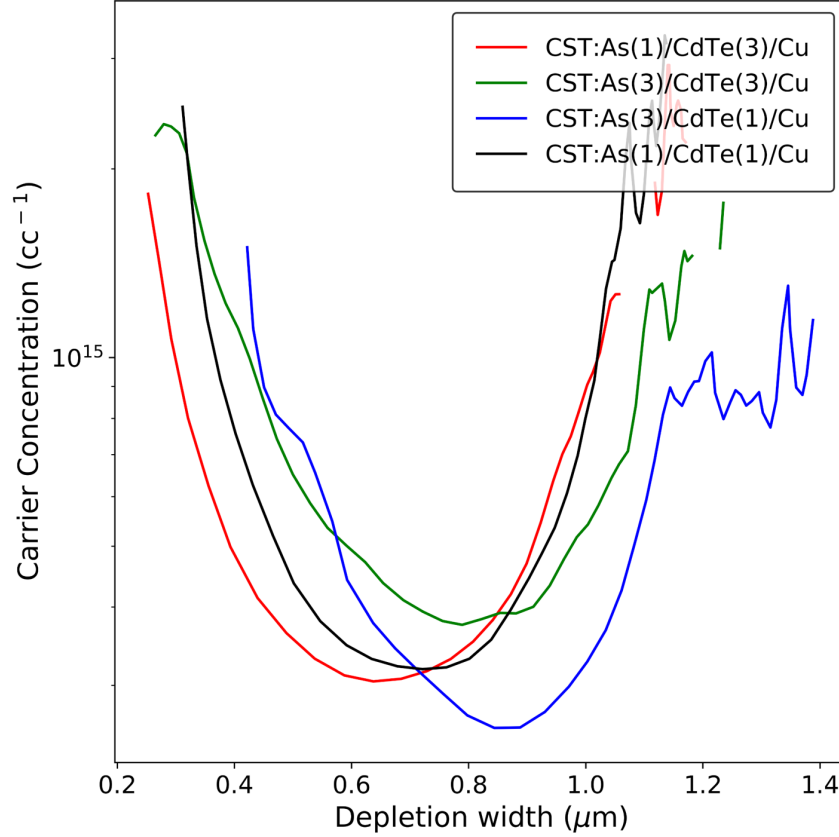


Figure 5.13: Carrier concentration versus depletion width plots for CST40:As/CdTe ratio experiment.

The effect summary in Figure 5.14 shows that the most influential factor is the CST40:As thickness, followed by CdTe thickness, and then the interaction factor. All are statistically significant. From the historical analysis mentioned earlier, the opposite result occurred that CdTe was more influential than CST40:As. This could be a difference between undoped and As-doped CST40, or because the historical analysis was inaccurate due to the long time period from which the data was taken. Whatever the cause, it is an interesting result and should be further investigated.

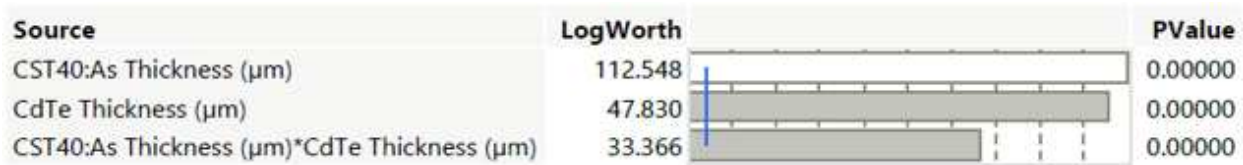


Figure 5.14: Effect summary for CST40:As/CdTe ratio experiment.

The model fit in this experiment was exceptional. Notably, the J_{sc} fit was the best with an R^2 value of 0.997, and an RMSE value of 0.643. The V_{oc} was next best with an R^2 value of .968, followed by FF with an R^2 value of 0.782. There was minimal unexplained variation in this experiment, yielding a high-confidence result. With both ANOVA and MLR, the P-values for the whole model as well as the individual factors are all less than 0.05. The model details are in Figure 5.15.

Summary of Fit

RSquare

0.99743

RSquare Adj

0.997342

Root Mean Square Error

0.643151

Mean of Response

17.23846

Observations (or Sum Wgts)

91

Analysis of Variance

Source

DF

Sum of Squares

Mean Square

F Ratio

Model

3

13968.608

4656.20

11256.59

Error

87

35.987

0.41

Prob > F

C. Total

90

14004.595

<.0001*

Parameter Estimates

Term

Estimate

Std Error

t Ratio

Prob> |t|

Intercept

45.107711

0.195713

230.48

<.0001*

CST40:As Thickness (μm)

-12.02866

0.067558

-178.0

<.0001*

CdTe Thickness (μm)

-2.079023

0.067525

-30.79

<.0001*

(CST40:As Thickness (μm)-1.96703)*(CdTe Thickness (μm)-1.98901)

-1.342556

0.06756

-19.87

<.0001*

Effect Tests

Source

Nparm

DF

Sum of Squares

F Ratio

Prob > F

CST40:As Thickness (μm)

1

1

13112.960

31701.19

<.0001*

CdTe Thickness (μm)

1

1

392.112

947.9478

<.0001*

CST40:As Thickness (μm)*CdTe Thickness (μm)

1

1

163.347

394.8999

<.0001*

Figure 5.15: ANOVA and MLR calculations for CST40:As/CdTe ratio experiment.

One of the purposes of this experiment was to diffuse Se almost to the back of the absorber to extract the maximum current while maintaining good V_{oc} and the electron reflector effect of CdTe [18]. The SEM and EDS images show that this was accomplished in Figure 5.16. The other elemental distributions were similar to the 19.44% cells, and were thus omitted. This confirms that $\sim 1 \mu\text{m}$ of CST40:As and $\sim 1 \mu\text{m}$ CdTe with the standard MZO, CdCl_2 , and Cu treatments yields very high J_{sc} because of the higher Se content in the film and fewer CdTe grain boundaries for recombination.

Lastly, the results from this experiment emphasize the benefits of DOE over OFAT. The response surface that was generated for FF is shown in Figure 5.17. If the experiment was run as

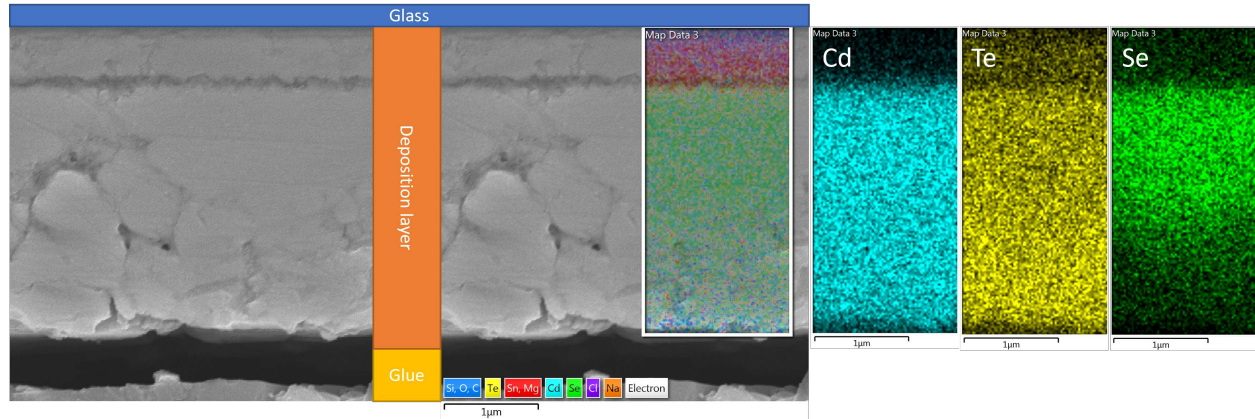


Figure 5.16: SEM image and the accompanying EDS elemental distribution map of Cd, Te, and Se.

OFAT, the conclusions would have been different. If the front left corner was run first and then the back left corner, the conclusion would be that CdTe thickness has minimal effect on FF. If the back right corner was run next, the conclusion would be that thinning the CST40:As layer has a positive significant impact on FF. If the order was front left to front right, the conclusion would be that thickening the CST40:As layer has a moderate positive impact on FF. Notice that these two conclusions are contradictory. If the back right corner was run next, the conclusion would be that thinning the CdTe layer has a significant positive impact on FF, whereas the original conclusion was that CdTe thickness had minimal impact on FF. This example emphasizes that observing the entire picture simultaneously is integral to making accurate and useful conclusions.

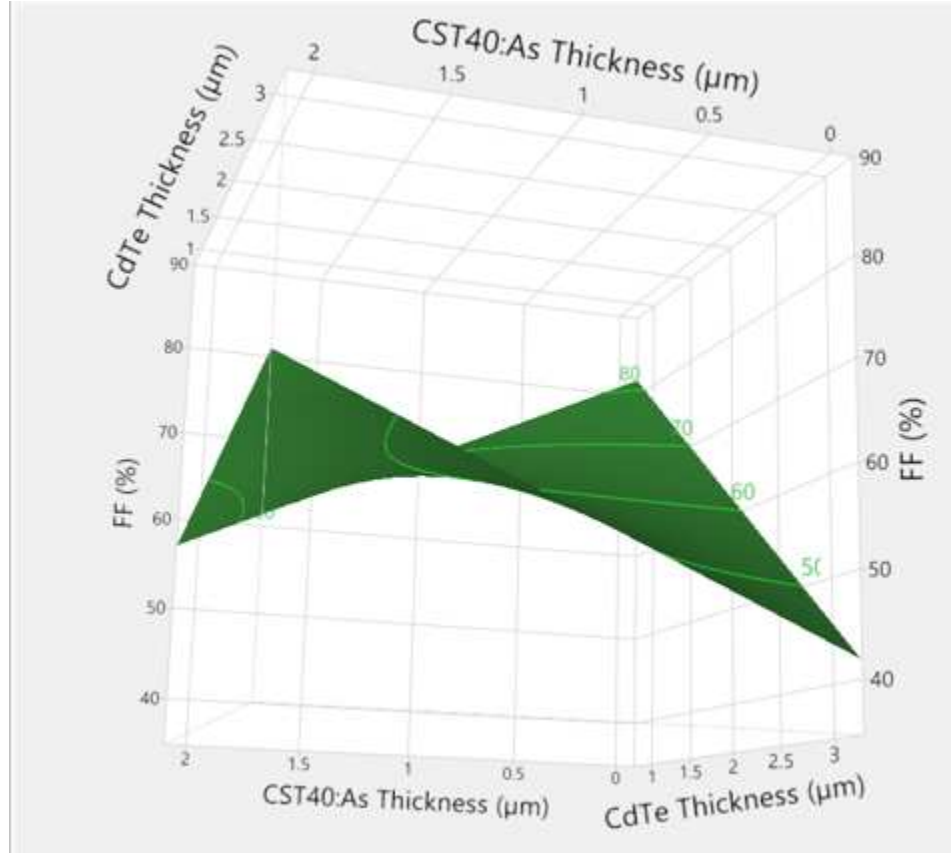


Figure 5.17: Response surface for FF for CST40:As/CdTe ratio experiment.

5.5 Oxides and Cd_3As_2

5.5.1 Methods

Another idea to increase longevity of PV modules in the field is to altogether eliminate dopants. Since their diffusion is inevitable, it would be worthwhile to research alternatives to doping. One active area of research is in various oxides at the back of the absorber, creating an electrical field effect on the diode achieving similar effects on the depletion width to that seen with As or Cu doping. Within the past 2 years, Cu-doped nickel oxide ($\text{NiO}:\text{Cu}$) has shown 32 mA/cm^2 while maintaining $824 \text{ mV } V_{\text{oc}}$, 69% FF, yielding 18.18% efficiency. TeO_x has also shown ~19% efficiencies. In this study, these two oxides were experimented with in structures involving CST40:As, something that has not been previously attempted. Various thicknesses of CST40:As and CdTe were fabricated

with 5 nm NiO:Cu at the back. Three superstrates were fabricated with 5 nm TeO_x at the back, all the same total thickness. One had no doping at all, one had CST40:As, and another had CST40:As and cadmium arsenide (Cd_3As_2) anneal at the back to further p-dope the absorber.

5.5.2 Results

In the NiO:Cu superstrates, thinner total thickness yielded higher efficiencies. Thicker CdTe at the back appeared to hurt all performance metrics. None of the cells reached above 13% efficiency, therefore additional exploratory experiments are required to discover a promising structure with NiO:Cu. The box plots for each of the four structures are shown in Figure 5.18.

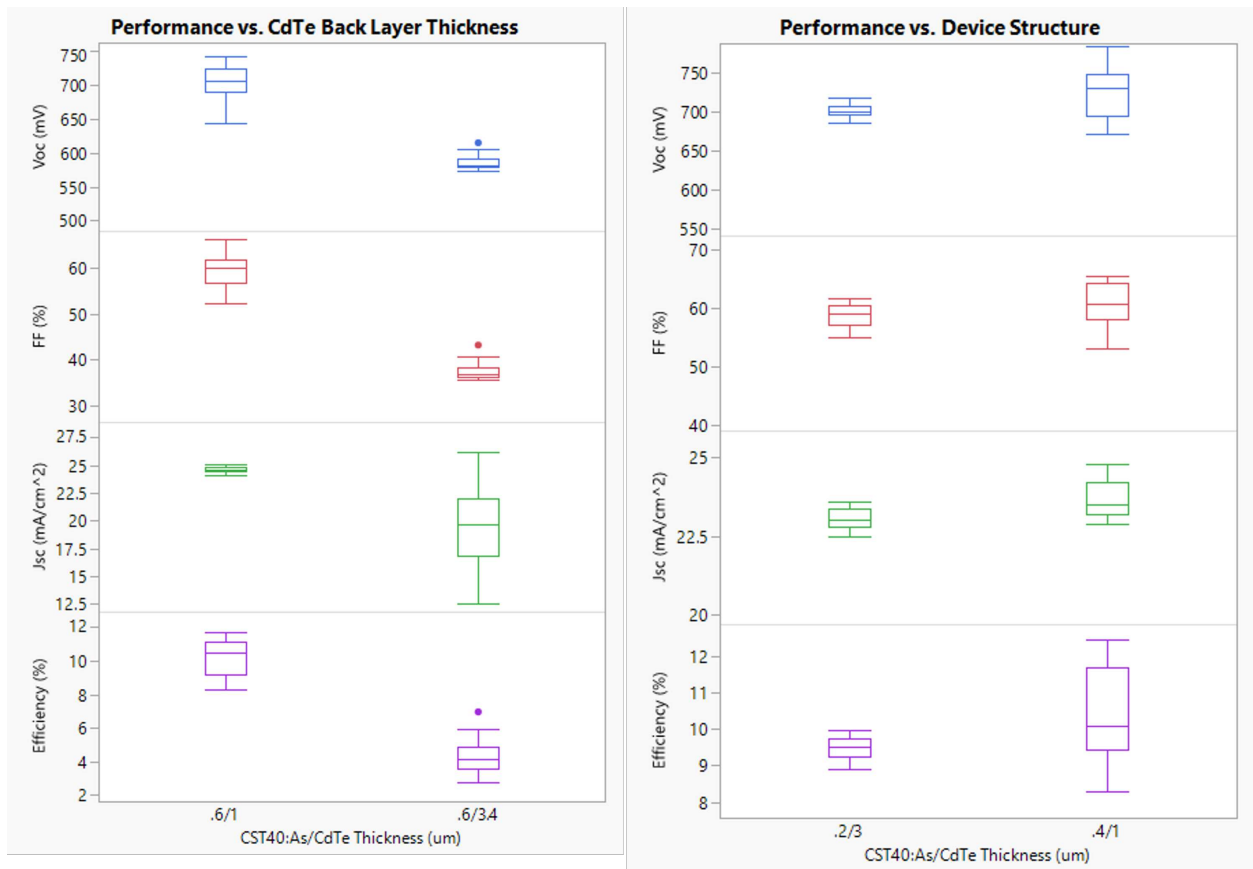


Figure 5.18: Performance box plots for different absorber structures and 5 nm NiO:Cu at the back.

The TeO_x outperformed NiO:Cu in every metric. This could have been due to the tool used, as NiO was deposited with a bell jar sputter tool and the TeO_x was deposited with the larger sputter

tool typically used for MZO. It could also simply be because the band alignment of TeO_x is better than NiO , or that Ni_2O_3 is being formed which has a less beneficial band alignment than NiO . The box plots, J-V curves, and performance metrics are shown in Figure 5.19, Figure 5.20, and Table 5.3, respectively.

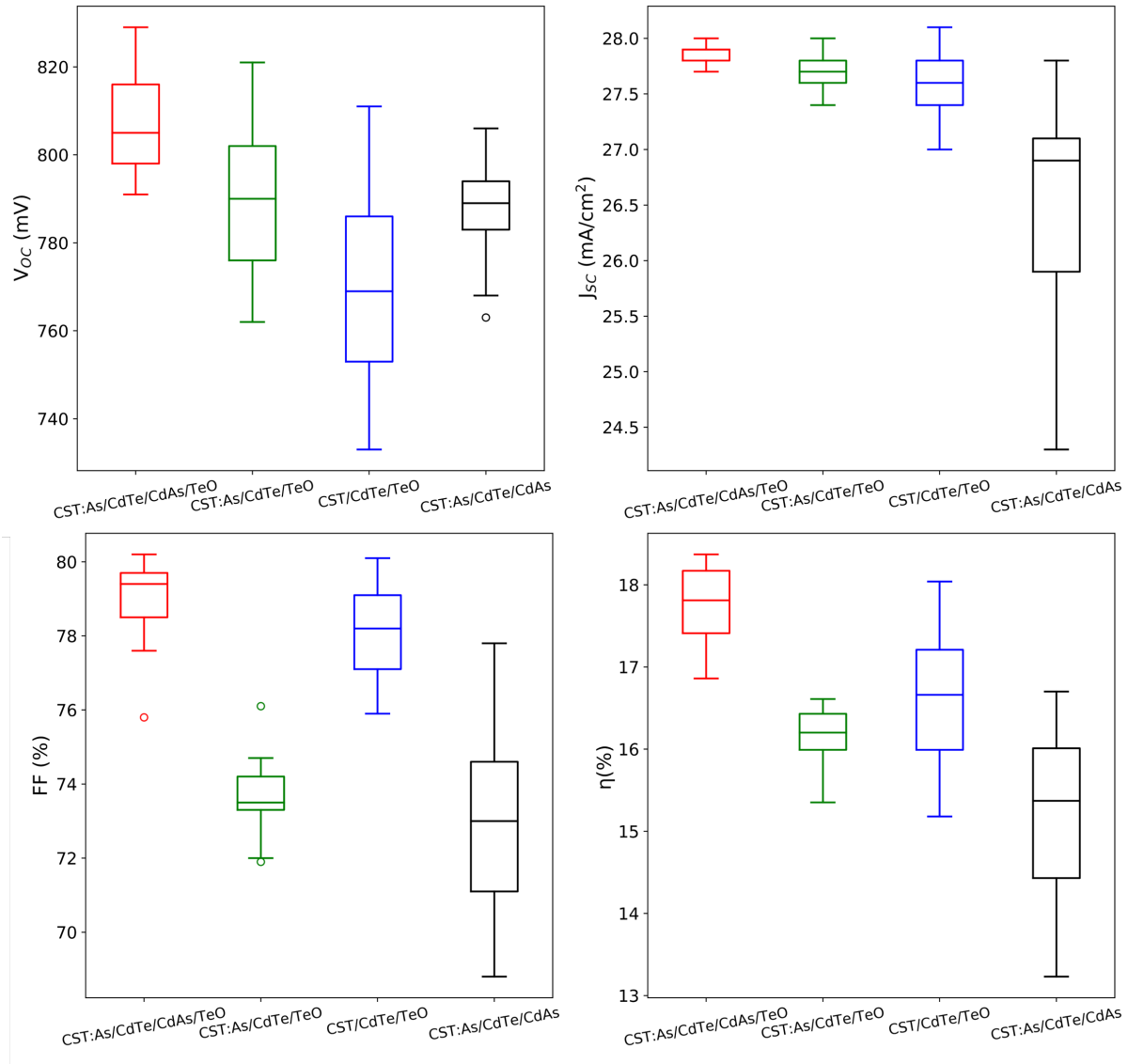


Figure 5.19: Performance box plots for different absorber structures and 5 nm TeO_x at the back.

Comparing within the TeO_x superstrates, the highest performing structure included CST40:As and Cd_3As_2 . The second best was undoped CST40 and no Cd_3As_2 , followed by CST40:As and no

Cd_3As_2 . With no TeO_x , the $\text{CST:As/CdTe/Cd}_3\text{As}_2$ structure was around 2% less efficient. There was a large spread in J_{sc} without TeO_x , indicating inconsistent charge carrier extraction among the cells. It appears that more As in the structure leads to higher V_{oc} , and TeO_x also led to higher V_{oc} . Some of the highest FF in lab history were recorded in the $\text{CST:As/CdTe/Cd}_3\text{As}_2/\text{TeO}_x$ and CST/CdTe/TeO_x superstrates, exceeding 80% in some cells.

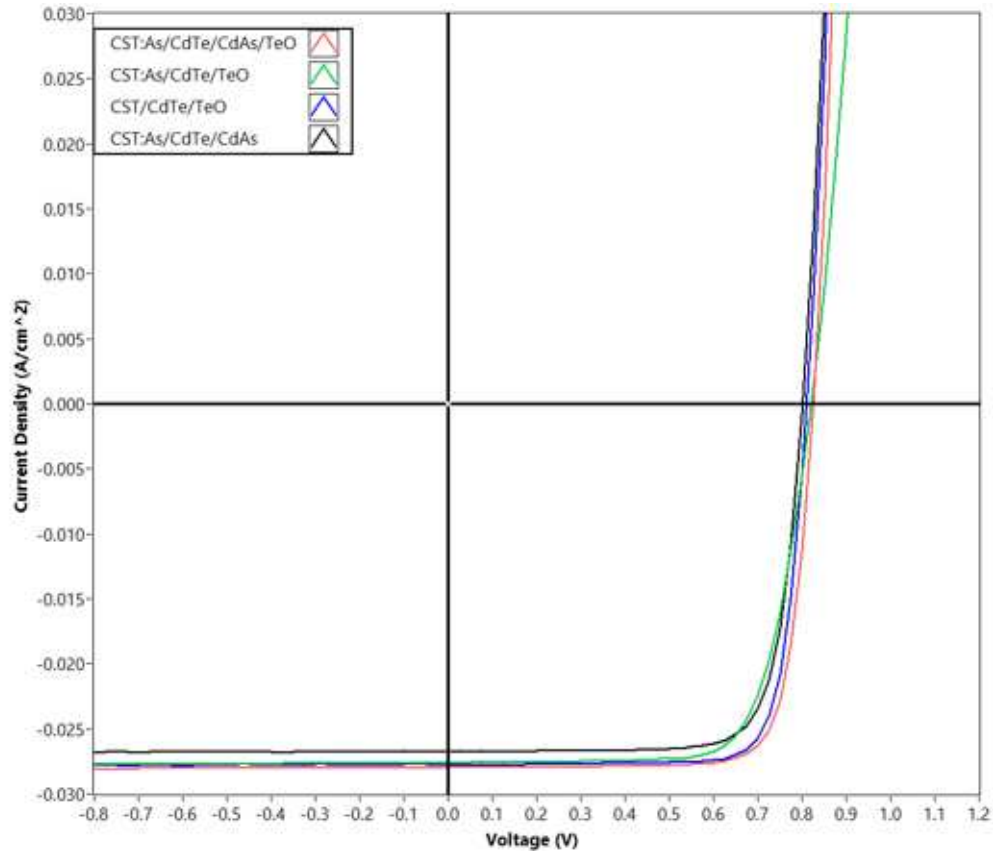


Figure 5.20: J-V curves for different absorber structures and 5 nm TeO_x at the back.

Table 5.3: Best Cell Performances from TeO_x Experiment

Sample	$V_{\text{oc}}(\text{mV})$	$J_{\text{sc}}(\text{mA}/\text{cm}^2)$	FF (%)	Efficiency (%)
$\text{CST:As/CdTe/Cd}_3\text{As}_2/\text{TeO}_x$	825	28.0	79.6	18.37
CST:As/CdTe/TeO_x	821	27.6	73.4	16.61
CST/CdTe/TeO_x	811	27.8	80.1	18.04
$\text{CST:As/CdTe/Cd}_3\text{As}_2$	802	26.8	77.8	16.70

Chapter 6

Conclusions

6.1 Summary of Results

The objective of these experiments was to utilize design of experiments (DOE) and statistical analysis to improve the baseline copper (Cu) doped solar cell structure and arsenic (As) doped structures, and explore new structures with oxides at the back. Multiple linear regression and analysis of variance on historical cell data led to a new thick 6 μm structure with a 600-second cadmium chloride (CdCl_2) that yielded 18%+ cells. New Cu doping process parameters were discovered through a 2-level 3-factor DOE that yielded 19%+ cells. A standardized painted electrode procedure was developed through a 2-level 3-factor DOE. Sputtered electrodes showed better stability over long periods of air exposure. A 33% faster fabrication process was developed through a 2-level 2-factor DOE as guided by the previous Cu doping DOE. Carrier concentration versus depletion width plots showed that high performance is predicated by a narrow depletion width shifted towards the front of the absorber. A 19.44% efficient Cu-doped cell was fabricated through the culmination of all previous DOE's, one of the best in published literature, and confirmed that a Se gradient through the absorber is critical for higher currents as shown in EDS maps. Exploratory runs revealed that $\text{CdSe}_{0.4}\text{Te}_{0.6}$ (CST40) doped with As (CST40:As) should be incorporated at the front of the absorber, the highest efficiencies of 18%+ were achieved with 0.5 μm CST40:As/3.5 μm cadmium telluride (CdTe) which is comparable to the Cu-doped baseline, and incorporating more selenium (Se) at the front leads to higher short-circuit current density (J_{sc}) values. Through a 2-level 2-factor DOE studying ratios of CST40:As to CdTe, cells of $30 \text{ mA/cm}^2 + J_{\text{sc}}$ were fabricated, some of the highest in lab history. Open-circuit voltage (V_{oc}) and J_{sc} were heavily influenced by CST40:As thickness, whereas fill-factor (FF) was more influenced by the interaction between CST40:As and CdTe thicknesses. With NiO:Cu at the back, thinner absorbers gave higher efficiencies, contrary to the trends observed in Cu-doped baseline structures. Tellurium oxide (TeO_x)

at the back increased V_{oc} and J_{sc} , and in conjunction with a cadmium arsenide (Cd_3As_2) annealed absorber, led to some of the highest FF seen in the lab of 80%+ and efficiencies of 18%+. The carrier concentration versus depletion width plots supported the conclusion that shifting the depletion width towards the front leads to better performance, and also the smoother more symmetrical curves led to higher J_{sc} .

6.2 Future Work

The As-doped absorber with TeO_x at the back should be further optimized with DOE to maintain 30 mA/cm² J_{sc} , 80% FF, and 860 mV V_{oc} . Each of these metrics has been observed on separate cells of relatively similar structures, and it is within reach to combine these into one cell of 20.6% efficiency. Advanced characterization of As-doped TeO_x structures would streamline research efforts, such as TEM, SIMS, and SKPM measurements. Undoped absorbers of CST40/CdTe or CST40 only with TeO_x at the back should be optimized with DOE to eliminate the dopant diffusion failure mechanism altogether. Thin absorbers with NiO:Cu at the back should be further optimized with DOE as NiO:Cu has shown the highest J_{sc} values in lab history and less material is required for manufacturing on a large scale. Sputtered metal electrodes should be explored as they have better consistency and longevity than the current painted electrode. An extensive study of all processing parameters with DOE is the best avenue in the future. DOE should be utilized to its fullest extent as it provides quantified effects of factors and their interactions which will make research efforts more efficient and fruitful, as well as distinguish lab members for industry careers in the future.

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Appendix A

Python Codes

A.1 Fetching Data for Historical Analysis

The following is the code utilized in acquiring J-V data in Section 3.2.

```
import os
import os.path
import numpy as np
from glob import glob
from os import listdir
from os.path import isfile, join
import pandas as pd

basedir = r'T:\VManufacturingLab\DATA\ARDS RUNS'
runfile = np.genfromtxt(r'C:\Users\Zach\Google Drive\JPHB\Massaged Data Deleting More.csv', delimiter=',')
runnumber = runfile[1:,1][:]
runnumber = runnumber[~np.isnan(runnumber)]
substrate = runfile[1:,2][:]
substrate = substrate[~np.isnan(substrate)]
# print(substrate)

firstrun = 1101
lastrun = 1900
perflist = []
i=0
for k in range(firstrun, lastrun, 50):
    for i in range(len(runnumber)):
        if runnumber[i]>k and runnumber[i]<=k+49:
            for f in listdir(basedir+'\\'+str(k)+'-'+str(k+49)+'\\Run '+str(int(runnumber[i]))+'\\JV Data'):
                if f.endswith('.txt'):
                    JVfile = join(basedir+'\\'+str(k)+'-'+str(k+49)+'\\Run '+str(int(runnumber[i]))+'\\JV Data', f)
                    JVdata = pd.read_csv(JVfile, sep='\t')
                    prefix = f.split('.')
                    perf = [f,float(JVdata[prefix[0][:-4]+str(int(runnumber[i]))][3])
                        ,float(JVdata[prefix[0][:-4]+str(int(runnumber[i]))][4])
                        ,float(JVdata[prefix[0][:-4]+str(int(runnumber[i]))][5])
                        ,float(JVdata[prefix[0][:-4]+str(int(runnumber[i]))][6])]
                    perflist.append(perf)
            print('Done with run '+str(int(runnumber[i]))+'. '+str(int(i*100/len(runnumber)))+' percent complete.')
perflistcopy = perflist
print('100 percent complete.')

perflist = perflistcopy
# perflist.append(['End'])
voc = []
ff = []
jsc = []
eff = []
vocnew = []
ffnew = []
jscnew = []
effnew = []
vocall = []
ffall = []
jscall = []
effall = []
perfav_alloutliers = []
cellperf_alloutliers = []
voccell = []
q=0
duplicates = []
sublist = []
while len(perflist) > 1:
    while perflist[q][0].split(' ')[0:2] == perflist[0][0].split(' ')[0:2]:
        duplicates.append(perflist[q][0].split(' ')[0]+' '+perflist[q][0].split(' ')[1])
        if perflist[0][0][0:3] == 'End':
            break
        if int(perflist[q][1]) < 900 and float(perflist[q][2]) < 90 and float(perflist[q][3]) < 32 and float(perflist[q][4]) < 22:
            voc.append(int(perflist[q][1]))
            ff.append(float(perflist[q][2]))
            jsc.append(float(perflist[q][3]))
            eff.append(float(perflist[q][4]))
            q+=1
        else:
            q+=1
            platenno = perflist[q-1][0].split(' ')[0]+' '+perflist[q-1][0].split(' ')[1]
    # voc = [voc]
    # ff = [ff]
```

```

#         vocav_long = np.mean(voc[i])
#         vocnew = [x for x in voc[i] if x >= vocav_long-2*voc_stddev]
#         voc.append(vocnew)
#         vocav = np.mean(voc[i])
#         a=voc[i]

#         for i in range(0,9):
#             ff_stddev = np.std(ff[i])
#             ffav_long = np.mean(ff[i])
#             ffnew = [x for x in ff[i] if x >= ffav_long-2*ff_stddev]
#             ff.append(ffnew)
#             ffav = np.mean(ff[i])
#             b=ff[i]
#         ffall.append(ff[i])

#         for i in range(0,9):
#             jsc_stddev = np.std(jsc[i])
#             jscav_long = np.mean(jsc[i])
#             jscnew = [x for x in jsc[i] if x >= jscav_long-2*jsc_stddev]
#             jsc.append(jscnew)
#             jscav = np.mean(jsc[i])
#             c=jsc[i]
#         jscall.append(jsc[i])

#         for i in range(0,9):
#             eff_stddev = np.std(eff[i])
#             effav_long = np.mean(eff[i])
#             effnew = [x for x in eff[i] if x >= effav_long-2*eff_stddev]
#             eff.append(effnew)
#             effav = np.mean(eff[i])
#             d=eff[i]
#         effall.append(eff[i])

#         perfav_alloutliers.append([plateno,vocav,ffav,jscav,effav])

#         cellperf_alloutliers.append([plateno,a,b,c,d])
#         print(a,b,c,d)

    voc = []
    ff = []
    jsc = []
    eff = []
    perflist = perflist[q:]
    q = 0

runfile = np.genfromtxt(r'C:\Users\Zach\Google Drive\JPHB\Massaged Data Deleting More.csv', delimiter=',')

df = pd.DataFrame(cellperf_alloutliers)
rundetails = pd.DataFrame(runfile[1:,:][:])
test = []
for g in range(len(rundetails.iloc[:,1])):
    for h in range(len(cellperf_alloutliers)):
        if str(int(np.array(rundetails.iloc[g,1]))[0:4]) in cellperf_alloutliers[h][0].split(' ')[0] and str(int(np.array(rundetails.iloc[g,1]))[4:6]) in cellperf_alloutliers[h][0].split(' ')[1]:
            yoooo = np.array(df.loc[h,:])
            test.append(yoooo)
        elif len(cellperf_alloutliers[h][0].split(' ')[1]) == 1 and str(int(np.array(rundetails.iloc[g,1]))[0:4]) in cellperf_alloutliers[h][0].split(' ')[0] and str(int(np.array(rundetails.iloc[g,1]))[5]) in cellperf_alloutliers[h][0].split(' ')[1]:
            yoooo = np.array(df.loc[h,:])
            test.append(yoooo)
df_perf = pd.DataFrame(test)
df_perf.columns = ['Substrate Number','Avg Voc (excluding outliers)','Avg FF (excluding outliers)',
                  'Avg Jsc (excluding outliers)','Avg Eff (excluding outliers)']
rundetails.columns = ['Run Number','Substrate','P1 Temp (°C)','CST40 Time (s)','CST20 Time (s)','CdTe Time (s)',
                      'Total Absorber Dep Time (s)','CdCl2 Time (s)','CdCl2 Anneal Time (s)','2nd CdCl2 Time (s)',
                      'Total CdCl2 Treat and Anneal Time (s)','Number Vacuum Breaks']
compiled = df_perf.join(rundetails)

writer = pd.ExcelWriter(r'C:\Users\Zach\Google Drive\JPHB\NEW Baseline Cells Avg Performance.xlsx', engine='xlsxwriter')
compiled.to_excel(writer, sheet_name='Substrate Average Performance', index=False)
writer.save()

```