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Manufacturing Process Optimization to Improve Stability, Yield and Efficiency of CdS/CdTe PV Devices

Final Report, December 2004 – January 2009

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Colorado State University
Fort Collins, Colorado

Subcontract Report
NREL/SR-520-45214
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1. SUMMARY

Under the Thin Film Partnership Program, we have made significant progress. The reproducibility of device efficiency and stability has been demonstrated during long duration operation of the system with a single charge loading for the CdS, CdTe and $CdCl_2$ process. In order to advance back contact processing, a significant upgrade to increase the processing space in our pilot scale system has been designed, fabricated and has been installed. A series of detailed studies on the effect of oxygen during the $CdCl_2$ treatment has been performed. Oxygen has been shown to improve the effectiveness of the $CdCl_2$ treatment. Mathematical modeling of a package design has yielded results that show that moisture can be kept from our device for 22 years at 65C temperature with saturated humidity. Hardware to perform steady state photocapacitance (PHCAP) has been designed, built and tested in our laboratory. The effect of processing on the deep states in CdTe devices can be seen quantitatively. Optimum process conditions lead to lower photocapacitance signals. The feasibility of cooling the substrate in vacuum for optimum processing of the back contact has been demonstrated. A large number of experiments have been performed on laser scribing of CdS/CdTe films. Mechanical scribing has yielded the lowest contact resistance between the scribed region and the metallization, to date. Researchers at National Starch and Chemicals (NSC) have performed many experiments to screen print carbon, nickel and silver films in patterns. The adhesion of these films was tested according to ASTM 3359B and achieved a 5B or "excellent" rating.

A fixture for automated cooling of the substrate in vacuum has been designed, fabricated, installed and tested. This is needed for optimum processing of the back contact. Large area devices (~ 4 sq. cm.) in the form of strips have been fabricated and tested at NREL. Efficiency of 10.9% has been measured on these strips. The air-to-vacuum-to-air seals in the pilot system have a glass filled teflon liner. These liners have experienced wear and this results in scraping of the glass substrates in the seal. Improved liners have been designed and fabricated, installed and tested in the system. Desiccant containing materials for the edge seal and sealing of the holes in the back glass have been tested in damp heat tests at NREL with very promising results. Hardware modifications to the pilot system for automated cooling of the substrate in vacuum have been completed and device efficiencies of 11.83 % have been made in "all forward" process.

Significant advances to the modeling of large area vapor sources and modeling of gas transport in the system have been made. Significant advances to the modeling of the substrate transport, temperature distribution and deflection in the glass substrate, large area vapor sources, diffusion of gases in the vapor source and modeling of gas transport in the system have been made. Significant progress has been made in characterizing films with ellipsometry and x-ray fluroscence (XRF) and the use of these methods for on-line process control is being investigated. In additio©n the use of reflection intensities for quality control is promising.

Efforts to improve device efficiency and advance device characterization are underway. Devices of efficiency 12.8% (NREL verified) have been fabricated on low iron glass with SnOx:F TCO. Devices of efficiency 13.7% (tested at CSU photovoltaics lab.) have been fabricated on low iron glass with SnOx:F TCO without AR coating.

A process for removing the coated films to reduce the amount of solid waste has been developed. Significant technical assistance was provided to AVA Solar.

2. INTRODUCTION

The aim of this Thin Film PV Partnership Program (TFPP) effort is to advance the understanding of device stability, efficiency and process yield for CdTe PV devices. Methodologies for reliably processing larger areas and increasing device efficiencies are being developed. We have actively participated in the National CdTe R&D Team activities. Our ongoing collaborations with the PV Testing Lab at CSU, NREL, Pacific Northwest Natl. Lab and other CdTe Team Members are resulting in further advances. The efforts in this project will be a significant step towards realizing the full potential of CdTe PV.

3. RESEARCH RESULTS

3.1. Improving Performance and Manufacturability

3.1.1 Process Reproducibility:

Reproducibility of efficiency and stability has been demonstrated during long duration operation of the system with a single charge loading for the CdS, CdTe and $CdCl_2$ process [Sampath 2004]. Currently efforts are underway to advance the back contact processing to the same level. An average efficiency of 11.4% with a standard deviation of 0.54% was demonstrated during nine hour processing with a single charge loading for the CdS, CdTe and $CdCl_2$ process [Sampath 2004]. The stability of these devices is shown in Figure 1.

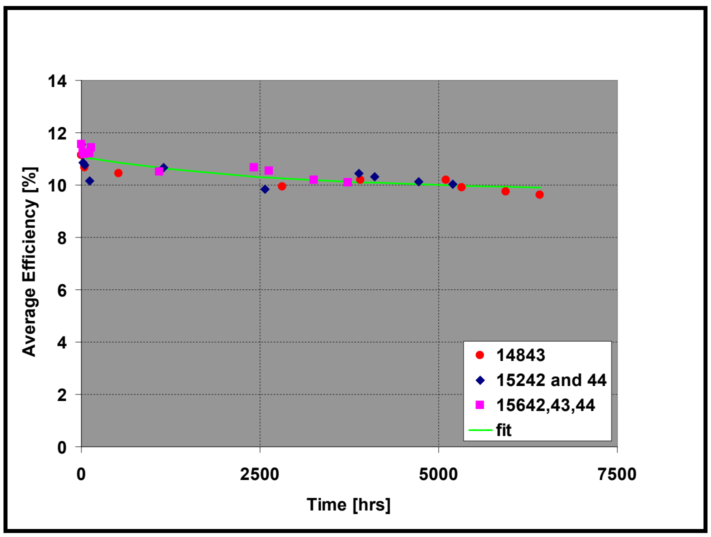


Figure 1: Average efficiency vs accelerated stress time for three groups of cells (12 cells total). Inset shows substrate IDs. The stress conditions are 65C, OC, 5 hours ON/ 3 hours OFF.

As shown in Figure 1, groups of cells fabricated with the same process conditions in three separate fabrication runs exhibit nominally the same stability performance during accelerated stress testing. Devices processed identically to the ones in Figure 1, but without the Cu back contact had Voc's $\geq$ 700 mV. We have shown earlier that devices with Voc greater than 700 mV without a Cu back contact have good stability [Barth 2005, Sampath 2004].

3.1.2. Oxygen and the $CdCl_2$ Treatment:

The presence of oxygen during the $CdCl_2$ treatment leads to better devices. In order to study the effect of oxygen during the $CdCl_2$ treatment, a system for introducing controlled amounts of oxygen directly into the $CdCl_2$ vapor source and the $CdCl_2$ annealing station was designed, built and installed. The system incorporated a mass flow controller for precise control and modification to the graphite sources. A series of studies were under taken which involved nearly 225 substrates.

These studies have shown that oxygen during the $CdCl_2$ treatment improves the device performance. The JV performance of two example cells is shown in Table 1 and Figure 2. A Cu containing back contact was not applied to either of the cells in Table 1 or Figure 2. However, the JV performance of devices with out intentional copper is predicative of the stability of fully processed devices [Barth 2005].

Table 1

Cell	Voc	Jsc	ff	Eff[
	[mV]	[mA/cm^2]	[%]	[%]
17638-3: 0.6% O2	685	19.68	40	5.55
17650-3: 2% O2	745	20.34	48	7.32

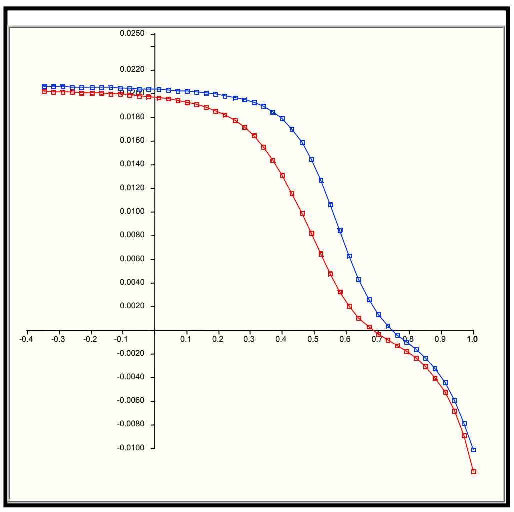


Figure 2: Light JV traces for devices with varied oxygen during the $CdCl_2$ treatment. Red trace: 0.6% O_2 ; blue trace: 2% O_2.

3.1.3. Process Optimization:

The process has been optimized with CdS from ASARCO. The earlier supplier (Balzers/Unaxis) discontinued the manufacturing of CdS pellets. In addition, the CdS from Unaxis was more expensive. The efficiency and stability of devices with CdS from ASARCO is comparable to device efficiency and stability with CdS from Unaxis. In addition, the process has been optimized with purer material for the back contact processing from a different supplier. The earlier supplier had lower purity. The efficiency and stability results with the newer material are comparable to the results with the older material. These optimization studies involved nearly 400 substrates. Efforts to obtain uniformity of back contact processing over long duration are currently underway. X-Ray Photoelectron Spectroscopy (XPS) at CSU has been used in these process optimization studies.

3. 2. Studies on Interconnection and Module Packaging

3.2.1 Studies on Interconnection:

Processes for creating a series interconnection for our modules is being developed. This work includes film scribing and the application of electrode materials for the "rollover" contact. A significant number of experiments on laser scribing of many of our films for interconnection has been performed at US Laser and Spectra Physics. As we reported earlier, for scribing the TO:F, the Nd:YAG laser has been found to be suitable. For scribing the CdS/CdTe films, experiments have been performed with both a Nd:YAG laser and a vanadate laser. The scribing experiments have been performed at 122 conditions. We have observed that scribing from the glass side results in better scribe quality and lower contact resistance for both flash lamp pumped Nd YAG and the diode pumped Nd vanadate laser. The CdS/CdTe scribes are characterized with optical microscopy, scanning electron microscopy and energy dispersive spectrometry. Though significant improvements have been demonstrated over previous experiments, the scribe parameters have not yielded a sufficiently low contact resistance (target 1 ohm for 1 cm) using the current spray applied electrode material. These experiments are continuing. Some of the experiments at Spectra Physics are being performed with "galvanometer scanning" system and this may lead to very high productivity.

Our group continues to collaborate with Dr. David Miles of NSC on optimizing the back electrode (metallization) and rollover interconnection process. The replacing of the current spray process for metallization with a screen print process is being investigated. This has advantages for process throughput, material utilization and lower volatile organic compound emissions. Since screen printing allows the metallization to be performed in patterns, a separate process for isolating the metallization in not needed. NSC is developing optimum formulations for screen printing for our CdTe PV application. It is envisioned that the back electrode will consist of screen printing of carbon and nickel in patterns. Many substrates have been provided to NSC for these studies.

3.2.2. Modeling Moisture Transmission and Encapsulation:

Significant progress has been made in the conceptual design of a package that keeps moisture away from our devices. Our 16.5 x 16.5 inch module is designed to have a 1" border around the edge. In this region, it is planned to use the Truseal solar edge tape which contains desiccant. Calculations based on the finite difference method have been performed. The aim of the calculations is to see how long a 1" edge seal will keep moisture away from our devices. For this, we calculated how long a 1" thick disc of the Truseal solar edge material will take to saturate with water if one side was exposed to saturated water at 65C and the disc was at 65 C was determined. The data for water transmission rate was obtained from Truseal. The finite difference calculations gave 22.3 years for the 1" thickness to saturate. These calculations were repeated by researchers at Truseal and similar results were obtained by them.

This is a conservative model because PV modules rarely reach 65C for a few hours in a year and this calculation is done assuming the side is exposed to saturated water on one side. Experiments are currently underway at Truseal to refine the data on water transmission. After the updated water transmission is obtained, the calculations will be refined, the model will be experimentally validated and results published.

Preliminary studies on encapsulation with EVA have been performed. A vacuum bag with an accumulator was used in these studies. In this approach, the glass/EVA/glass is placed in the vacuum bag and the bag with the accumulator is evacuated and placed in the furnace. The purpose of the accumulator is to provide a vacuum reservoir for the gases that are evolved during the encapsulation to accumulate. These experiments have resulted in bonding between the glass and the EVA. However the bubbles could not be fully removed. In addition when the temperature of the EVA was measured with a thermocouple, a high degree of variability was observed.

A fixture to quantitatively measure the moisture ingress through the encapsulation has been developed. The fixture consists of a closed glass container placed in a temperature controlled furnace. The container has a small amount of water to saturate the container to 100% relative humidity (RH). This fixture is capable of testing encapsulated 3" X 3" specimens at different temperatures and 100% RH. A measured quantity of indicating desiccant is placed in the specimen. The indicating desiccant with $CoCl_2$ and $CaSO_4$ changes color when a certain quantity of moisture has penetrated through the encapsulation. By estimating moisture ingress at different temperatures and using well known mathematical approaches, the ability of encapsulants to protect the devices from moisture under field conditions can be predicted.

3.2.3 Studies on Interconnection:

Processes for creating a series interconnection for our modules is being developed. This work includes film scribing and the application of electrode materials for the "rollover" contact. Many experiments on laser scribing of many of our films for interconnection have been performed at US Laser and Spectra Physics. For scribing the TO:F, the Nd:YAG laser has been found to be suitable. For scribing the CdS/CdTe films, experiments have been performed with both a Nd:YAG laser and a vanadate laser. Recent scribing experiments have been performed at Spectra Physics application lab. Over 115 different conditions have been explored. The results of the laser scribing conditions on the contact resistance to the spray applied electrode is shown below in Figure 3.From the figure, it can be seen that the scribe parameters have not yielded a sufficiently low contact resistance (target 1 ohm for 1 cm) using the current spray applied electrode material. The laser wavelength was 1064 nm. Experiments are continuing with laser light wavelength of 532 nm. Initial results show improved contact resistance values to approximately 5 ohm -cm of contact.

As we reported earlier, we have demonstrated the feasibility of mechanical scribing to produce contact resistance of 1 ohm for 1 cm. Recently mechanical scribing at high speeds has been performed and the measured contact resistance between the mechanical scribe and the sprayed electrode material was measured at 1 to 2 ohms for 1 cm of scribe length.

Researchers at NSC under the guidance of Dr. David Miles are optimizing the back electrode (metallization) and rollover interconnection process. Replacing of current spray process for metallization with a screen print process is being investigated. This has advantages for process throughput, material utilization and lower volatile organic compound emissions. Since screen printing allows the metallization to be performed in patterns, a separate process for isolating the metallization in not needed. NSC is developing optimum formulations for screen printing for our CdTe PV application. NSC has performed many experiments to screen print carbon, nickel and silver films in patterns. Initial samples have recently been received from NSC.

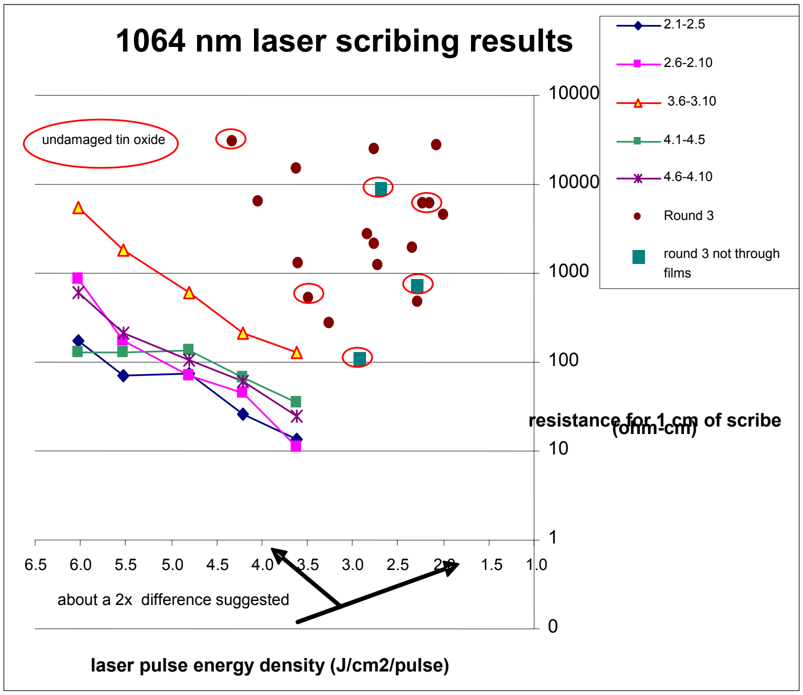


Figure 3: Contact resistance as a function of laser pulse energy density at 1064 nm wavelength. The different symbols denote different laser power, repetition rate and scan speed

The samples show that the screen printing technique can provide adequate line width resolution and accuracy. Adhesion was measured for all the materials on Pilkington Tec 15 glass and of the carbon material on CdS/CdTe following ASTM 3359B. The results were "5B" or excellent adhesion. The resistance values for interconnection of the silver based ink are excellent; however the resistance of the nickel and possibly the carbon need further optimization. This is currently under investigation at NSC.

3.2.4 Hail Impact Studies:

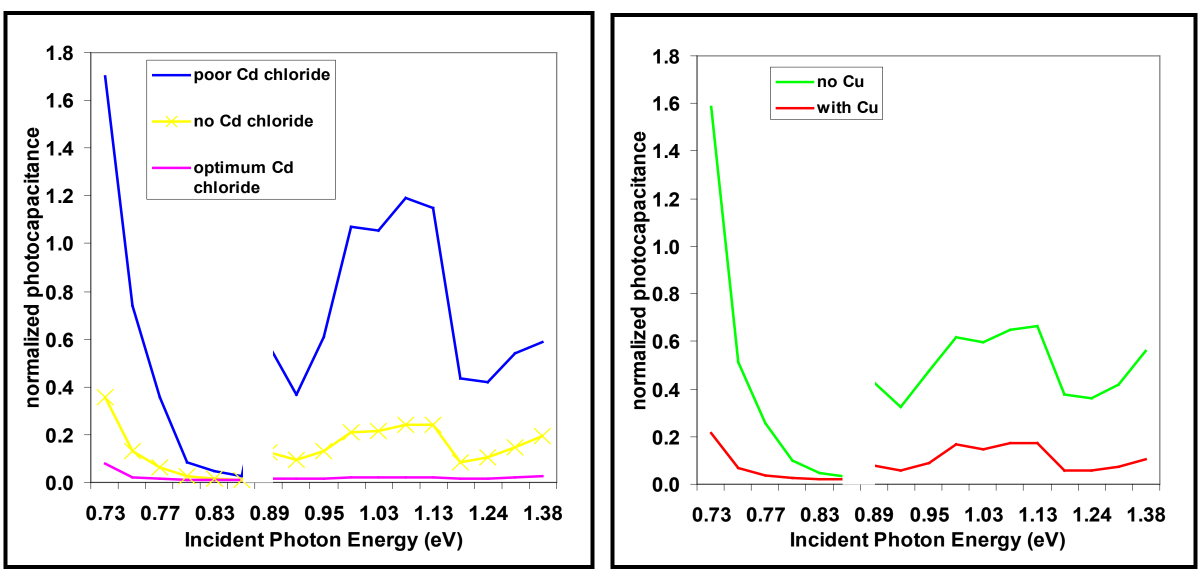
Many glass/EVA/glass specimens of size 16.5"X16.5" were fabricated and tested at ASU-PTL with the hail impact test. The hail impact tests did not cause any mechanical damage to the specimens. The top glass was tempered and passed thru the system. Many 16.5 x 16.5 inch tempered substrates have been transported with the load lock system and heated to 500 ºC in 2 minutes. Vendors with expertise in tempering TEC15 substrates with minimal distortions have been identified. A residual stress of 2700 psi. remained after processing. In addition, the 16.5" X 16.5" laminates withstood 80 lbs. of load (static load for passing IEC 61646). Some specimens were tested to failure in the static test. The failure load was 400 lbs. The studies on hail impact tests and static loading will be part of MS thesis for Mark Armijo.

3.2.5 Encapsulation:

Initially the design of the packaging for our modules will utilize glass/EVA/glass packaging. In order to reduce moisture ingress into the device, polymers with desiccants will be used for sealing the edges and also the holes in the back glass. Fixtures simulating the package design with the desiccant containing materials have been fabricated and are being tested at NREL under damp heat (85/85). A small quantity of moisture indicating material placed inside the fixture has not changed color after 3000+ hours of testing for the fixtures simulating the edge seal. The fixtures without the desiccant containing materials have failed (the moisture indicating material inside the fixture has changed color). The tests are continuing. This result is very promising. An advanced method for encapsulation is also being developed by National Starch and Chemicals (NSC) with our input. Based on our input and their past expertise, NSC has developed a promising approach for encapsulation. The new method involves screen printing a polymer based material (developed by NSC for OLED applications) at the edges on the back side of the front glass and then pressing the back glass to the front glass. Subsequently, the polymer is cured by UV exposure for fraction of a second. One glass/glass package with 0.25" wide encapsulant has been tested in the damp heat test (85/85) for 1300 hours. A small quantity of indicating desiccant placed in the middle between the two glass plates has not changed color. In addition to studies on packaging, the feasibility of scribing our films with automated systems has been demonstrated.

3.3 Detailed Device Analysis, Steady State Photocapacitance:

Hardware to do steady state photocapacitance (PHCAP) has been designed, built and tested in our laboratory. The photocapacitance technique measures changes in device capacitance under the illumination of sub-bandgap monochromatic illumination. The measurements are done at 77K. The relative magnitudes of the capacitance changes in the PHCAP spectrums are proportional to the defect densities. The PHCAP spectrums for our devices processed at various conditions are shown in Figure 4. The yellow curve with X markers in Figure 4(a) is a device that received no $CdCl_2$ treatment. The blue and pink curves are devices that received poor and optimum $CdCl_2$ treatment respectively. The poor $CdCl_2$ treatment shows greater defect density than those with the optimum $CdCl_2$ treatment. As shown in Figure 4(b) the devices with Cu back contact have lower photocapacitance than the devices without copper. A correlation between initial device efficiency and defect densities has also been shown. The photocapacitance has been normalized to the intensity of illumination at different wavelengths.



(a) (b)

Figure 4: Normalized PHCAP spectrum of deep states with (a) varied $CdCl_2$ treatment, (b) with and without the Cu back contact.

The capacitance increases with incident light in Figure 4 are related to the emission of holes from deep states and the decreases in capacitance are related to the emission of electrons from deep states. However due to the complex interactions of multiple deep levels (both majority and minority traps) with possible overlap of optical cross sections it is difficult to assign exact emission threshold energies. Further work is underway to understand the PHCAP spectrums. Taru Takamia has completed a MS thesis on PHCAP and Jim Sites served in his committee. Some of the thesis work is presented here. Two cells processed identically to cells from the PHCAP study were sent to Steve Johnston at NREL for DLTS characterization.

3.3.1 Device Characterization Studies:

A summary of the preliminary work on the transient ion drift (TID) method of characterizing mobile Cu ions was presented in the poster session on May 8th at the 2006 WCPEC4 in Kona Hawaii, (paper enclosed). The WCPEC presentation was an an extension of the results presented in the talk, "Observations of Cu Diffusion in CdTe PV Devices" at the 2006 CdTe R&D Team at NREL. The TID method is well known as a means of characterizing the drift of Cu ions in c-Si material. Using TID it is possible to obtain the density and the diffusion coefficient of Cu ions. The work in our lab is an attempt to adapt the TID method to thin (2 µm) polycrystalline CdS/CdTe devices. An initial study of CdS/CdTe devices using TID indicates that increasing the quantity of Cu applied during the back contact formation process increases the Cu_i^+ density. However, for devices with an optimum $CdCl_2$ treatment the Cu_i^+ density is on the order of 2E13 cm^{-3}. Also a preliminary estimate of the Cu ion diffusion coefficient is $D(Cu_i)$ = 1.3E-6 [cm^2/sec] * exp(-0.29 eV/KB*T) which closely matches the value found by others for Cu_i diffusion in c-CdTe. The WCPEC4 paper qualitatively discusses the possible effects of grain boundaries, a thin neutral region and a non-uniform doping profile on TID measurements. In order to use TID as a practical method for characterizing Cu diffusion in CdTe PV devices more work is needed to quantitatively address these issues. Al Enzenroth met with Xuanzhi Wu and Su-Huai Wei at NREL on June 29th to discuss Cu diffusion mechanisms in CdTe.

Some of the preliminary work on the photocapacitance (PHCAP) method of characterizing deep states or traps was presented at the 2006 EMRS in Nice France (paper enclosed). The EMRS presentation was an extension of the results presented at the 2005 CdTe R&D Team at NREL,in the talk, "Steady State Photocapacitance (PHCAP) Study of CdS/CdTe PV Devices".

The introduction to the EMRS paper discusses problems in using deep level transient spectroscopy (DLTS) and thermal admittance spectroscopy (TAS) to characterize thin CdTe PV cells that have nearly depleted absorbers. Photocapacitance and optical DLTS with sub-bandgap light are shown to be promising techniques for characterization of deep levels in thin CdTe devices. Both steady state and transient PHCAP were used to characterize deep states related to the $CdCl_2$ treatment in thin CdTe PV devices. In the study it was found that a non-optimum $CdCl_2$ treatment increased the density of deep states while an optimum treatment decreased the density of deep states over an untreated sample. Three distinct deep levels were found the upper half of the band gap in all devices surveyed. A discussion of possible assignments of defects to these deep levels is presented.

A collaboration has been initiated with Anura Samantilleke of the Department of Chemistry at the University of Bath in the UK to characterize our CdTe devices using modulated electroreflectance (ER). The ER technique was described in a presentation by Ramesh Dhere entitled "Study of CdS/CdTe Junction by Modulated Reflectance", at the 2006 CdTe R&D Team meeting. Initial ER results from the University of Bath are promising. An example ER spectrum is shown in Figure 5 below. There are two critical points for CdTe in Figure 5 at 1.482 eV and 1.525 eV. These values would indicate that there is little or no intermixing of S into the CdTe layer. The fit to the ER data also indicates that the crystalline quality of the CdTe is very good. Also there is a "lift off" of the ER spectrum at ~ 2.4 eV near the band edge energy of CdS. Since the spectrum continues to increase towards higher energies this is an indication of intermixing of the SnO:F TCO and the CdS layer.

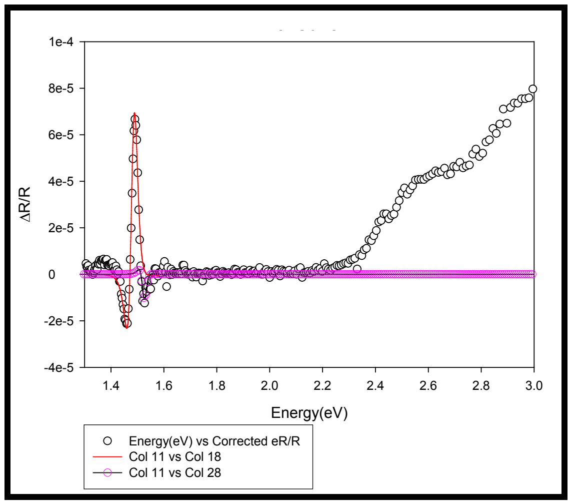


Figure 5: Electroreflectance spectrum of fully processed CdS/CdTe PV cell. Colored traces are fits to the ER data (black)

Fred Seymor of Colorado School of Mines has performed admittance spectroscopy measurements on several cells fabricated at the CSU MEL. These cells included poor $CdCl_2$ without Cu and good $CdCl_2$ with and without Cu. A brief summary of the results follows. For poor $CdCl_2$ without Cu there was a uniform spatial distribution of deep states with an activation energy of 0.320 eV. For a cell with good $CdCl_2$ treatment there was a uniform spatial distribution of deep states with an activation energy of 0.130 eV. This deep state may be assigned to the Cl A-center complex or other states related to Cl. The addition of Cu to a cell with a good $CdCl_2$ treatment introduces a deep state at 0.350 eV. This deep state has a relatively high density and a non-uniform spatial distribution. The decrease in capacitance signal with increasing temperature indicates a steep concentration gradient near the back contact. This deep state may be assigned to Cu_{Cd}. In all three cells there was evidence of deep states with a continuous energy band with activation energies deep in the band gap. The concentration of this distributed band was lowest for the cell with good $CdCl_2$ with Cu.

3.4 Modification of the Pilot System.

The pilot system for processing 3.6 x 3.1 inch substrates is being modified to more closely simulate the back contact processing for actual industrial manufacturing. With the current configuration of the pilot system, Cu is introduced immediately after the $CdCl_2$ treatment steps. The substrate enters the copper process at too high a temperature resulting in devices with high Rs. To avoid this, a pause is introduced after the $CdCl_2$ treatment step to allow the substrates and process sources to cool. After a nominal 3 hour wait, the substrate motion direction is reversed and the now cool samples are exposed to a vapor flux of the Cu compound followed by annealing. This completes the formation of the Cu containing back contact.

To simulate the Cu back contact process for actual production the pilot system is being lengthened to allow fabrication of devices without the pause and change in substrate motion ("all forward" process). The modified pilot system would also allow processing of devices in a manner which emulates a continuous production system. In addition, new process methodologies can be investigated which can not be performed on the unmodified system. These include longer $CdCl_2$ treatment times and copper processing. The current system is not long enough to apply the back contact with the longer $CdCl_2$ processing. The longer $CdCl_2$ processing times have resulted in devices with higher Voc and Jsc without the Cu back contact processing. This milestone will enable precise definition of conditions for all the semiconductor processing steps (including the back contact) needed to fabricate high efficiency, stable CdTe devices. This process definition will be implemented in the 2 MW/yr. production prototype system for 16.5 x 16.5 inch substrates.

A large number of experiments have been performed to explore the feasibility of reducing the time needed to cool the substrate before the copper processing. This will reduce the length of the "all forward" system. Active contact conduction cooling of the substrate (rather than radiation cooling) has been investigated. This would lead to a reduction in the length of the vacuum system and an increase in process control. Many thermal interface materials were explored including silicone polymers with fillers. These materials were not suitable for repeated contact with the substrate. A structure made from water cooled copper plate and multiple foils extending for contacting the substrate was also tested. Preliminary heat transfer analysis and experiments suggest that contacting the substrate with a copper plate with a flat, smooth surface should be adequate for cooling the substrate.

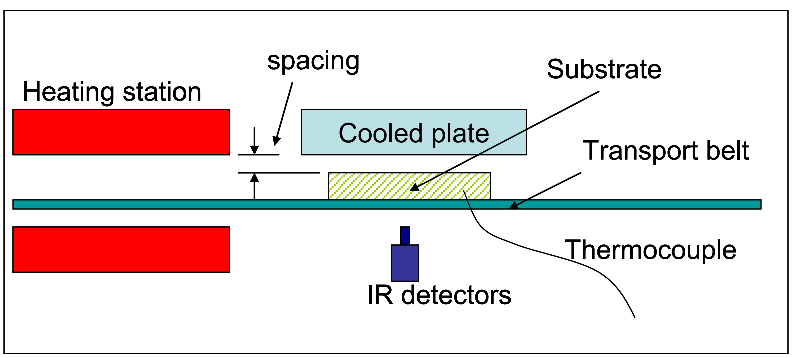


Figure 6: Schematic of contact cooling test apparatus in vacuum chamber

A series of measurements of the cooling rate of glass substrates were performed with the test apparatus shown schematically in figure 6. The apparatus was installed in our pilot system. This allowed for the transport the glass substrates through the heating station and then under the water cooled plate. During measurements, the pressure was varied between 1 Torr and 40 mTorr and one measurement was done at atmospheric pressure as a control. The spacing between the water cooled plate and the glass substrate indicated in Figure 6 was a close contact in most of the cases. In one case a space of 0.010 inch was maintained. The substrate was heated to 170 C in the heating station and then indexed under the contact cooling plate. Measurements of the substrate temperature were performed with either a thermocouple or with two infrared (IR) sensors. The water cooled plate was maintained at approximately 20 C.

The results of the temperature measurements are shown in Figure 7. As shown in Figure 7 there is an increase in cooling rate with and increase in background pressure. The fastest cooling rate was at atmospheric pressure. In this case convection from the bottom of the substrate can not be neglected. However other tests at atmospheric pressure where the bottom of the substrate was insulated to prevent convection (not shown) closely match the result shown in Figure 6 for atmospheric pressure. Also shown is the predicted cooling rate for radiation alone. The contact cooling rate in all cases was faster than simple radiation. At a background pressure of 1 Torr the substrate cooled to 37 C in two minutes and 30 C after 4 min. Also shown is a case at 1 Torr pressure where the cooling plate was spaced away from the substrate by 0.010 inches. In this case the cooling rate closely matches the rate of a substrate in direct contact to the cooling plate at a pressure of 300 ~ 400 mTorr.

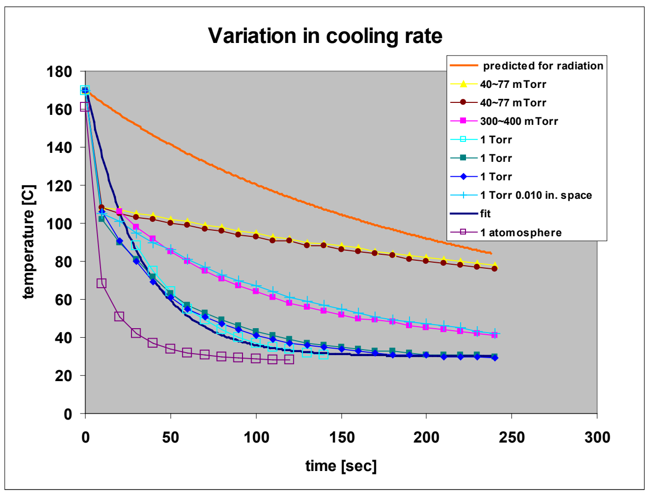


Figure 7: Plot of substrate temperature with time for different background pressure and cooling plate spacing. Open symbols indicate thermocouple measurements; closed symbols indicate IR sensor measurements. All substrates used for the IR measurements had a CdTe film.

The results indicate that an adequate cooling rate can be obtained with a minimum pressure of 1 Torr of nitrogen gas. The cooling plate is best maintained in close contact to the top surface of the substrate. No glass cracking was observed during any of the testing. A reasonable fit to most of the data could be obtained by using a temperature difference model $dT = K*(T1-T2)*dt$ where the T2 is the cooling plate temperature and T1 is the substrate temperature, dT is the change in substrate temperature in time dt. The constant K is dependant on the ambient pressure. A comparison of the substrate temperature measured by the two IR sensors indicates that the cooling of the substrate is uniform within approximately 4 C. Based on the above experiments a fixture to contact cool the substrate that allows the contact cooled regions to be raised to 1 Torr ~ 10 Torr pressure is being designed and will be fabricated and implemented in the pilot system. Since the operating pressure is typically 40 mTorr, the fixture will be sealed against the substrate using O ring seals.

3.4. Large Area Processing:

A production prototype system has been developed to process larger substrates. This activity is supported by DOE-EERE and cost shared by National Starch and Chemicals (NSC).

This is an Inventions and Innovation Program award to AVA Technologies LLC and is the only Category 3 award ever granted by this program. The results described in this Section 3.4 are partially supported by this program and performed by AVA Technologies in collaboration with CSU's Materials Engineering Lab.

3.4.1. Processing Larger Substrates

The semiconductor deposition system for the 2MW/Yr production line was designed to be fabricated in modular sections. One section of the vacuum chamber including the substrate transport and four deposition stations has been fabricated and two stations have been tested. Load locks to bring substrates into and out of the vacuum space have also been fabricated and substrate motion has been tested. The new modular section includes all pump ports, feedthroughs, access doors, water cooling plates and a support frame is currently being fabricated. Many 16.5 X 16.5 inch substrates have been heated from 25C to ~500C in two minutes with no glass cracking.

3.4.2 Thermal Uniformity Measurements in the large area substrates

In order to obtain consistent device performance, a high degree of thermal uniformity is desired. Steady state temperature measurements of the graphite blocks in our deposition sources showed a ± 1.5° C variation on a 400º C base across the 14.5 x 14.5 in. pocket. In order to develop a model of the temperature distribution in the substrate, finite element analysis (FEA) simulation of substrate temperatures have been done at CU Boulder. The preliminary results predict that the substrate temperature difference would be larger during transient motion than during steady state conditions. A series of temperature measurements were undertaken to provide feedback to the FEA model and to give an initial map of thermal uniformity during transient substrate motion.

The temperature measurements were performed by using thermocouples mounted in the glass substrates. A diamond coated drill bit was used to drill 0.040 in. diameter holes 0.125 in. ~ 0.25 in. deep into the glass substrates and the thermocouples were inserted into the holes. The measurements were performed at pressures and source temperatures that would be used during prototype production. The experimental setup is shown in Figure 8. It was not possible to pass the thermocouples through the load locks so the substrate was placed in position 1) in Figure 8 during warm-up of the heater.

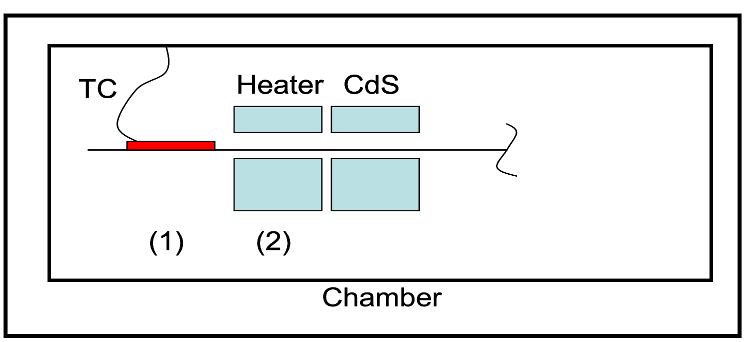


Figure 8: Schematic of temperature measurement setup

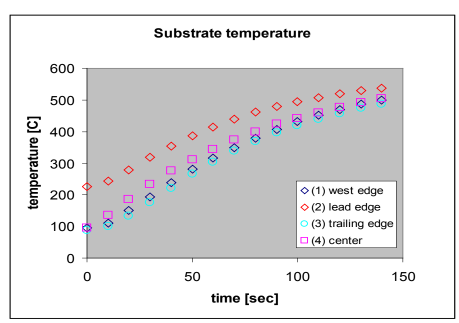


Figure 9: Measured substrate temperatures at selected points.

After the heater and CdS source had reached operating temperature the substrate was moved from position 1) to position 2) in 6 seconds. The substrate was held in position 2) for 140 seconds to acquire the temperature data for the substrate heating sequence. At the end of 140 seconds the substrate was moved back to position 1). Figure 9 shows temperature vs. time data for selected points on a substrate during the heating sequence. The initial temperatures at t = 0 are for the substrate in position 1) of Figure 8. The heating sequence begins at t = 10 sec when the substrate is in position 2) of Figure 8. As can be seen in Figure 9 there is a large spread (~ 125º C) in initial temperatures. This is due to the fact that for the sources to reach operating temperature requires about 2 hours. This initial temperature difference will be much smaller during actual process operation when the pause time will be 2 minutes.

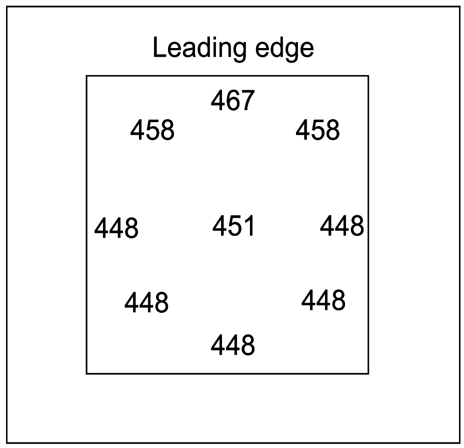


Figure10: Predicted substrate temperature [ºC] exiting heater, entering CdS station.

The most pertinent temperature difference in the raw data shown in Figure 8 is between the center and the west edge since these points start at t = 0 within 1º C of each other. The final temperature difference is 3º C after 120 seconds. This is an acceptable amount of variation.

As mentioned above the initial temperature difference between the leading edge and the other points is large. One other factor that affects the raw data shown in Figure 8 is that the leading edge has been heated for six seconds more than the trailing edge. This slow indexing time was used to eliminate damage to the thermocouple probes. In actual operation the substrate index time to move from station to station will be faster. In order to use the raw data to predict actual substrate temperatures during a process run the raw data was "normalized". This was done by using a data fit to the measured raw data. The data fit was a bulk Euler integration model using glass parameters from the manufacturer.

The initial substrate temperatures were predicted using calculations based on radiation heat transfer. The time of heating the glass was normalized to 120 seconds of heating time. This is valid since all points on the substrate will have received 120 seconds of heating as the substrate passes into the CdS station. The bulk model was then used with the estimated initial starting temperatures and a uniform heating time to predict substrate temperatures as the substrate enters the CdS station. The center to edge temperature difference of 3º C was preserved. The resulting substrate temperature uniformity map is shown in Figure 9. As can be seen in Figure 9 the predicted temperature for the center of the leading edge is 16º C hotter than the center of the substrate. This is the greatest predicted variation.

The FEA model predicts that substrate uniformity will only increase as the substrate passes through the CdS and CdTe stations. So the thermal variation shown in Figure 9 should decrease as the substrate continues to be processed. However, it is desirable to decrease the thermal variation of the substrate in the heating station. Efforts are currently underway to reduce the temperature variation. The radiation shielding in the heater is being modified to reduce the heating of the leading edge of the substrates before they enter the heater. The real time measured data is also being used to refine the FEA model.

3.5. Cost Estimates for Large Scale Manufacturing with our Technology

A detailed cost analysis was conducted to determine the manufacturing and facility costs for manufacturing CdTe PV by our technology. In addition the development costs to advance the technology from the current pilot stage to a manufacturing stage was estimated. These analysis were performed by AVA Technologies LLC of Fort Collins. The methodology and results are summarized here.

3.5.1 Manufacturing Cost Analysis Background:

A detailed cost analysis was performed for a 20 MW/yr. PV manufacturing facility using our technology. This analysis uses knowledge developed from the operation of the pilot scale manufacturing facility since 1997 and the development of a production prototype system for processing 16.5x16.5 inch substrates. A manufacturing plant with an annual throughput of nominally 20 MW/yr. processing 120x60 cm frameless modules with a 63 watt rating is the basis for the analysis. This plant throughput was chosen because it represents an incremental step towards large scale manufacturing and is comparable to other facilities. Please note that in this analysis no building or land capital costs are included. However, equipment costs and rent are included.

- Nominally 20 MW/yr. facility
- Operating 2 shifts/day, 7 days/week, 49 weeks/yr.
- 120x60 cm thin film modules
- Module rating of 63 watts
- Glass/glass laminate package without frame (typical for CdTe PV)

3.5.2 Methodology: Significant effort was taken to ensure the accuracy of the data and the validity of the estimations used to generate this analysis. With almost no exceptions, all the equipment and materials costs and labor requirements used in this analysis were obtained from direct quotes or consultation with reputed vendors. This was augmented with the combined 35+ years experience of CSU's Materials Engineering Lab in thin film PV and vacuum equipment design. The analysis was performed using a spreadsheet which was provided to Ken Zweibel of NREL.

- The equipment and materials costs and labor requirements used in this analysis were obtained from direct quote or consultation with reputed vendors.

- Detailed, automated spreadsheet was utilized to generate costs.
- There are 25 processes to produce modules with this advanced technology. Most of the processes utilize commercially available standard industrial equipment optimized for high throughput.
- Thin film modules are monolithically integrated and have no "cell" stage of processing. There are many significant differences in both the semiconductor and packaging processing between c-Si and thin film modules.

The results of the analysis demonstrates that this CdTe thin film PV manufacturing technology has significantly lower manufacturing and equipment costs than other PV technologies.

- The manufacturing costs for modules are less than $1.00/Watt.
- These manufacturing costs are significantly lower (approximately 3-4 times) than other technologies according to data from another study [NREL 2005].
- The one time equipment costs are less than $10 million for 20 MW/yr. facility.
- These one time equipment costs are at least 5 times lower than the published costs for other technologies.

The equipment cost for the 10 MW Antec CdTe thin film facility in Germany was estimated at $27 million [Bonnet 1992]. This facility has only half the throughput of the facility described here. A 30 MW Q-cells factory (crystalline silicon cells and modules) is approximately $75 million [Solarbuzz 2005]. Wurth Solar intends to invest approximately $66 million in a 15 MW thin film CIS facility [Solarbuzz2 2005].

Technology	Facility cost ($ million, normalized to 20 MW/yr.)
CdTe thin film reported here	**approx. $10**
Antec (CdTe)	$54
Q-Cell (silicon)	$50 (May include building, not all modules, some cells)
Wurth Solar (CIS)	$88 (May include building)

The module packaging and the substrate preparation processes are quite similar between the different technologies. The difference is primarily in the semiconductor processing. Since 1991, the focus of our efforts has been to reduce the cost of the thin film semiconductor PV processing. The cost advantages of our in-line, continuous, lean manufacturing technology can be clearly seen from the above numbers.

3.6 Modification of the Pilot System

3.6.1. Cooling Substrates in Vacuum.

The pilot system for processing 3.6 x 3.1 inch substrates has been modified to more closely simulate the back contact processing suitable for actual industrial manufacturing. With the old configuration of the pilot system, the Cu back contact process head is located immediately after the $CdCl_2$ treatment heads. If the substrate enters the copper process at too high a temperature, the resulting devices have a high series resistance. To avoid this, a pause to cool the substrate was introduced in the old configuration of the pilot system. After a nominal 3 hour wait, the substrate motion direction is reversed and the now cool samples are exposed to a vapor flux of the Cu compound followed by annealing. This completed the formation of the Cu containing back contact in the old configuration. The old configuration is not suitable for large volume manufacturing.

To simulate the Cu back contact process for actual production the pilot system has been lengthened to allow fabrication of devices without the pause and change in substrate motion ("all forward" process). The modified pilot system would also allow processing of devices in a manner which emulates a continuous production system. An automated system for cooling substrates in vacuum has been designed, fabricated, installed and tested. The cooling fixture was tested with automated substrate movement. The substrates were heated to 200 C and after 4 minutes of radiation cooling were cooled with the fixture to 26 C in two minutes. The results indicate that an adequate cooling rate can be obtained to maintain a cycle time of 2 minutes. The measurements of substrate temperatures were performed with infrared sensors. The cooling of the substrates during processing was measured by IR detectors. A journal article has been drafted on the in-situ cooling approach and has been published by the Journal of vacuum Science and Technology. A patent application has also been filed. Device efficiencies of 11.83% have been obtained with an "all forward" process. **It is noted that the total time for processing the 11.83% device is only 22 minutes.** This includes glass heating, CdS deposition, CdTe deposition, CdCl2 treatment and back contact processing.

The modified pilot system will enable precise definition of conditions for all the semiconductor processing steps (including the back contact) needed to fabricate high efficiency, stable CdTe devices. This process definition will be implemented in the 2 MW/yr. production prototype system for 16.5 x 16.5 inch substrates.

3.6.2. Modification of the Seals:

The pilot system for processing 3.1 X 3.6 inch substrates has a differentially pumped air-to-vacuum-to-air seal that has a glass filled teflon liner for supporting the belt. This system has been operational since 1997. This system has been used to process nearly 10,000 substrates. The wear in the liner is causing the substrate to contact the seal and this leads to pinholes. In addition, the adhesive bond between the teflon liner and the aluminum support plate had also degraded. A new teflon liner with improved attachment to the aluminum support plate has been designed, fabricated and tested .

3.6.3. Strip Cells:

Many large area devices in the form of narrow strips of ~0.7 cm. wide and 4 sq. cm. total area were processed to study the performance of these devices. The widths are representative of cells in modules. Devices were tested at NREL and the efficiency of 10.88% was measured and efficiency of 11.1% was also measured independently at IEC. These measurements indicate that module efficiency of 10% based on active area is feasible with our technology. The 10% module efficiency was utilized in the cost calculations developed for our technology. These calculations were sent earlier and summarized in the recent AVA Tech. team presentation.

3.7 Higher Efficiency

We have demonstrated NREL verified efficiencies of 12.44% on unmodified Pilkington TEC15 glass. In order to obtain higher efficiencies, low iron sodalime (white glass) glass plates have been obtained and cut to size suitable for our pilot system. Fifty substrates have been sent to Sierratherm for APCVD (atmospheric pressure CVD) coating with TO:F. The coated substrates have been received and have been given to Professor Sites' group for optical studies. Coated samples have also been received from Solaronix. Deposition experiments with these substrates will be performed soon. The APCVD process is suitable for low cost high volume processing. After the current batch of samples, the use of barrier layer deposited by APCVD and other methods will be investigated. Discussions have been held with Pillkington and PPG and they have indicated that they may produce white glass with "TEC" type tin oxide coating in the future.

The coated substrates have been studied and the results are:

A. The optical transmission of low iron glass in the visible spectrum is comparable to 7059 borosilicate glass (nearly 92% without AR coating). 7059 glass has been used in many high efficiency devices.

B. MgF_2 AR coating has been used in many high efficiency devices. MgF_2 is slightly soluble in water and may not be suitable for outdoor applications. The MgF_2 could be replaced with an oxide AR coating made by a pyrolytic process. Oxide AR coated substrates were obtained from Denglass and these substrates have very similar transmission to MgF_2 coated glass.

C. Significant decrease in the transmission (~ 3 mA/sq. cm.) has been observed due to the TO:F coating. Efforts to reduce the transmission losses in the transparent conducting oxide are currently underway.

Deposition experiments with substrates from Sierratherm have been performed. In one run the average efficiency of devices with the Pilkington TEC 15 substrates was 10.8%. The efficiency with white glass substrates was 12%. Cross-sectional SEM studies showed that the white glass had a higher thickness for CdS (nearly 1800 angstroms). This indicates that optimization of CdS thickness would result in higher efficiency. These efforts are currently underway. After the current batch of samples, the use of barrier layer will be investigated. A few substrates with intrinsic tin oxide barrier coating have been obtained from Chris Ferekides. The coated substrates have been studied and the results are shown in Figure 11 below.

Three different substrates have been investigated for higher efficiency. These are: TEC15, Low Fe, and Low Fe with i-SnOx coating. The i-SnOx coatings were provided by Chris Ferekides of USF. Our current standard process produces Jsc of 20 mA/sq. cm. at ~800mV.(open blue squares have slightly smaller CdS thickness compared to the standard). When the CdS thickness was reduced, an increase in Jsc was observed, but the Voc decreased. Nearly 100 substrates and 24 devices were part of the thin CdS study. Six devices have been provided to Prof. Sites' group for LBIC and QE studies.

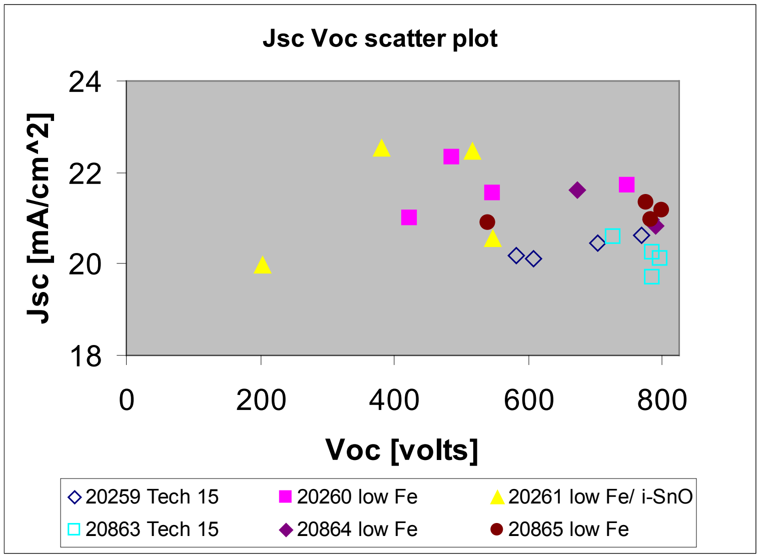


Figure 11: Jsc Voc scatter plot of devices with thinner CdS on three different substrates

Further optimization of the TCO and CdS will be needed for obtaining higher efficiencies. Four 3 X 3 inch. Low Fe substrates with ITO/i-SnOx coating are being provided by Chris Ferekides of USF. Xuanzhi Wu of NREL has supplied four 3 X 3 inch LOF TEC 15 substrates with a ZTO buffer layer. These substrates will be used for future efforts to increase device efficiency.

In order to obtain higher efficiencies, more transparent glass plates with ITO applied by planar magnetron sputtering and ZnO:B by LPCVD have been obtained. These substrates have transmission greater than 90% between wavelengths of 500 to 800 nm as compared to ~74% for TEC15. These substrates did not produce devices with higher efficiencies.

Devices that have 25 mA/sq. cm. current density with Voc of 800 mV. (JV plot shown in Fig. 12) have been made in our laboratory. The values were also got from the JV tester at AVA. Both testers are calibrated with devices from NREL. These use ITO coated glass that is more transparent and commercially available. This current density is nearly 25% higher than the normal 20 mA/sq. cm. These do not have the AR coating and with AR coating we can get to 26 mA/sq. cm. The glass is low iron white glass and back contact processing was not applied to the device. With optimization, we should be able to make 14 to 15% small area devices and 11 to 12% modules and these efforts are currently underway.

Devices of efficiency 12.8% (NREL verified) have been fabricated on low iron glass with SnOx:F TCO. Devices of efficiency 13.7% (tested at CSU photovoltaics lab.) have been fabricated on low iron glass with SnOx:F TCO without AR coating.

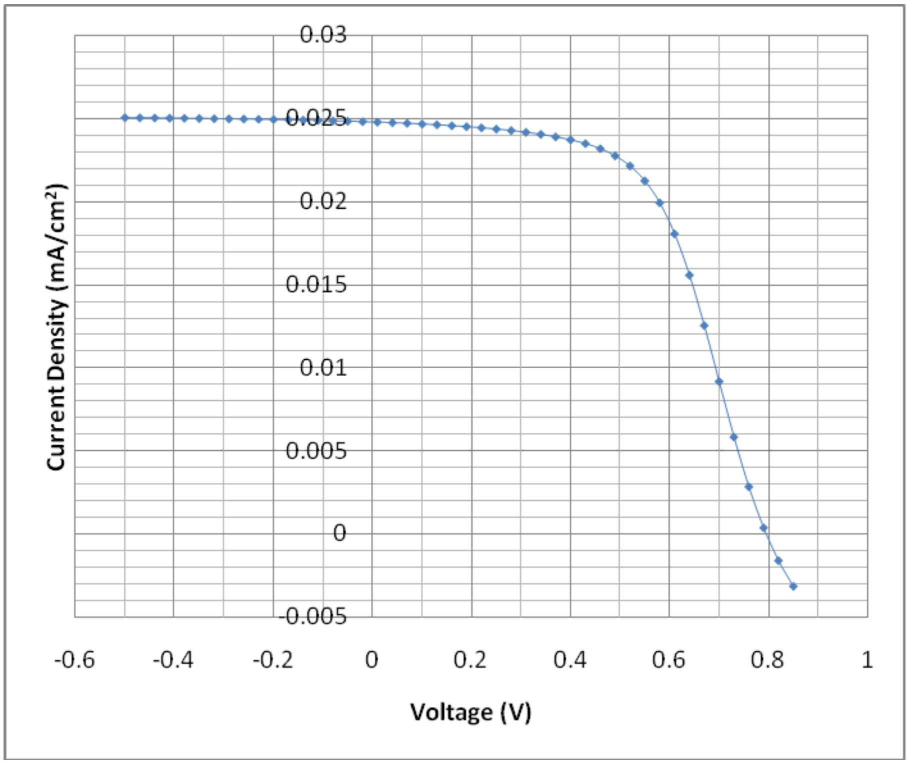


Figure 12. J_V curve for devices with more transparent ITO.

<u>3.8. On-Line Process Control:</u>

Spectroscopic ellipsometry is being investigated as a tool for on-line process control. It is hoped that ellipsometry would provide a nondestructive means of measuring thickness uniformity of CdS/CdTe films on large areas. It is also possible that by tracking optical constants measured by ellipsometry it would be possible to correlate this data to process variation. Efforts are underway to qualify the technique and verify its usefulness.

In order for ellipsometry to predict layer thicknesses and optical constants for a multi-film stack an analytical model must be developed. Sandeep Kohli of the CSU central instrumentation facility has used a J. A. Woollam Vase ellipsometer to collect experimental spectrums from several samples processed in our laboratory. Working in collaboration with the Woollam Co. Sandeep constructed an analytical model to predict the optical constants and layer thicknesses for the measured samples. The model fit to the experimental data for a representative sample is shown in Figure 13. The model has 14 layers and the mean squared error for this fit is 24.22, which is considered to be a good fit.

The most difficult part of developing the analytical model was to obtain a good fit to the glass/SnOx substrate. Sandeep eventually used 6 layers including one layer with graded optical constants to fit the measured data. Initial profilometry measurements of the CdS/CdTe layer thickness match the CdS/CdTe thickness predicted by the model. Cross sectional SEM characterization of the samples is also underway to verify the ellipsometry data.

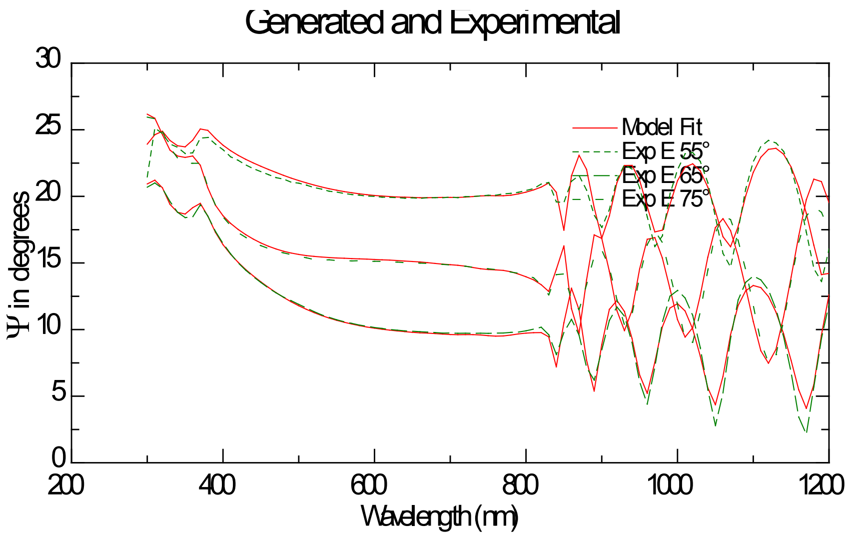


Figure 13: Spectroscopic ellipsometry data and model fit for a LOF Tec 15 substrate with SnO:F/CdS/CdTe:Cu which had received $CdCl_2$ treatment.

At this point a reasonable model has been obtained and now the predictive capability of the model must be further verified. Optimization and further development of the model will also be pursued. Al Enzenroth of the CSU Materials Engineering Laboratory attended a four day spectroscopic ellipsometry short course on data analysis presented by the Woolam Co. at Arizona State University. In order to exercise the model more samples with varied film thicknesses will be fabricated. Ellipsometry data will be obtained from these samples and the model predictions will be checked. Multiple ellipsometry measurements on 3 in. X 3 in. samples will also be performed to measure uniformity.

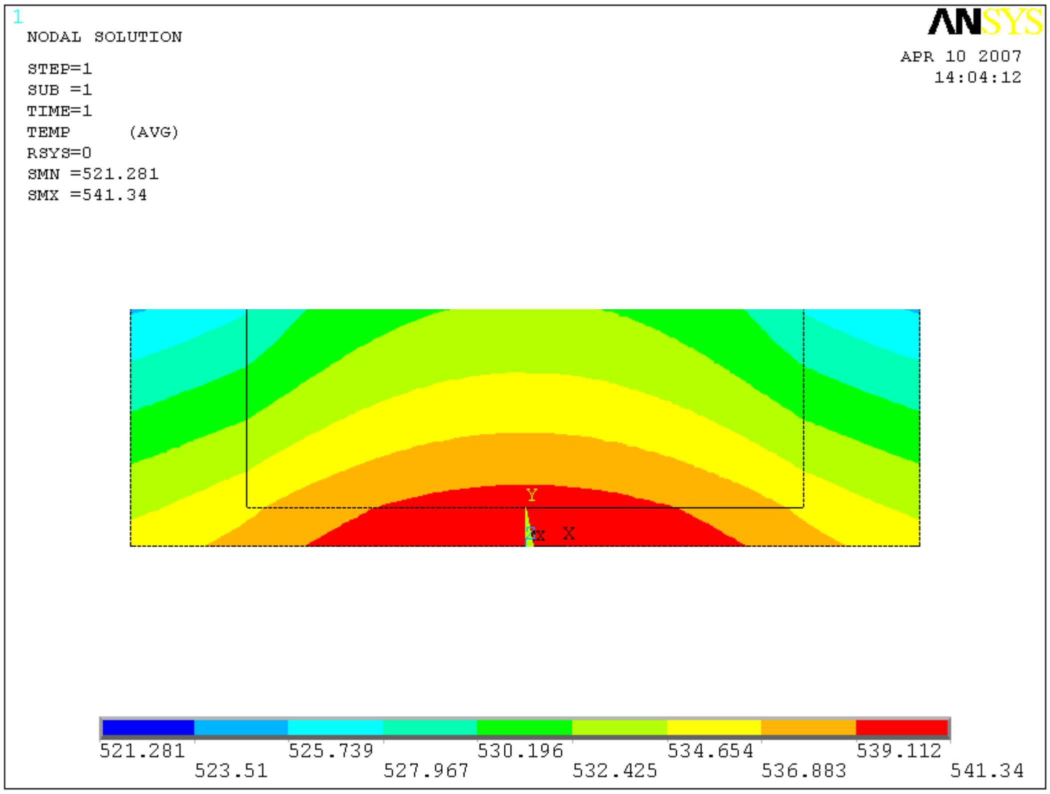
It has been shown that the refractive index n and the extinction coefficient k change with the processing and n and k values approach single crystal values after the chloride treatment. In addition to ellipsometry where changes in polarization are measured, the use of total intensity for on-line process monitoring is being investigated and the results are promising. Two journal articles have been written on the ellipsometry results and both have been accepted for publication.

In addition to the use of ellipsometry, the use of x-ray floroscence (XRF) for process monitoring and control has been demonstrated. Quantitative relationship between the film thicknesses and the x-ray signal in XRF has been developed. The feasibility of measuring the amount of copper in the samples used for the back contact has also been shown. The studies with XRF was performed by Nathan Schuh, a graduate student in our laboratory.

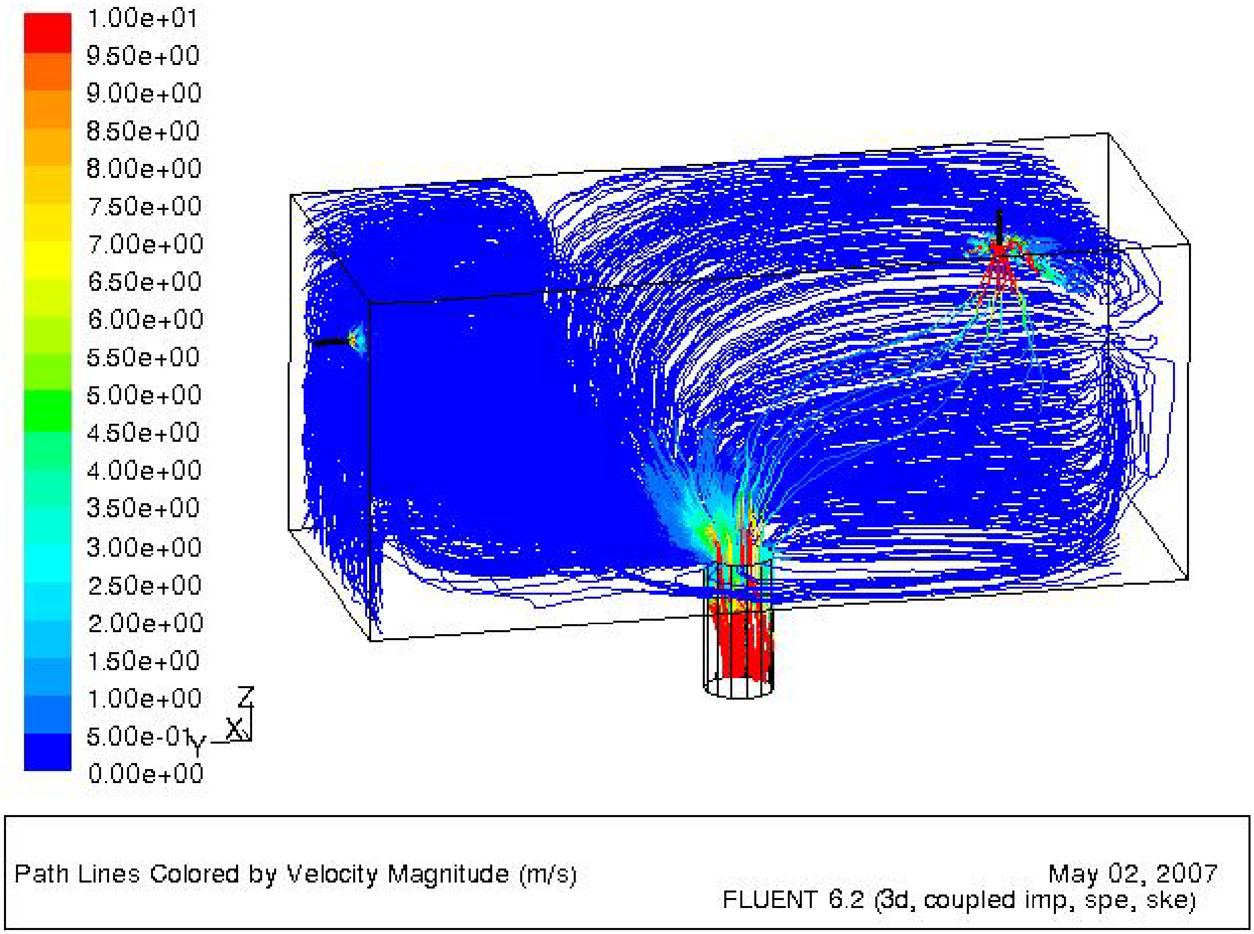
3.9 Numerical Modeling:

3.9.1. Thermal Modeling: Many designs of the large area (2' X 4') vapor sources have been analyzed with the finite element method (FEM) for thermal uniformity. These models included non-linear radiation boundary conditions and body to body radiation. The designs were analyzed with the ANSYS finite element software. More than 18 different cases were analyzed. A typical result of the analysis is given below. The temperatures are in degrees C. The results shown below are for the bottom plate of the CdTe source perpendicular to the substrate motion in the center.

The results are for a design with adequate radiation shielding that results in good thermal uniformity. The results indicate that thermal uniformity of ± 2 C can be obtained on a horizontal plane.



3.9.2. Modeling Gas Flow: A detailed modeling of the gas flow in the 3" X 3" pilot system using computational fluid dynamics (CFD) using the software FLUENT has been completed. The modeling was performed by a senior Dan Sweeney in our department with the help of his advisor Prof. Hiroshi Sakurai. The modeling showed that the pressure distribution within the pilot system was very uniform. There was a concern that the numerous vapor sources and other structures combined with the gas flow could lead to non-uniformities in pressure and the modeling showed that this was not the case. Currently nitrogen and oxygen are injected into two separate ports in the system. Based on the modeling it was decided to mix the gases prior to the injection to obtain more uniform distribution of the composition. A gas mixing unit has been designed with CFD modeling. CFD modeling of the larger system has been completed. An example of the flow patterns from the CFD modeling is shown below. The modeling showed that the use of commercially available gas diffusers significantly reduce the exit velocities at gas injection.



In addition to the above, many modeling studies have been completed. These include:
a. Calculation of the sticking coefficient show that only one in 50 condense. This is for the CdTe source. This explains why the film uniformity is better than the temperature uniformity.
b. The vapor pressure of CdS in the CdTe source is likely to incorporate 0.7% CdS in the CdTe film and this will lower the bandgap of the film slightly. The vapor pressure of CdTe in the CdCl2 source is likely to incorporate 0.017% CdTe in the CdCl2 film. This is unlikely to hurt the Cdcl2 treatment.

3.10 Miscellaneous Studies:
3.10.1 Outdoor testing:

Eleven optimally processed devices are being tested outdoors under open circuit conditions. These devices were recently measured and the results are shown below in Figure 14. It is noted that most of the devices have maintained an efficiency of 10% after nearly 5 years outdoors at open circuit conditions. Accelerations factors of 7 to 100 have been reported in the literature for CdTe devices between open circuit and max. power condition.

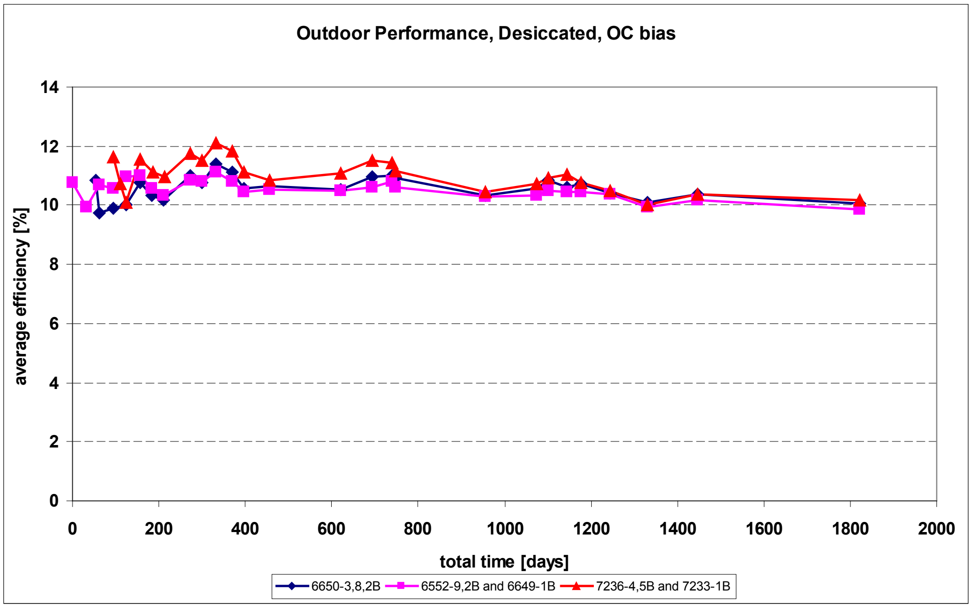


Figure 14: Average efficiency versus time for groups of cells in outdoor test conditions

3.10.2. New Vendor for CdS and CdTe:

Until now, we have obtained CdS and CdTe from ASARCO. Since ASARCO no longer produces CdS and CdTe, we are obtaining these materials from 5N Plus Inc. The new materials have been tested on the pilot system and preliminary results indicate that the optimum process conditions with the new materials are close to that of the old materials.

3.10.3.Cleaning films: We actively looked into removing the coating from waste coated plates prior to diposal. This will substantially reduce the solid waste to be to blast the surface and the CdS and CdTe can be filtered. Five 16 X 16 plates processed by AVA were cleaned by a service provider using abrasive blasting with water. They have constructed a setup to do the cleaning. It takes 30 sec. to remove the coating and overall 2 mins. to place, clean and remove the samples. The cleaned glass plates, water and sand have been tested by the federal TCLP test and found to be non-hazardous. The hazardous material collects at the bottom of the waste water and can be collected for recycling if needed. This provides an attractive means for removing the films before disposal. It is pointed out that the coated films pass the TCLP test and the procedure was developed to keep Cd from landfills. These results have been reproduced in our laboratory using a traditional sand blaster with abrasive slurry. There was no detectable change in the thickness implying that only the coating has been removed.

3.10.4. Thermal Gradient Testing of Glass: A fixture for testing glass under thermal gradients (colder at the edges and vice-versa) have been constructed. Glasses of size 16.5” X 16.5” have been tested. The surface condition of the edge has a significant effect on the glass breakage due to thermal gradients. The #2 ground samples have been found to withstand a gradient of 70C (colder at the edges). No failure was observed when 10 substrates were tested.

4. REFERENCES

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5. APPENDICES

5.1. Description of Activities with the National CdTe Team

Our group supported the basic research efforts of the CdTe Team. We continue to supply devices, films and substrates as well as experimental data to the Team members. A selection of the research efforts supported are listed below:

1) Nine cells and 24 samples were sent to Larry Olsen at PNNL for studies with the moisture barrier
2) Two samples and two devices to CS Jiang of NREL for SKPM
3) Two substrates to C Corwine of CSU PV group for PL
4) Two cells to T. McMahon for Rsh characterization
5) Four cells to A. Fahrenbruch for transient current characterization
6) Twenty cells to A. Davies of CSU PV group for micro LBIC characterization
7) One substrate to Tim Gessert
8) 12 cells with an outdoor fixture to N. Dehre of FSEC for outdoor condition testing
9) Eight full 3.1 x 3.5 in. substrates to CSM for various studies

10) 19 cells were provided to Alan Davies (Prof. Sites' group) and these cells were stress tested and it was shown that at optimum processing, good stability can be obtained. This was presented at the CdTe Team Meeting.
11) Many interactions with Larry Olsen of PNNL regarding the application of CdTe devices for another application have occurred.
12) Graduate student Tushar Shimpi graduated with a MS degree and Jim Sites served on his committee.
13) Two presentations (one by CSU and one by AVA Tech.) were given at the CdTe Team meeting.
14) Twenty slides on our research were provided to Ramesh Dhere of NREL for his tutorial at the IEEE PV Conference.
15) Marc Landry and Ramesh Dhere (both of NREL) and visitors from Ziyax Corp. were given a tour of our laboratory and possibilities of collaboration were discussed. Other visitors include: Steve Johnson, researchers from PPG, etc.
16) Our group has developed a technique for defining CdTe cell areas on glass substrates. The technique consists of applying a contact mask and removal of unmasked areas with an abrasive blast. Xuanzhi Wu supplied four CdTe substrates for initial testing of the abrasive blast technique on NREL devices. Circular areas of ~ 0.69 cm^2 were defined and the cells were returned to NREL for evaluation.
17) Many interactions with Larry Olsen of PNNL regarding the application of CdTe devices for another application have occurred.
18) Al Enzenroth from our group presented papers at the IEEE meeting and E-MRS meeting (discussed above). He also attended the CdTe workshop in France.
19) Collaborations continued with CSM, X. Wu of NREL and a new collaboration with Anura Samantilleke of the Department of Chemistry at the University of Bath in the UK has been initiated.
20) . Five substrates processed upto the chloride treatment were provided to Tim Gessert of NREL for his studies with ZnTe:Cu with a summer student.
21) 2. Alan Davies from the CSU Photovoltaics laboratory has been participating in processing devices in the laboratory.

5.2. Description of Interactions with Industry

Specialty electronic coatings are used as an electrode for our PV devices. These materials are supplied by Acheson Industries which is a part of National Starch and Chemical (NSC is the US subsidiary of the approximately $10 Billion/yr, ICI Group). NSC manufactures critical products for the semiconductor, electronics and photonic industries. Our group has a continuing involvement with NSC to advance CdTe PV under the I and I program. During this last year, 126 substrates to NSC for metallization studies.

A large corporation capable of very large scale manufacturing had expressed interest in pursuing a potential partnership for PV manufacturing with our technology. Numerous teleconferences and site visits have been conducted with high level representatives of the company. Documentation was also provided which includes:

A. A detailed review of any environmental and occupational safety aspects with our technology

B. A detailed break down of the cost to manufacturing large volumes of PV with our technology.

C. A non-disclosure agreement.

D. Description of the advantages of our technology over competing technologies.

E. Details on the intellectual property ownership.

These requests are in support of developing a potential partnership relationship. The environmental analysis was prepared with the assistance of an industrial hygienist and demonstrated that only simple, industry standard environmental health and safety practices are needed for to protect workers in a large scale manufacturing facility using our technology. This effort was enabled by the materials available at http://www.nrel.gov/cdte/.

Peter Meyers and Roger Green of First Solar visited our facility and were given a full tour and presentation on our activities. This was followed with a conference call from Nelson Devoe for possible consulting.

Southwall Technologies and an investor group represented by Jim Frantz were given detailed presentations on the advantages of CdTe PV manufacturing.

Based on their request, Solar Fields has been provided details of our metallization and they were put in touch with NSC.

Five cells were provided to Trace Photonics for Beta radiation studies.

John Bleem from the local utility, Platte River Power Authority, was given a facility tour.

5.3. Additional Activities

The deputy director and two program managers of the Colorado Office of Energy Management and Conservation (OEMC) visited our laboratory and were given a demonstration and brief presentation. They have offered to assist with the technology transfer efforts.

In November 2005, the well known CdTe PV researcher, Dr. D. Bonnet, visited CSU. In addition to visiting J. Sites lab, Dr. Bonnet was given a full tour of the Materials Engineering Lab. A demonstration of our pilot scale CdTe manufacturing system was conducted. The current status of the 2 MW/yr. prototype manufacturing line being developed by AVA Tech. and CSU demonstrated. Dr. Bonnet gave a presentation to our group on CdTe manufacturing facilities of ANTEC of Germany.

We are collaborating with Prof. Roop Mahajan of University of Colorado, Boulder. He is an internationally renowned authority in the field of heat transfer in processing semiconductors. This work through the International Center for Science, a UN agency, in collaboration with our group has been selected for funding. The funding will support two students and demonstration projects in Mexico and India. This will provide more opportunity for studying stability under field conditions.

A series of measurements of the residual stress in the glass substrates after processing through our continuous pilot scale system have been completed as per ASTM C1279. Glass substrates with different levels of residual stress have been sent to the ASU Photovoltaic Testing Lab for hail impact tests. These studies will establish the stress levels needed to pass the hail impact test for modules as per IEC 61646.

Prof. Wilbur's group at Colorado State University was supported with 11 devices and characterization for high altitude balloon studies and the devices performed well in these studies.

These studies were part of the Colorado Space Grant program and efficiencies of 15% were measured at high altitudes at temperatures of -23 degrees C. The results were presented at Jet Propulsion Laboratory.

5.4. Student Activities

Graduate students, Tushar Shimpi, Mark Armijo and Rick Lueb were supported through this project. They have assisted in the activities described in this report. Tushar Shimpi and Toru Takamiya have performed their graduate research on this project and have graduated with Masters degree. The objective of Tushar Shimpi's thesis was to develop an understanding of the hail impact test and Toru Takamiya conducted research on the Photocapacitance method described earlier. Hershel Shelly is conducting his Ph. D. research on this project. His research is to study the pilot scale process from an industrial engineering perspective. Chetan Malhothra of CU Boulder has completed his Ph.D. through thermal and deposition modeling of the process. Marh Armijo has made significant progress towards completing his MS thesis and his study is to understand the mechanics of the composite module.

5.5 Collaborative Studies and Other Activities:

During this phase, the following collaborative activities were conducted:

1.Brian Murphy, Fred Seymour and Russell Black of Primestar Solar were given a detailed tour of the lab. and many insights on the effect of processing on device stability were discussed.
2. Our laboratory was part of an organized self guided tour of the American Solar Energy Society. Nearly 100 visitors visited the laboratory over a six hour period.
3. Mani Manivannan from the Global Research Center of GE has joined our department and is continuing his research on CdTe photovoltaics.
4. Many substrates and devices were processed for a large glass manufacturer with significant interest in developing TCOs for the CdTe PV industry.
5. Three seminars were arranged by Jim Sites, Tim Gessert and Dean Levi. These were well attended by CSU and AVA personnel. These were well received and tapes were sent to researchers in the glass industry.
6. Many substrates and devices were processed for a large glass manufacturer with significant interest in developing TCOs for the CdTe PV industry.
7. Alan Davies from the CSU Photovoltaics laboratory has been participating in processing devices in the laboratory and has accepted a position with AVA Solar. Many devices have been provided for the graduate studies of Alan Davies and Lei Chen from the photovoltaics laboratory under Jim Sites and Sampath served on the committee. Alan has completed his Ph. D. Lei Chen has also accepted a position with AVA Solar.
8 Many substrates with different processing conditions have been processed for Prof. Manivannan for his collaborative studies with NREL on the effect of processing conditions on the films. In his studies with NREL researchers, the lifetimes increased with longer times in the $CdCl_2$ Treatment but the efficiency had an optimum $CdCl_2$ treatment. His article on the diffusion of copper in the solar energy journal has been accepted for publication.

9. Many devices have been provided to Dr. Sanjeev for radiation studies.

10. Many small area devices and modules from AVA Solar are being tested under accelerated testing in our laboratory.

11. Collaborative research on the use of evaporated films for metallization have been conducted in collaboration with Prof. Amy Prieto on chemistry at CSU. Dr. Srinivas, a newly hired post-doctoral fellow in the laboratory conducted the experiments.

12. Collaborative research on the use of ion beam sputtered films for metallization have been conducted with Prof. John Williams of the mechanical Engineering Dept. of CSU .

13. Nearly 40 representatives from the Denver South Chamber were given a lecture and tour of the laboratory.

5.6 Presentation to Senator Salazar:

A detailed presentation was made to senator Salazar and the presentation was well received. The presentation was attended by Harin Ullal and Bolko Vonrodern of NREL and many senior administrators from CSU, City and the County.

5.7. Publications and Presentations from this project:

Sampath, W. S., K. L. Barth, R. A. Enzenroth, "Progress in Continuous In-Line Processing of CdS/CdTe Devices, Including Large Area (16” X 16”) Deposition" presentation to the Solar Program Review Meeting, Denver CO, November 2005. available at

http://www.nrel.gov/ncpv/thin_film/docs/sampath2005solarreview.ppt

Barth, K. L, R. A. Enzenroth, and W. S. Sampath, "Progress in Continuous In-Line Processing of CdS/CdTe Devices Including LargeArea (16 x 16 inch) Deposition" paper for the Solar Program Review Meeting, Denver CO, November 2005. Published in proceedings.

Malhotra, C. P., Mahajan, R. L., Sampath, W. S., “Use of a Commercial Finite Element Software for Predicting Deposition Rates and Uniformity in High Knudsen number PVD”, accepted to IMECE 2005: ASME International Mechanical Engineering Congress Orlando, FL, November 5–11, 2005

"Mass Production of CdTe Solar Photovoltaics" Presentation and facility tour for the Fort Collins, Colorado Chamber of Commerce Chamber Environmental Committee, Oct 12, 2005.

Malhotra, C. P., Mahajan, R. L., Sampath, W. S., Barth, K. L., Enzenroth, R. A., “Prediction of Spatial Evolution of Temperature across Substrates during the Deposition Process for Manufacturing large area CdTe Photovoltaic panels,” submitted to IHTC-13: 13th International Heat Transfer Conference Sydney, August 13-18, 2006

Barth, Kurt, W. S. Sampath, Robert "Al" Enzenroth, "Project Update Facility Tour", Presentation, Discussion and Facility Tour with the with representatives of US DOE, and Industry, April 5, 2005.

Enzenroth, R. Albert, K. L. Barth, and W. S. Sampath, "Correlation of Stability to Varied $CdCl_2$ Treatment and Related Defects in CdS/CdTe PV Devices as Measured by Thermal Admittance Spectroscopy", Journal of Physics and Chemistry of Solids, pp 1883-1886, 66 (2005).

Barth, Kurt, "Mass Production of Thin Film Solar Photovoltaics", Invited seminar For US DOE Golden Field Office March 17, 2005.

Malhotra, C. P., Mahajan, R. L., Sampath, W. S., Barth, K. L., Enzenroth, R. A., "Control of Temperature Uniformity during the Manufacture of Stable Thin-Film Photovoltaic Devices", submitted to International Journal of Heat and Mass Transfer in March 2005

Sampath, W. S., Robert. A. Enzenroth and Kurt L. Barth, "Mass Production of Thin Film Solar Photovoltaics", Presentation, Discussion and Facility Tour with the Fort Collins Utilities, and CSU Facilities, March 3, 2005.

Enzenroth, R. A., K. L. Barth and W. S. Sampath, "Thermal Admittance Spectroscopy Study: Preliminary Observations of a Meyer-Neldel Relationship in CdTe Devices", Invited talk to senior Researchers and managers, NREL Golden CO, February, 16, 2005.

Barth, K. L., R. A. Enzenroth, and W. S. Sampath, "Consistent Processing and Long Term Stability of CdTe Devices", presented at the 31 IEEE PVSC, January 3-7, 2005, Lake Buena Vista, Florida.

Enzenroth, R. A., K. L. Barth and W. S. Sampath, "Thermal Admittance Spectroscopy Study: Preliminary Observations of a Meyer-Neldel Relationship in CdTe Devices", presented at the 31 IEEE PVSC, January 3-7, 2005, Lake Buena Vista, Florida.

Barth, K. L., R. A. Enzenroth, and W. S. Sampath, "Advances in Continuous In-Line Processing of CdS/CdTe Devices: Stability and Scale-Up", DOE Solar Energy Technologies Program Review Meeting, October 25-28, 2004, Denver, Colorado.

Sampath, W. S. K. L. Barth, "Mass Production of CdTe Solar Photovoltaics", American Society of Mechanical Engineers (ASME), Centennial Section Laboratory tour and presentation, Nov. 18, 2004.

Malhotra, C. P, R. L. Mahajan, W.S. Sampath, K. L. Barth, R. A. Enzenroth, "Control of Temperature Uniformity during the Manufacture of Stable Thin-film Photovoltaic Devices", ASME International Mechanical Engineering Congress & Exposition, (IMECE 2004), November 13-19, 2004, Anaheim, California.

Barth, K. L., "Mass Production of CdTe Solar Photovoltaics", Mechanical Engineering Seminar Series, Colorado State University, October 15, 2004.

Enzenroth, R. Albert, K. L. Barth, W. S. Sampath, "Correlation of Stability to Varied $CdCl_2$ Treatment and Related Defects in CdS/CdTe PV Devices as Measured by Thermal Admittance Spectroscopy", 14th International Conference on Ternary and Multinary Compounds, September 27-October 1, 2004, Denver, Colorado, USA.

5.7.1. National CdTe R&D Team Meeting Presentations

Sampath, W. S, R. Albert Enzenroth, and Kurt L. Barth, "Advances in Continuous In-Line Processing of CdTe PV Devices" National CdTe Team Meeting, Sponsored by the DOE through the National Renewable Energy Laboratory, Golden, CO, May 5 and 6, 2005. Available at NREL website: www.nrel.gov/ncpv/thin_film/docs/Sp-top-Sampath.ppt

Barth, Kurt L., R. Albert Enzenroth and W. S. Sampath, "Progress at AVA Technologies LLC" National CdTe Team Meeting, Sponsored by the DOE through the National Renewable Energy Laboratory, Golden, CO, May 5 and 6, 2005. Available at NREL website: /www.nrel.gov/ncpv/thin_film/docs/Ind-AVA%20Tech.ppt#366,1,Progres

Enzenroth, R. A., K. L. Barth, and W. S. Sampath "Estimation of Acceleration Factors by Comparison of Performance During Accelerated Stress and in Outdoor Conditions", National CdTe Team Meeting, Sponsored by the DOE through the National Renewable Energy Laboratory, Golden, CO, May 5 and 6, 2005. Available at NREL website: /www.nrel.gov/ncpv/thin_film/docs/Stab-Al%20Enzenroth.ppt

Enzenroth, R. A. T. Takamiya, K.L. Barth, and W.S. Sampath, "Steady State Photocapacitance (PHCAP) Study of CdS/CdTe PV Devices", National CdTe Team Meeting, Sponsored by the DOE through the National Renewable Energy Laboratory, Golden, CO, May 5 and 6, 2005. Available at NREL website: www.nrel.gov/ncpv/thin_film/docs/Mat-chem-Al%20Enzenroth.ppt

Enzenroth, R. Albert, K. L. Barth, W. S. Sampath, "Stability Sub-Team Meeting" October 25, 2004, Denver, Colorado, USA.

Barth, K. L., R. A. Enzenroth, and W. S. Sampath, "Advances in Continuous In-Line Processing of CdS/CdTe Devices: Stability and Scale-Up", DOE Solar Energy Technologies Program Review Meeting, October 25-28, 2004, Denver, Colorado.

5.7.2 Refereed Journals**:**

Enzenroth, R. A.T. Takamiya, K. L. Barth, and W. S. Sampath, "Photocapacitance Study of Deep Levels in Thin CdTe PV Devices", accepted in Thin Solid Films (2006)

Robert A. Enzenroth, Kurt L. Barth, W. S. Sampath and V. Manivannan, "Measurement of cooling rates of a superstrate cooling apparatus for an integrated in-line manufacturing process for thin-film photovoltaic devices", Accepted to the Journal of Vacuum Science and Technology, 2006

R.A. Enzenroth, K.L. Barth, W.S. Sampath and V. Manivannan, " In-line manufacturing of CdTe thin film photovoltaic devices", Submitted to Journal of Manufacturing Science and Engineering, under review.

R.A. Enzenroth, K.L. Barth, W.S. Sampath and V. Manivannan, " Performance of in-linemanufactured CdTe Thin Film Photovoltaic devices", Journal of Solar Energy Engineering, vol 129, (2007) 327.

R. A. Enzenroth, Kurt L. Barth, W.S. Sampath and V. Manivannan, " Measurement of cooling rates of a superstrate cooling apparatus for an integrated in-line manufacturing process for thin film photovoltaic devices". J. Vac. Sci. Technol. A 25(2)(2007);0734-2101/2007/25(2)L9/3.

R. A. Enzenroth, Kurt L. Barth, W.S. Sampath and V. Manivannan "Thermal model for a superstrate cooling apparatus for an integrated in-line manufacturing process for thin film photovoltaic devices". J. Vac. Sci. Technol. B 25(6) 2007.

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V. Manivannan, Robert A. Enzenroth, Kurt L. Barth, Sandeep Kohli, Patrick McCurdy and W. S. Sampath, " Microstructural features of CdTe Photovoltaic thin film devices", Thin Solid Films, 516 (2008) 1209-1213.

Tushar M. Shimpi, Kurt L. Barth, Robert Al. Enzenroth, W.S. Sampath and V. Manivannan; "Effect of Hail Impact on Thermally Tempered Glass Substrates Used for Processing CdTe PV Modules". J. of Testing and evaluation, vol.36 No.2 paper ID JTE101036

R. A. Enzenroth, Kurt L. Barth, W.S. Sampath and V. Manivannan "Thermal model for a superstrate cooling apparatus for an integrated in-line manufacturing process for thin film photovoltaic devices" J. Vac. Sci. Technol. B 25(6) 2007.

5.7.3 Refereed Conferences:

Enzenroth, R. A., K. L. Barth, and W. S. Sampath, "Transient Ion Drift Measurements of Polycrystalline CdTe PV Devices", presented 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion-4, (2006).

Enzenroth, R. A.T. Takamiya, K. L. Barth, and W. S. Sampath, "Photocapacitance Study of Deep Levels in Thin CdTe PV Devices", presented European Materials Research Society (EMRS) Spring meeting, Strasbourg France (2006)

Barth, Kurt L., R. Albert Enzenroth and W. S. Sampath, "Brief update of progress at AVA Technologies LLC" National CdTe Team Meeting, Sponsored by the DOE through the National Renewable Energy Laboratory, Golden, CO, March 2006. Can be got from: http://www.nrel.gov/pv/thin_film/docs/cdte_team_march_2006.pdf

Enzenroth, R. A., K. L. Barth, and W. S. Sampath, " Observation of Copper Diffusion in CdTe PV Devices", National CdTe Team Meeting, Sponsored by the DOE through the National Renewable Energy Laboratory, Golden, CO, March 2006. Can be got from: http://www.nrel.gov/pv/thin_film/docs/cdte_team_march_2006.pdf

Sampath, et. al; "Advances in Continuous In-Line Processing of Stable CdS/CdTe Devices", 33rd IEEE PV Specialists Conference, May 2008.

Sampath, et. al; "Continuous In-Line Processing of CdS/CdTe Solar Cells", Invited Talk at American Vacuum Society (AVS), Boston, October 2008.

5.7.4 Other Presentations**:**

Barth, K. L, R. A. Enzenroth, and W. S. Sampath, "Advancing Thin Film CdTe PV Manufacturing", Thin Film PV Kickoff Meeting, GE Global Research Center, April 4, 2006.

W. S. Sampath, "Mass Production of CdTe Solar Photovoltaics" Presentation for the Northern Colorado chapter of IEEE January 17, 2007.

Sampath, W. S., Robert. A. Enzenroth and Kurt L. Barth, "Mass Production of Thin Film Solar Photovoltaics", Presentation, Discussion and Facility Tour for numerous groups including GE, Reliance Industries, NEA, Sequel, Murphy and Durier, Blackstone, Barings, local investment group, Primestar Solar, Nanosolar and many others.

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The reproducibility of CdTe device efficiency and stability has been demonstrated during long-duration operation of the system with a single charge loading for the CdS, CdTe, and CdCl2 process. A fixture for automated cooling of the substrate in vacuum has been designed, fabricated, installed, and tested. Significant advances to the modeling of large-area vapor sources and modeling of gas transport in the system have been made. Efforts to improve device efficiency and advance device characterization are under way. A process for removing the coated films to reduce the amount of solid waste has been developed.

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