Fabrication of Stable, Large-Area Thin-Film CdTe Photovoltaic Modules

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ABSTRACT

During the period of this subcontract, May 1991 through February 1995, Solar Cells, Inc. has developed and demonstrated a low-cost process to fabricate stable large-area cadmium telluride based thin-film photovoltaic modules. This report summarizes the final phase of the project which is concentrated on process optimization and product life tests. One of the major post-deposition process steps, the CdCl_2 heat treatment, has been experimentally replaced with alternative treatments with vapor chloride or chlorine gas. Material and device qualities associated with alternative treatments are comparable or superior to those with the conventional treatment. Extensive experiments have been conducted to optimize the back-electrode structure in order to ensure long term device stability. Numerous small-area cells and minimodules have been subjected to a variety of stress tests, including but not limited to continuous light soak under open or short circuit or with resistive load, for over 10,000 hours. Satisfactory stability has been demonstrated on 48 cm^2 and 64 cm^2 minimodules under accelerated tests and on 7200 cm^2 large modules under normal operating conditions. The conversion efficiency has also been significantly improved during this period. The total area efficiency of 7200 cm^2 module has reached 8.4%, corresponding to a 60.3W normalized output; the efficiency of 64 cm^2 minimodules and 1.1 cm^2 cells has reached 10.5% (aperture area) and 12.4% (total area), respectively.

1.0 INTRODUCTION

In late 1990 Solar Cells, Inc. (SCI) selected CdTe as the principal semiconductor layer in PV devices due to its record of high efficiency and stability, and its flexibility with respect to deposition techniques. This flexibility allowed SCI the freedom to choose a manufacturing process based on attributes of low cost, high throughput, and reliability. Elemental vapor deposition, EVD, was chosen due to its high deposition rate and its capability of producing state of the art efficiency devices. Shortly after SCI's commitment to this technique, the University of South Florida group made significant improvements in efficiency of small area CdTe/CdS device fabricated by close spaced sublimation (CSS), which was the prior art. During the first two years of this subcontract, SCI designed, built and installed equipment and developed procedures for consistent deposition of CdTe and CdS films on commercial SnO_2 -coated soda lime glass. Several significant modifications have been made to the conventional CSS to satisfy the requirements of a manufacturing environment. The suitability of the chosen technique to manufacturing has been demonstrated by the fact that the scale-up from 100 cm^2 to 7200 cm^2 film deposition was completed in one step and in one year.

Although CdTe is known to be a stable material there has been evidence that CdTe/CdS device stability is dependent on process details, especially on the choice and preparation of the back electrode [1]. During the last phase of this subcontract, research effort has been devoted to the improvement and verification of device stability through process optimization. In order to demonstrate a product life of more than 10 years within a limited testing period, methods of accelerated stress testing have been investigated. Modifications aimed to further simplify and streamline the manufacturing process have also been studied and implemented. Experiments of reducing the CdS thickness in large area film deposition have been conducted in order to improve device efficiency which is largely limited by optical losses in the window layers. During this period SCI has also been proactive in addressing the Cd related safety, health and environmental issues.

2.0 PROCESS OPTIMIZATION

The purpose of process optimization is two fold. First, the device and module performance can only be improved through continuous optimization of all processes involved. This is particularly true when device performance is measured not only by conversion efficiency but also by long term stability, an issue somewhat neglected in the pre-commercialization research community. For example, it has been observed that CdTe/CdS device stability is strongly affected by the structure and application of the back electrode contact. The second major purpose of process optimization is to meet low-cost, high-throughput requirements of large-scale commercial production. One major process step that required improvements was the conventional CdCl_2 heat treatment of CdTe/CdS films. A number of alternative methods have been explored during the last 18 months of this subcontract.

2.1 Back Contact Process

A back contact process usually includes one or more steps of surface treatment that are necessary to prepare the CdTe film prior to metallization. However, caution must be exercised when one refers to surface treatment of polycrystalline CdTe films since such a treatment may affect the device in a way that can not be solely accounted for by back contact characteristics.[2] For example, it is common to observe more than 0.2 V difference in V_{oc} on devices prepared identically with the exception of back contact process. These processes, especially the chemical and thermal treatments, will very likely affect grain boundaries which in turn may influence device characteristics. Therefore, the back contact application should be regarded as an integral part of material and device optimization such as the well studied $CdCl_2$ treatment.

We have observed that in some cases device degradation starts and is localized in the neighborhood of back contact. For example, some aged devices can be rejuvenated by stripping off the back contact and remetallizing with the original contact materials. It was suspected that interdiffusion and/or interaction between the CdTe and metal contact were the cause of device degradation. Therefore, it was desirable to insert an electronically compatible and chemically inert buffer layer between the CdTe and metal to prevent such interactions without sacrificing electronic properties. We discovered that with a proper application of the interfacial layers (IFL) the choice of back electrode material could be more flexible than without, thus making the selection process complicated. Several elemental and compound semiconductor materials have been tested as IFLs. Initial studies have enabled us to narrow down to a small selection of IFL contact structures for further optimization. Extensive stress tests have been used to examine and qualify the contact structures and will be discussed in Section 3 of this report.

2.2 Chloride Treatment

This section is largely adapted from Ref. [3]. Heat treatment near 400°C with $CdCl_2$ has been routinely used to improve electronic characteristics of polycrystalline CdTe/CdS films. The $CdCl_2$ treatment usually results in grain growth in small grain films prepared with a number of methods such as electrochemical deposition or vacuum evaporation [4]. In the case of high-temperature vapor deposition such as close-spaced sublimation (CSS) and its variations, the as-deposited average grain size is large (~1 μm). Nonetheless the $CdCl_2$ heat treatment is still necessary in order to achieve consistently good device characteristics, i.e., $V_{oc} > 750$ mV and FF > 60%. There is evidence that, in large grain films, the treatment promotes grain boundary re-growth and small grain elimination. In either case, $CdCl_2$ is believed to act as a flux agent that increases the atomic mobility of CdTe at annealing temperatures.

The conventional $CdCl_2$ treatment (hereafter referred to as solution treatment) usually involves the following steps: 1) Application of $CdCl_2$ in methanol solution; 2) Heat treatment in air at about 400 °C for 30 to 60 minutes; 3) Removal of the $CdCl_2$ residue from the treated film. Incorporation of these processes may cause substantial delay in mass production. This subsection summarizes the initial investigation at SCI of alternative post-

deposition chloride treatments which are potentially better suited to manufacturing. All PV devices reported in this subsection have been fabricated using SCI's standard process with the exception of chloride treatments.

2.2.1 Immediate post-deposition treatment by vapor CdCl_2

Cadmium chloride preserves its linear molecular structure in the vapor phase and exhibits a high vapor pressure as shown in Fig. 2.1. Thus at 400 °C a significant amount of CdCl_2 exists near the CdTe surface in the conventional CdCl_2 annealing step. The interaction of CdCl_2 vapor with a heated CdTe film may be sufficient to affect the polycrystalline grain structures in a manner similar to the conventional CdCl_2 treatment if the adsorbed CdCl_2 molecules have a sufficiently long dwell time on the film surface.

The CdCl_2 vapor treatment of 100 cm² CdTe films was tested in SCI's multistage CSS deposition system described in a previous publication[5]. The CdS and CdTe were deposited at 1 to 10 Torr of N_2 at superstrate temperature near 600 °C. Immediately following deposition the chamber was back-filled with N_2 to pressures at 1 to 200 Torr while allowing the film to cool to about 400 °C. The film was then inserted into a CSS zone loaded with anhydrous CdCl_2 for the treatment. The upper and lower heaters of the CdCl_2 zone were set between 420 and 450 °C to maintain a sufficient CdCl_2 vapor pressure. The treatment lasted between 5 to 20 minutes. If the treated film is allowed to cool quickly, fine grains of CdCl_2 in the form of a dark powder remain on the surface and can be easily rinsed off with de-ionized water.

The vapor treated films appear very uniform whereas the solution treated films usually exhibit swirl marks formed during the drying of the solvent. SEM studies show subtle but definite differences between the vapor and solution treated samples (see Fig. 2.2). In general the vapor treatment leaves smoother compact grains and lower chlorine residue (undetectable by EDS). On the solution treated surface, however, certain Cl-containing fine structures are often observed. It is important to note that the conventional CdCl_2 treatment is usually conducted in an oxygen and moisture containing environment. Several chlorine and oxygen related compounds on the CdTe surface after CdCl_2 heat treatment in room air have been identified by X-ray analysis [6]. We have also observed that a CdTe film exposed to room air prior to the vapor treatment would appear similar to a conventionally treated film in terms of surface inhomogeneity. This suggests that surface oxides may have an effect which develops during the vapor CdCl_2 treatment. Clearly the immediate post-deposition treatment significantly reduces the possibility of contamination on as-deposit films.

Table 2.1 lists typical vapor treatment parameters along with small-area cell performance measured under simulated AM1.5 illumination. The listed average efficiency is obtained from six 1.1 cm² cells. It has been found that treatment times longer than 5 minutes and ambient pressures higher than 10 Torr tend to result in best and most consistent device performance.

Fig. 2.1 CdCl₂ vapor pressure.

(a)

(b)

Fig. 2.2 SEM photograph of a) solution CdCl₂ treated, b) vapor CdCl₂ treated CdTe surface.

Table 2.1. Representative data of vapor-CdCl₂ treatment experiments conducted immediately following the CSS deposition of CdTe

Sample	T(heater) (°C)	T(sample) (°C)	P (Torr)	t (min.)	Avg. Eff (%)
N2017	440/450	396	200	10	10.2
N2018	440/450	397	200	5	10.0
N2059	400/440	377	10	4	9.3
N2033*	440/440	398	200	10	10.7
N2031	440/440	392	1	2	8.4
N2043	400/460	385	1	1	8.3

* CdTe deposition was in air at 10 Torr.

2.2.2 Vapor CdCl₂ treatment of 7200-cm² films

The vapor CdCl₂ treatment has also been applied to 7200 cm² CdTe films in the large-area deposition system described in Ref. 7. Due to equipment limitations the CdS/CdTe depositions and the vapor treatment were not conducted in a single vacuum cycle. To perform the vapor treatment the semi-cylindrical boats normally used for CdS and CdTe source materials were loaded with powder CdCl₂. A pre-deposited CdS/CdTe film, re-heated to ~400 °C, was slowly oscillated under the CdCl₂ boats. The treatment was conducted at different N₂ ambient pressures for several minutes. Three 7200 cm² modules with total area efficiencies between 6.7% and 6.9% have been made with this process (See Table 2). In this case the ambient pressure did not seem to be a critical parameter. It must be pointed out that the effective anneal time may be ~3 times longer than indicated in the table due to a CdCl₂ dwell time longer than the period of oscillation.

Table 2.2. Vapor CdCl₂ treated 7200 cm² modules

Sample	T(heater) (C)	T(sample) (C)	P (Torr)	t (min.)	Total Area Eff.
B9418	450/430	400	200	3.5	6.8%
B9419	450/430	400	10	2	6.9%
B9421	450/420	400	1	1.1	6.7%

2.2.3 Vapor treatment by hydrogen chloride or chlorine

In the conventional CdCl₂ treatment the amount of CdCl₂ applied to CdTe surface is low, usually no more than 2 molar percent of the CdTe. It is also possible to form a CdCl₂ layer by reaction of chlorine (Cl₂) or certain chloride vapors with the CdTe surface. It has been observed that even at room temperature HCl vapor renders the CdTe surface

hydrophobic and electrically more conductive. Although an aqueous HCl solution does not etch CdTe, a certain amount of Cd leaching is believed to occur, resulting in a slightly Te-rich surface.

The interaction of HCl and CdTe were first investigated in a simple apparatus involving a Pyrex tube and a heater. A flow of N₂ was established in the tube until the sample temperature reached 400 °C. The gas flow was then diverted through a bubbler containing a concentrated HCl solution. The HCl:N₂ flow was maintained at about 500 sccm for < 5 minutes. The sample was then allowed to cool in N₂ ambient. After the reaction, the film was covered with powdered CdCl₂ residue similar to that on CdCl₂ vapor treated films. The small cell (0.25 cm²) average efficiency was 8.4% with V_{oc} > 750 mV. These devices are considerably better than those made on untreated films.

Production-scale HCl treatment experiments were then performed in the large-area deposition system. A pre-deposited 7200 cm² CdTe/CdS film was heated to 400 °C in N₂. A flow of premixed HCl:N₂ was bled into the chamber through a shower head gas distributor approximately 1 cm above the film surface. The film was oscillated with respect to the gas distributor which was held at a temperature slightly higher than the film temperature. The effective time that a particular section of film was directly in the stream of the incoming HCl flow was < 10 minutes. As shown in Fig. 2.3 the treated film appeared to be homogeneous with little or no Cl residue detectable by EDS. Small cells with efficiencies above 10% have been repeatedly produced from HCl-treated CdTe 7200 cm² films. Satisfactory spatial uniformity of treatment was indicated by an average 48-cm² aperture-area efficiency of 8.4% (± 0.4%) over 59 minimodules randomly selected from a single 7200 cm² film.

A dilute mixture of Cl₂ with N₂ has also been used to treat the CdTe/CdS film in a similar manner. The Cl₂-treated film appeared non-uniform. Isolated area of films, however, have been made into cells with efficiency in the range of 9 - 10%. Apparently a considerable amount of CdCl₂ was formed during the treatment. This has been expected given the strong reaction between CdTe and Cl₂ (elemental halogens and their solutions are known to etch CdTe at room temperature). While reaction control may be difficult chlorine remains a viable candidate as a processing gas for the post-deposition treatment of CdTe.

Capacitance-Voltage (CV) and Quantum Efficiency (QE) have been measured on samples processed with the various chloride treatments with all other process steps being identical. For cells with similar efficiencies and I-V characteristics, there are no significant differences in the CV or QE curves for the solution, vapor or HCl treated samples.

Accelerated life tests indicate that stability of vapor chloride treated devices is comparable or better than the conventionally treated devices. Various back contact processes have been experimented on vapor chloride treated films to ensure that these process modifications are mutually compatible and complementary. The vapor chloride process has been and continues to be optimized at SCI by the Manufacturing Group to meet the production requirements such as yield, throughput and safety.

Fig. 2. 3 SEM micrograph of CdTe surface after a heat treatment in HCl:N₂.

3.0 ACCELERATED DEVICE LIFE TESTS

SCI has recognized the importance of product stability and durability for successful commercialization of the CdTe PV technology from the beginning of its operation. Although CdTe has no known intrinsic instability problem such as the Staebler-Wronski effect seen in amorphous silicon, the device stability is strongly influenced by the preparation process.(Ref. 1) Devices made during the early stage of this subcontract suffered degradation of varying degrees depending on process conditions. Therefore, it has been found that conversion efficiency is not and should not be the only measurement of device performance. Continuous illumination near AM1.5 intensity has been routinely applied to the majority of cells and mini-modules, especially those prepared under intentionally modified conditions. The reason to subject single cells to stress testing is to distinguish possible device aging process from interconnect related failures. The light source is an array of stadium xenon lamps that provide approximately 80 mW/cm² with reasonable spatial uniformity ($\pm 10\%$). Without active control, the device temperature reaches 60 - 70 °C in summer and 40 - 50 °C in winter. Special chambers with glass windows and temperature controls have been made to facilitate light soak at specified temperatures. Modules under light soak are biased at open circuit, short circuit or near maximum power point with resistive load. In addition, thermal stress at various bias voltages has also been applied at temperatures up to 140 °C in N₂ atmosphere.

3.1 Empirical modeling

It is our goal for the near future to be able to guarantee that 90% of SCI's PV modules retain 90% of their initial power output for at least 10 years of normal field operation. In order to verify the 10+ year stability from a limited time period of testing, an empirical model was conceived and tested such that the future device performance could be extrapolated from stress testing data. The basic assumption of the model was that the average device performance could be expressed as a unique function of time and the set of conditions under which the devices were stressed. Specifically, efficiency η could be written as a parametric function

$$\eta \equiv \eta(t; V, \Phi, T),$$

where t = time, Φ = light intensity, V = bias voltage and T = temperature. A typical sample set consists of 20 to 50 minimodules with 48-cm² aperture prepared under identical conditions. Usually a 60 cm x 120 cm film was processed with special laser scribe pattern and then minimodules were obtained by mechanical cleaving. Members of each set were subject to light or heat stress at various bias conditions with I-V characteristics measured periodically. Table 3.1 is a list of stress conditions for Test Set 9. Due to equipment limitations, the data were only collected on several lines in the parameter space spanned by V , T and Φ . For example, the intensity assumes only two values, 0 for dark and 1 for normal light soak (80 mW/cm²); bias voltage per cell under thermal stress assumes three discrete values, -0.5, 0, and 0.5 V. Bias per cell under light soak at open circuit, short circuit and with resistive load was assumed to be 0.75, 0, and 0.5 V, respectively. The model was assumed to be a polynomial function of terms such as t , $\log(t)$, $1/t$, $1/T$, V and Φ . It was strictly empirical such that numerous functions had to be tested by fitting to data using a commercial computer algorithm to determine the coefficients. For example, the first 4000 hours of stress test data collected under the conditions listed in Table 3.1 (Set 9) were fit to the following form,

$$\eta = 1.35 + 786.6/t + 8.11V + 1890/T - 3138/t^2 - 2820 V/T - 40.5 V/t + 0.81V\log(t) - 233000/tT - 0.22\Phi$$

Fig. 3.1 plots the above function at $V = 0.5$ V (~max. power point), $T = 333$ K (=60 °C) and $\Phi = 1$, against data collected from 6 minimodules of Set 9 under light soak with resistive load. The fit was good considering the function was expected to fit data at all conditions listed in Table 3.1. However, extrapolation of the model curve beyond 5,000 hours failed to agree with the actual data later generated from the same samples. This implies that the model functional is of little value for predicting modules behavior under stress.

Several reasons may be responsible for the failure of the model to correctly predict long term device behavior. First, as pointed above, the parameter space was not properly sampled by the test set. Specifically, as indicated in Table 3.1, temperature dependence, if any, of the aging process had been only monitored on samples under thermal rather than light stress. The intensity variable only took one non-zero value therefore making any estimate of intensity dependence essentially impossible. Secondly, certain module failure such as busbar deterioration could be abrupt, therefore inexpressible by any analytical

function. While the model's inability to predict long term device behavior was disappointing, it was by no means surprising since the model was not based on any physical mechanism that might describe the aging process. The attempt was made only to investigate the possibility of developing a global model that could describe device behavior under all stress conditions. The model was hoped to be universal so that devices made with different procedures could be evaluated by the same method. The existence of such a universal model is now questionable given the above results. However, stress testing under a wide range of conditions with statistical analysis remains the best and perhaps the only method to demonstrate and verify module stability. Even in the absence of a simple, quantitative relationship between stress conditions, such as illumination and temperature, it is always desirable to find module stability to be insensitive to extreme external conditions possible in the field. In the next subsection several examples of stable module performance will be discussed.

Table 3.1 Stress test conditions for a sample set

Illumination	Bias	Temperature	Encapsulation	Number of Samples
1	OC	~60 C	No	2
1	SC	~60 C	No	2
1	R-Load	~60 C	No	6
1	R-Load	~60 C	Yes	6
0	OC	Room T	No	6
0	OC	Room T	Yes	6
0	0.5V/cell	Room T	N ₂	2
0	-0.5V/cell	Room T	N ₂	2
0	OC	60 C	N ₂	2
0	0.5V/cell	60 C	N ₂	2
0	-0.5V/cell	60 C	N ₂	2
0	OC	100 C	N ₂	2
0	0.5V/cell	100 C	N ₂	2
0	-0.5/cell	100 C	N ₂	2
0	OC	140 C	N ₂	2
0	0.5V/cell	140 C	N ₂	2
0	-0.5V/cell	140 C	N ₂	2

3.2 Stress test results

Fig. 3.2 shows the efficiency history of two mini-modules, without encapsulation, under light soak with resistive load for 14,000 to 15,000 hours, equivalent to more than 6-7 years of field operation. These samples were prepared more than one and a half years ago, preceding many steps of process optimization. However, only minor degradation has been observed. Fig. 3.3 plots the average efficiency of 6 encapsulated mini-modules of Set 13 under light soak with resistive load, showing little variation in efficiency between 2,000 and 7,500 hours after some initial stabilization. As a contrast, 6 encapsulated

minimodules of set 9 under the same stress condition suffered considerable degradation after 5,000 hours of testing as shown in Fig. 3.4. The two sets of samples were processed identically with the exception of busbar material and application. Comparison between the two groups of minimodules indicates that degradation in set 9 was very likely caused by deterioration in busbar connections.

As indicated by the preceding figures it was possible for device performance to improve during the first few hundred hours. In some cases, when the process was not optimized, device performance could improve for even a longer period of time as shown in Fig. 3.5. In this case, the samples had received CdCl_2 vapor treatment as opposed to conventional solution treatment while the rest of the process remained unchanged and might not be optimized. The modules started with aperture efficiency below 6%, mainly limited by short circuit current, but continue to improve for 7,000 hours under light soak. Devices processed with the newly developed HCl vapor treatment have also been subject to long term stress tests. Fig. 3.6 shows the average efficiency of six HCl vapor treated minimodules of Set 16 under light with resistive load. Comparison of Set 16 with either the baseline (Fig. 3.2) or Set 13 modules (Fig. 3.3) clearly indicates improved stability of the HCl treated devices.

In addition, good stability has been demonstrated on SCI's 0.72 m² modules. The performance of three modules subject to over one year of field testing at NREL is shown in Fig. 3.7. The 24-module 1kW array installed in August, 1994 at SCI's Toledo, Ohio, facilities is stabilized at normalized output above 1250 Watts as shown in Fig. 3.8. The demonstrated stable performance has reassured us that reliable CdTe-based PV cells and modules can be produced consistently.

3.3 Reversible effects under bias stress

The wealth of data collected during stress tests reveal an interesting and possibly important phenomenon. It was observed that CdTe/CdS devices prepared with several different processes all degraded under reverse bias but improved under forward bias, both quite significantly, at slightly elevated temperatures (60 - 140 °C). Furthermore, the degradation incurred at reverse bias could be recovered under forward bias and the cycle could be repeated many times. Fig. 3.9 shows efficiency vs. time over 11 such cycles at 100 °C of a mini-module processed with those shown in Fig. 3.3. When biased at room temperature, the degradation and recovery cycle are very slow with a time scale measured in weeks. It had been hypothesized that the reverse bias condition could be considered as a rapid aging process equivalent to an accelerated light soak because it generally resulted in decreased V_{oc} and increased series resistance similar to what a prolonged light soak would have caused. However, a comparison between Fig 3.3 and 3.9 indicates that modules stable under light soak could still degrade under reverse bias. Although it is unlikely for a module in operation to encounter a reverse bias condition over any extended period, the study of this reversible phenomenon may provide useful information on device operation and aging mechanisms. The reversibility of the bias-induced effects suggests that the change is localized near the back contact region, consistent with C-V measurements which indicate that the bulk of the film does not change during these cycles. Two

mechanisms may be responsible for this reversible process: solid state electrolytic reactions near the back contact or a long-lived trapping process. The former seems more likely given the long time constant involved (~ 10 hours). However, this phenomenon is largely independent of process details that it is difficult to identify the elements involved in such chemical reactions.

Fig. 3.1. The empirical model vs. efficiency history of six 48 cm^2 minimodules of Set 9 under light soak with resistive load.

The Longest Tested Modules

Fig. 3.2. The longest stress-tested unencapsulated 64 cm² minimodules

Fig. 3.3. Average efficiency of six 48 cm² minimodules under light soak with resistive load.

Fig. 3.4. Average efficiency of the same modules as shown in Fig. 3.1 over extended period of light soaking.

Fig. 3.5. Average efficiency of six 48 cm² minimodules with CdCl₂ vapor treatment under light soak with resistive load.

Fig. 3.6. Average efficiency of six 48 cm² minimodules with HCl treatment under light soak with resistive load.

Fig. 3.7. Stable performance of three 0.72 m² modules monitored at NREL.

04/18/95

Fig. 3.8. Normalized power output of the 24-module array # 2 at SCI's Toledo, Ohio, facility.

Fig. 3.9 Degradation-recovery cycles under reverse and forward bias at 100 °C

4.0 CADMIUM RECOVERY EXPERIMENTS

Exploratory experiments of methods to effectively and cheaply recycle off-specification modules have been performed. The general strategy investigated is to first separate Cd-containing semiconductor films from the SnO_2 -coated glass by means of an acid etch and to then treat the effluent. Nitric (HNO_3), hydrochloric (HCl) and ethylene diaminetetraacetic (EDTA) acids were tested as potential etchants. Samples were cut from 7200 cm^2 modules in six-inch by six-inch squares - but these samples generally broke into three to six pieces in the process. Agitation was provided using a shaker table or a standard toxicity characteristic leaching procedure (TCLP) agitator unit.

Initial trials were performed with nitric acid and EDTA. The 0.1M EDTA prove to be rather ineffective. However, nitric acid at the 10% concentration level is very effective at dissolving the semiconductor and nearly all of the Cd is removed from the glass. Weaker acids, down to 0.1 % concentration, were also successfully used to strip the semiconductors. While Cd is more soluble in the more concentrated acid, the weaker acid is still effective at Cd removal due to CdTe flaking off the glass, presumably by dissolving the underlying CdS layer. This result is expected as HNO_3 is an oxidizing acid, when in concentrations greater than 2M, and therefore attacks the CdTe directly. Dilute HNO_3 and HCl , on the other hand, only dissolve the CdS. Fig. 4.1 shows the amount of soluble Cd removed with agitation for 30 and 60 minutes with 2, 5, and 10% concentration nitric acid on six separate samples. Note that the 10% solution dissolves the majority of the Cd within 30 minutes and that the amount dissolved is far greater than with the 2 and 5% solutions. (Note that for SCI modules, $1.3 \pm 0.3 \text{ mg/cm}^2$ of Cd is initially present on the glass). Within the normal variations of the measurement, the samples had no change in the amount of soluble Cd.

To determine if the acid etch removes enough Cd to permit the glass substrate to be classified as non-hazardous, samples were subjected to TCLP tests using an acetic acid leachate, the more rigorous of the TCLP tests. Present regulations permit a maximum of 1.0 mg/l of Cd in the leachate. All treated samples clearly passed with the highest reading being 0.65 mg/l for the 0.1% HNO_3 , and the lowest reading being 0.01 mg/l for 5% HCl .

Removal of the regulated materials from the glass substrate by acid etching leaves yet another challenge. The Cd concentration is still too low for economical recycling by conventional means; therefore, further processing is required. The two approaches taken were electrolytic deposition and ion exchange. The electrolytic deposition results were discouraging. Only a small fraction of the soluble Cd was recovered from the extraction fluids. A number of combinations of voltage to the electrodes and pH of the extraction fluids were tried with only marginal improvement in Cd removal. Since electroplating of Cd is commonly performed, further experiments are needed.

The results of the ion exchange are much more encouraging. Two commercially available cation exchange resins were tested with similar results. The first resin is Amberlite IRC-718 produced by Rohm and Haas Company and is a weakly acidic

chelating exchange resin with a high affinity for heavy metal cations. The resin can only be used for aqueous solutions with no more than 0.5% nitric acid content. Fig. 4.2 shows a comparison of the Cd concentration of the influent and effluent for a period of 50 minutes. The resin removes over 99.9% of the Cd from the influent over the test period. The expected capacity of the resin is about 2 meq/ml resin. A second ion exchange resin produced by Sybron Chemicals Inc. was also tested. This resin has the advantage of tolerating higher influent acid concentrations. The performance was comparable to the Amberlite. The disadvantage of the ion exchange process is the high cost of the resin. If, however, a weak acid is used to strip a high percentage of the CdTe off the glass in solid form that can be removed by physical processes, the amount of resin required can be minimized and therefore the cost minimized.

Fig. 4.1 The amount of soluble Cd removed from CdTe modules with agitation in different concentration of nitric acid.

Ion Exchange Column Performance

Fig 4.2 Cd concentration of the influent and effluent in the ion exchange process.

5.0 SUMMARY

During the final phase of this subcontract SCI has concentrated on issues pertinent to commercialization of CdTe PV technology such as long term device stability and process optimization. Major modification of conventional CdCl₂ heat treatment has been demonstrated not only technically possible but potentially beneficial to device stability. Extensive stress tests have been applied to numerous cells and modules of different sizes. The baseline device has withstood more than 14,000 hours of continuous illumination stress while initial tests indicate that devices fabricated with various innovative methods are more stable. Through continuous optimization the conversion efficiency of cells and modules of all sizes have improved during this period as shown in Fig. 5.1. Optimized techniques have been constantly transferred to the manufacturing process (partially supported by PVMaT). As a result of combined efforts of process optimization and manufacturing quality control the average efficiency of production modules has been greatly improved. As shown in Fig. 3.8, the second 1kW PV array at SCI's Toledo, Ohio, facility is producing more than 1.25 kW at AM 1.5. This corresponds to an average efficiency of 7.2% which is 34% improvement over our first outdoor array.

Fig. 5.1: Steady improvement in conversion efficiency of SCI's photovoltaic cells and modules.

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