Processing Issues for Thin-Film CdTe Cells and Modules

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ABSTRACT

Among emerging thin-film PV technologies, CdTe-based modules have displayed perhaps the most flexibility with respect to their method of manufacture. Device efficiencies have reached >15% and there appears to be no inherent device instability. Nonetheless, there remain serious technical challenges which must be met if CdTe modules are to be manufactured at a commercially attractive level. This paper identifies and discusses these issues.

INTRODUCTION

Thin film CdTe-based photovoltaic technology continues to attract serious attention within the photovoltaic community. Solar cells with an area of 1 cm^2 have been made with efficiency over 15% and modules have been made with efficiencies over 10%. In addition, CdTe solar cells with efficiencies over 11% have been made by a variety of deposition methods and several of these methods have been adapted to module manufacturing. Table 1 summarizes the performance of CdTe solar cells and modules fabricated by a variety of methods and lists the research groups involved. In this paper the status of CdTe technology is discussed with emphasis on key technical issues relating to device fabrication and commercialization.

MATERIALS AND DEVICE ISSUES

All high efficiency CdTe/CdS solar cells have a superstrate device configuration shown schematically in Figure 1 along with the processing steps required to fabricate the device. In this section, we discuss several material and device issues associated with the fabrication of CdTe cells with respect to processing and developing a manufacturing process for producing modules.

Leading CdTe Deposition Technologies [1,2]

CdTe Deposition Process	Academic Interest	Industrial Interest	Efficiency/Area
Compound Sublimation and Vapor Transport (CSS)	USF [1], NREL, IEC, Stanford	SCI, Antec [3]	15.8% / 1.05 cm^2 [4] 8.4% / 7200 cm^2 [5]
Electrodeposition	CSM, Queensland	BP Solar, A.D. Plating	14.2% / 0.02 cm^2
Atomic Layer Epitaxy		Microchemistry	14.0% / 0.12 cm^2
Screen printing	KAIST, U. Gent [7]	Matsushita	12.8% / 0.78 cm^2 8.1% / 1200 cm^2
Spraying		Golden Photon	12.7% / 0.3 cm^2 8.1% / 832 cm^2
MOCVD	GIT, USF, U Durham, RPI [8]		11.9% / 0.08 cm^2 [9]
PVD - vacuum evaporation	IEC, Univ Parma,New Castle-on-Tyne, Stanford		11.8% / 0.3 cm^2 [10]
Laser Driven PVD	U Toledo		10.5% / 0.1 cm^2 [11]
MBE	NREL [12], Swiss Fed. Inst. Tech, GIT		10.5% / 0.08 cm^2 [13]
Sputtering	NREL, U Toledo		10.4% / 0.1 cm^2 [11]
APCVD	USF [14]	Batelle [15], SCI [16]	9.9% / 1 cm^2 [14]

CdS Window Layer and J_{SC}

Based on the standard AM1.5 Global spectrum, the maximum J_{SC} of a CdTe solar cell is about 30.8 mA/cm^2 [19] where approximately 7.1 mA/cm^2 of that current is due to photons with energy above the CdS absorption edge· Thus absorption losses in the CdS layer can have a significant effect on J_{SC}.

The highest efficiency CdTe/CdS solar cells are distinguished by their high short circuit current - >25 mA/cm^2. This has been achieved using thin CdS, ~70 nm, deposited from an aqueous solution, by a method called chemical bath deposition or CBD [1, 20]. The use of the thin CdS is often accompanied by reduced yield of devices which is, in turn, attributed to pinholes or other defects in the CdS. The use of thin CdS is also complicated by a further reduction in the thickness of the CdS which occurs during CdTe film growth or post deposition $CdCl_2$ heat treatment (21).

From a manufacturing perspective, CBD film growth of CdS has certain disadvantages :

1) the deposition rate of CBD films, ~10 A/s, is relatively slow;

2) the process is complicated since the best cell results are achieved only when the CdS film is heat treated in H_2 [1] or with $CdCl_2$ [22];

3) the CdS grows heterogeneously on the glass/TCO superstrate and vessel walls as well as homogenously forming particulates in the solution which can subsequently adhere to the superstrate; and

4) the materials utilization of precursor chemicals is low requiring recycling or disposal of a hazardous waste.

Thus there is a clear need to develop alternative methods to deposit pinhole free thin CdS or to identify a suitable wider bandgap heterojunction/window layer if the high solar cell efficiencies achieved in the laboratory are to be translated to a manufacturing environment.

$CdCl_2$ Heat Treatment

In fabricating high efficiency CdTe/CdS solar cells, there is a post deposition heat treatment in the presence of $CdCl_2$ or a chloride is present during the growth of the CdTe layer. The $CdCl_2$ treatment improves the overall performance of the solar cells and appears to improve the yield and uniformity of devices.

Typically, the CdCl2 heat treatment consists of: 1) coating the surface of the CdTe/CdS with CdCl2 from an alcohol solution containing CdCl2, [24], by laser ablation [25] or by vacuum evaporation [26] or by performing the heat treatment in a CdCl2 vapor [27]; 2) annealing the coated CdTe/CdS at 400°C for 10 to 30 min in air or in an oxygen containing atmosphere; and 3) the residual CdCl2 is removed by a water rinse or mild etch.

The effect of the CdCl2 heat treatment on the structural and optical properties of evaporated CdTe/CdS has been documented. The heat treatment promotes grain

growth of both the CdS and CdTe films; Figure 2 is a schematic representation based on TEM results showing the film [ ] structure before and after heat treatment. In the as-deposited state, the CdTe grows pseudo-epitaxially on the CdS most likely creating a strained interface due to the ~10% lattice mismatch between the CdS and CdTe. After heat treatment there is no longer a correlation between the CdS and CdTe grain structures and the grain size of the CdTe has increased from 200 nm to over a 1 micron. further, based on spot EDS of the TEM samples and shifts in the lattice parameter of the CdTe measured by XRD, S has diffused into the CdTe layer creating a CdTeS layer. The incorporation of S into the CdTe reduces the optical bandgap of the CdTeS as can be seen in Figure 3. This shift in bandgap is also seen in spectral response measurements on completed devices. Additionally, there is diffusion of Te into the CdS, reducing the optical bandgap or 'softening' the CdS absorption edge. Based on Auger/SIMS measurements there are oxygen and chloride incorporated into the CdTe/CdS structure. Rohatgi [10] has suggested that the Cl acts as a deep level trap in the CdTe. The effects of the O and Cl on the properties of the CdTe/CdS are not well understood.

The CdCl2 heat treatment or use of CdCl2 during film growth is a complex, yet critical process in fabricating CdTe/CdS solar. In fact it could be argued that it is the CdCl2 heat treatment which enables the use of the wide variety of CdTe deposition procedures. A quantitative understanding of the roles of CdCl2, O and Cl on the fabrication and operation of CdTe solar cells is needed to effectively design manufacturing facilities to produce CdTe modules.

Back Contact

The most difficult to process and most vulnerable component of CdTe solar cells is the stable low resistance back contact [5, 28]. There are many procedures - some proprietary - for producing a back contact to CdTe, but most researchers admit that fabrication of the low resistance contact is more art than science. Most procedures to form a back contact include 1) an etch or surface preparation step; 2) application of a film containing Cu, Hg, Pb, or Au [18, 33-35]; and 3) a subsequent heat treatment above 150°C.. The contact fabrication process can be interpreted as: 1) the etch produces a Te rich surface resulting in a highly doped or degenerate p+ interfacial layer; 2) the incorporation of a p-type dopant into the contact material may have two functions- formation of a degenerate Te compound with the dopant and modification of the 'bulk' CdTe properties by diffusion of the dopant into the CdTe making it more p-type; and 3) the heat treatment promotes reaction and diffusion of the contact materials.

Based on this interpretation, it is not surprising that most contact procedures depend on the specific CdTe deposition process since film parameters such as thickness and grain size vary with fabrication procedures. The empirical nature of the CdTe contact fabriaction process makes it difficult to define a suitable procedure for contacting CdTe. A clear understanding of the interfacial chemistry including an understanding of the mechanisms of dopant diffusion in a polycrystalline film is needed in order to develop aprocedure for producing a robust contact suitable for modules.

COMMERCIALZATION ISSUES

In this section, technical issues regarding commercialization of CdTe technology are discussed

STABILITY

Reports in the literature attest to the inherent stability of CdTe/CdS PV devices [36-40]. Figure 4 shows the performance of a CdTe module during ?? of exposure. Nonetheless, at this time no thin film technology has established the field track record for stability and reliability that single and large-grained polycrystalline silicon PV has demonstrated. The reported results of stable CdTe-based PV modules should be viewed as "existence proofs" and do not eliminate the need for more rigorous testing.

The principal concerns regarding CdTe device stability center on the low resistance back contact. Degradation of the contact is manifested by increases in series resistance or by the emergence of a second diode in the current voltage characteristics. There are several plausible explanations for these effects including oxidation of the metal at the CdTe-metal interfaceand migration of species which alter the chemistry or electrical properties within the interfacial region. At this point it is not clear that all CdTe devices are susceptible to this form of degradation or if there are other degradation mechanisms which could contribute to reduce power conversion over time. In addition there may be durability issues associated with encapsulation. However, it is important for the CdTe PV community to analyze stability issues, to build upon the existence proofs of stable CdTe modules and to develop an in-depth understanding of the fundamental issues affecting stability.
There are two major goals of this analysis:

1) The stability of specific device structures should be demonstrated to enable researchers to optimize device structures and processing to maximize stability.
2) Procedures for accelerated life testing must be established to shorten the time required to assess stability from years to months or to even days. The way to establish a credible accelerated testing procedure is to determine the physical mechanisms responsible for degradation, establish their dependence on stress factors such as temperature, voltage bias, humidity or light level, and then to extrapolate the results obtained at elevated stress levels to those levels anticipated in normal use.

Production Technology Issues

One of the greatest attractions of CdTe PV technology for the design engineer is the freedom that it provides

with respect to its method of semiconductor deposition. The evidence to date suggests that, if one is willing to include a post deposition CdCl2 heat treatment step, any process which will deposit essentially stoichiometric CdTe can be adapted to produce 10% efficient cells.Thus prospective PV module manufacturers have wide latitude to adapt existing high throughput deposition technologies to the deposition of CdTe/CdS films. Production technology must be established to achieve large area and high throughput. In this case, large area is defined as one square meter and high throughput is defined as one square meter per minute. At 8% efficiency this is equivalent to about 10 MW/yr per 8 hr shift.) At present there are industrial activities directed toward commercialization of CdTe devices deposited by electrodeposition, screen printing, spraying, and CSVT. However this does not exhaust the list of attractive options.

Potential alternatives include sputtering, vacuum evaporation and atmospheric pressure chemical vapor deposition (APCVD). Sputtering is widely used for coating millions of square feet per year of architectural glass [46]. Vacuum evaporation has not only been used commercially for coating large area architectural glass and automobile sunroofs, but has also been shown to be suitable for deposition of thin film CdS for PV [47]. APCVD is used to apply TCO to glass while it is still on the float line at the rate of >20 square meters per minute[48].

At this point there are many attractive options but no clear cut leader.Important parameters in selecting a deposition technology might include throughput, equipment cost, operating cost, source material cost, source material utilization efficiency, process yield, environmental impact, equipment up-time (or cycle time), equipment reliability, equipment lifetime, and compatibility with other process steps. An analysis of the pros and cons of the various procedures could be a useful tool in quantifying the relative merits of each and might possibly serve as a tool to focus the CdTe PV development effort.

Environmental Concerns

One technical and perceptual barrier to the widespread utilization of CdTe PV technology is related to the toxicity of the semiconductor materials and specifically to cadmium. There is a legitimate concern that at the end of their useful life, CdTe modules might be disposed of in locations and under conditions in which cadmium might enter the environment; a particular concern is the water supply.

The EPA defines waste to be toxic based upon the results of the Toxicity Characteristic Leaching Procedure, TCLP [42]. With respect to cadmium in PV modules, this means that spent modules are defined to be toxic if 1 ppM of Cd can be leached from crushed modules under conditions that are intended to mimic those which might be encountered in a landfill. Preliminary results are mixed [43,44], but they suggest that CdTe PV modules may have difficulty meeting this standard. Future standards may be even more stringent. Although it is by no means certain that defective or discarded CdTe PV modules will be regarded as regulated wastes, it is prudent for the CdTe PV community to prepare for that contingency. Concerns of potential manufacturers, distributors and users would be greatly allayed by the demonstration of technology by which CdTe-based PV modules can be disposed of in a manner which captures Cd-bearing wastes, promotes recycling, and is cost-effective. The most widely suggested solution is to use the spent modules as flux in smelting operations in which the cadmium and tellurium would not affect the toxicity of the byproducts of existing operations. While this solution satisfies existing requirements, it has the shortcoming of relying on the continued existence and good will of the smelter operator.

Given these environmental concerns and their potential to significantly impact the commercial viability of CdTe PV technology, it seems prudent to demonstrate that alternative means of disposing of CdTe PV modules are available. The technology is straight treatment-forward [44, 45] and new science is not required. In addition to providing additional options to existing industrial operations, a well-documented, carefully controlled, laboratory scale demonstration would address the concerns of environmentalists and potential investors in existing or future CdTe PV enterprises. Conversely, if the proposed procedures are not cost effective, then the industry is best served by taking this information into consideration as soon as possible.

SUMMARY

CdTe continues to be a strong candidate in the competition to set the standard for the next generation of thin film PV technology. It has some very strong points in that it has high demonstrated efficiency, no inherent problems with stability, and provides wide flexibility in terms of its method of manufacture. Nonetheless, significant technical issues remain unresolved. These issues, which are all being actively investigated, include establishing improved process control over the CdS window layer thickness and the CdCl2 heat treatment, controlling the formation and stability of the low resistance back contact, and demonstration of cost-effective and environmentally responsible methods for dealing with the environmental issues surrounding cadmium. There appear to be no "show stoppers" to the commercialization of CdTe PV. It is a technology well suited to high throughput manufacturing and is well poised to play a significant role in the future of PV.

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