

Role of Process Chemistry and Stability on CdTe-based Solar Cell Performance

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ABSTRACT

CdTe-based solar cell research at the Institute of Energy Conversion (IEC) has focused on optimization of vapor transport deposition (VTD), high band gap CdZnTe alloys, etching of CdTe surfaces, and relating stress studies to module performance. A research-scale VTD reactor has been operated for the deposition of CdTe onto moving substrates with an area of 10 cm x 10 cm at temperatures from 400° to 600°C with growth rates of >1 μm/min. Baseline performance of 9-10% has been established. Wide band gap Cd_{1-x}Zn_xTe films have been deposited by physical vapor deposition (PVD) or VTD. HNO₃/H₃PO₄ (NP) and Br₂/methanol (BM) etching of CdTe films have been evaluated using variable angle spectroscopic ellipsometry (VASE). Etching in NP initially results in the formation of amorphous-Te, which crystallizes after treatment. NP-etched CdTe is fairly stable to atmospheric oxidation, compared to BM, but NP etch penetrates down GBs. Increasing NP acidity rapidly produces significant Te without grain boundary (GB) etching. Both First Solar (FS) and BP Solar (BP) devices degrade independent of ambient: bottled air, H₂/Ar, or vacuum. Both FS and BP devices can show a daily cyclic variation in V_{oc} of 30-50 mV during stress, with recovery following 16 hours in the dark at 65°C.

1. Introduction

The Institute of Energy Conversion (IEC) has an extensive research program on CdTe-based thin-film solar cells to support DOE's thin-film R&D efforts on the commercialization of CdTe PV technology. The IEC program addresses two areas to meet these objectives: 1) research under the NREL Center of Excellence Thin-Film Partnership Program is directed at addressing the critical issues regarding performance and stability of CdTe solar cells; and 2) research under the NREL High Performance Program is directed at the development of Cd_{1-x}Zn_xTe solar cells as the wide bandgap cell for tandem solar cells. This paper provides an overview of the research at IEC related to CdTe and Cd_{1-x}Zn_xTe devices.

2. Vapor Transport CdTe

Two decades of research and development of CdTe thin-film solar cells have demonstrated that there are

three critical parameters for CdTe processing needed to obtain both high performance and high throughput in-line manufacturing: 1) annealing CdTe/CdS in the presence of Cl-containing vapor at a temperature ~400°C to form the junction; 2) use of Cu as a dopant and contact reactant; and 3) sufficiently high deposition rate [1]. VTD, in which deposition occurs by de-saturation of a carrier gas containing Cd and Te vapors satisfies the processing temperature and growth rate criteria [2]. The method is being employed by First Solar, LLC, for commercial development of CdTe thin-film cell modules. IEC has implemented a research-scale reactor for the deposition of CdTe by VTD onto moving substrates with an area of 10 cm x 10 cm at temperatures from 400°C to 600°C. The CdTe films deposited in this reactor are used to support research on the effects of post-deposition processing and contacts on cell performance and stability.

The VTD system was designed and modeled by IEC and built by MVSystems, Inc., of Denver Colorado. The CdTe source consists of a ceramic manifold with a slit arranged above and perpendicular to the translating substrate, whose motion is externally programmed. Within the source manifold, a quartz ampoule contains CdTe crystallites. A Kanthal-A wire filament is used to heat the source material. The deposition process relies on saturation of the carrier gas, which can be inert such as argon, helium, or nitrogen or a reactive gas, containing oxygen or hydrogen. The gas is transported to the substrate and de-saturated since the substrate is colder than the gas. To achieve a static growth rate of 1 μm/min, the CdTe source must reach ~800°C, at a gas flow rate of 20 sccm and total pressure of 20 T. The deposition process is controlled by regulating the total system pressure. CdTe film growth occurs at 20 T and is stopped by increasing the pressure to 100 T. For baseline operation, the average thickness over the 10 x 10 cm area for 2 cm/min translation rate, is 4 μm and is uniform ±10% in the cross direction and ±5% in the translation direction, with a CdTe utilization of >60%. Baseline cells are fabricated on LOF TEC-10 soda-lime glass coated with SnO₂ with 80 nm thick CdS, completed with Cu/Au contacts and have V_{oc} = 750 mV, J_{sc} = 20 mA/cm² and FF = 64%. Emphasis is presently on raising baseline efficiency by optimizing the CdS and post-CdTe deposition processes. The VTD system can be operated

in a multiple pass mode, for experimental situations where different deposition conditions are desired for different film regions, e.g., high growth temperature at the CdTe/CdS junction followed by low growth temperature for the remainder of the film.

3. Cadmium Zinc Telluride

High performance multi-junction solar cells based on polycrystalline thin films will require a top cell with optical band gap E_g in the range of 1.7-1.9 eV, with high sub-band gap transmission. IEC is developing wide band gap solar cells based on $Cd_{1-x}Zn_xTe$ as a possible absorber layer since ZnS and CdTe forms a continuous solid solution, and E_g can be varied from 1.45 to 2.25. The research strategy consists of: 1) deposition of single phase alloy films; 2) evaluating effects of thermal and chemical treatments on film properties; 3) fabrication of solar cells with CdS window layers and Cu/Au contacts; and 4) analysis of device operation to determine processing modifications.

PVD and VTD are being used to deposit $Cd_{1-x}Zn_xTe$ thin films with x between 0.35 and 0.6 resulting in E_g from 1.7 to 1.9 eV. PVD $Cd_{1-x}Zn_xTe$ films are deposited at 325°C from CdTe and ZnTe sources where source temperatures control effusion rate and, thus, film composition [3]. The PVD films exhibit a dramatic loss of crystallinity for alloy composition for $0.1 < x < 0.9$; however, by annealing in argon at $T > 500^\circ C$ the crystallinity is restored with random orientation. VTD $Cd_{1-x}Zn_xTe$ films are deposited at 550°C from a 1:1 mixture of CdTe and ZnTe, resulting in films with $x \sim 0.35$, corresponding to E_g of 1.7 eV. This composition represents a steady-state between the CdTe and ZnTe saturation pressures within the source and Cd and Zn sticking coefficients at the substrate. VTD films are randomly oriented and have similar crystallinity as annealed PVD films.

Post-deposition treatment of $Cd_{1-x}Zn_xTe$ films in $CdCl_2$ vapor at 400°C results in removal of Zn from the film as volatile $ZnCl_2$. Treatment in $ZnCl_2$ vapor at 400°C results in no change to the alloy composition and causes recrystallization, i.e., re-orientation and grain growth, similar to that observed for CdTe films treated with $CdCl_2$. Devices made from PVD and VTD $Cd_{1-x}Zn_xTe$ films with $x \sim 0.35$ and CdS window layers exhibit similar properties, with $V_{oc} = 0.78V$ and $J_{sc} < 10$ mA/cm². Analysis of the spectral response indicates a $Cd_{0.65}Zn_{0.35}Te$ band gap of 1.7 eV.

4. CdTe Surface Chemistry

A critical aspect of CdTe cell processing is the preparation of a Te-rich CdTe surface to allow back contact formation. Wet oxidizing etches, including NP and BM, are often used. The action of CdTe etching is not completely understood, and a thorough knowledge of etch chemistry of CdTe surfaces is needed for the optimization devices.

The effect of chemical etching of CdTe films is being analyzed by surface sensitive methods, glancing incidence x-ray diffraction (GIXRD), and VASE to determine structure and phase distribution. Initial NP etches contained 1:70:29 $HNO_3:H_3PO_4:H_2O$ (NP1) and BM etches consisted of 0.05% Br_2 . As NP1 etching proceeds, bubbles are observed on the CdTe surface after ~20 sec and the CdTe becomes silvery-gray. BM forms a polished CdTe surface.

Figure 1 shows ϵ_2 vs. energy plots from VASE measurements of a CdTe film before and after 20 sec. in NP1. Since ϵ_2 is proportional to the absorption coefficient, changes in the ϵ_2 vs. energy spectrum coupled with GIXRD measurements can be correlated with changes in surface composition. In Fig. 1, the spectrum of unetched CdTe shows two peaks between 3 and 4 eV, while after the etch, only a single peak near 2 eV, due to Te, is seen. This suggests significant Te is present at the surface. VASE and GIXRD indicate for time >40s, NP1 etches produce crystalline Te films. For shorter etch times, the Te films contain an amorphous phase that spontaneously crystallizes due to its instability at room temperature [4]. Curve b of Fig. 1 shows that Te crystallization occurred within 10 mins of etching. In contrast, BM etching of CdTe is known to produce very thin Te films [5]. After 60s in BM, no surface Te was detected, though the VASE spectral intensities increased due to the enhanced reflectivity of the BM polished surface.

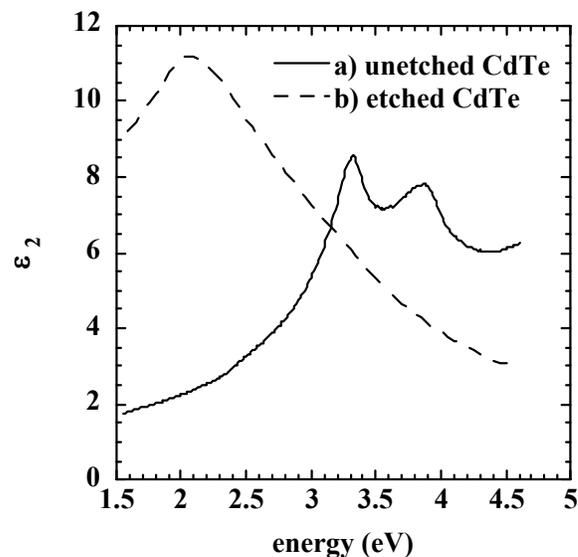


Figure 1 ϵ_2 vs. photon energy from VASE measurements of CdTe (a) unetched and (b) following 20s NP1 etch.

NP1 etched films are stable in the air for 3-4 hours before a decrease of Te begins due to atmospheric oxidation. Complete oxidation occurs after 7-8 hrs. BM etched CdTe begins to oxidize immediately, and is completely oxidized after 3-6 hrs. Thus, cells should be contacted immediately following etching.

NP1 etches of ~60s are needed to produce good cells [6]. This, however, produces significant GB etching [6],

Table 1 Conditions for cyclic stressing of FS and BP CdTe/CdS solar cells.

Condition	Hours light/temp	Hours dark/temp	Comments
1	24 hrs @ 65°C	None	Standard lab stress cycle
2	16 hrs @ 65°C	8 hrs @ 20°C	8 hrs dark, low T recovery
3	8 hrs @ 65°C	16 hrs @ 20°C	16 hrs dark, low T recovery
4	8 hrs @ 65°C	16 hrs @ 65°C	16 hrs dark, high T recovery

which may affect cell performance. To avoid GB etching, NP solutions of increased strength were considered. This would allow a fast etching of the CdTe surface, while minimizing GB diffusion of the HNO₃ due to the much shorter etch times required. Two NP etches of higher acidity, 1% and 0.5% HNO₃ in H₃PO₄ (NP2 and NP3, respectively) have been used. NP2 and NP3 produced a maximum amount of amorphous-Te following 2-4s and 4-6s, respectively, and longer times resulted in consumption of Te by the etch solution. Te crystallization occurs following etching. Unlike for NP1, CdTe peaks remain in the VASE spectra of NP2 and NP3 etched samples, indicating less net Te is produced. This may be the result of fast etching of surface Te, coupled with less GB etching. Scanning electron microscopy shows GB etching only occurs after >6s in NP2 and >8s in NP3. Preliminary analysis indicates that better devices are produced with etches that form the thickest Te.

5. Effect of Atmosphere and Light Cycling During Stress

There are two significant differences between the accelerated stress conditions used in most laboratories for CdTe research and the actual conditions experienced by CdTe modules in the field. One is the atmosphere: either room air or bottled dry air in the lab vs. encapsulated modules. The second is the duration of the illumination: continuous light exposure in the lab vs. cyclic daily sunlight illumination. IEC has built a system for accelerated stress studies of thin film solar cells under controlled conditions of ambient, light, bias voltage, and temperature. The effect of bias voltage during stress has been previously reported [7].

CdTe/CdS devices manufactured at FS or BP were stressed at either 65° or 85°C, for 30 days, at open circuit (OC), 1 sun illumination in bottled air, H₂/Ar, or in a vacuum. In general, no significant dependence of the device degradation on ambient was observed, suggesting that neither oxidation nor reduction play a crucial role in device degradation during accelerated stress.

Typically, lab stressing has been done at 70-100°C under continuous stress conditions while modules in the field see temperatures up to 60°C with cyclic light exposure and power generation. It is possible that some relaxation effects occur during the dark portion of the cycle which could result in slower degradation. Therefore, a series of stress experiments were performed

with various cycles of light (L), dark (D) and temperature (65° or 20°C) as shown in Table 1. Two sets of BP and FS devices with their own contacting process were stressed at each of the above conditions for 30 days. In each case, there was one device at OC and one at 1/2 OC bias. V_{oc} was monitored daily at 65°C after 24, 16, or 8 hours of light exposure. Condition 4 allows measurement of V_{oc} at 65°C after 16 hours dark or after 8 hours light

Figure 2 shows V_{oc} at 65°C for FS devices stressed at OC for the first 3 cycles in Table 1. V_{oc} decreases rapidly for 5 days regardless of cycle, then more slowly. The 8 or 16 hr. dark cycle seemed to have little effect. Thus, V_{oc} measured at 65°C during the stress degraded ~60-80 mV. However, upon removing and testing these cells on the simulator at 28°C at the end of 30 days, it was found that V_{oc} actually increased as much as 20 mV compared to the initial V_{oc}. Note that the devices were in the dark at room temperature in the lab for ~24 hours before testing. This apparent recovery is seen explicitly in Fig. 3 which shows the V_{oc} measured at 65° for the fourth stress condition. It is measured at 9 a.m. after the cells have been in the dark for 16 hrs. and at 5 p.m. when they have been in the light at OC for 8 hours. The FS devices clearly show a daily dark recovery of 30-50 mV followed by 30-50 mV decrease in V_{oc} during 8 hours illumination. Similar dark recovery in V_{oc} occurs in BP devices except that their V_{oc} doesn't degrade as much. Some BP devices were re-tested after 9 days storage in the dark. Devices with the greatest degradation recovered nearly all of their original performance; i.e. devices starting with 10% efficiency which then degraded to 9% during stress recovered to 9.7-9.8% after 9 days storage.

A key result is that V_{oc} in both FS and BP devices can show a daily cyclic variation. Observation of this metastable behavior implicates changes in the physio-chemical configuration, leading to changes in deep level traps or complexes, as partly responsible for stress-induced degradation, and suggests caution is needed in designing stress experiments and interpreting changes in device performance. The time between stress and measurement can allow for relaxation and partial recovery to occur. The variation of 30-50 mV seen here corresponds to 2-3 V in a 60 cell module. BP confirmed daily changes of this magnitude in an array between morning and afternoon.

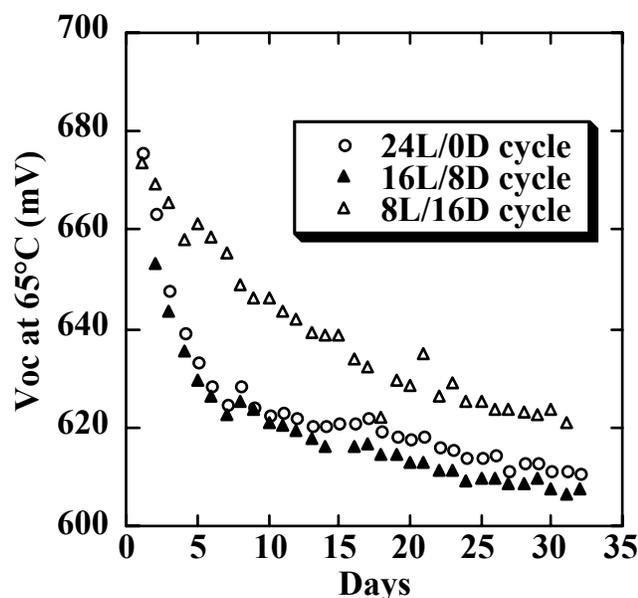


Figure 2. V_{oc} at 65°C in situ for 3 different light cycles for FS CdTe device.

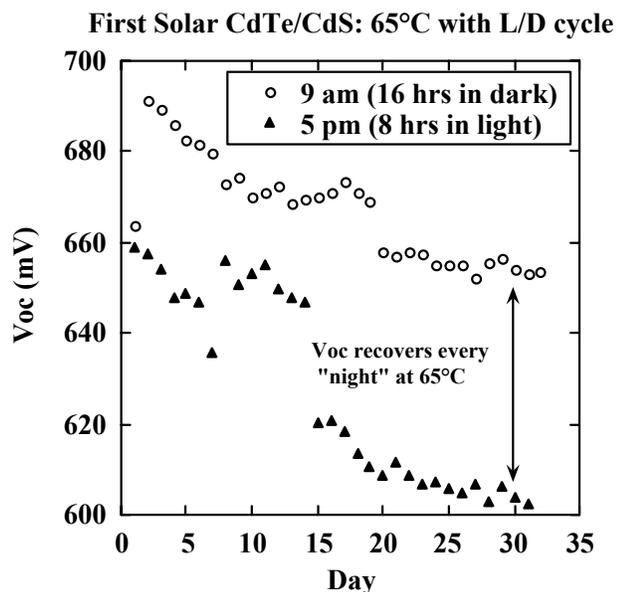


Figure 3. V_{oc} at 65°C in situ for FS device at 65°C data taken at 9 a.m. (following 16 hours of dark) and 5 p.m. (following 8 hours of light). Cell was continuously at 65°C.

6. Collaborations and Teaming

IEC actively participates in the National CdTe R&D Team by carrying out experiments and providing films and analysis to other groups. Until the recent closure of the BP Solar facility in Fairfield, California, IEC had provided them with close technical support and

collaboration, through independent interactions and as part of the National CdTe Team. IEC has performed numerous accelerated stress studies and device characterization for First Solar. Under the High Performance project, IEC serves as a lower-tier subcontractor to the University of Toledo by characterizing their ZnTe:N films.

7. Acknowledgment

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8. References

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