

PROGRAM AND PROCEEDINGS



NCPV Program Review Meeting 2000

April 16-19, 2000

Adam's Mark Hotel

Denver, Colorado



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Analysis of Moisture and CO₂ Uptake in Anhydrous CdCl₂ Powders Used for Vapor CdCl₂ Treatment of CdS/CdTe PV Devices

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ABSTRACT

Water and CO₂ uptake in CdCl₂ powder precursors was investigated using thermogravimetric analysis/Fourier transform infrared spectroscopy (TGA/FTIR). Exposure of powders under ambient conditions shows that a steady-state hydration level near 9 % (by weight) is achieved after brief exposure to room air, with minimal absorption and/or adsorption of CO₂. TGA has also shown that storage in a desiccator with Mg(ClO₄)₂ preserves the anhydrous form. Water is rapidly devolved from hydrated powders, with the pure anhydrate reappearing at temperatures below 150°C under N₂ flow and a modest heating rate of 10°C/min. Water present in raw-powder precursors is shown to affect the appearance of source plates manufactured by the close-spaced sublimation (CSS) method.

1. Introduction

A number of techniques exist to make thin-film CdTe solar cells and the majority utilize cadmium chloride in a post-deposition heat treatment. The use of cadmium chloride in the various "heat treatments" is related to the experience-based expectation that it will lead to optimal performance of the n-CdS/p-CdTe heterojunction. In many cases, recrystallization and reduction of grain boundary area via grain growth have been associated with the chloride treatment. As such, the mechanisms associated with the role of cadmium chloride as a sintering aid (fluxing agent) are only qualitatively understood at the present time and more fundamental knowledge of basic properties of this compound is clearly needed.

CdS/CdTe devices produced at the National Renewable Energy Laboratory (NREL) currently use a vapor process for the CdCl₂ treatment. The process begins by depositing a thick CdCl₂ film (~1 mm thick) onto a 2" x 2" Corning glass plate (7059 or 7059 F) by CSS of CdCl₂ powders from a graphite boat. This glass substrate plate is then used in the same chamber as a source plate for vapor treatment of a CdS/CdTe device using a CSS-like process. Although this process works well, anecdotal evidence suggests that moisture may be an important and uncontrolled parameter of both the source-plate fabrication and vapor-treatment processes. Although this evidence is contrary to preliminary data [1], it should not be a surprise because CdCl₂ is a strongly hygroscopic material. Specifically, we have observed that source powders can erupt (decrepitate) from the graphite boat during source-plate fabrication if the moisture content of the powder is high. This decrepitation

leads to considerable non-reproducibility during CdCl₂ source-plate production. Further, there appear to be significant differences between the source-plate films formed with old (hydrated) CdCl₂ powders and new powder sources. Finally, the vapor process appears to commence more rapidly when the laboratory humidity is high (i.e., the summer months). To isolate effects of moisture on the NREL vapor CdCl₂ process, this study uses TGA to measure the moisture content of CdCl₂ powders following controlled exposures to various environmental conditions. The CdCl₂ powders used at NREL are Alfa-Aesar products of 4N purity, anhydrous, and packed under argon. Two batches of the powders were investigated for this study. These batches were manufactured separately, and the major distinction between the two is the length of time they have been stored in the laboratory. Henceforth, any reference to "old" or "new" powders refers to these different batches.

2. Experimental Procedure

Anhydrous CdCl₂ powder samples were stored under controlled conditions including exposure to room air, storage in a desiccator charged with Mg(ClO₄)₂, and storage in a helium-filled glove box. For the air-exposed samples, an hygrometer was placed in the open container to monitor air humidity and temperature. Thermogravimetry, coupled with FTIR, was used to determine (in situ) species evolution and rate-of-loss when the powders were heated. A constant heating rate of 10°C/min from ambient to 500°C under an N₂ flow of 100 cc/min was used in all experiments.

3. Results and Discussion

As shown in Figure 1., fresh anhydrous powder and samples stored in protected environments exhibit little or no hydration. Regardless of exposure conditions, mass loss observed below 200°C is attributed to water evolution. This is demonstrated by real-time FTIR absorbance spectra correlating well with the TGA data. The steady "baseline" at intermediate temperatures is indicative of the pure anhydrate, and mass loss at temperatures above 450°C is due to sublimation of CdCl₂ (m.p. 568°C). CO₂ has been observed in some cases during the initial heating (low temperature) but at this time, it is uncertain if the CO₂ is present in the CdCl₂ or simply an artifact from the brief exposure of the TGA/FTIR system to the atmosphere during sample loading. No absorbance peaks are observed that correspond to the sublimation of CdCl₂ as it is an IR-inactive species.

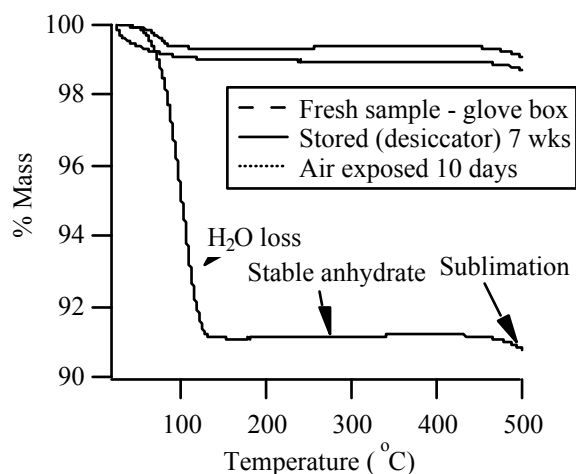


Figure 1. Thermogravimetric profiles of CdCl₂ stored under various conditions and heated at 10°C/min under N₂ flow.

Figure 2 shows the rate of hydration of CdCl₂ exposed to air. It is not clear at this time if the scatter in the data for exposure <5 days is related to some physical process. In any case, a steady-state value of ~9% (by weight) hydration was achieved after 1 week of exposure. This agrees well with preliminary analysis of the old powder source used to make source plates at NREL. In that case, no special precautions were used to preserve the anhydrous state of the powder and thermogravimetric analysis showed the water content to be ~8 wt.%. For reference, a fully hydrated compound (CdCl₂·2.5 H₂O, stable up to 34°C) contains ~20 wt.% H₂O.

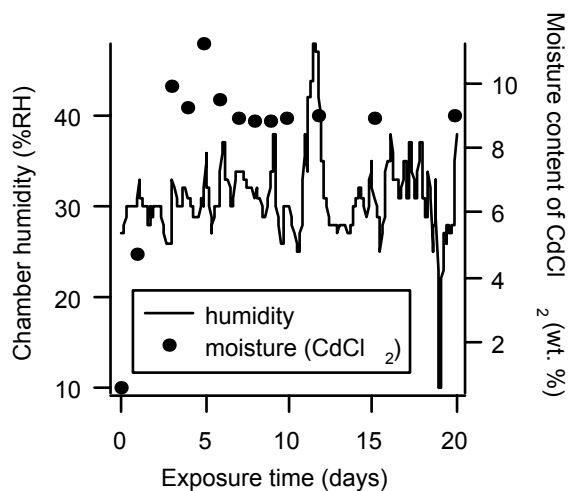


Figure 2. Moisture uptake in CdCl₂ exposed to ambient air.

The hydration level of CdCl₂ powder impacts the appearance of newly fabricated source plates. The old powder source (~8 wt.% water) produced more desirable source plates in the sense that the sublimated layer was thicker and more uniform as compared to plates made with the new powder (~2 wt.% water). However, as shown in Table 1, net-transfer efficiency (ratio of mass deposited on glass to total mass lost)

was much lower with the old CdCl₂. In other words, though more material was deposited under the same conditions with the old powder, a correspondingly larger amount of the powder was simply wasted. It is believed that the old-source powder is forcibly expelled (decrepitation) from the boat during a rapid heating (ambient to 200°C in 2 minutes) portion of the source-plate manufacturing process. In that case, the rapidly-evolved water vapor could enhance the transport of CdCl₂ from the graphite boat in an aerosol at the low temperatures. Indeed, solid particles were observed in the deposition chamber to a much greater degree with the old powder. Further, it is speculated that the aerosol coats the glass substrate to an appreciable degree or at least nucleates the surface for more efficient transfer at higher temperatures where CdCl₂ vapor sufficiently exists (e.g. 500°C).

Table 1. Mass transfer of different CdCl₂ powders using the same time-temperature profile for source-plate fabrication.

Source Powder	Transfer Efficiency	Mass Distribution (% initial mass)		
		Glass	Boat Residue	System Loss
Old	54.3	20.2	62.8	17.0
Old	71.2	22.5	68.4	9.1
Old	54.3	21.3	60.7	18.0
Old	44.3	17.8	59.8	22.4
Old	58.6	23.9	59.2	16.9
Old	45.1	19.3	57.3	23.5
Old	31.2	16.9	45.9	37.2
New	75.5	8.2	89.1	2.7

4. Conclusions and Further Work

Water is readily absorbed by anhydrous CdCl₂ under ambient conditions. However, CdCl₂ source powders do not achieve full hydration. CO₂ absorption is minimal for the short-term exposure used in this study. The decrepitation phenomena will be further explored by controllably hydrating new material and assessing its impact on source-plate characteristics. An additional study will focus on the impact of water vapor in the process ambient when treating CdS/CdTe devices, with emphasis on chlorine diffusion into the device.

5. Acknowledgements

The author would like to thank Dave Albin for discussions related to this work. This research was supported by DOE Contract #DE-AC36-99GO10337.

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- [1] Y. Mahathongdy, D.S. Albin, C.A. Wolden, and R.M. Baldwin, "Vapor CdCl₂ – optimization and screening experiments for an all dry chloride treatment of CdS/CdTe solar cells, AIP Conf. Proceedings #462, (AIP, New York) (1998) 236-241.