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*J.D. Webb, J. Keane, R. Ribelin, L. Gedvilas,
A. Swartzlander, K. Ramanathan, D.S. Albin,
And R. Noufi*

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National Renewable Energy Laboratory (NREL), Golden, CO 80401-3393

Abstract. Impurities in cadmium sulfide (CdS) films are a concern in the fabrication of copper (indium, gallium) diselenide (CIGS) and cadmium telluride (CdTe) photovoltaic devices. Devices incorporating chemical-bath-deposited (CBD) CdS are comparable in quality to devices incorporating purer CdS films grown using vacuum deposition techniques, despite the higher impurity concentrations typically observed in the CBD CdS films. In this paper, we summarize and review the results of Fourier transform infrared (FTIR), Auger, electron microprobe, and X-ray photoelectron spectroscopic (XPS) analyses of the impurities in CBD CdS films. We show that these impurities differ as a function of substrate type and film deposition conditions. We also show that some of these impurities exist as 10^2 micron-scale precipitates.

INTRODUCTION

Cadmium sulfide (CdS) plays an essential role in the creation of junctions, buffers, or passivation layers in thin-film photovoltaic (PV) devices (1). The best device performance has historically been achieved with solar cells incorporating CdS films grown by CBD, rather than CdS films grown using other methods, such as physical vapor deposition (PVD) (2), although CdTe devices with near-record efficiencies have recently been grown on close-spaced sublimated CdS films (3). Recently, considerable attention has been focused on the effects of components of the CBD solution on CIGS PV films (4) and on side products of the CBD reaction. Typical CBD solutions contain a soluble cadmium salt, ammonia, and thiourea (4), and sometimes use triethanolamine as a complexing agent for cadmium ion (1) or an ammonium salt as a pH buffer (2). Cadmium cyanamide (CdNCN) and $\text{Cd}(\text{OH})_2$ have been identified (1,5) in CBD CdS films. Urea (1) and cyanamide (HNCNH , 5) have been identified as the primary products of the CBD reaction. Hydroxyl ions (OH^-), water (H_2O), cyanamides, and carbonates were detected in CBD CdS films, but not in evaporated CdS films (6,7).

The variety of possible products and by-products of the CBD reaction, and the potential for aqueous ammonia to act as a complexing agent for both cadmium (1,8) and copper (8) ions, suggest that minor variations in the CBD process chemistry may have a significant influence on the CdS/CIGS interface and on the performance of the resulting devices (8). In CdTe thin-film PV devices, which are grown on CdS substrates to form an active heterojunction, the CBD process for CdS has produced high efficiencies (9), although alternatives to the CBD process, such as close-spaced sublimation, are being actively pursued (9, 10) and have excelled in some cases (3).

EXPERIMENTAL APPROACH

FTIR micro-spectroscopy was used in this work in concert with micro- and macroscale surface analytical techniques (11). The samples analyzed nominally consisted of IR-transparent films on IR-reflective substrates (Mo or SnO₂); any film contaminants will absorb IR radiation at frequencies characteristic of the particular contaminant(s). The Nicolet NicPlan FTIR microscope can obtain infrared reflectance (R) spectra of sample areas as small as 20 x 20 μm. The R spectra were converted to reflection-absorbance (RA = -log [1/R]) spectra to facilitate comparison with infrared spectral databases (which are stored in absorbance units) for pure chemical compounds. The FTIR microscope can be set to automatically scan a preset traverse or grid of the sample, record the spectra at each traverse or grid point, and prepare a two- or three-dimensional map of the intensity of infrared absorbance associated with a given chemical species versus sample position. FTIR specular reflectance (SR) spectroscopy enables RA analysis of a 1-cm² area of the samples for overall contaminant detection. An electron probe microanalysis (EPMA) system operated at 10 kV, a scanning Auger nanoprobe, and an XPS system were also used in this work (11).

RESULTS AND DISCUSSION

In (11), we used scanning FTIR micro-spectroscopy and EPMA to identify absorbed water and copper carbonates in one of numerous 150-μm orange inclusions visible in an experimental CBD CdS/CIGS/Mo PV device without a ZnO overlayer. Figure 1 shows a map of carbonate absorbance (shaded peak) vs. position. Our EPMA analyses show that the spot protrudes many times the EPMA sampling depth (~ 1 μm for CdS) above the CdS film surface, that it contains carbon, oxygen, copper, indium, and selenium in addition to cadmium and sulfur, but does not contain nitrogen or gallium. EPMA analyses of areas near the spot show only CdS.

Our interpretation of these results is that the spot contains normal or basic copper carbonate (12), which could have resulted from a side reaction between the CIGS film (or its surface oxides and selenides, 13) and the CBD bath. The CBD process for this sample involved the reaction of thiourea with cadmium acetate in ammonia-buffered aqueous solution at 75°C. Copper oxides and selenides are soluble in aqueous ammonia (12). Carbonates and bicarbonates can precipitate from solutions containing CO₂ and metal ions, and CO₂ is readily evolved from heated basic solutions of acetates (14), such as the ammoniated CBD bath. An alternative route for carbonate ion formation has been postulated as a result of absorption of atmospheric CO₂ by the basic CBD solution (6). Carbonates have been observed on the surfaces of similar devices by using large-area FTIR and XPS analyses (6). Our work indicates that the carbonates are in the form of localized precipitates on the device surfaces. We note that the CBD solution will preferentially dissolve copper from stoichiometric CIS (15); similar dissolution of copper from CIGS could result in precipitation of copper-containing impurities onto CIGS films in some CBD recipes.

To further investigate the CBD reaction chemistry, we prepared a series of 50-nm-thick CdS films on Mo/glass substrates using our standard CBD process for CIGS substrates, with CdSO₄ as the cadmium source, 40-70°C deposition temperature, and 100:1 molar ratio of thiourea to Cd (15). The glass substrates were either cerium oxide-polished soda-lime glass or Corning 7059 sodium-free glass. We analyzed these

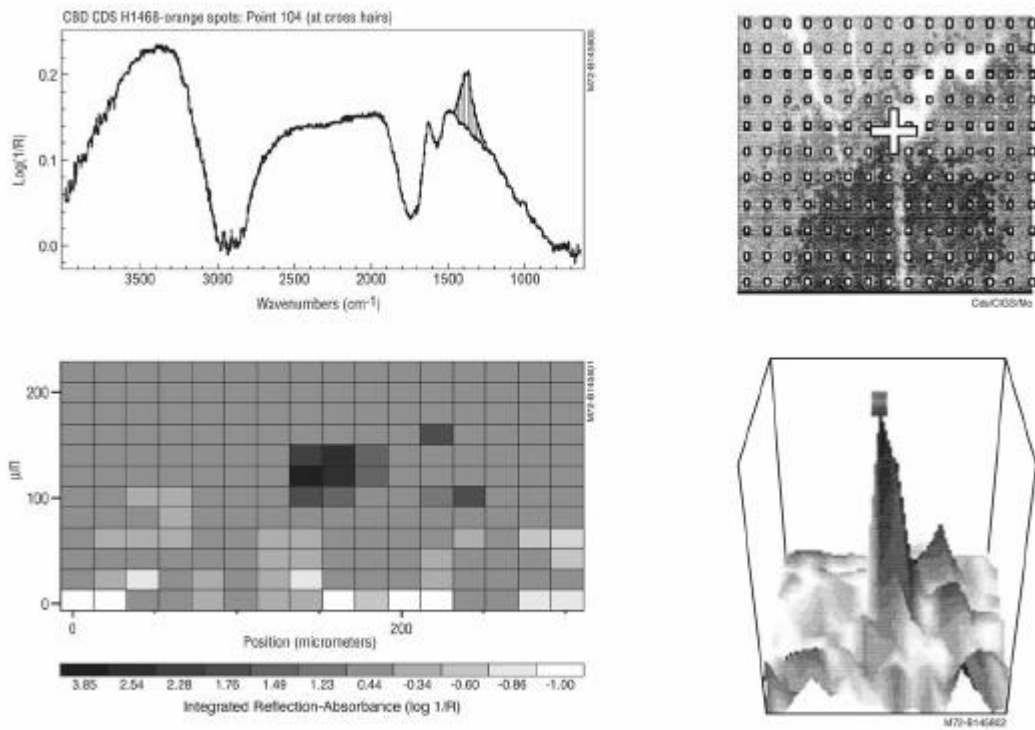


Fig. 1. FTIR microspectroscopic analysis of 50- μm orange spot on CdS/CIGS/Mo sample.

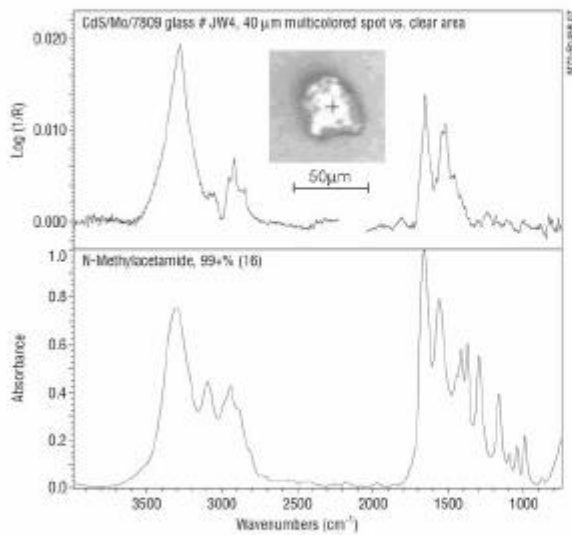


Fig. 2. Micro-FTIR-RA spectrum of 40 μm spot on CdS/Mo/7059 glass, compared to spectra of possible constituents.

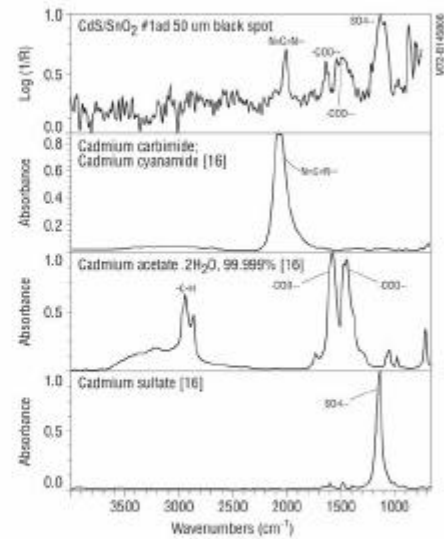


Fig. 3. FTIR microreflectance spectrum of 50- μm black spot on as-deposited CdS/SnO₂ sample, with library spectra [16] of probable contaminants.

samples using FTIR SR and micro-reflectance spectroscopy in conjunction with spectral database searches (16). The large-area SR spectra of the samples versus a gold-coated silicon wafer exhibited no contaminant absorbance peaks. However, when viewed through the visible-light optics of the FTIR microscope, the samples exhibited a number of precipitates large enough for FTIR microanalysis, i.e., with diameters > 20 μm . Precipitate coverage of about one large particle/ cm^2 was observed, and many more particles too small to analyze were visible on the samples. Database searching (16) of the FTIR spectra of the particles found matches to acetamide (Figure 2) or urea compounds for both substrate types. In addition to these particulate types, sulfate or molybdate-containing particles were identified in the CdS films on Mo/soda-lime glass, while hydrocarbons and silicates were found in particles in the CdS films on Mo/7059 glass. Precise matches to carbonates were not found in the CdS/Mo samples, in contrast to the CdS/CIGS/Mo sample (Figure 1). It is possible that carbonate formation is favored when a CIGS film, which makes soluble metallic counter-ions available during CBD, is present. We have found good matches to carbonate and bicarbonate species in the FTIR micro-reflectance spectra of large (100-400 μm), sodium-containing dark spots on the surfaces of CIS/Mo films prepared both with and without added sodium (17,18). This indicates that carbonates could even be present before CBD on some CIGS films, as a product of the reaction of sodium with atmospheric oxygen and carbon dioxide. Work in this area is continuing, with spectroscopic microanalyses of additional CIGS/Mo and CdS/CIGS/Mo samples currently in progress.

We also examined a series of CBD CdS films, 0.07-0.10- μm thick, on Corning 7059 glass substrates coated with $\text{SnO}_2\text{:F/iSnO}_2$ (19). These samples are typical substrates for CdTe deposition, and contained numerous visible anomalies in the form of spots 50-100 μm in diameter. The CBD process for these samples involved the reaction of a 2:1 molar ratio of thiourea and cadmium acetate in ammonia-ammonia acetate buffered aqueous solution at 86-90°C, followed by ultrasonic agitation and rinsing in deionized (DI) water ("standard" CdS/SnO₂ procedure, see 20). Using FTIR micro-spectroscopy and searches of spectral databases (16), we have identified acetate, sulfate, and cyanamide ionic species in black spots visible on or in the as-deposited CBD CdS films (Figure 3). The cyanamide ionic species (probably cadmium cyanamide) can be distinguished from cyanamide, the expected reaction product, by its lower vibrational frequency (16). The FTIR analyses were confirmed using the scanning Auger nanoprobe and XPS. The failure to remove the soluble acetate and sulfate precipitates through DI water rinsing could be explained if these precipitates were encapsulated by a thin CdS overlayer. In (11) we described the effects of annealing and hydrochloric acid rinsing in removing the various precipitate types. FTIR analyses showed that among the various annealing and rinsing procedures, only acid rinsing plus annealing in oxygen at 600°C completely removed the organic precipitates. Auger analyses showed that the acid rinse plus 600°C oxygen anneal left tin-rich spots on the sample surfaces, which are apparently voids through the CdS films to the SnO₂ substrates. Some of these voids were probably created by oxidation of included organic precipitates, as well as by evaporation of SnS phases from the CdS films (19).

We performed a study of the effect of variations in the CBD recipe for the CdS/SnO₂ films on impurity type and prevalence using FTIR SR spectroscopy and FTIR micro-spectroscopy. The "standard" CBD recipe (19) was modified by varying the thiourea/Cd and Cd/ammonium acetate molar ratios, by varying the bath agitation procedures, or by adding a rinse with 100% acetic acid following the CBD process.

The SR RA spectra of the samples, computed versus an uncoated SnO₂/glass background sample, showed a peak at 2000 cm⁻¹, similar to the cadmium cyanamide absorbance shown in Figure 3. The intensity of this peak, normalized for film thickness, was used to gauge the level of cyanamide contamination in the samples. Varying the thiourea/Cd molar ratio from 0.7B8.0 had little effect on the cadmium cyanamide band intensity, but increasing the Cd/ammonium acetate ratio to 0.15 from its standard value of 0.06 correlated to an increase in cadmium cyanamide band intensity. FTIR-RA measurements showed that attempting to remove the cadmium cyanamide by rinsing the samples in glacial (100%) acetic acid per (1) were unsuccessful, perhaps because the precipitates are encapsulated within the CdS film. The acid-rinsed samples also exhibited an FTIR-RA band at 757 cm⁻¹, which is similar to the 816 cm⁻¹ absorbance band that we measured using FTIR transmission micro-spectroscopy for stannous oxide (SnO, Aldrich Chemical Co.) particles dispersed in a potassium bromide pellet. Our measurement of the 816 cm⁻¹ SnO absorbance band is confirmed in the literature (21). The 757-cm⁻¹ band observed in the acid-rinsed samples is nearly identical in frequency to the 761-cm⁻¹ absorbance band characteristic of the stannous oxide trimer, Sn₃O₃ (21). The presence of stannous oxide in CdS/SnO₂ films has been postulated (19); encapsulation by CdS and the presence of reducing impurities in the CdS films may inhibit the expected oxidation of SnO to SnO₂ in air. The SnS and CdO phases detected in the CdS films using x-ray techniques (19) cannot be confirmed using FTIR micro-spectroscopy because of the low frequency of their characteristic lattice absorbance bands (22).

A CdS sample grown using ultrasonic agitation plus magnetic stirring during the standard CBD process exhibited much higher cadmium cyanamide band intensity relative to the standard process, and also showed the stannous oxide peak. A sample grown using the standard procedure, with ultrasonic agitation but no stirring during CBD, yielded a CdS film exhibiting low cyanamide band intensity and no stannous oxide RA peaks, similar to results obtained using the standard procedure. From the FTIR-SR results, we suspect that stirring deposits contaminants on the CdS films, which are then encapsulated during later stages of CBD. In comparison with the FTIR-SR results from the CBD CdS/Mo samples, the standard process for the CdS/SnO₂ films yielded much higher contaminant levels. However, attempts to use the CBD process developed for CdS/CI(G)S (15) initially did not yield uniform CdS/SnO₂ films, apparently because the SnO₂ films have a much lower density of nucleation sites than CIGS films (23), although good quality CdS/SnO₂ films were obtained subsequently by slightly modifying this process (24). Our present “standard” CBD recipe for CdS/SnO₂ (20) was developed to overcome the uniformity problem (25).

Using the visible light optics of the FTIR microscope, we counted surface coverages of about 70B80 particles/cm² with diameter > 20 μm on most of the CdS/SnO₂ samples—far higher than the precipitate coverage of about 1 particle/cm² observed on the CdS/Mo samples. In addition to the ionic cyanamide and stannate absorbances present in the FTIR-SR spectra, the micro-FTIR RA spectra of the CdS/SnO₂ samples exhibited bands characteristic of ionic cyanates, sulfites, and sulfates, and also acetamides similar to the library spectrum bands shown in Figure 2. There was no clear correlation between the presence of these species and the variations in the CBD recipes described previously.

CONCLUSIONS

The wide variety of chemical species observed in the CdS films is ascribed to variations in the CBD conditions and substrates. These species occur primarily as precipitates or precipitate clusters with diameters up to 200 μm . In the CdS/CIGS device, the dimensions and prevalence of the impurity-containing spots suggest that a fairly extensive reaction occurred between the CBD solution and the absorber film or its soluble contaminants to yield carbonates. In the CdS/SnO₂ samples, post-CBD annealing treatments alter the composition of the impurity precipitates, but do not remove them without leaving tin-rich spots behind. We infer from these results that modification of the CBD process to prevent codeposition of impurity precipitates in the CdS films, rather than post-CBD treatments, will prove most effective in producing clean, uniform CdS films. Although the CBD process for CdS yields high-quality devices in many cases (25), the size and extent of the precipitates observed suggest potential performance problems. The evidence for incorporated water and ionic salts in the precipitates, as well as their size, indicate that they could function as shunts or initiate delamination in a finished device. Although the low density of particulate contaminants found on the CdS/Mo samples is adequate for laboratory-scale devices, a particle density of 1/cm² would be of concern during CIGS module manufacturing if the particles act as shunts or delamination centers. We have evidence that impurities in CBD CdS films facilitate delamination of CdTe from CdS (23). These observations provide impetus for developing alternatives to the CBD process for CdS, while gaining an understanding of the positive effects of the CBD process on device performance. We expect that FTIR and surface spectroscopic techniques will continue to provide useful insights into these issues.

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