



## Effect of CdCl<sub>2</sub> passivation treatment on microstructure and performance of CdSeTe/CdTe thin-film photovoltaic devices

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### ABSTRACT

The effects of the CdCl<sub>2</sub> passivation treatment on thin-film CdTe photovoltaic films and devices have been extensively studied. Recently, with an addition of CdSeTe layer at the front of the absorber layer, device conversion efficiencies in excess of 19% have been demonstrated. The effects of the CdCl<sub>2</sub> passivation treatment for devices using CdSeTe has not been studied previously. This is the first reported study of the effect of the treatment on the microstructure of the CdSeTe /CdTe absorber. The device efficiency is < 1% for the as-deposited device but this is dramatically increased by the CdCl<sub>2</sub> treatment. Using Scanning Transmission Electron Microscopy (STEM), we show that the CdCl<sub>2</sub> passivation of CdSeTe/CdTe films results in the removal of high densities of stacking faults, increase in grain size and reorientation of grains. The CdCl<sub>2</sub> treatment leads to grading of the absorber CdSeTe/CdTe films by diffusion of Se between the CdSeTe and CdTe regions. Chlorine decorates the CdSeTe and CdTe grain boundaries leading to their passivation. Direct evidence for these effects is presented using STEM and Energy Dispersive X-ray Analysis (EDX) on device cross-sections prepared using focused ion beam etching. The grading of the Se in the device is quantified using EDX line scans. The comparison of CdSeTe/CdTe device microstructure and composition before and after the CdCl<sub>2</sub> treatment provides insights into the important effects of the process and points the way to further improvements that can be made.

### 1. Introduction

Thin film CdTe based photovoltaics have recently demonstrated lowest cost of electricity for utility scale energy generation. The technology is recognized to be an important contributor to the global need for sustainable renewable energy. The technology is low cost and has proven industrial scalability [1]. With improvements in fabrication processes, research scale small devices with device efficiency up to 22.1% [2] have been reported while commercial module efficiencies of 18.6% [3] have been achieved. The average efficiency of commercial production modules has increased from 13.5% to 16.2% between 2014 and 2016 [4,5]. Device efficiency has been improved recently by modifying the cell architecture by introducing new materials into the buffer layer and into the absorber. These modifications have not resulted in increased manufacturing complexity or cost. The most significant improvement has involved the introduction of Se to form a CdSeTe layer at the interface with an intrinsic but fully transparent

buffer layer such as magnesium doped zinc oxide (MZO). These devices have demonstrated a conversion efficiency above 19% with short-circuit current density ( $J_{SC}$ ) of over 28 mA/cm<sup>2</sup> [6]. Devices fabricated using a CdTe-only absorber using similar fabrication conditions with efficiency 18.6% have been reported by the authors [7]. This suggests incorporation of Se is an important improvement in device fabrication technology. Optimization of the CdSeTe/CdTe absorber is required to further optimize the composition of these films and achieve improvement in device efficiency. It is important to understand the behavior of these CdSeTe/CdTe films under processing conditions. It is well known that the cadmium chloride annealing process is vital to obtain good efficiencies with conventional CdS/CdTe devices. Here we report on the effects of the treatment on the microstructure and composition of CdSeTe/CdTe devices and relate these effects to device performance using direct evidence from device cross sections investigated using Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray Analysis (EDS).

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In this study, two thin-film devices were deposited with CdSeTe and CdTe using sublimation under identical process conditions. One as deposited device was characterized while the second device was treated with CdCl<sub>2</sub> and then characterized. The CdCl<sub>2</sub> treatment is a critical process step in fabrication of high efficiency CdTe photovoltaic devices [8,9]. In this study cross-sections of the CdSeTe/CdTe devices, as deposited and CdCl<sub>2</sub> treated, were analyzed using cross-section scanning transmission electron microscope (STEM) imaging, energy dispersive X-ray spectroscopy (EDS) elemental mapping, EDS line scans and EDS selected area analysis. In addition, the electrical performance of these research scale small devices was obtained to correlate with the structural analyses. The analysis of these devices show similar behavior between the CdSeTe/CdTe graded absorber devices and the CdTe-only devices. Effect of CdCl<sub>2</sub> passivation treatment on grain structure of these films is thoroughly studied. The CdCl<sub>2</sub> passivation treatment also causes removal of stacking faults in CdSeTe as previously observed in CdTe films. Elemental analysis of fabricated films using cross-section TEM and EDS is used to understand the effect of CdCl<sub>2</sub> treatment on material composition of the film. Behavior of chlorine observed in CdSeTe/CdTe films with CdCl<sub>2</sub> is similar to CdTe-only films [10]. Electrical characterization of these devices shows a steep improvement in device performance after the CdCl<sub>2</sub> passivation treatment.

## 2. Experimental

The cells used in the study were deposited on NSG TEC 10 soda lime glass coated with fluorine-doped tin oxide (FTO) to function as a transparent conducting oxide (TCO). A 100 nm thick Mg<sub>z</sub>Zn<sub>1-x</sub>O (MZO) buffer layer was deposited using RF sputter deposition [11,12]. Identical CdSeTe films were sublimated on 2 TEC 10 glass substrates that were coated with MZO using an optimized deposition process followed by sublimation of the CdTe layer. On one of these substrates, CdSe<sub>x</sub>Te<sub>1-x</sub> (CdSeTe) and CdTe depositions were followed by CdCl<sub>2</sub> passivation, performed in-line without breaking vacuum. The substrate was heated to ~530 °C before starting the sublimation of CdSeTe. The temperature of the substrate was measured in-situ using a pyrometer located outside the pre-heating station. The thin-films for this study were deposited using the advanced deposition system with 9 process stations at Colorado State University previously optimized for fabrication of CdTe based thin-film devices [13].

The CdSeTe composition used for this study had 40% CdSe in the source material and the as-deposited films had a band-gap of ~ 1.41 eV measured using optical transmission measurements and the Tauc plot method. The CdSeTe vapor source was heated to 575 °C while the substrate heater was maintained at 420 °C and CdSeTe films of ~ 1.5–2.0 μm thickness were deposited. After deposition of CdSeTe, the substrate was moved to the CdTe sublimation vapor source and a film ~3.5 μm thick was deposited. The total thickness of CdSeTe and CdTe film stack was measured to be ~5 μm using a profilometer. The CdTe sublimation source temperature was maintained at 555 °C and the substrate heater for this source was maintained at 500 °C. One of the substrates was moved to the CdCl<sub>2</sub> vapor passivation treatment station in-situ without breaking vacuum after the CdTe film deposition. The CdCl<sub>2</sub> sublimation source was maintained at 447 °C while the substrate heater for this source was heated to 430 °C. The CdCl<sub>2</sub> passivation treatment was performed for 600 s. These temperatures were determined after several experimental iterations to optimize the CdCl<sub>2</sub> treatment such that at the end of the 600 s treatment there was a thin film of CdCl<sub>2</sub> deposited on the substrate. Following the CdCl<sub>2</sub> passivation treatment, the substrate was moved to a cooling station without any active heating and allowed to cool for 180 s. No post CdCl<sub>2</sub> treatment annealing was performed during this experiment. After this process step, the substrate was removed from the vacuum chamber and the residual CdCl<sub>2</sub> film was rinsed using de-ionized water.

Thereafter, the films were heated to ~ 140 °C, and CuCl was deposited on the film surface for 110 s. This was followed by 220 s of

annealing at 220 °C, both in vacuum, to form a Cu doped back contact. A ~ 30-nm Te film was evaporated to improve the back-contact [14]. After the deposition of Te, the substrates were cut in half. One half was used for materials characterization using TEM and TEM/EDS. Carbon and nickel paint in a polymer binder was sprayed on the second half of these films to form the back electrode. These halves with carbon and nickel back electrode were masked and delineated to form 10 small scale devices with an area of ~ 0.55 cm<sup>2</sup>, that were tested for electrical performance using current density vs voltage measurements using a 1.5 AM spectrum. ABET Technologies 10,500 solar simulator with uniform illumination accessory was used to illuminate the devices for measurements. The lamp used for illumination as ozone free DC xenon arc lamp that produces 1Sun power output over 35 mm diameter field and, met ASTM, IEC and JIS Class A AM1.5 G output requirements. Current density v/s voltage curves were generated based on electrical measurements performed using Keithley 2420 SourceMeter controlled by a LabView program. Short-circuit current density was calibrated to cells measured by NREL. Device areas were measured using a webcam that took an image of a backlit solar cell and counted the pixels below certain brightness. Both the light intensity and area were calibrated for each set of measurements. The cells were contacted by a fixture of spring loaded gold pins that provided a 4-point connection and collect current from all around the front contact of the device. The setup accurately measures the J-V parameters and the agreement of these measurements with an externally certified photovoltaic device is shown in the [Supplementary section](#).

Specimen foils for scanning transmission electron microscopy (STEM) were prepared using an FEI focused ion beam (FIB) dual beam system using a standard in-situ lift out method [7]. STEM specimen preparation and imaging were performed at Loughborough University, U.K. STEM imaging was performed using a FEI Tecnai F20 S/TEM equipped with Gatan Bright and Dark field STEM detectors, Fischione High Angle Annular Dark Field (HAADF) STEM detector and an Oxford Instruments X-Max 80 mm<sup>2</sup> windowless energy-dispersive spectrometer (EDX). STEM imaging was performed at 200 kV with a camera length of 100 mm and condenser aperture size of 70 μm using a spot size of 7. Such an aperture size provides a good resolution with lower depth of field. However, the specimen being thin TEM specimen lower depth of field does not affect the image quality. HAADF images were collected in conjunction with STEM bright field images. HAADF imaging gave a unique perspective as the higher the atomic weight of the material, the more the electrons pass through the sample to be detected. Therefore the amount of signal collected depends on the atomic weights of the elements within the sample, providing atomic weight contrast in the image.

The STEM system was equipped with a Silicon Drift Detector (SDD) allowing high spatial resolution Energy Dispersive X-ray (EDX) measurements and chemical mapping. This was useful to map the diffusion of elements such as chlorine and selenium in the absorber matrix. EDX spectra were collected for 120 s. Elemental maps were collected using the largest condenser aperture (150 μm) with the largest spot size. Strength of condenser lens controls probe size and final probe current. Larger condenser aperture allows more current to pass through to become probe current on the specimen. Large condenser aperture and spot size were used to achieve high EDS output signal while maintaining lower dead time. The dead time was further controlled by changing the process time; each frame took approximately 120 s to collect. Maps were collected from 10 min up to 1 h with no discernible sample drift.

## 3. Characterization

Cross-sections of as deposited CdSeTe/CdTe films and devices following the CdCl<sub>2</sub> passivation treatment were imaged using STEM (Fig. 1). Fig. 1A shows the grain structure of an as deposited CdSeTe/CdTe absorber layer. Large number of small grains can be observed near the CdSeTe/CdTe and MZO interfaces. In the as-deposited film, the

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