Antimony Chloride Treatments of CdTe-Based Solar Cells

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***Abstract* — Development of a new $SbCl_3$-based solution treatment for chloride activation of CdTe-based solar cells is described. Activation was confirmed with CdSeTe:Sb devices exhibiting V_{OC} > 550 mV and J_{SC} > 25 mAcm^{-2}. Treatment optimization showed strong effects of annealing time and temperature on cell properties. Material characterization indicated surface conversion of CdSeTe to $CdCl_2$ and Sb_2Te_3 with $SbCl_3$ treatment. However, no reaction products were formed with treatment under inert conditions, which was coupled with poor device performance. Drying the $SbCl_3$ films at controlled humidity conditions confirmed that exposure to high relative humidity is critical for CdSeTe activation, through hydrolysis of $SbCl_3$. Mechanistic details of $SbCl_3$ speciation during hydrolysis and annealing to activate CdSeTe are discussed.**

I. Introduction

Chloride-based treatments are ubiquitous for the processing of thin film CdTe solar cells and are critical to achieve high device performance [1]. Treatment with $CdCl_2$ can result in grain recrystallization and growth, promotion of layer inter-diffusion, modification of defects, and passivation of grain boundaries. However, Cl^- treatments of alloyed-CdTe species can be limiting. For example, it has been shown that $CdCl_2$ treatments of CdZnTe result in stripping of Zn from the material lattice [2]. This was overcome by using $ZnCl_2$, which successfully maintained alloy composition, though handling $ZnCl_2$ is complicated by its highly hygroscopic nature. There is a need to identify alternate and manufacturable halide activation chemistries with the flexibility for application to CdTe and its alloys.

$SbCl_3$ has been highlighted as a possible alternate chloride flux for CdTe alloys [3], with the potential to maintain both alloy composition, as well as Sb doping that has been developed in our laboratories [4]. Its less hygroscopic nature also allows for easier material handling. Li et al. [5] demonstrated post-deposition chloride solution treatments as an approach for ex-situ Sb-doping of CdTe, demonstrating device performance improvements compared to Cu-doped cells. Ciris [3] considered the use of $SbCl_3$ solutions as an alternate chloride treatment for CdTe, with treated films showing significant grain growth, coarser grain morphology, and Sb inclusion into the lattice.

In this paper, $SbCl_3$-based solution treatments for Sb-doped CdSeTe (CdSeTe:Sb) are described which activate CdSeTe photovoltaic performance, particularly through improvement of device J_{SC}. Optimization of treatment chemistry, however, showed the critical involvement of water vapor in CdSeTe:Sb activation. The chemical effects of humidity on $SbCl_3$ speciation and its potential role for CdSeTe film activation are discussed.

II. Materials and Methods

$SbCl_3$ treatments were carried out on vapor transport (VT) CdTe:Sb deposited on a front stack of thermal-evaporated 500 nm $CdSe_xTe_{1-x}$ (x~0.25) and 250 nm CdTe bilayer on a TEC-12D glass substrate, with the absorber designated as CdSeTe:Sb. Sb-doping is carried out during CdTe VT deposition, controlling in-situ Sb vapor concentration in the presence of a Cd vapor excess to assist Sb incorporation [6]. Processing details are provided elsewhere [4].

$SbCl_3$ solution-based treatments of CdSeTe:Sb were carried out, unless otherwise noted, using 0.1 M solutions of $SbCl_3$ (≥99.0%, Sigma Aldrich) with either air-exposed methanol (Electronic Grade, Fisher) or anhydrous methanol (99.9%, Thermo Scientific). Dry solutions were prepared in a N_2-glovebox using the anhydrous solvent. $SbCl_3$ films were prepared by drop-casting 200 µL aliquots of $SbCl_3$ solution onto 1"x1" CdSeTe:Sb substrates and dried at ~60°C on a hotplate in the glovebox (dry treatment) or drop-cast in room ambient and dried at ~65°C in an air-filled oven (air treatment). For controlled relative humidity (RH) experiments, $SbCl_3$ films were dried in air in an oven at ~65°C over saturated solutions [7] in a closed petri dish. Saturated aqueous solutions of LiCl (99%, Sigma-Aldrich), NaBr (ACS Grade, Fisher) and KCl (99.0-100.5%, Sigma-Aldrich) were used to control RH at ~10%, ~50%, ~80%, respectively, while use of pure H_2O is designated as 100% RH in this report. The solutions were pre-warmed at 65°C for ~30 mins in a smaller petri-dish in the covered larger vessel, after which drop-cast $SbCl_3$ solution-coated CdSeTe samples were placed in the larger vessel, quickly replacing the cover, and allowed to dry. The $SbCl_3$ films generally dried within 15 min.

Dried $SbCl_3$/CdSeTe samples were stored and transported in an Ar-filled box. Anneal treatments were carried out by covering samples with a glass slide and heating in a tube oven at 460°C for 30 min under flowing Ar, unless otherwise stated. Following treatment, samples were rinsed in methanol and then contacted for cells by 10 min dips in 10^{-2} M aqueous $CuCl_2$ (>98%, Alfa Aesar) before briefly rinsing with water and annealing at 260°C for 30 min in Ar. On cooling, cells were immediately contacted with graphite paste with area = 0.36 cm^2.

Current-voltage (JV) measurements were obtained using an Oriel Xenon solar simulator at AM1.5 and 25°C. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were obtained using an Amray 1810T Digital Scanning Electron Microscope. Symmetric x-ray diffraction (XRD) and glancing incidence XRD (GIXRD) were measured using a Rigaku D/Max 2500 system with para-focusing optical configuration and Cu K_α radiation at 40 kV.

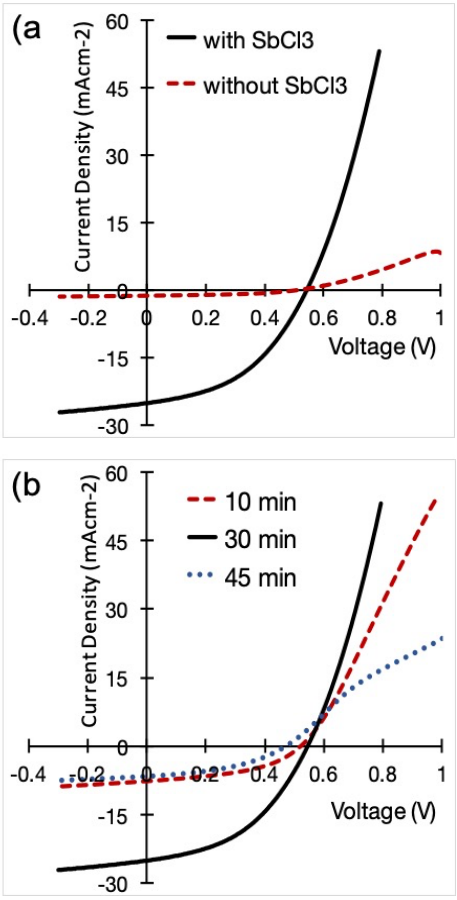

Fig. 1. Light JV curves of CdSeTe:Sb solar cells (a) no Cl^- treatment and with 0.1 M $SbCl_3$ air treatment at 460°C for 30 min, and (b) with 0.1M $SbCl_3$ air treatment at 460°C for 10, 30, and 45 min.

III. Results and Discussion

A. Development of $SbCl_3$ treatments

Fig. 1a shows the JV curves of an untreated CdSeTe:Sb cell, and a device processed with $SbCl_3$ air treatment, using air-exposed methanol solution and $SbCl_3$ film dried in air prior to annealing, with the treated device exhibiting V_{OC}=544 mV and J_{SC}=25.2 mAcm^{-2}. For comparison, the non-treated cell has J_{SC}<10 mAcm^{-2}; the low J_{SC} is due to poor carrier transport and the significant J_{SC} improvement indicates electronic activation of CdSeTe. While performance of the $SbCl_3$-treated cell is below our current best $CdCl_2$-treated cells, which have V_{OC}>830 mV, J_{SC}>25 mAcm^{-2} (not shown), a similar J_{SC} has been obtained with the new $SbCl_3$ treatment. Preliminary optimization of air treatment conditions was carried out. Resultant cells showed anneal time and temperature had a significant effect on JV performance, with J_{SC} improving from 10 min to 30 min treatments at 460°C (Fig. 1b), however treatments of >30 min or >460°C significantly decrease both V_{OC} and J_{SC}. Varying [$SbCl_3$], from 0.01 M – 1 M, showed little effect on cell performance.

SEM characterization of CdSeTe:Sb films with and without $SbCl_3$ air treatment is shown in Fig. 2. A roughening of grain morphology is seen, indicating $SbCl_3$ interaction or reaction with the CdSeTe:Sb surface. EDS analysis at 20 kV of the treated sample following a methanol rinse confirmed a near-surface uptake of 3-4 at% Sb.

XRD analysis of CdSeTe:Sb following $SbCl_3$ air treatment is shown in Fig 3. Aside from primary CdTe-related reflections, peaks are observed that are assigned to newly formed phases, confirmed from GIXRD to be on the CdSeTe surface, of Sb_2Te_3 and $CdCl_2$ along with smaller levels of Cd- and Te-oxychloride-based phases. A methanol rinse of the sample resulted in a decrease in intensity of peaks assigned to soluble $CdCl_2$. These observations confirm that $SbCl_3$ is reactive at the CdSeTe surface, producing the reaction products via Eq. (1), and with further optimization, is a potential agent for chloride treatments of CdTe.

$$3CdTe + 2SbCl_3 \rightarrow Sb_2Te_3 + 3CdCl_2 \qquad (1)$$

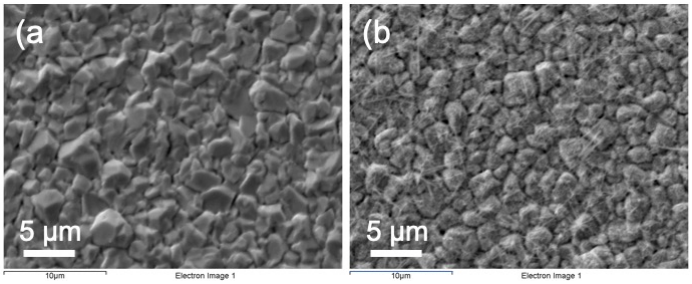

Fig. 2. SEM images of CdSeTe:Sb films (a) without treatment, and (b) following 0.1 M $SbCl_3$ air treatment at 460°C for 10 min.

The presence of oxychloride phases following air treatment of CdSeTe:Sb suggests a role of O_2 or H_2O vapor in the $SbCl_3$ chemistry. To confirm this, different approaches for $SbCl_3$ film preparation were compared. Fig. 4. shows the light JV curves of a CdSeTe:Sb cell following dry $SbCl_3$ treatment, using a dry methanol solution and $SbCl_3$ film prepared in the N_2 glovebox, and a second cell prepared using the same dry $SbCl_3$ methanol solution but with the $SbCl_3$ film dried in air. Both cells were

annealed at 460°C for 30 mins in Ar. The JV data of the dry processed cell shows low activation (J_{SC}≈5 mAcm^{-2}), while the device treated with the air-dried film showed improved JV performance (J_{SC}≈17 mAcm^{-2}). XRD of a dry $SbCl_3$-treated CdSeTe:Sb film (Fig. 5) showed only CdTe-related reflections, compared to a CdSeTe:Sb film treated with an air-dried $SbCl_3$ film, indicating that no surface chemistry occurred during treatment, consistent with the observed poor JV performance.

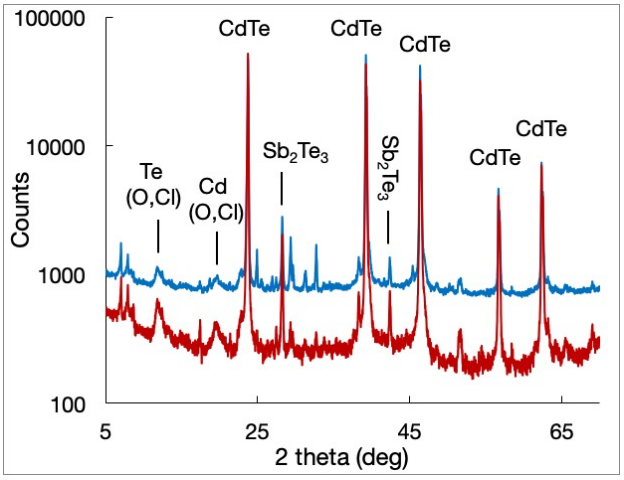

Fig. 3. XRD patterns of CdSeTe:Sb film (blue) directly following $SbCl_3$ air treatment, and (red) following methanol rinse. Plots are offset for clarity.

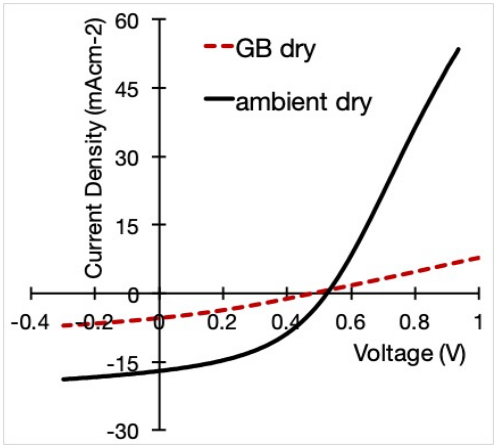

Fig. 4. Light JV curves of $SbCl_3$-treated CdSeTe:Sb cells with $SbCl_3$ films prepared from dry methanol solution and dried either in the glovebox or in air prior to annealing at 460°C for 30 min in Ar.

Other approaches to introduce ambient exposure of $SbCl_3$ films were tested. Annealing of a glovebox-dried $SbCl_3$ film in ambient air gave JV curves with strong blocking behavior likely due to oxidation of the CdSeTe surface, while exposing samples with glovebox-dried $SbCl_3$ films to humidity during annealing by bubbling the Ar purge gas through H_2O, resulted in no cell activation. Controlled addition of liquid H_2O to a $SbCl_3$ / dry methanol solution ([H_2O] up to 0.55 M) was also tested, however, after drying films in the N_2 glovebox followed by annealing, no CdSeTe activation was observed.

A further approach was to dry the $SbCl_3$ films in air at controlled RH. $SbCl_3$ films were prepared on CdSeTe substrates by drying aliquots of $SbCl_3$/dry methanol solution over various saturated solutions [7] at ~65°C in a closed petri dish to vary RH from ~10% to 100% RH. Treatment anneals were then carried out at 460°C for 30 mins. Fig. 6 shows V_{OC} and J_{SC} from the resultant devices with $SbCl_3$ films dried for 15 mins at varying RH. V_{OC} shows a steady increase of ~100 mV with increasing RH, while cells exhibit almost no J_{SC} at RH<50%, indicating no chloride activation. However, at RH>50%, a rapid J_{SC} increase in observed, indicating that exposure to high humidity is critical for $SbCl_3$ activation of CdSeTe. Optimization of drying conditions indicated that longer film drying times of 45 min generally produced improved cell performance. Drying films at high humidity was incorporated as part of the baseline process for $SbCl_3$ treatments.

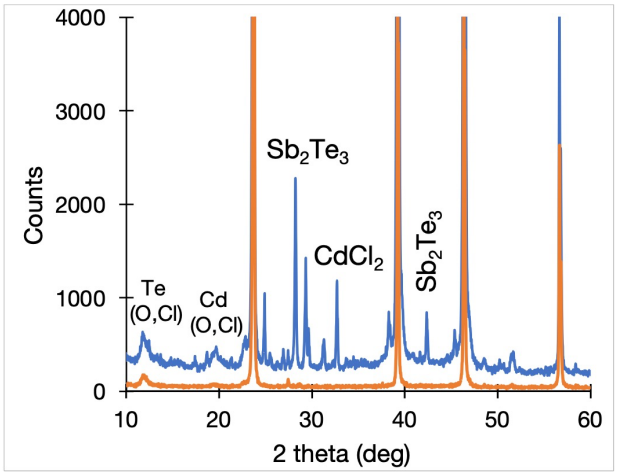

Fig. 5. XRD patterns of $SbCl_3$-treated CdSeTe:Sb films with $SbCl_3$ films prepared from dry methanol solution and dried either in the glovebox (orange) or in air (blue) prior to annealing at 460°C for 30 min in Ar. Plots are offset for clarity.

To assist understanding of $SbCl_3$ treatment chemistry, the effects of high RH drying and annealing of $SbCl_3$ films were monitored. Films were deposited on glass microscope slides from $SbCl_3$/dry methanol solutions and dried at 65°C, either in the N_2 glovebox or in air at 100% RH for 45 mins. Both films were then annealed at 460°C for 30 min. The glovebox-dried film was transparent to the eye after drying and remained so following annealing. XRD measurements (not shown) indicated the film remained amorphous, likely as $SbCl_3$,

throughout processing. In contrast, after drying at high RH, the other sample had dried as a uniform opaque white film, which became more transparent following annealing. Analysis of the XRD data (not shown) indicates the presence of the SbOCl in the as-dried film, an expected product of $SbCl_3$ hydrolysis, which converts to $Sb_8O_{11}Cl_2$ during the anneal step. The formation of the higher order oxychloride phase is consistent with reported thermal degradation pathways for SbOCl [8 and discussion below].

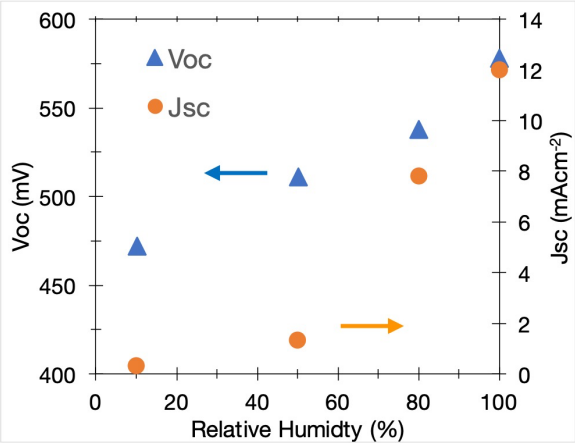

Fig. 6. Effect of controlled RH during drying of $SbCl_3$ films at ~65°C on V_{OC} and J_{SC} of resultant $SbCl_3$-treated devices.

B. Chemical mechanisms of $SbCl_3$ treatments

These observations show humidity exposure during treatment is critical to drive $SbCl_3$-activation of CdSeTe. While high RH during film drying gives improved cell performance, it must be well controlled to achieve consistent results. The solution behavior of $SbCl_3$ was considered to understand the observed $SbCl_3$ treatment chemistry, particularly the role of humidity exposure, and to guide further optimization of treatment conditions. Tian et al. [9] modeled speciation of $SbCl_3$ with varying pH in aqueous solution, showing that $SbCl_x^{(3-x)}$ complexes dominate at acidic pH, while at neutral and alkaline conditions, Sb-O phases (e.g. SbO^+, $Sb(OH)_3$, etc.), along with free Cl^-, are formed. Though methanol solutions are employed in this work, an effective solution pH can be assumed to estimate the majority species present at particular solution conditions. With exposure to H_2O vapor during film drying, $SbCl_3$ will react to form small levels of SbOCl or similar species, as confirmed from XRD analysis, along with small levels of HCl or free Cl^- (Eq. (2)). At low [HCl], the effective pH of the solution will remain nearly unchanged (essentially neutral) and the SbOCl phase remains dominant [9] with liberated HCl/Cl^- available for CdSeTe activation. Removal of $SbCl_3$/SbOCl films from CdSeTe by rinsing in methanol following just film drying at high RH, reveals discoloration of the CdSeTe surface, consistent with etching by HCl. If significantly large levels of water are added, a larger HCl concentration will be generated via Eq. (2), which decreases the effective pH of the solution, and $SbCl_x^{(3-x)}$ complexes will now dominate and largely reduce levels of free Cl^- [9].

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \qquad (2)$$

How this speciation affects the chemistry of Cl^- activation can be estimated from the thermal decomposition of Sb-oxychlorides [8 and references therein]. SbOCl degrades at temperatures >245°C to produce higher oxychlorides, before forming Sb_2O_3 near 600°C. At each decomposition step, $SbCl_3$ is formed as a secondary phase [8], highlighting its high thermal stability compared to the oxychlorides, and preventing further formation of free Cl^- for CdSeTe activation. In the absence of humidity exposure, the thermal stability of $SbCl_3$ prevents generation of Cl^- and, as observed, no activation is expected. The degradation of SbOCl to $Sb_8O_{11}Cl_2$ was confirmed from XRD analysis in this work.

These considerations highlight the need to ensure the presence of SbOCl or similar species through controlled hydrolysis of $SbCl_3$ during treatment. Further analysis of $SbCl_3$ chemistry is being carried out and findings will be used to guide characterization and optimization of $SbCl_3$-based treatments. With exposure to humidity during film drying, $SbCl_3$ hydrolysis forms SbOCl along with generation of free Cl^-. It may be expected, with generation of Cl^- at these benign conditions, as opposed to relying on thermal degradation of the chloride phase, that lower anneal temperatures could now achieve CdSeTe activation. However, preliminary re-optimization of anneal conditions for high RH dried $SbCl_3$ treatments at lower temperatures down to 400°C have so far shown poor devices through insufficient Cl^- activation. Treatment optimization is continuing and will be presented in a later publication

III. Summary

$SbCl_3$ is shown to be a viable activation agent for CdTe-based solar cells. Optimization of solution $SbCl_3$-based air treatments of CdSeTe:Sb show promising performance, with cells of $J_{SC} \approx 25$ $mAcm^{-2}$ demonstrated. Optimization of treatment conditions showed strong effects of annealing time and temperature on JV performance. Exposure to high RH during $SbCl_3$ film drying was found to be critical for the activation of CdSeTe cells. The role of water vapor in treatment chemistry was confirmed by XRD characterization, which indicated hydrolysis of the $SbCl_3$ film coupled with the formation of $CdCl_2$ and Sb_2Te_3 majority surface phases on activated CdSeTe, though no reaction was observed after dry $SbCl_3$ processing. Mechanistic details of $SbCl_3$ speciation in solution and during annealing highlights the roles of H_2O vapor

on CdSeTe activation. These findings will guide further optimization and understanding of treatment chemistry.

III. Acknowledgements

Funding was provided by the Alliance for Sustainable Energy, LLC, Managing and Operating Contractor for the National Renewable Energy Laboratory for the U.S. Department of Energy, and was supported in part by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office Award Number 37989. The authors thank K. Dewberry and G. Obikoya for JV measurements.

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