



Evolution of oxygenated cadmium sulfide (CdS:O) during high-temperature CdTe solar cell fabrication

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ABSTRACT

Oxygenated cadmium sulfide (CdS:O) produced by reactive sputtering has emerged as a promising alternative to conventional CdS for use as the *n*-type window layer in CdTe solar cells. Here, complementary techniques are used to expose the window layer (CdS or CdS:O) in completed substrate devices and combined with a suite of materials characterization to elucidate its evolution during high temperature device processing. During device fabrication amorphous CdS:O undergoes significant interdiffusion with CdTe and recrystallization, forming CdS_{1-y}Te_y nanocrystals whose Te fraction approaches solubility limits. Significant oxygen remains after processing, concentrated in sulfate clusters dispersed among the CdS_{1-y}Te_y alloy phase, accounting for ~30% of the post-processed window layer based on cross-sectional microscopy. Interdiffusion and recrystallization are observed in devices with un-oxygenated CdS, but to a much lesser extent. Etching experiments suggest that the CdS thickness is minimally changed during processing, but the CdS:O window layer is reduced from 100 nm to 60–80 nm, which is confirmed by microscopy. Alloying reduces the band gap of the CdS:O window layer to 2.15 eV, but reductions in thickness and areal density improve its transmission spectrum, which is well matched to device quantum efficiency. The changes to the window layer in the reactive environments of device fabrication are profoundly different than what occurs by thermal annealing in an inert environment, which produced films with a band gap of 2.4 eV for both CdS and CdS:O. These results illustrate for the first time the significant changes that occur to the window layer during processing that are critical to the performance of CdTe solar cells.

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1. Introduction

Cadmium telluride (CdTe) has emerged as the leading thin-film photovoltaic (PV) technology and is poised to reach grid parity soon with record device efficiency currently at 21.5% [1]. Cadmium sulfide (CdS) is the most commonly used window layer in CdTe photovoltaic devices [2]. This layer provides a receptive surface for CdTe nucleation and growth, and forms a high quality heterojunction with the absorber. Light absorbed by CdS does not generate photocurrent, so quantum efficiency (QE) is attenuated at wavelengths below the CdS band gap (520 nm) [3]. Photocurrent losses can be decreased by reducing thickness, but only to a

degree. As the CdS thickness is reduced efficiency can decline due to deterioration in both open circuit voltage (V_{oc}) and fill factor (FF) [4,5]. The CdS window layer can be deposited by several techniques, including chemical bath deposition (CBD) [6], close-spaced sublimation (CSS) [7], evaporation [8], and sputtering [9]. Sputtering offers numerous advantages over alternative deposition methods. Like CSS and evaporation it is vacuum-based and scalable for in-line manufacturing, and uniformity and waste management are less problematic for vapor deposition compared to solution-based methods. Most significantly, sputtering enables the ability to finely tune the window layer composition and properties by simply varying the argon/oxygen fraction [10].

The role of oxygen in CdS has been a focus of study for decades. It has been observed that CdS deposited by physical vapor deposition in the absence of oxygen undergoes extensive interdiffusion with CdTe during high temperature processing [11,12].

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Interdiffusion reduces the effective thickness of the window layer, creating CdS_{1-y}Te_y alloys whose optical band gap E_g is given by

$$E_g(y) = 2.40(1-y) + 1.51(y) - b(1-y)(y) \quad [\text{eV}] \quad (1)$$

where y refers to the atomic concentration in CdS_{1-y}Te_y and b is a bowing parameter equal to ~ 1.8 [13]. Alloying reduces the band gap of the window layer, and excessive interdiffusion degrades device performance by reducing the short circuit current density (J_{sc}) and/or by shunting caused by localized disappearance of the window layer [8,14].

The presence of oxygen in CdS has been found to have a dramatic impact on the interdiffusion process. McCandless and Birkmire [15] showed that annealing CdS in a CdCl₂:O₂:Ar environment prior to CdTe deposition eliminated the formation of CdS_{1-y}Te_y on the S-rich side of the junction, attributing this behavior to oxide formation along grain boundaries. Oxygen is present in CBD films at levels of 5–15 at%, and its presence is credited with retarding interdiffusion in a similar manner as O₂ annealing [14]. The higher level of oxygen in CBD CdS is thought to be responsible for producing higher efficiency than devices fabricated using CdS deposited by CSS or evaporation. Oxygenated cadmium sulfide (CdS:O) was first introduced in 2002 by Wu and co-workers [10], who prepared window layers by reactive sputtering using a CdS target in an O₂/Ar ambient. Based on transmission electron microscopy (TEM) images, these authors also attributed the observed improvements in J_{sc} to the ability of CdS:O to suppress Te interdiffusion and alloy formation [16].

CBD has remained one of the leading techniques to prepare CdS, particularly in research laboratories, though in recent years several groups have turned to sputtered CdS:O to produce high efficiency devices [17–21]. With increasing amounts of oxygen in the sputter ambient, film crystallinity is reduced and the optical band gap increases. Performance gradually improves with increasing optical band gap, reaches a maximum, and then drops dramatically [17,19,20]. The oxygen content in as-deposited CdS:O can reach 45 at% via sulfate group (CdSO₄) incorporation [19,20,22]. The efficiency gains are achieved primarily through increases in J_{sc} due to improvements in short-wavelength quantum efficiency without compromising V_{oc} or FF. The successful use of CdS:O requires careful optimization of sputter conditions, but high performance devices with power conversion efficiencies ranging from 15.2 to 16.4% have been achieved independently by several groups [16,17,19,23].

The trends discussed above have been well documented, but the underlying reasons controlling the observed behavior are not fully understood. It has been suggested that the catastrophic failure observed at high oxygen levels is caused by an excessive conduction band offset between the CdTe and CdS:O layers [19], while there are several possible explanations for the improvements in J_{sc} at moderate oxygenation levels. Changes in device performance could simply reflect the enhanced transparency of as-deposited CdS:O. Alternatively, CdS:O may decompose and release oxygen during subsequent high temperature processing, resulting in a CdS layer of reduced thickness. Finally, as discussed above, the degree of interdiffusion with CdTe appears to be highly dependent on the amount of oxygen in the window layer. The evolution of the window layer during device processing has been studied fairly extensively for CBD and evaporated CdS, but has not been examined in detail for CdS:O.

In the conventional superstrate architecture, the CdTe absorber is deposited directly on CdS:O at high temperature (500–600 °C) by CSS or vapor transport deposition, which is followed by an annealing step in the presence of CdCl₂ at $T \sim 400$ °C. These high-temperature, reactive environments likely cause significant changes to the underlying CdS:O material. For example, thermal

annealing in an inert environment appears to convert CdS:O back to intrinsic CdS. Paudel et al. [21] varied the optical band gap of sputtered CdS:O films from 2.0 to 3.2 eV through manipulation of both oxygen content and substrate temperature. After annealing at ~ 600 °C in the He/O₂ ambient used during CSS all of these films exhibited properties that were characteristic of intrinsic CdS based on their crystal structure and band gap (~ 2.4 eV). Similar changes in optical properties were reported by Kephart et al. when annealing their films at 500 °C, but interestingly they observed that the SO_x content of these films was not significantly changed by annealing [19]. However, since CdTe vapor was not present in these experiments, it is not clear if these thermally-induced changes are truly representative of device processing.

Direct characterization of the window region with high fidelity in completed devices is extraordinarily difficult because this ~ 100 nm layer is sandwiched between a TCO-coated glass superstrate and several microns of the CdTe absorber. To better understand the evolution of CdS:O during processing and its impact on device performance we make use of two recently developed approaches to expose both sides of the window layer in completed devices [24]. It is shown that oxygenated cadmium sulfide (CdS:O) undergoes significant interdiffusion and recrystallization during CdTe device fabrication, forming CdS_{1-y}Te_y nanocrystals with a band gap of 2.15 eV. Substantial oxygen is retained throughout processing, concentrating in sulfate clusters dispersed throughout the window layer. These results illustrate for the first time the significant changes that occur to the CdS:O window layer during processing that are critical to the performance of CdTe solar cells.

2. Materials and methods

2.1. Device fabrication

Devices in this work were fabricated in the superstrate configuration using Corning 7059 glass coated with a fluorinated and intrinsic tin oxide bilayer using chemical vapor deposition. The properties of un-oxygenated CdS were compared with moderately oxygenated CdS:O whose as-deposited optical band gaps were 2.4 and 2.8 eV, respectively. In previous studies, it was found that the 2.8 eV CdS:O produced optimal device performance using our process [20]. Films were deposited by rf magnetron sputtering using a stoichiometric CdS target (Materion, 99.99% purity) in a Unifilm PVD-300 sputtering system. The sputtering ambient was pure argon for the intrinsic CdS films, and a 4% O₂/Ar mixture was used to produce the 2.8 eV CdS:O. Prior to deposition the system was evacuated to $\sim 2 \times 10^{-7}$ Torr and backfilled with the desired ambient. Gas flow rates were maintained at a total of 100 sccm, and a throttle valve was used to set the pressure to 15 mTorr. The sputter power density was 1.1 and 2.2 W/cm² for CdS and CdS:O films, respectively, and the film thickness was fixed at 100 nm for device fabrication. A subset as-deposited CdS/CdS:O films were subjected to thermal annealing performed at 600 °C for 5 min in an inert ambient. In device fabrication, ~ 4 μm of CdTe was deposited on CdS/CdS:O layers using CSS. The source and substrate temperatures were held at 660 and 600 °C, respectively, for 150 s in an oxygen/helium ambient at 16 Torr. Vapor-phase CdCl₂ annealing was also performed in a CSS configuration with source and substrate temperatures fixed at 400 °C for 10 min in an oxygen/helium ambient at 400 Torr. To complete fabrication an evaporated Cu/Au back contact was used followed by annealing at 260 °C for 30 min to promote Cu diffusion [25]. All devices with CdS:O had very similar performance, yielding photovoltaic conversion efficiency of $\sim 14\%$ as described previously [20,24]. The device analyzed by transmission electron microscopy in this work was processed identically to those described above with the exception of

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