Solar Energy Materials & Solar Cells 117 (2013) 300–305

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

The influence of cadmium sulfide and contact annealing configuration on the properties of high-performance cadmium stannate

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ARTICLE INFO

Article history:
Received 8 March 2013
Received in revised form
16 May 2013
Accepted 5 June 2013

Keywords:
Cadmium stannate
Transparent conductive oxide
Cadmium telluride
Thin-film photovoltaics
Annealing
Sputtering

ABSTRACT

The sensitivity of cadmium stannate (CTO) performance to both sputtering and annealing conditions was investigated. Films treated by the standard proximity anneal in contact with a CdS film displayed an electrical resistivity of $\sim 2.2\times10^{-4}\,\Omega$ cm, high mobility ($\sim$57 cm^2/V s), and $>$90% transmission throughout the near infrared ($\lambda \le 1350$ nm). Film properties were insensitive to annealing temperature and sputtering ambient when O_2 was present during deposition. Next, we demonstrated process modifications to the proximity anneal. CTO and CTO/CdS bilayer films were annealed either uncovered or covered with a bare glass plate. CTO/CdS bilayers annealed in the covered configuration had comparable or superior conductivity to the proximity anneal, with optimal performance achieved with 10 nm of CdS. The resistivity of uncovered films and films produced without CdS was insensitive to CdS thickness ($\sim 3\times10^{-4}\,\Omega$ cm), and displayed higher mobility and improved transparency, particularly in the near infrared. The electrical properties were well correlated with X-ray diffraction measurements of film crystallinity and purity. These high-conductivity films are promising for photovoltaic applications, transmitting 92–95% of solar radiation $>$1 eV.

1. Introduction

Glass coated with a transparent conductive oxide (TCO) serves as the foundation for solar cell technologies that employ the superstrate configuration. Cadmium stannate (CTO, Cd_2SnO_4) possesses excellent electrical and optical properties, and is therefore a potential alternative to conventional TCOs such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO) [1]. Its high mobility ($\sim$60 cm^2/V s) enables extremely low resistivity ($\sim 2\times10^{-4}\,\Omega$ cm) while providing high transmission across both the visible and near infrared (IR) [2]. CTO is an attractive TCO for a range of optoelectronic applications, particularly cadmium telluride (CdTe) solar cells, because it is comprised of earth-abundant elements and displays robust chemical and thermal stability [2–4]. As a case in point, substitution of the conventional fluorine-doped tin oxide (FTO)/tin oxide (TO) bilayer with a CTO/zinc tin oxide bilayer enabled the National Renewable Energy Laboratory (NREL) to produce a then-world-record 16.7%-efficient CdTe solar cell in 2001 [5,6].

CTO has comparable resistivity and significantly greater mobility and transmission than FTO [7,8], but large-scale commercialization has been hindered in part by processing constraints. The standard procedure for producing state-of-the-art films involves a two-step batch process: (1) room-temperature sputtering in an Ar, O_2, or Ar/O_2 ambient followed by (2) high-temperature annealing in which the CTO film is placed in direct contact with a glass plate coated with CdS [2,9–13]. The latter step is commonly referred to as the proximity anneal. Although CTO sputtering targets usually have the thermodynamically stable orthorhombic structure, sputtered films are often amorphous or crystallize in the cubic inverse spinel structure [14,15]. Previous researchers credited the proximity anneal with promoting crystallization and shifting the Cd:Sn composition to the stoichiometric 2:1 ratio [2,10,11,13]. The annealing temperature is also important. Crystallization begins around 550 °C, and previous work reported optimum conductivity at $\sim$650 °C [2,10,11,13,16]. Decomposition of the spinel structure begins at $\sim$700 °C, leading to the formation of a SnO_2 phase [13,16]. The role of sputtering ambient is also unsettled, and it is most likely target dependent. Whereas previous work at NREL reported CTO films sputtered in pure O_2 [2,12], others demonstrated high-quality films using sputtering ambient compositions up to 90–100% Ar [10,11,16].

The proximity anneal is a major limitation for in-line processing of large-area substrates. Manufacturing would require the

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0927-0248/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.solmat.2013.06.009

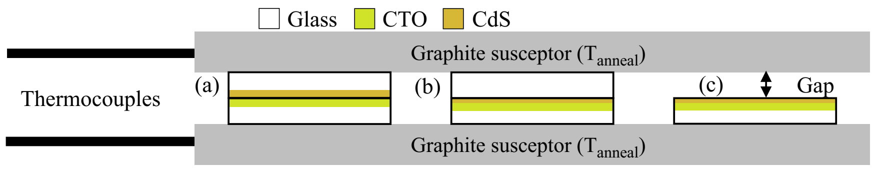

Fig. 1. Schematic orientation for (a) proximity, (b) covered, and (c) uncovered anneals.

production of large, uniform auxiliary CdS films. Moreover, these CdS films are depleted during processing, generating additional process complications. The proximity anneal also presents significant challenges for roll-to-roll production due to the requirement of physical contact between the CTO and CdS films. Though not completely understood, the proximity anneal likely provides two necessary functions: a Cd source to compensate for stoichiometric deviations in the sputtered film and/or a physical barrier to prevent Cd evaporation during film crystallization [17]. The goals of this work are to better understand this process and develop alternative processing routes that are more compatible with large-scale manufacturing and roll-to-roll production.

First, we examine the impact of sputtering ambient and annealing temperature for the standard proximity anneal. Next, we explore the potential of sputtering CTO/CdS bilayers as an alternative to the proximity anneal, and examine annealing these bilayers with and without a glass cover plate. Detailed evaluation of the films' structural, optical, and electrical properties is provided to help understand the process–structure–performance relationships in this system.

2. Materials and methods

We used a CVC SC-3000 sputtering system with a target-to-substrate distance of 7 cm. The CTO films were radio frequency (RF) magnetron sputtered on 1.5×1.5 in.^{2} pieces of Corning Eagle XG glass at room temperature and a power of 110 W to a nominal thickness of 175 nm. Upon reaching a base pressure of 2×10^{-6} Torr, Ar and/or O_2 flow (total 15 sccm) commenced and the plasma was ignited. Gas flow was controlled by calibrated mass flow controllers, and the chamber pressure was set to 15 mTorr by a hand-operated gate valve. The sputtering target was a 2-in. diameter hot-pressed target (Cerac Inc.) consisting of a pre-reacted 2:1 CdO:SnO_2 molar ratio, as described by Haacke and coworkers [13]. CdS films were sputtered in the same chamber at room temperature at 15 mTorr and 15 sccm Ar flowing ambient. The CdS target was a 2-in. diameter hot-pressed target (99.99% purity, Cerac Inc.). Whereas CdS films used in the proximity anneal were deposited on larger 3×3 in.^{2} plates at 70 W with a target-to-substrate distance of 9 cm, these values were 50 W and 7 cm, respectively, for CdS films in CTO/CdS bilayers. After sputtering, the 3×3 in.^{2} plates were cut into four 1.5×1.5 in.^{2} plates to supply CdS films for the proximity anneal. We estimate that the proximity anneal removes a layer of about 10 nm from the CdS film.

High-temperature annealing was performed in a close-spaced sublimation chamber for 15 min in a 30 Torr He ambient. Fig. 1 displays schematic diagrams of the geometric configurations used for the (a) proximity, (b) covered, and (c) uncovered annealing procedures. The proximity anneal was performed by placing the CTO and CdS films in contact between two temperature-monitored graphite susceptors. Four heating lamps supplied heat to the assembly. Covered annealing of CTO and CTO/CdS bilayers was performed by placing a Corning Eagle XG glass plate directly in contact with the film. CTO and CTO/CdS films were also annealed without a glass cover. The uncovered configuration allows for a variable gap between the CTO film or bilayer and the upper graphite susceptor. The thermal stability of the Corning Eagle XG substrate enabled the CTO films to be successfully annealed up to 700 °C because of the glass's high annealing point (722 °C) [18]. In contrast, films annealed at 700 °C using Corning 7059 (639 °C annealing point) [19] had more than double the resistivity, and this process caused visible damage to the glass itself.

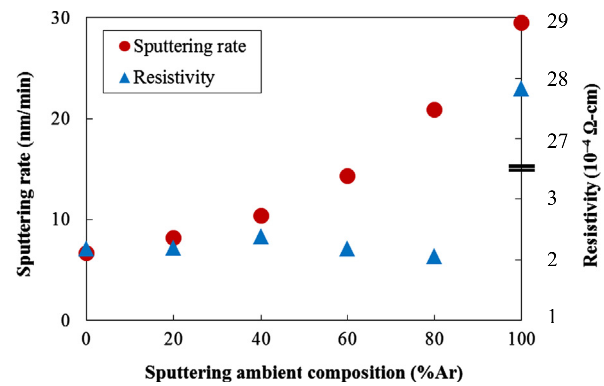

Fig. 2. Sputtering rate and resistivity as a function of ambient composition.

Film thickness, transmittance/reflectance, and optical band gap were measured using variable-angle spectroscopic ellipsometry (J.A. Woollam Co., Inc. alpha-SE), spectrophotometry (Cary 5000), and Tauc plot analysis, respectively. Electrical properties (resistivity, mobility, and carrier concentration) of a 1×1 cm^2 section of each sample were determined using Hall measurement (Bio-Rad HL5500PC). Film composition and crystallinity were evaluated by energy-dispersive X-ray spectroscopy (EDAX; JEOL JSM-7000F SEM) and X-ray diffraction (XRD; Siemens Kristalloflex 810), respectively. The results shown below pertain to single-sample measurements.

3. Results and discussion

A set of films was sputtered under varying ambient compositions ranging from pure O_2 to pure Ar, and subsequently proximity annealed under identical conditions. Fig. 2 plots the sputtering rate and resistivity of these films as a function of argon content in the sputter ambient. The CTO sputtering rate increased monotonically with the Ar fraction. Using a pure Ar ambient, the sputtering rate was more than four times greater than using a pure O_2 ambient. Sputtering with at least 20% O_2 produced films with resistivities of $\sim 2.2 \times 10^{-4}$ Ω cm, and the resistivity was not very sensitive to oxygen content in the range of 20–100%. Films sputtered in pure Ar were an order of magnitude less conductive (2.8×10^{-3} Ω cm); note the axis break in Fig. 2. Sputtering in Ar/O_2 mixtures provides a means of increasing sputtering rate by more than a factor of three without negatively affecting film conductivity. We also investigated the sensitivity of film electrical and optical properties to proximity-annealing temperature from 600 °C to 700 °C for films sputtered in pure O_2. Neither film resistivity ($2.2–2.4 \times 10^{-4}$ Ω cm) nor the optical band gap (3.1–3.2 eV) varied significantly as a function of annealing temperature. These data, along with Fig. 2, demonstrate that CTO sputter