Thin Solid Films 574 (2015) 43–51

Contents lists available at ScienceDirect

Thin Solid Films

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

High rate deposition of thin film cadmium sulphide by pulsed direct current magnetron sputtering

F. Lisco [a,*], P.M. Kaminski [a], A. Abbas [a], J.W. Bowers [a], G. Claudio [a], M. Losurdo [b], J.M. Walls [a]

[a] Centre for Renewable Energy Systems Technology (CREST), School of Electronic, Electrical and Systems Engineering, Loughborough University, Leicestershire LE11 3TU, UK
[b] Institute of Inorganic Methodologies and of Plasmas, IMIP-CNR, via Orabona 4, 70126 Bari, Italy

ARTICLE INFO

Article history:
Received 15 May 2014
Received in revised form 19 November 2014
Accepted 20 November 2014
Available online 28 November 2014

Keywords:
Cadmium sulphide
Pulsed direct-current magnetron sputtering
Scanning electron microscopy
Transmission electron microscopy
Refractive index

ABSTRACT

Cadmium Sulphide (CdS) is an important n-type semiconductor widely used as a window layer in thin film photovoltaics Copper Indium Selenide, Copper Indium Gallium (di)Selenide, Copper Zinc Tin Sulphide and Cadmium Telluride (CdTe). Cadmium Sulphide has been deposited using a number of techniques but these techniques can be slow (chemical bath deposition and Radio Frequency sputtering) or the uniformity and the control of thickness can be relatively difficult (close space sublimation). In this paper we report on the development of a process using pulsed Direct Current magnetron sputtering which allows nanometre control of thin film thickness using time only. The CdS thin films deposited in this process are highly uniform and smooth. They exhibit the preferred hexagonal structure at room temperature deposition and they have excellent optical properties. Importantly, the process is highly stable despite the use of a semi-insulating magnetron target. Moreover, the process is very fast. The deposition rate using 1.5 kW of power to a 6-inch circular magnetron was measured to be greater than 8 nm/s. This makes the process suitable for industrial deployment.

1. Introduction

Cadmium Sulphide (CdS) is an important semiconductor material widely used in thin film photovoltaics as a window layer [1,2]. Cadmium Sulphide is an n-type semiconductor with a band gap of 2.42 eV. Cadmium Sulphide exists in two crystalline phases, hexagonal wurzite and the cubic zinc-blend structure. Cadmium sulphide has a bulk refractive index (n) of 2.52 at wavelength 600 nm [3] which is well suited for its application in solar cells. The refractive index value is between the index of the absorber and the Transparent Conducting Oxide (TCO) contact, which allows light trapping by refractive index matching. Radio Frequency (RF) Sputtered CdS films with refractive index in the range of 2.25–2.51 have been reported [4,5]. Sprayed films have been reported with a refractive index of 2.12 [3] and refractive indices in the range 2.19–2.32 have been reported for vacuum evaporated CdS [3,6].

Thin film CdS has been used as a n-type material to form a heterojunction in a number of photovoltaic systems including copper indium selenide (CIS) [7], copper indium gallium (di)selenide (CIGS) [8–10], copper zinc tin sulphide (CZTS) [11,12] and cadmium telluride (CdTe) [1,13–16]. Although research is being conducted to evaluate alternatives to CdS in CIGS [7,9,10], the highest efficiency devices utilise a CdS window layer [2,8]. The CdS window layer is required to provide good transmission of light through to the absorber layer in a thin film photovoltaic (PV) stack. The material must uniformly cover the absorber to avoid shunts between the absorber and the front electrode. The deposition technique is required to allow fine control of thickness since films between 40 nm and 150 nm are usually required in solar cells. The precise thickness of the CdS layer determines the degree of light absorption. A compromise is needed between uniformity of coverage of the CdS, its thickness, and light transmission into the absorber layer.

CdS has been deposited using a number of methods including: metalorganic vapour phase epitaxy [17], chemical bath deposition [7,12], close space sublimation [13,18–20], vacuum evaporation [6,16,21], and Radio Frequency (RF) magnetron sputtering [1,22–24]. RF sputtered films can be deposited at room temperature but they usually exhibit a small grain size. Magnetron sputtering deposits dense films with uniform surface coverage avoiding pinhole formation. It also offers good control of thin film thickness. RF sputtering has been used to date since CdS is a semi-insulating material and the use of DC power leads to charge build up, arcing and process instability. Unfortunately, magnetron sputtering using RF power results in low deposition rates (for example a rate of 0.3 nm/s has been reported at 250 W [24]) and involves the use of complex matching circuits. Although suitable for research purposes, the technique is not well suited to industrial deployment. In this paper, we report on the use of pulsed DC magnetron sputtering. A previous study using pulsed DC magnetron sputtering of CdS has been reported but this work focused on the wavelength and lifetime of transient species [25]. We have developed a process using pulsed DC power that can be used to sputter thin films of CdS in process

* Corresponding author.
E-mail address: F.Lisco@lboro.ac.uk (F. Lisco).

http://dx.doi.org/10.1016/j.tsf.2014.11.065

conditions which are highly stable. The major advantage is that the process produces high deposition rates suitable for use in solar module manufacturing. These rates are over an order of magnitude faster than those obtained by RF sputtering. In common with other applications we also find that the energetics of the pulsed DC process produce favourable thin film properties and the power supply configuration avoids the need for matching circuits [26,27].

2. Experimental details

CdS thin films were deposited by pulsed DC magnetron sputtering in a 'PV Solar' sputtering system (Power Vision Ltd., Crewe UK). The system is equipped with four six-inch diameter circular magnetrons mounted vertically, with an option to replace one of the magnetrons with a plasma source for reactive sputtering. The samples are mounted vertically on a rotatable carrier, designed for 5 cm × 5 cm substrates. The target to substrate distance is typically 10 cm. During the deposition process the carrier rotates at typically 120 rpm. This provides excellent uniformity in the horizontal direction. Uniformity in the vertical direction is achieved using disposable masks mounted in front of the magnetron target. The CdS thin films were sputtered using a pulsed DC power supply (Advanced Energy Inc. Pinnacle plus, 5 kW) using argon as the working gas [28].

The CdS thin films were deposited on NSG-Pilkington Transparent Electrically Conducting (TEC15 and TEC10) Fluorine doped tin oxide (FTO) coated glass substrates. Prior to the CdS deposition, the substrates were cleaned in a two-step ultrasonic bath process consisting of a 5 min

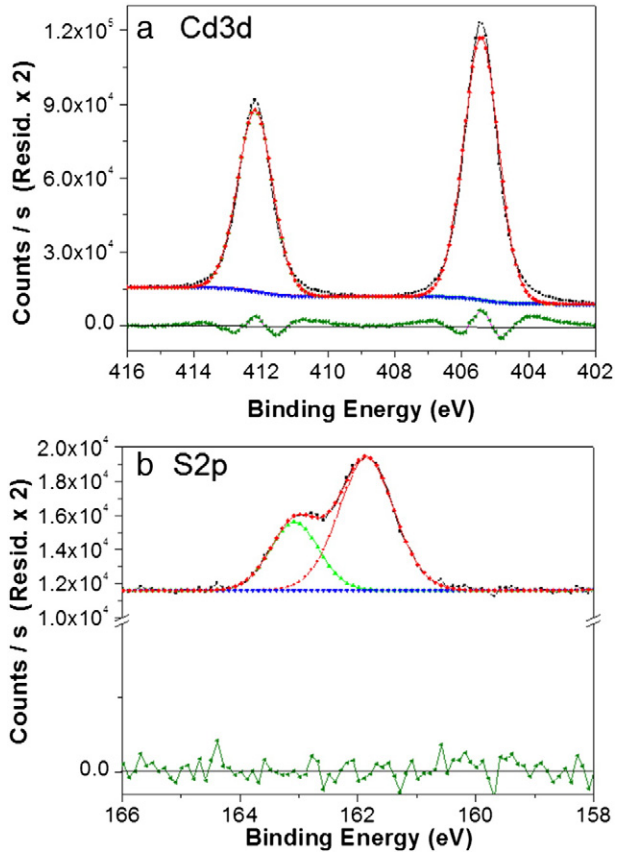

Fig. 1. The XPS spectra measured for pulsed DC deposited CdS, was not affected by the deposition conditions, showing photoelectron core levels of (a) Cd3d5/2 and Cd3d3/2 and (b) S2p for CdS thin films deposited at 10 sccm Ar, 500 W and 150 kHz. For (a) the fitting is achieved with a single Gaussian peak due to CdS and for (b) the fitting shows the splitting of S2p3/2 and S2p1/2. The green line below shows the error fitting function.

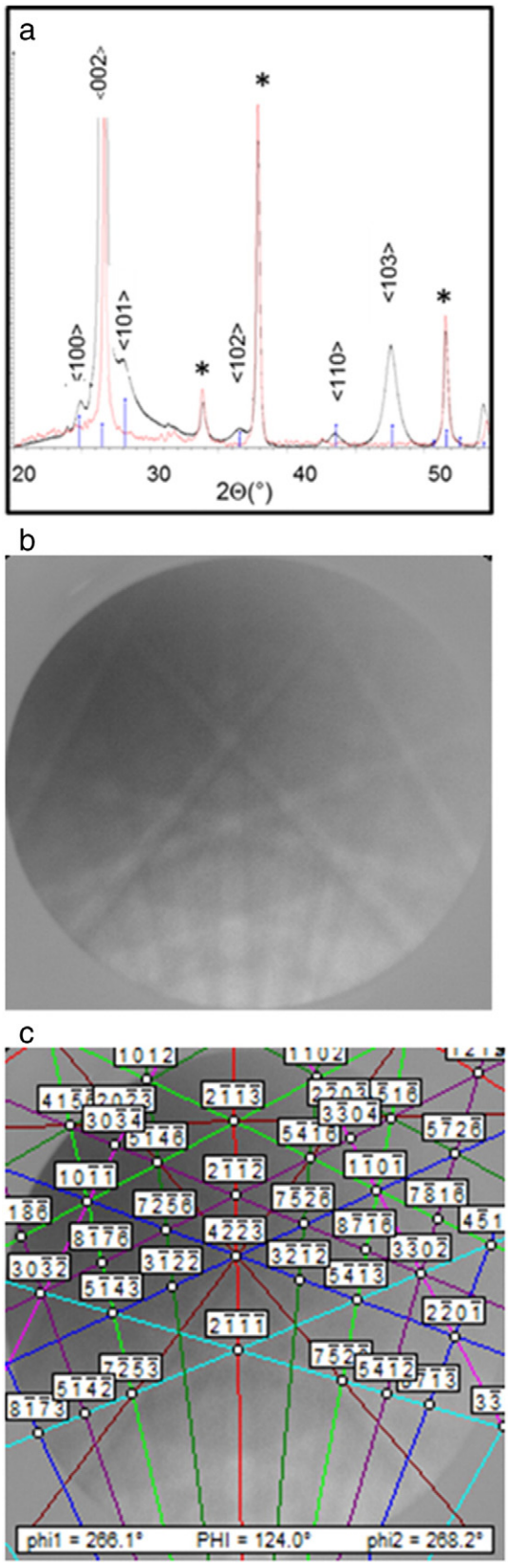

Fig. 2. (a) XRD pattern, (b) Kikuchi pattern and (c) Kikuchi phase map of a CdS film sputtered on TEC15 coated glass for 3600 s, 10 sccm Ar, 500 W, 150 kHz, 2 s (ramp time), 2 μs (reverse time). The * in (a) indicates peaks due to the TEC 15 glass substrate.