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The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering

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ABSTRACT

Cadmium sulphide (CdS) thin films were deposited by two different processes, chemical bath deposition (CBD), and pulsed DC magnetron sputtering (PDCMS) on fluorine doped-tin oxide coated glass to assess the potential advantages of the pulsed DC magnetron sputtering process. The structural, optical and morphological properties of films obtained by CBD and PDCMS were investigated using X-ray photoelectron spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, spectroscopic ellipsometry and UV–Vis spectrophotometry. The as-grown films were studied and comparisons were drawn between their morphology, uniformity, crystallinity, and the deposition rate of the process. The highest crystallinity is observed for sputtered CdS thin films. The absorption in the visible wavelength increased for PDCMS CdS thin films, due to the higher density of the films. The band gap measured for the as-grown CBD-CdS is 2.38 eV compared to 2.34 eV for PDCMS-CdS, confirming the higher density of the sputtered thin film. The higher deposition rate for PDCMS is a significant advantage of this technique which has potential use for high rate and low cost manufacturing.

1. Introduction

Cadmium sulphide (CdS) is an important II–VI compound semiconductor material with applications in several heterojunction photovoltaic systems including cadmium telluride (CdTe), copper indium diselenide/sulphide and copper indium gallium diselenide/sulphide (CIGS) solar cells [1]. It has also applications in various electro-optic and infrared devices [2]. There are several deposition techniques used for the deposition of thin film CdS including RF sputtering [3,4], chemical bath deposition (CBD) [5], thermal evaporation [6], chemical vapour deposition [7], close space sublimation (CSS) [8], molecular beam epitaxy [9] and spray pyrolysis [10]. Each deposition process produces different structural, electrical and optical properties of the CdS thin films. In most heterojunction devices, high efficiency cells utilise a CdS window layer [11,12]. For example, First Solar has reported CdS deposited high-rate vapour transport deposition (HRVTD) [13]. A 14.2% efficient thin film CdTe solar cell with CdS deposited by CSS has been reported [14]. Use of RF sputtered CdS in CdTe solar cells resulted in an efficiency of 15.8% [15,16]. Interestingly, an efficiency of 21.7% has been reported for CIGS devices with CdS layers grown by CBD [17].

We have developed a process using pulsed DC magnetron sputtering (PDCMS) [18] to sputter thin films of CdS in highly stable process conditions. In this paper, we report on the differences in the properties of CBD and PDCMS deposited CdS thin films. The major advantage of the PDCMS process is that it produces high deposition rates which are much higher than those obtained using RF sputtering [19]. This makes the use of pulsed DC sputtering suitable for high throughput solar module manufacturing [18]. We also find that the energetics of the pulsed DC process produce favourable thin film properties. In addition, the use of pulsed DC power supplies avoids the need for complex matching circuits necessary when using radio frequency power supplies.

2. Experimental details

Transparent electrically conducting (TEC 10) glass supplied by NSG-Pilkington (http://www.pilkington.com/) was used as the substrate (superstrate) material. The substrates were cleaned in a two-step ultrasonic bath process followed by a plasma surface treatment prior to the CdS film growth [20]. CdS thin films of ~100 nm thickness were deposited by pulsed DC magnetron sputtering in a 'PV Solar' magnetron sputtering system (Power Vision Ltd., Crewe UK); details of the system have been provided elsewhere [18]. The deposition conditions were set using the following process parameters: 10 sccm of Ar gas flow, 500 W, 150 kHz, 2 s (ramping time), 2.5 μs (reverse time).

Thin films of CdS of ~100 nm thickness were deposited by chemical bath deposition (CBD); the reaction occurred in a beaker immersed in a water jacket to ensure constant temperature (70 °C). The bath solution consisted of 200 ml of de-ionised water, 15 ml of $Cd(CH_3COO)_2$ 0.01 M,

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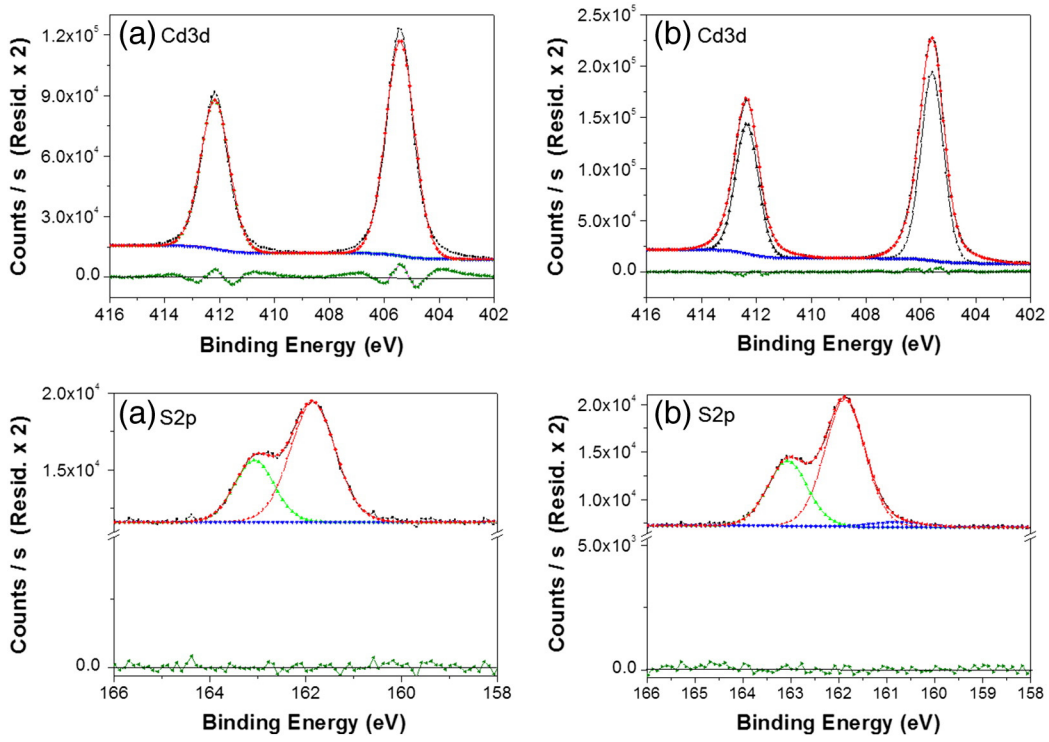

Fig. 1. The XPS spectra measured for pulsed DC and chemical bath deposited CdS films, were not affected by the deposition conditions, showing photoelectron core levels of (a) $Cd3d_{5/2}$ and $Cd3d_{3/2}$ and S2p for CdS thin films deposited at 10 sccm Ar, 500 W and 150 kHz and (b) $Cd3d_{5/2}$ and $Cd3d_{3/2}$ and S2p for CdS thin films deposited by chemical bath. For $Cd3d_{5/2}$ and $Cd3d_{3/2}$, the fitting is achieved with a single Gaussian peak due to CdS and for S2p the fitting shows the splitting $S2p_{3/2}$ and $S2p_{1/2}$. The green line at the bottom shows the error fitting function. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

25 ml of NH_4OH 25% and 10 ml of $CS(NH_2)_2$, 0.1 M. An ultrasonic probe was immersed in the solution to accelerate the reaction kinetics [20].

The chemical composition, microstructure and optical properties of CdS thin films prepared by CBD and PCDMS were investigated and compared. The microstructure was studied with a high-resolution field emission gun scanning electron microscope (FEGSEM), Leo 1530 VP FEG-SEM, which provides the ability to visualise surface features of the material with nanometre resolution, operating at 5 kV. X-ray photoelectron spectroscopy (XPS) was used to obtain the surface chemical composition of the layers. The analysis was performed using a Thermo Scientific K-Alpha XPS surface analysis tool. An electron flood gun was used to reduce charging that would cause peak shifts to occur. An argon ion surface etch at 1 keV, for 30 s, was carried out prior to analysis to remove surface contamination. The X-ray source used was Al K_α radiation $h\nu = 1486.6$ eV with a beam diameter of 200 microns. The High Resolution Multiplex Scan was used to evaluate the chemical state(s) of each element through its core electron binding energies. Precise determination of binding energies was made through the use of curve fitting routines applied to the peaks in the multiplex scan and sensitivity factors were taken into account to determine elemental composition. A dual beam FEI Nova 600 Nanolab was employed to prepare the transmission electron microscopy (TEM) samples. A standard in situ lift off method was used to prepare cross-sectional samples through the coating into the glass substrate. A platinum over-layer was deposited to define the surface and homogenise the final thinning of the samples. TEM images were obtained using a Jeol JEM 2000FX operating at 200 kV, with an integrated camera above the phosphor screen to obtain digital images. The TEM technique provided morphological analysis of the grain structure of the sputtered and CBD CdS films on fluorine doped tin oxide (FTO) coated glass substrates (TEC 10). Scanning transmission electron microscopy (STEM) was carried out using a FEI Tecnai F20 (S) TEM, equipped with a silicon drift detector, in the common imaging mode for the STEM bright field imaging (BF). The X-ray diffraction analysis (XRD) was performed, using a Bruker D2 Phase bench-top XRD using copper X-rays with a 1.542 nm wavelength, to investigate the crystalline structure of the materials. Each sample was scanned using an angular range of 20–90 ° with a step size of 0.02 ° and a dwell time of 0.1 s. The transmission, reflection and energy gap (Eg) measurements were carried out using a spectrophotometer Varian Cary® UV–Vis 5000. The energy band gap E_g, was calculated by a graphic extrapolation by using the Tauc plot [21].

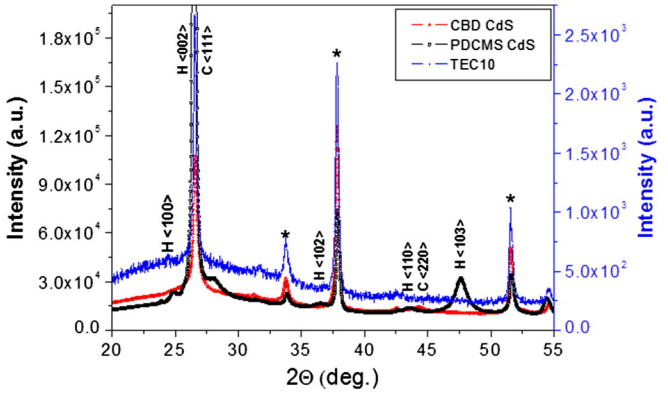

Fig. 2. XRD spectra of CBD and PDCMS CdS films. The peaks due to the hexagonal and cubic structure are indicated by H and C, respectively. The peaks due to the subtrate are indicated with *.

The optical properties of the thin films were measured using spectroscopic ellipsometry (SE) (Horiba, Jobin Yvon, UVISEL); which provided information about the thickness and refractive index (and uniformity) of the deposited films. The dispersion of the real and imaginary part of the refractive index was measured in a wavelength range between 248 nm and 2100 nm. The transparent electronic conductive (TEC 10) glass has a complex multilayer structure, being coated with successive layers of undoped SnO_2, SiO_2 and F-doped SnO_2, to achieve the desired sheet resistance. The optical properties of each component layer have been reported

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