This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

Comparison of Cadmium Selenide Thin Films deposited by chemical bath and pulsed DC sputtering for use in Cadmium Telluride devices

PLEASE CITE THE PUBLISHED VERSION

<https://doi.org/10.1109/pvsc45281.2020.9300466>

PUBLISHER

IEEE

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

LICENCE

All Rights Reserved

REPOSITORY RECORD

Morris, Kerrie, Rachael Greenhalgh, Vladislav Kornienko, Christos Potamialis, Jake Bowers, and Michael Walls. 2021. "Comparison of Cadmium Selenide Thin Films Deposited by Chemical Bath and Pulsed DC Sputtering for Use in Cadmium Telluride Devices". Loughborough University.
<https://hdl.handle.net/2134/13603001.v1>.

Comparison of Cadmium Selenide Thin Films Deposited by Chemical Bath and Pulsed DC Sputtering for use in Cadmium Telluride Devices

Kerrie M. Morris

*Centre for Renewable Energy Systems
Technology (CREST)
Loughborough University
Loughborough, UK
k.morris@lboro.ac.uk*

Rachael C. Greenhalgh

*Centre for Renewable Energy Systems
Technology (CREST)
Loughborough University
Loughborough, UK
r.c.greenhalgh@lboro.ac.uk*

Vladislav Kornienko

*Centre for Renewable Energy Systems
Technology (CREST)
Loughborough University
Loughborough, UK
v.kornienko@lboro.ac.uk*

Christos Potamialis

*Centre for Renewable Energy Systems
Technology (CREST)
Loughborough University
Loughborough, UK
c.potamialis@lboro.ac.uk*

Jake W. Bowers

*Centre for Renewable Energy Systems
Technology (CREST)
Loughborough University
Loughborough, UK
j.w.bowers@lboro.ac.uk*

John M. Walls

*Centre for Renewable Energy Systems
Technology (CREST)
Loughborough University
Loughborough, UK
j.m.walls@lboro.ac.uk*

Abstract—Cadmium selenide (CdSe) thin films deposited using chemical bath deposition and pulsed DC magnetron sputtering are compared for use in cadmium telluride/selenide (CST) photovoltaic (PV) devices. Full devices were made from the bath and sputtered films using a cadmium chloride (CdCl₂) treatment temperature of 425°C, this gave an overall efficiency of 9.3% and 3.2% respectively. Photoluminescence (PL) of the sputtered sample confirmed a bandgap was present of 1.58 eV which suggested poor diffusion at 425°C. A (CdCl₂) treatment temperature of 465°C gave a large PL peak at 1.37 eV which corresponds to the bandgap of CST, indicating diffusion was more effective at this temperature.

Index Terms—cadmium selenide, thin film, chemical bath, pulsed DC magnetron sputtering

lower bandgap allows a greater portion of the solar spectrum to be utilized which effectively raises the short circuit current density (J_{sc}). In our previous work chemical bath deposition (CBD) of the CdSe layer has been shown to produce CST devices with good initial efficiencies [8] however the rate is very slow with films of 280 nm deposited in 4 hours. Pulsed DC magnetron sputtering offers a way of giving uniform thin films at a much faster rate with better control over the process. This study will compare the microstructure and electronic properties of CdSe deposited by sputtering and CBD, as well as final device properties.

I. INTRODUCTION

Cadmium telluride (CdTe) based photovoltaics have seen an increase in efficiency in recent years with a record breaking 22.3% [1]. The increase in efficiency has been attributed to, in part, to alloying the CdTe with cadmium selenide (CdSe) [2]. When CdTe (bandgap 1.50 eV) [3] is alloyed with CdSe (bandgap 1.74 eV) [4] and treated, a bowing effect occurs and a bandgap of 1.36 eV presents when the mole fraction (x) of CdSe is 0.4. This is described by Vegard's law where b is the bowing factor (Fig. 1) [5], [6].

$$E_{g,CST} = xE_{g,CdSe} + (1-x)E_{g,CdTe} - bx(1-x) \quad (1)$$

This has been attributed to the Se substituting Te sites in the CdTe layer [7] with the ternary compound CST forming. The

Fig. 1. Bandgap bowing described by Vegard's law.

Funding provided through a studentship from the EPSRC CDT in New and Sustainable Photovoltaics. Sponsorship provided by the EPSRC SuperSolar Network

II. EXPERIMENTAL

A. CdSe Deposition

The chemical bath deposition followed a method previously reported [8] and was optimized to increase the deposition rate. 4 mmol of cadmium acetate, 8 mmol of sodiumselenosulphite and 10 ml of ammonium hydroxide were added to 275 ml of de-ionized water. Pilkington TECTM12D low iron glass substrates, with a F-doped SnO₂, SnO₂ buffer layer (FTO) were inserted vertically into the bath and kept at 88°C for 2 hours under stirring.

The sputtered CdSe films were deposited using a pulsed DC magnetron sputtering system. The process was optimized to give the fastest rate that would still result in a film quality that could be used in a full device. The deposition was completed under the following conditions, 60 sccm of Ar gas flow giving a gas pressure of 4.2 mTorr, power density 5.5 W cm⁻², frequency of 250 kHz, 15 s ramping time, to reach full power, 1.5 μ s reverse time and a base pressure of 2.2×10^{-5} Torr.

B. Device Fabrication

The devices were then completed with a 2-4 μ m CdTe layer deposited using close space sublimation (CSS) with a substrate temperature of 515°C, a source temperature of 630°C for 3 minutes deposition time at a pressure of 1 Torr with a 6% oxygen in argon gas mix. This was followed by a CdCl₂ treatment at 425°C for 1 minute. The devices were completed with 85 nm thick gold back contacts, deposited using thermal evaporation. No intentional copper doping was included in these devices.

III. RESULTS AND DISCUSSION

A. CdSe Layer Characterization

Scanning electron microscope (SEM) cross sections were obtained for both samples. The sputtered sample (Fig. 2a) shows a dense uniform thin film approximately 400 nm thick with no pinholes or voids present.

Fig. 2. SEM images of the DC sputtered (a) and CBD CdSe thin films (b) and (c).

Conversely the CBD samples were very uneven and crystallites ranged in size up to 500 nm and were not densely packed. CdSe clusters are shown over 500 nm taller than the surrounding CdSe layer (Fig. 2c). A CdSe sample deposited using CBD with an average thickness of approximately 400 nm was selected for further comparisons with sputtered films.

Transmission data collected was used to estimate the bandgap of the CdSe layers using a Tauc plot [9] (Fig. 3). The film deposited using CBD gave a bandgap of 1.91 eV whilst the sputtered film gave a bandgap of 1.68 eV.

X-ray diffraction (XRD) analysis was also completed on each film (Fig. 4) with diffraction peaks of the CBD deposited film observed at 2θ values of 24.4°, 25.5°, 26.5° and 42.5° which can be indexed to (100), (002), (101) and (110) CdSe hexagonal crystal planes (PDF 08-0459).

The sputtered thin film was seen to have both hexagonal and cubic character with diffraction peaks observed at 2θ values of 23.9°, 26.6°, 45.6° indexed to (100), (101) and (103) hexagonal and 2θ values of 25.4°, 41.9°, 49.8° indexed to (111), (220) and (311) (cubic PDF 65-2891)

Fig. 3. Tauc plots of as-deposited thin film CdSe by CBD and DC sputtering.

Fig. 4. XRD of as-deposited thin film CdSe by CBD and DC sputtering, The FTO XRD has been included for comparison.

TABLE I
EFFICIENCY (η), SHORT CIRCUIT CURRENT DENSITY (J_{sc}), OPEN CIRCUIT VOLTAGE (V_{oc}), AND FILL FACTOR (FF) OF THE CBD AND SPUTTERED CdSe/CdTe DEVICES.

CdSe deposition	η (%)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (%)
CBD	9.3	23.3	696	57
DC sputtered	3.2	7.4	682	63

B. Full Device Characterization

Efficiency, (η), open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) were measured for each device and are shown in Table I. The efficiency for the device using CBD deposited CdSe was higher than the sputtered CdSe device, with the sputtered device only achieving a J_{sc} of 7.4 mA cm⁻². Although it suffered from a low J_{sc} , it did have comparable V_{oc} at 682 mV and an improved FF of 63%.

An EQE of both devices (Fig. 5), shows that the device using CdSe deposited by CBD had no parasitic absorption at short wavelengths, which suggests the CdSe diffused fully into the CdTe layer. The increased response at 850 nm and 900 nm is due to the reduction in the absorber bandgap when compared to CdTe/CdS devices.

Fig. 5. EQE of the CdSe/CdTe devices using CdSe deposited by CBD and DC sputtering.

Fig. 6. PL measurements of DC sputtered CdSe devices, CdCl₂ treated at variable temperatures.

Fig. 7. Bandgaps of variable temperature treatment of CdCl₂ plotted on the Vegard's law graph.

In comparison the sputtered device has a poor EQE with little response at shorter wavelengths suggesting low diffusion of the CdSe layer. Only at wavelengths greater than the CdSe bandgap does the EQE improve to 75%.

It was anticipated that increasing the temperature of the CdCl₂ treatment would improve the diffusion of CdSe into CdTe for the sputtered CdSe device and so was repeated at temperatures of 445°C and 465°C. Photoluminescence (PL) was used to investigate opto-electronic properties of the material (Fig. 6). At 425°C two peaks were noted corresponding to 1.58 eV and 1.40 eV, at 445°C peaks can be seen corresponding to 1.50 eV and 1.38 eV.

The PL completed on the film annealed at 465°C had a large peak corresponding to 1.37 eV. When these values are plotted on the graph from Fig. 1 (Fig. 7) it is clear that increasing the temperature improves diffusion as the bandgap tends towards 1.36 eV as the mole fraction of CdSe approaches 0.4.

J-V measurements of the increased CdCl₂ treatment temperatures (Fig. 8) showed that when the treatment temperature was raised to 445°C it resulted in a decrease in V_{oc} , J_{sc} , FF and efficiency but when increased to 465°C a slight recovery in J_{sc} and overall efficiency was seen (Fig. 9.)

Fig. 8. J-V curves of the CdCl₂ treated CdSe/CdTe devices using DC sputtered CdSe.

Fig. 9. Box plots showing Efficiency (η), short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) of the CBD and DC sputtered CdSe/CdTe devices with variable CdCl₂ treatment temperatures.

The rollover was also improved which suggests the higher temperature was beneficial for the CdTe/back contact interface.

C. Summary

CdSe films deposited by CBD and pulsed DC magnetron sputtering were compared. CBD films tend towards a hexagonal crystal structure with low density and uneven surface with a large range of crystallite sizes. The bandgap of the CBD CdSe film was estimated to be 1.91 eV using transmission data. The CBD full device showed effective diffusion of the CdSe layer into CdTe at a CdCl₂ annealing temperature of 425°C with a top efficiency of 9.3% but a low FF. Both the ease of diffusion and the low FF may be attributed to low CdSe film density which resulted in a low shunt resistance but further analysis is required.

Sputtering provided a highly uniform dense film that had both hexagonal and cubic character. The bandgap was estimated to be 1.68 eV using transmission data. The sputtered device showed low diffusion at a CdCl₂ treatment temperature of 425°C with a poor EQE response. PL was used to analyze the opto-electronic response of sputtered devices annealed at 425°C, 445°C and 465°C.

At 465°C a single peak occurred at 1.37 eV. This suggests as the annealing temperature increases diffusion is more efficient as the signal tends towards one large peak close to the expected bandgap for CST of 1.36 eV.

Further work will focus on improving the deposition procedure for the sputtered CdSe thin-film and film thickness to promote the most effective diffusion and analyzing higher temperatures and longer CdCl₂ treatment times.

REFERENCES

[1] M. A. Green, E. D. Dunlop, D. H. Levi, J. Hohl-Ebinger, M. Yoshita, and A. W. Ho-Baillie, "Solar cell efficiency tables (version 54)," *Progress in Photovoltaics: Research and Applications*, vol. 27, pp. 565–575, Jul 2019.

[2] R. M. Geisthardt, M. Topic, and J. R. Sites, "Status and potential of CdTe solar-cell efficiency," *IEEE Journal of Photovoltaics*, vol. 5, pp. 1217–1221, Jul 2015.

[3] S. Rühle, "Tabulated values of the Shockley-Queisser limit for single junction solar cells," *Solar Energy*, vol. 130, pp. 139–147, Jun 2016.

[4] S. Ninomiya and S. Adachi, "Optical properties of cubic and hexagonal CdSe," *Journal of Applied Physics*, vol. 78, no. 4681, 1995.

[5] T. Baines, G. Zoppi, L. Bowen, T. P. Shalvey, S. Mariotti, K. Durose, and J. D. Major, "Incorporation of CdSe layers into CdTe thin film solar cells," *Solar Energy Materials and Solar Cells*, vol. 180, pp. 196–204, Jun 2018.

[6] L. Vegard, "Die konstitution der mischkristalle und die raumfüllung der Atome," *Zeitschrift für Physik*, vol. 5, pp. 17–26, Jan 1921.

[7] T. A. M. Fiducia, B. G. Mendis, K. Li, C. R. M. Grovenor, A. H. Munshi, K. Barth, W. S. Sampath, L. D. Wright, A. Abbas, J. W. Bowers, and J. M. Walls, "Understanding the role of selenium in defect passivation for highly efficient selenium-alloyed cadmium telluride solar cells," *Nature Energy*, vol. 4, pp. 504–511, Jun 2019.

[8] K. M. Morris, C. Potamialis, F. Bittau, J. W. Bowers, and J. M. Walls, "Chemical bath deposition of thin film CdSe layers for use in Se alloyed CdTe solar cells," *IEEE Journal of Photovoltaics*, in press.

[9] J. Tauc, "Optical properties and electronic structure of amorphous Ge and Si," *Materials Research Bulletin*, vol. 3, pp. 37–46, Jan 1968.