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# High Rate Deposition of CdSe Thin Films by Pulsed DC Magnetron Sputtering

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**Abstract** — The efficiency of cadmium telluride solar cells has recently been increased by adding selenium as a CdSeTe alloy at the front of the device. In this paper, we report on the use of pulsed dc magnetron sputtering to deposit thin films of Cadmium Selenide from a compound target. The deposition rates are surprisingly high and exceed 10nm/sec at a power of only 1.5kW on a 6 inch diameter target. The deposited thin films are dense and columnar. The thin films have been characterized using X-Ray diffraction, UV-vis Spectrophotometry, SEM, and Hall effect to analyse the structural, optical and electrical properties. Magnetron sputtering is widely used in thin film manufacturing and the high rates reported here make the use of pulsed dc sputtering an attractive industrial production technique for CdSe deposition in the CdSeTe device stack.

## I. INTRODUCTION

The efficiency of Cadmium Telluride photovoltaics has increased recently by alloying selenium at the front of the absorber and by replacing CdS with a transparent metal-oxide buffer layer. The CdSeTe (CST) alloy at the front of the device creates a graded band-gap absorber which allows the solar cell to make greater use of higher wavelengths, similar to CIGS device band gap grading [1]. Replacing the CdS layer with a transparent oxide increases transmission to the absorber at lower wavelengths. Both have the effect of increasing the current density  $J_{sc}$ . Se in CdTe devices improves lifetimes and defect tolerance of grain interiors [2], [3]. The Se concentration in the ternary CST alloy reduces towards the back of the device. This CST layer has been created using two methods; sublimation of CdSeTe followed by a CdTe cap [4], [5], or the deposition of a CdSe layer at the front of the device, followed by CdTe. In both methods the grading occurs during the CdCl<sub>2</sub> activation treatment by diffusion of Se towards the back of the device [2], [6]. CdSe has also been used as a window layer for Sb<sub>2</sub>Se<sub>3</sub> thin film solar cells [7]. CdSe films have previously been deposited by continuous D.C. sputtering [8], R.F. sputtering [6] chemical bath deposition [9], evaporation [10] and solvothermal method [11].

In this study, CdSe has been deposited using pulsed DC magnetron sputtering. The pulse frequency has been selected to create stable process conditions, particularly to avoid arcing, Uniform thin films can be deposited at high deposition rates using pulsed dc power. Magnetron sputtering is used

extensively for high throughput manufacturing applications and the process developed here is industrially scalable.

## II. EXPERIMENTAL

The thin films were deposited by pulsed DC magnetron sputtering using a sputtering system with the substrates held vertically on a rotating carrier. The deposition chamber has 3 vertically mounted six-inch circular magnetrons (Power Vision Ltd., Crewe UK). The sputtering target used was 50:50 Cd:Se (Plasmaterials Inc, 99.999%). Up to four substrates can be mounted on a carousel which rotates at 100rpm. The substrates used were 1 mm thick 5x5 cm soda lime glass (SLG) (ThermoFisher) and a 3mm thick 5x5 cm TEC12D glass (NSG Pilkington). TEC12D has an architecture of glass followed by a fluorinated tin oxide layer (FTO) and an undoped intrinsic tin oxide layer. The CdSe was deposited at a pulse frequency of 200 kHz, with a 2  $\mu$ s reverse time and 15 second ramp time. The powers used were 250 W, 500 W, 750 W, 1000 W and 1500 W. The argon gas flow used was 60 sccm. Scanning Electron Microscope (SEM) images were obtained using a JEOL-7800F Field Emission Gun Scanning Electron Microscope (FEGSEM) at 5 kV accelerating voltage. Specimens for Transmission Electron Microscopy (TEM) were prepared by Focused Ion Beam (FIB) milling. TEM was carried out using a FEI Technai

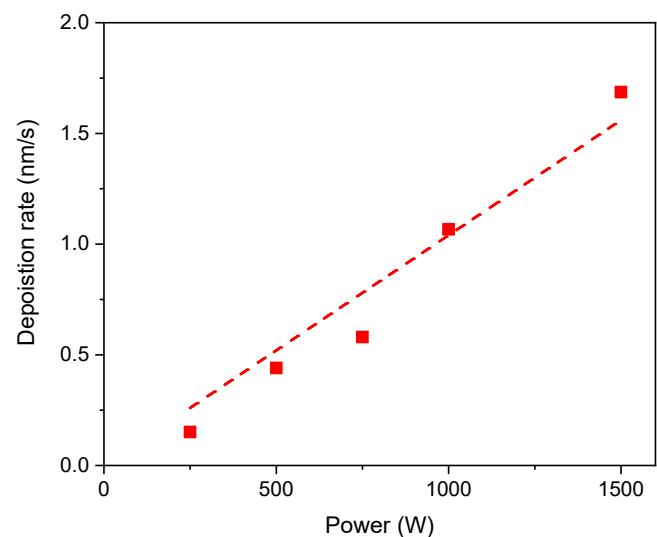


Figure 1 Rotated deposition rates for CdSe sputtered by Pulsed DC Magnetron sputtering for different deposition powers

F20, equipped with an Oxford Instruments X-max N8 TLE SDD for energy dispersive X-ray Spectroscopy (EDX). The X-ray diffraction (XRD) characterization was performed on a Bruker- D2 benchtop XRD, utilizing Cu K $\alpha$  X-rays  $\lambda = 1.542\text{\AA}$ . The spectrophotometry measurements were taken on a Varian Cary 5000 UV-Vis-NIR. The Hall Effect measurement was taken on a Semilab PDL Hall System. These samples required an insulating surface, so the Hall Effect measurement could only be performed on a soda lime glass substrate. The thickness measurements used to calculate the deposition rates were performed using a stylus profilometer (Ambios XP2 Profiler). These thickness measurements were verified with cross section SEM images. X-ray photoelectron spectroscopy (XPS) was performed on Thermo Scientific K-alpha XPS surface analysis tool. These spectra were charge corrected to reference the C 1s peak at 248.8 eV. A monochromated X-ray Al K alpha source with energy of 1.48 keV was used.

### III. RESULTS AND DISCUSSION

The deposition rates of thin films sputtered on SLG substrates were between 0.15 nm/s (250W) and 1.69 nm/s (1.5kW) on a rotated substrate carrier with space for 4 substrates (Figure 1). The estimated equivalent deposition rates, when the substrate is stationary are between 0.98 (250W) and 10.1 nm/s (1.5kW) respectively. Note that the Advanced Energy Pinnacle Plus power supply is capable of delivering 5kW, so the power could be increased further if required. The deposition rates obtained with pulsed dc power are surprisingly high and industrially attractive.

The structure of the thin films produced on soda lime glass (SLG) is highly oriented. This is shown in the XRD and the TEM cross section (Figures 2 and 3). The XRD pattern for the CdSe film on SLG at room temperature shows two peaks – one at  $2\theta = 25.3^\circ$  and one at  $52.05^\circ$  (Figure 2). These can correspond to either the cubic phase  $(111)_c$  and  $(222)_c$  planes, or the hexagonal phase  $(002)_h$  and  $(004)_h$  planes. The absence of any other peaks indicates this film is highly oriented, and depending on the phase the  $(002)_h$  or the  $(111)_c$  plane is preferentially oriented parallel to the substrate. It is difficult to separate the two phases in this pattern.

CdSe deposited on the TEC12D substrate has a mix of cubic and hexagonal phases. The most intense peak in hexagonal CdSe is the  $(100)_h$  peak, and the most intense peak in cubic CdSe is the  $(111)_c$  peak. If this film was purely hexagonal there would be much less intensity at the  $(002)_h/(111)_c$  peak. Therefore the cubic phase is indicated by the intense  $25.27^\circ(111)$  peak and the hexagonal phase is indicated by the peaks at  $23.881^\circ(100)$ ,  $27.097^\circ(101)$ ,  $35.136^\circ(102)$ ,  $45.81^\circ(103)$ , and  $55.879^\circ(202)$ .

The XRD pattern for CdSe deposited on SLG at  $150^\circ\text{C}$  indicates the presence of both phases with the  $(111)_c$  and  $(101)_h$  peaks. Other peaks at  $41.8^\circ$ ,  $45.4^\circ$  and  $49.3^\circ$  are present, but not intense. The presence of these peaks indicates the film is less preferentially orientated compared to the SLG sample deposited at room temperature. The broad region between  $20^\circ$

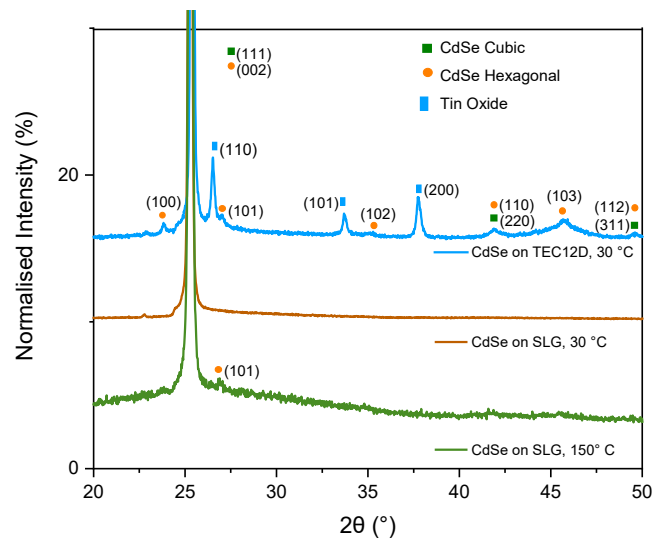


Figure 2 XRD patterns for CdSe deposited on SLG at room temperature, on TEC12D at room temperature, and on SLG at  $150^\circ\text{C}$

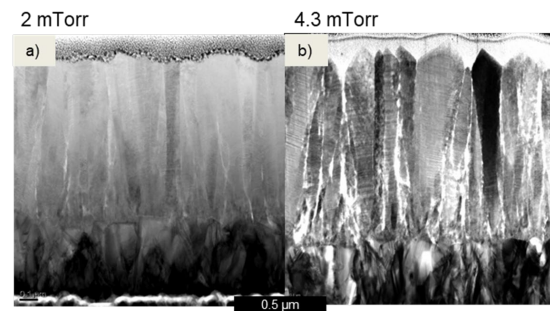


Figure 3 TEM micrograph of a cross section of CdSe deposited on TEC12D at room temperature at a) a working gas of 2 mTorr of Ar and b) 4.3 mTorr of Ar

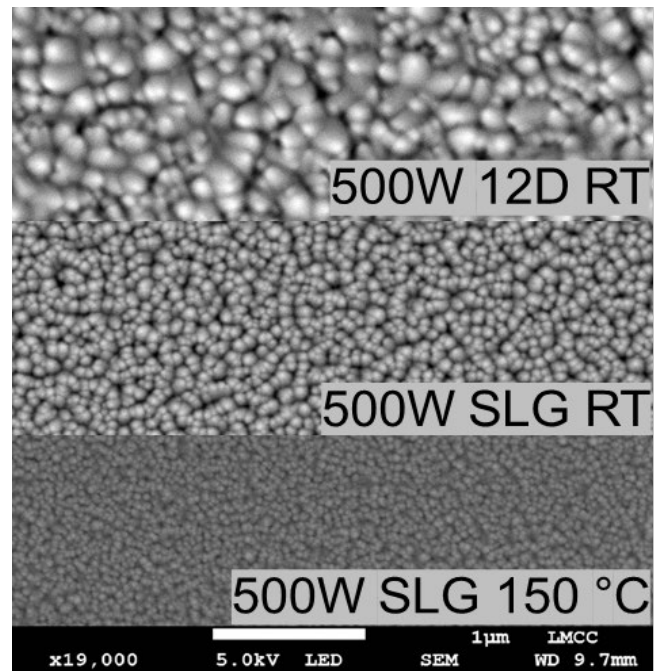


Figure 4 Planar SEM micrographs of CdSe deposited at 500 W deposition power onto TEC12D and SLG at room temperature, and CdSe deposited on SLG at  $150^\circ\text{C}$

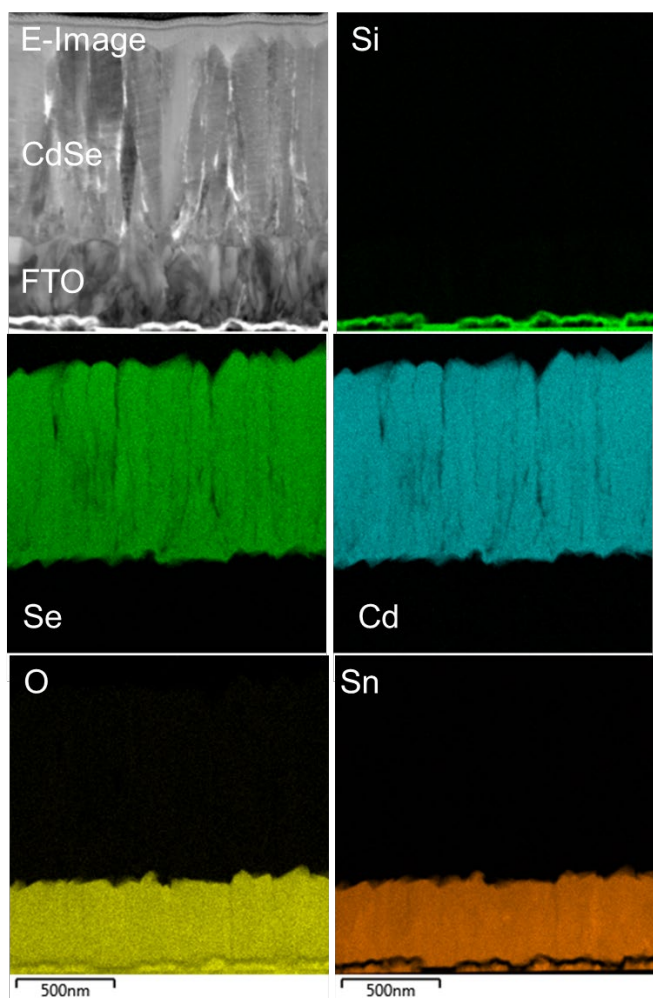


Figure 6 TEM cross section EDX compositional maps of CdSe on TEC12D. TEM and EDX data taken on FEI Technai F20 with Oxford Instruments X-max N8

and 30° may be due to substrate effects from the SLG, due to the thickness of the CdSe, or it may be due to microcrystalline grains in the CdSe.

The TEM cross section of the CdSe deposited on TEC12D at room temperature (Figure 3) shows strong columnar growth on this substrate, which corresponds to the preferential growth observed in the XRD pattern. A high density of stacking faults can be observed, especially visible in the 4.3 mTorr image. The XRD data supports this, with the stacking faults a mix of cubic and hexagonal phases, similar to stacking faults observed in CdTe [12]. This growth has also been observed in CdS thin films sputtered by PDCMS [13]. The film deposited at a

TABLE 1 – Comparison of different compositional techniques, the differences in these values may be due to the sensitivity of the technique, coupled with slight differences in the surface and bulk composition.

Measurement Technique	25 °C Cd : Se	150 °C Cd : Se
EDX SEM	54.42 : 45.58	54.65 : 45.35
XPS	62.13 : 37.87	61.28 : 38.72
EDX TEM	58.2 : 41.8	x

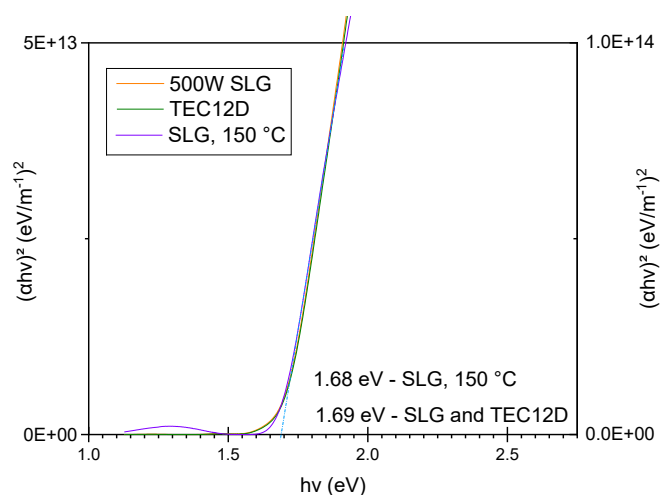


Figure 5 Calculated band gaps for CdSe films deposited on SLG at room temperature and at 150 C, and CdSe deposited on TEC12D. The 12D and SLG samples are using the Left axis, and the heated sample is using the right-hand axis

working gas pressure of 4.3 mTorr has more voids than the film deposited at 2 mTorr. This shows optimization of the gas pressure will dramatically improve the film quality and reduce the voids.

The planar-view SEM micrograph of the CdSe film grown on SLG at room temperature shows rounded grains, with consistent grain sizes and shapes (Figure 4). The SEM images for the CdSe films deposited at powers between 250 W and 1500 W are consistent and appear very similar. The CdSe deposited on TEC12D however shows much larger grains, and there is much more variation in the shape of the grains. This corroborates with the XRD characterization showing less preferential orientation. The CdSe film grown at 150 °C on SLG shows much smaller grains than the thin films deposited at room temperature on SLG.

TEM EDX maps shown in Figure 3 show the Cd and Se in the CdSe layer, with Sn and O in the FTO layer below.

Alongside the TEM EDX, the composition was also characterised with SEM EDX and XPS. All techniques showed the films to be cadmium rich, with 8% difference in the values between the techniques. The XPS is a surface technique, which indicates the surface may be more cadmium rich than the bulk, however an XPS depth profile will provide more insight. The difference between the SEM EDX and the TEM EDX is caused by the different spatial resolution of the techniques, and the SEM EDX was performed on a planar surface and the TEM EDX was performed on a cross section.

Spectrophotometry transmission measurements have been used to calculate the band gaps as shown in Figure 5. The CdSe

TABLE 2 - Hall effect data for a 1 µm thick CdSe film on SLG

Carrier type	N
Carrier density	-1.98e <sup>+18</sup> cm <sup>-3</sup>
Mobility	6.211 cm <sup>2</sup> /Vs
Sample Resistivity	0.575 Ohm.cm
Conductivity	1.739 Ohms <sup>-1</sup> cm <sup>-1</sup>

deposited on the TEC12D substrate and the SLG substrate produce very similar transmission spectra, and so the calculated band gap is the same for both. The SEM images show much smaller crystallites in the sample heated during deposition, so these small crystallites may also have an effect on the bandgap. [8]. The Tauc plots have produced bandgaps of 1.69 eV and 1.68 eV for room temperature and 150 °C depositions, respectively.

The electrical properties were obtained with a Hall Effect system with a CdSe film deposited on an insulating substrate (SLG). The sample resistivity is the reciprocal of the conductivity, so the conductivity is  $1.739 \text{ Ohms}^{-1}\text{cm}^{-1}$ . CdTe has a conductivity of between  $0.0001$  and  $0.000001 \text{ Ohms}^{-1}\text{cm}^{-1}$  [14], so the CdSe film is  $10^5$  times more electrically conductive. The carrier density of this CdSe film is also  $10^2$  times higher than that of CdTe. The CdSe is a relatively conductive n-type film with a low mobility.

#### IV. CONCLUSIONS

A full characterization of the structural, compositional and electronic properties of pulsed dc sputtered CdSe has been performed. The deposition rates of 10nm/s at 1.5kW from a 6 inch target is surprisingly high and pulsed dc magnetron sputtering is an industrially viable process for the deposition of thin film CdSe. SEM images show a decrease in the grain size after deposition at 150 °C, and CdSe deposited on TEC12D has more randomly oriented and larger grains. Changing the power used during the deposition process has little effect on the grain size, with a calculated deposition rate of up to 10 nm/s. The phases present in the CdSe films on SLG appears to be only cubic, however deposition on TEC12D produces a mix of cubic and hexagonal phases due to the presence of a high density of stacking faults. The films are more electrically conductive than CdTe with a conductivity of  $1.739 \text{ Ohms}^{-1}\text{cm}^{-1}$ . The CdSe films are Cd rich, which may encourage intermixing with CdTe when turned into full devices, due to  $V_{\text{Se}}$  providing space for Te to diffuse easily into the CdSe film.

Further work includes in-depth analysis of samples deposited at increasing temperature, and further optimization of the working gas pressure during deposition. EBSD analysis will be useful to examine in more detail the crystal phase as deposited at different temperatures, photoluminescent spectroscopy to examine the bandgap and electrical characterization and

ellipsometry to fully understand the pure as deposited CdSe material, and the effects of post-annealing.

#### V. ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] M. Gloeckler and J. R. Sites, "Band-gap grading in Cu(In,Ga)Se<sub>2</sub> solar cells," *J. Phys. Chem. Solids*, vol. 66, no. 11, pp. 1891–1894, 2005.
- [2] J. Munshi, Amit; Kephart *et al.*, "Polycrystalline CdSeTe / CdTe Absorber Cells With 28 mA/cm<sup>2</sup> Short-circuit Current," *IEEE J. Photovoltaics*, vol. 8, no. 1, pp. 310–314, 2018.
- [3] T. A. M. Fiducia *et al.*, "Understanding the role of selenium in defect passivation for highly efficient selenium-alloyed cadmium telluride solar cells," *Nat. Energy*, vol. 4, no. 6, pp. 504–511, 2019.
- [4] D. E. Swanson, J. R. Sites, and W. S. Sampath, "Co-sublimation of CdSe x Te 1 Å x layers for CdTe solar cells," *Sol. Energy Mater. Sol. Cells*, vol. 159, pp. 389–394, 2016.
- [5] A. H. Munshi *et al.*, "Polycrystalline CdTe photovoltaics with efficiency over 18% through improved absorber passivation and current collection," *Sol. Energy Mater. Sol. Cells*, vol. 176, pp. 9–18, 2018.
- [6] T. Baines *et al.*, "Incorporation of CdSe layers into CdTe thin film solar cells," *Sol. Energy Mater. Sol. Cells*, vol. 180, no. February, pp. 196–204, 2018.
- [7] L. Guo *et al.*, "Improved stability and efficiency of CdSe/Sb<sub>2</sub>Se<sub>3</sub> thin-film solar cells," *Sol. Energy*, vol. 188, no. January, pp. 586–592, 2019.
- [8] M. K. Khalaf, B. A. M. Alhilli, A. I. Khudiar, and A. A. Alzahra, "Influence of nanocrystalline size on optical band gap in CdSe thin films prepared by DC sputtering," *Photonics Nanostructures - Fundam. Appl.*, vol. 18, pp. 59–66, 2016.
- [9] M. Dhanam, R. R. Prabhu, and P. K. Manoj, "Investigations on chemical bath deposited cadmium selenide thin films," *Mater. Chem. Phys.*, vol. 107, no. 2–3, pp. 289–296, 2008.
- [10] H. L. Wilson and W. A. Gutierrez, "Cadmium Selenide Thin Film Field Effect Transistors," *J. Electrochem. Soc.*, vol. 112, no. 1, pp. 85–91, 1965.
- [11] S. Suresh and C. Arunseshan, "Dielectric Properties of Cadmium Selenide (CdSe) Nanoparticles synthesized by solvothermal method," *Appl. Nanosci.*, vol. 4, no. 2, pp. 179–184, 2014.
- [12] A. Abbas, "The microstructure of thin film cadmium telluride photovoltaic materials," 2014.
- [13] F. Lisco, "High rate deposition processes for thin film CdTe solar cells," 2015.
- [14] G. G. Rusu and M. Rusu, "On the electrical conductivity of CdTe thin films evaporated onto unheated substrates," *Solid State Commun.*, vol. 116, no. 7, pp. 363–368, 2000.