



# Thin films of CdTe/CdS grown by MOCVD for photovoltaics

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## Abstract

A doped CdTe/CdS photovoltaic structure has been grown onto ITO coated glass substrates by metal organic chemical vapour deposition (MOCVD). CdS is nucleated from dimethylcadmium and ditertiarybutylsulphide at 290°C followed by CdTe growth from DMCD and diisopropyltelluride at 300–310°C. The grain size of the CdTe is approximately the same as the underlying CdS layer and with a strongly preferred (1 1 1) orientation. This has been achieved without post growth annealing or chemical treatment. Similarly, doping of both the CdS and CdTe layer have been achieved during growth to form a n–p junction. The dopant precursors are n-butylchloride for the CdS layer and dimethylaminoarsenic for the CdTe layer. Preliminary photovoltaic devices show good rectification, with an open circuit voltage of 0.14 V, and fill factors of 35–50%. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

This paper reports on the first MOCVD (metal organic chemical vapour deposition) grown CdS/CdTe photovoltaic cells which includes doping both sides of the p–n junction. This material system has attracted considerable attention as an alternative thin film photovoltaic material to amorphous silicon as it offers a near optimum

absorption band gap in CdTe, excellent transmission properties of the CdS layer and high absorption coefficient in CdTe [1]. The potential photovoltaic efficiency is in excess of 30% (AM1.5), the best achieved so far in the laboratory is 15.8% by Britt and Ferekides [2] but on a production scale it is less than 10% [3]. One attraction of the CdS/CdTe system is the ability to deposit onto glass substrates which helps in achieving the low cost objectives for terrestrial photovoltaic cells of < \$1/W. Another factor in working towards the low cost objective is the use of low cost deposition methods for CdTe such as electrodeposition [4]

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and close space sublimation [2], and chemical bath deposition for CdS [5]. The films, as deposited, are not electrically active and the grain size is small. These layers require annealing at over 400°C under CdCl<sub>2</sub> to convert the CdTe layer to p-type and promote grain growth to achieve approximately 10 µm size grains [6]. It has been shown by Galloway et al. [7], using EBIC and cathodoluminescence, that the grain boundaries are effectively passivated but the exact mechanism is unclear and difficult to study since the anneal causes diffusion of a number of elements, including S, Cl and O, in addition to the formation of point defects.

Very little previous work has been carried out using MOCVD to deposit either the CdS or CdTe layers, probably because it is a higher cost deposition process than those previously mentioned and would not help in achieving the cost goal for terrestrial applications. In the present study, we are interested in thin film CdTe/CdS photovoltaics on glass substrates for space applications where the cost can be higher but the efficiency must be greater than even the best reported to date for CdTe/CdS cells. The eventual goal is for a low cost, high efficiency thin film photovoltaic technology which, using glass substrates, would be cheaper than the present GaAs/Ge photovoltaics. MOCVD offers the advantages of greater control over the nucleation and the growth process while offering the opportunity for controlled doping during growth. This offers a path for systematically studying the limitations to photovoltaic efficiency with the potential for achieving devices that are closer to the theoretical efficiency. Previous reports of MOCVD growth of CdTe layers for photovoltaics have not involved doping and thus require a post growth anneal [8,9]. Relatively little work has been carried out on the MOCVD growth of CdS with one recent report on CdS grown at 300°C using DMCd and DES [10], which showed promising transmission and conductivity properties. Recent reports from our own laboratory show that CdS can be grown onto ITO (indium tin oxide) coated glass at 290°C from DMCd and DTBS [11,12]. It was found that good grain growth could be achieved in the deposited films and doping with n-butylchloride (nBuCl) could achieve a sheet resistivity of 1 Ω/square. This paper reports on progress with the MOCVD

growth of CdTe onto CdS and preliminary results of photovoltaic characterisation.

## 2. Experimental procedure

CdS layers, approximately 1000 Å thick were grown onto ITO coated glass substrates supplied by Pilkington Space Technology. The ITO, having a sheet resistivity of 10 Ω/square was deposited using plasma deposition by Applied Films Corporation and the thickness of the glass substrates was 200 µm. The substrates were rinsed in aristar grade methanol and dried with nitrogen before loading into the MOCVD reactor chamber. The precursors were DMCd and DIPTe supplied by epichem ltd and DTBS purified by distillation over CaH<sub>2</sub> at the University of St. Andrews. The dopants were n-butylchloride (nBuCl) (purified by distillation at the University of St. Andrews) for doping CdS with chlorine and *tris*-dimethyl-aminoarsenic (DMAAs) (supplied by Epichem Ltd) for doping CdTe with arsenic. CdS and CdTe layers were deposited in a horizontal, atmospheric pressure reactor with a rotating graphite substrate holder. The substrate holder was heated with a graphite resistance heater and the top wall of the reactor and liner tube were modified, to permit the reflectance of a 650 nm diode laser beam, for in situ interferometer monitoring. The organometallic concentrations were calibrated prior to growth using an Epison (Thomas Swan Ltd) ultrasonic concentration monitor. This was also used during growth to check that the organometallic mixture was maintained at a constant concentration. The carrier gas was palladium diffused hydrogen at a reactor pressure of 1 atm.

## 3. CdTe growth

A series of CdTe growth runs were carried out at different growth temperatures. Prior to growing the CdTe layers, a 1000 Å thick layer of CdS was grown with a 1 : 1 VI : II ratio at 290°C. This has been shown to give optimum grain size and transmission for the CdS layer [11,12]. Growth rates were measured using in situ interferometry in the

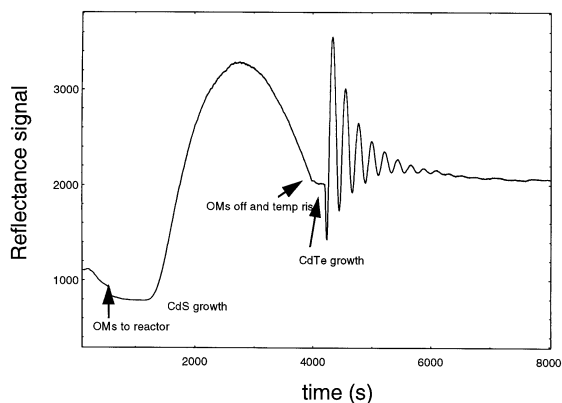


Fig. 1. Interferogram of CdS/CdTe MOCVD growth where the CdTe layer was grown at 340°C

temperature range from 270 to 410°C. An example from one of these growths is shown in Fig. 1 where the CdTe was grown at 340°C. The organometallic partial pressures were  $2 \times 10^{-4}$  atm for both precursors. The features of this time resolved reflectance give a history of the growth of this structure. From the time when the organometallics were detected by the Epison to be flowing into the reactor cell, to the time where the increase in reflectance indicates that the film was growing for approximately 12 min. This nucleation delay appears to be a critical part of the process for achieving good grain growth in the CdS layer [11]. After growing 1000 Å of CdS, the organometallics were switched to vent and after a pause of three minutes, in which time the temperature was reset from 290 to 340°C, the DMCD and DIPTe organometallics were switched into the reactor to start the CdTe growth. No nucleation delay was observed at the start of any of the CdTe growths. The more rapid oscillations indicate that the growth rate is higher for CdTe at 340°C ( $10 \text{ Å s}^{-1}$ ) than CdS at 290°C ( $0.2 \text{ Å s}^{-1}$ ). The attenuation of the CdTe oscillations is expected due to absorption at the laser wavelength of 650 nm. The constant reflectance as the CdTe layer grows thicker is indicative of smooth growth. All the films grown in this way had a mirror smooth finish.

The results from CdTe films grown at different temperatures are plotted as  $\log(\text{growth rate})$  versus

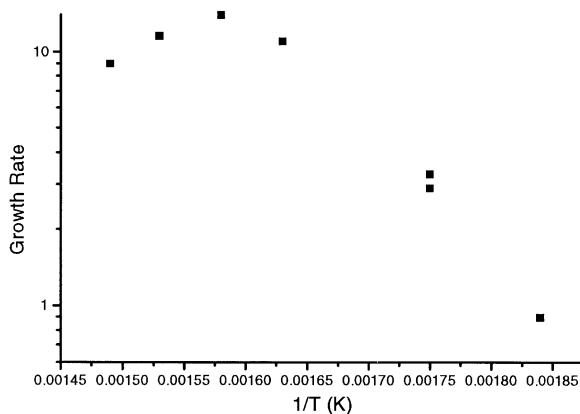


Fig. 2. Plot of CdTe growth rate as a function of  $1/T$  on CdS/ITO/glass substrates.

$1/T$  in Fig. 2. The curve follows the same general trend as has been observed for epitaxial layers [13]. The low temperature regime indicates first order kinetics with an activation energy of 25.3 kcal/mol. This is higher than the value reported for epitaxial growth onto (1 0 0) substrates, from a VI/II ratio of 1 : 1 and is closer to the activation energy achieved for 2 : 1 [13]. The difference may be due to the different film orientation. The high temperature regime also shows a similar behaviour to epitaxial CdTe with a decrease in growth rate with increasing temperature. This has been attributed to the desorption of unreacted tellurium organometallics where the surface reaction depends on radical reactions with adsorbed DIPTe [13]. From Fig. 2 it can be seen that to grow at the same temperature as the CdS layer (290°C) would give a CdTe growth rate of  $2 \text{ Å s}^{-1}$ . Thus it would take 167 min to grow a thickness of 2 µm, the target thickness for CdTe. There are also issues of the poor efficiency of using the organometallics when the growth rate is nearly an order of magnitude lower than the maximum achieved at higher growth temperatures. High temperature growth would be undesirable because of the diffusion of impurities from the glass substrate and interdiffusion at the CdS/CdTe interface. For the purpose of these experiments, a compromise was chosen with a CdTe growth temperature of 300 to 310°C, giving a growth rate around  $5 \text{ Å s}^{-1}$ .

#### 4. CdTe characterisation

The grain structure was revealed by etching the CdTe films in the Inoue defect revealing etch [14]. This preferentially etched the grain boundaries which could be seen in an SEM. An example is shown in Fig. 3 for a layer of CdTe grown at 300°C onto the standard CdS layer. The revealed grain structure is similar to that observed for CdS [11] with an approximate grain size of 10  $\mu\text{m}$ , which is similar to layers that have been given the 400°C bake in  $\text{CdCl}_2$  [6]. In this case the grain growth has been achieved at 100°C below the conventional bake temperature and without chemical treatment. The similarity in grain size between the CdTe and CdS layers is consistent with a columnar structure with epitaxial registration between the CdTe and CdS grains but more detailed characterisation would be needed to clearly establish this relationship.

An X-ray powder diffraction profile is shown in Fig. 4 for a 2  $\mu\text{m}$  thick layer grown at 310°C. The

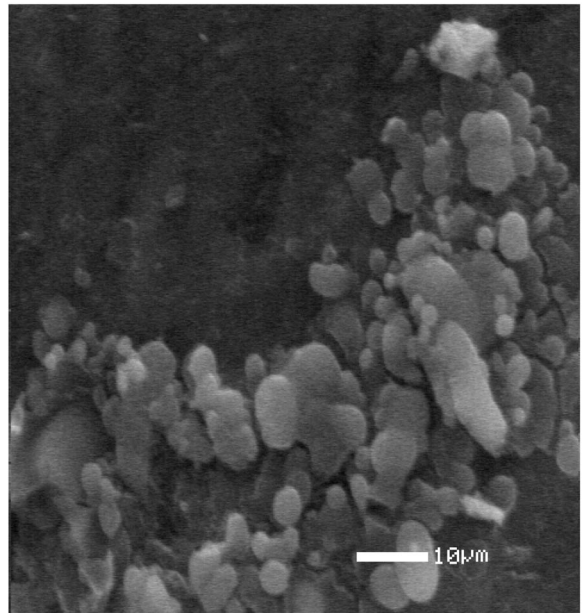


Fig. 3. SEM image of etched CdTe layer grown at 300°C.

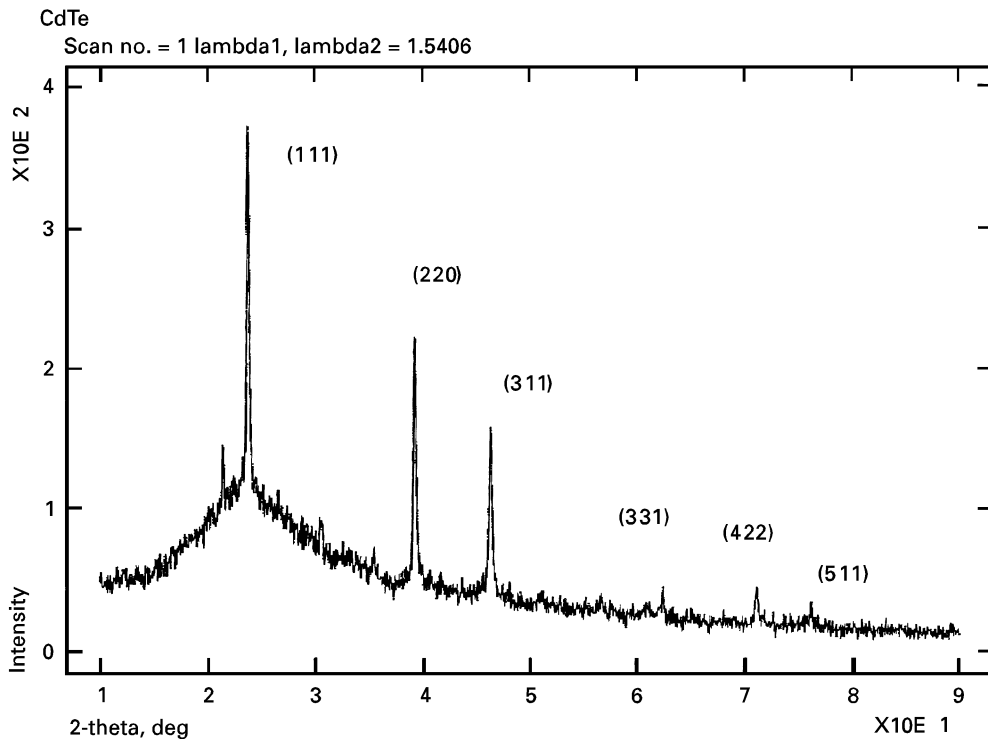


Fig. 4. X-ray powder diffraction profile for 2  $\mu\text{m}$  CdTe layer grown onto CdS/ITO/glass.

main peaks have been indexed according to the CdTe zinc blende cubic structure and indicate that there is a preferred (1 1 1) orientation. The CdS X-ray diffraction trace has been assigned previously to a hexagonal structure with a preferred (1 0 0) orientation. We can tentatively suggest from these results that there is a CdTe(1 1 1)//CdS(1 0 0) orientation relationship. Further studies using TEM would be needed to establish if this relationship is true. Some coherence between these layers would be an advantage for reducing defect density at the junction and obtaining good diode characteristics. Simmons et al. [9], using MOCVD growth of CdTe onto CdS substrates, observed the CdTe(1 1 1)||CdS(0 0 0  $\bar{1}$ ) and CdTe(3  $\bar{7}$   $\bar{5}$ )||CdS(0 1  $\bar{1}$   $\bar{6}$ ) relationships but CdS(1 0 0) was not studied.

## 5. Growth of doped photovoltaic junctions

Having successfully established that a suitable grain structure of CdTe/CdS could be grown onto ITO/glass substrates, the final step was to dope both layers to form a junction. The CdS layer was

doped with nBuCl and the CdTe layer with DMAAs. The conditions used for the DMAAs doping were 1 sccm of DMAAs at  $-14^{\circ}\text{C}$  into a total gas flow of 3400 sccm. A SIMS profile using a Cameca IMS with  $\text{Cs}^+$  primary ions was used to profile through the complete structure; profiles for the matrix elements S and Te, and dopant elements Cl and As are shown in Fig. 5. The buried CdS layer can be seen by the sharp rise and fall in the S counts. The dip in the Te counts is probably shallow due to roughening at the ion beam interface rather than interdiffusion of the Te and S matrix elements. This is supported by the 5 decades fall of the S counts in the CdTe layer. Ion beam interface roughening is likely to be a problem with polycrystalline material with different erosion rates at the grain boundary compared with the bulk of the grains. The Cl concentration shows a similar sharp rise into the CdS layer as the S signal. The residual concentration in the CdTe layer of  $2 \times 10^{16} \text{ cm}^{-3}$  may be due to residual contamination within this layer rather than Cl diffusion. The As profile closely follows that of Te which again shows that the dopant profile is abrupt, within the

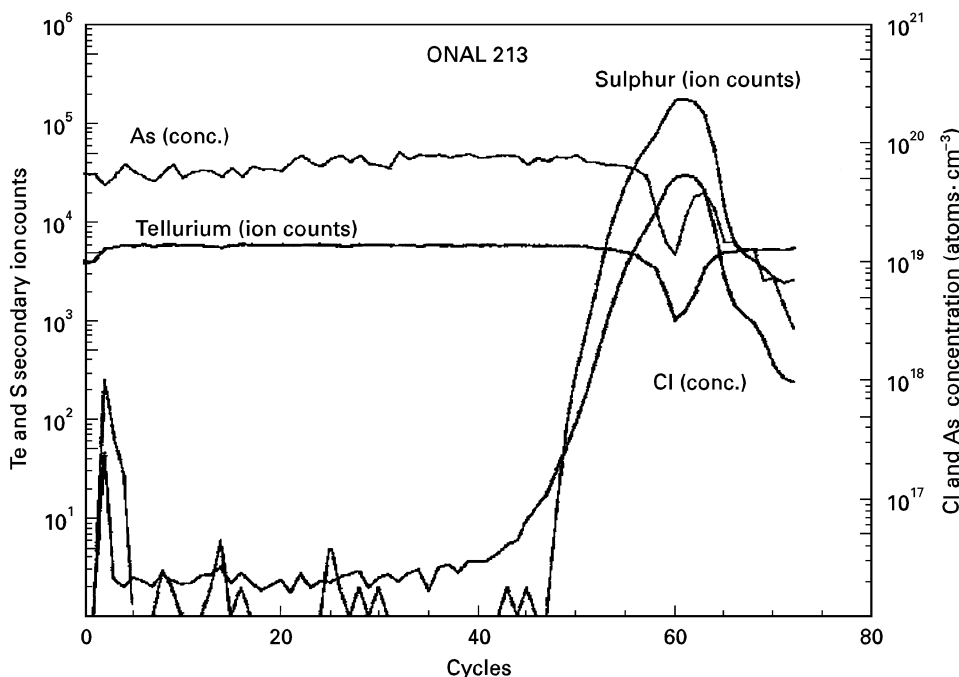


Fig. 5. SIMS depth profile for CdTe/CdS doped photovoltaic structure.

limitations of resolution of this experiment. The calibrated concentrations are estimated based on HgCdTe calibrations and show that the dopant concentrations are very high for both Cl and As. The As concentration of  $1 \times 10^{20} \text{ cm}^{-3}$  is likely to cause a short minority carrier diffusion length which would limit photovoltaic efficiency. Considering the low concentration of DMAAs in the gas stream, these results indicate that the incorporation efficiency is very high. Further experiments are in progress to reduce the As and Cl concentrations.

Test diode structures have been fabricated by selectively etching CdTe and CdS from the edge of the sample to expose the conducting ITO layer, followed by evaporating gold contact pads onto both the CdTe and ITO layers. These devices were contacted with gold probes and the current–voltage ( $I$ – $V$ ) characteristics measured using an HP4140B meter with computer control to scan the applied voltage. The  $I$ – $V$  curves show good rectification in both the dark and under illumination from a 500 W quartz halogen lamp. The current device geometry does not permit efficiency measurement but typical parameters were: short circuit photocurrent of  $0.2 \text{ mA/cm}^2$ , open circuit voltage of 0.14 V, forward bias series resistance of between 3 and  $30 \text{ } \Omega/\text{cm}^2$  and FF of between 35% and 50%. The gold contacts on the ITO layers give the expected  $10 \text{ } \Omega/\text{square}$  and four point probe measurements on the CdS layers indicate low impedance, approximately  $1 \text{ } \Omega/\text{square}$ . The reverse bias impedance indicates a soft breakdown which could be attributed to the very high doping concentrations on each side of the junction. These results are encouraging for the first attempts in producing MOCVD grown and doped CdTe/CdS photovoltaic structures.

## 6. Conclusions

A doped CdS/CdTe photovoltaic structure has been grown for the first time by MOCVD onto ITO coated glass substrates. Grain growth and dopant activation are achieved without the need for a high temperature anneal or chemical treatment after growth. The CdTe grain size is approximately  $10 \text{ } \mu\text{m}$  which is the same as the underlying CdS

layer. X-ray powder diffraction has shown that the CdTe layer has a preferred (111) orientation which appears to form a CdTe(1 1 1)∥CdS(100) relationship with the underlying CdS layer. It appears that the CdS polycrystalline layer forms an epitaxial template for the CdTe layer.

Dopant profiles for Cl and As appear to be abrupt, within the resolution of the present measurements, thinner CdTe layers would enable better depth resolution at the interface. Both dopant concentrations appear to be very high, indicating efficient dopant incorporation, but would have to be much lower for an optimum structure. Device characterisation shows that the diodes have good rectification with photo-response from a 500 W quartz halogen lamp. The versatility and control, inherent in MOCVD, will enable optimisation of this structure with the prospect of achieving photovoltaic efficiencies suitable for space applications.

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