In situ deposition of cadmium chloride films using MOCVD for CdTe solar cells

V. Barrioz *, S.J.C. Irvine, E.W. Jones, R.L. Rowlands, D.A. Lamb

School of Chemistry, University of Wales, Bangor, Deiniol Road, Bangor, Gwynedd, LL57 2UW, Wales, United Kingdom

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Abstract

This paper reports on the first deposition of cadmium chloride ($CdCl_2$) films by metal organic chemical vapour deposition (MOCVD). As the p–n junction can be deposited by MOCVD, the *in situ* $CdCl_2$ treatment of the device allows for containment of the whole process. MOCVD allows a high level of control over material properties and excellent repeatability. Deposition of $CdCl_2$, on glass and silicon, at different II:VII precursor ratios and substrate temperatures are reported. The precursors used are dimethylcadmium and tertiarybutylchloride or *n*-hexylchloride, respectively for the cadmium and chlorine species. Results are presented on the surface morphology and layer structure. $CdCl_2$ was in its hydrate form once exposed to ambient air. Preliminary results on the effects of *in situ* $CdCl_2$ treatment on MOCVD CdS/CdTe:As devices are reported and compared with untreated devices, using current–voltage characterisation. The $CdCl_2$ treatment successfully resulted in MOCVD devices having open-circuit voltage higher than 600 mV and fill factor above 50%.
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1. Introduction

Cadmium telluride (CdTe) is one of the contender materials for thin film photovoltaic (PV) solar cells with a near optimum direct band gap of 1.5 eV and low cost of raw materials. The p–n heterojunction is conventionally formed using cadmium sulphide (CdS) as a window layer (n-type) and CdTe as the absorber layer (p-type). As a consequence, both layers are polycrystalline with grains of the order of the layer thickness. To reduce the photocurrent losses by carrier recombination at the grain boundaries [1,2], a thin $CdCl_2$ layer is deposited on the CdTe layer using physical vapour deposition [3,4], or by spraying aqueous solution [5], followed by an annealing of the device at around 400 °C under nitrogen or oxygen. Alternatively, vapour transport of chlorine (Cl) or cadmium chloride during annealing can also be used [6,7]. This $CdCl_2$ treatment has the effect of passivating the grain boundaries and may provide a flux to promote lateral grain growth (i.e. depending on the initial grain size) [1–8].

The current dilemma of the overall p–n junction process and activation is that each step is carried out in a different environment with potential for process variability. Typically, the process steps are as follow: (i) the CdS is deposited at low temperature by chemical bath deposition (CBD) before being annealed; (ii) the CdTe is then deposited at high temperature ($\sim$ 500 °C) by closed space sublimation (CSS); (iii) the $CdCl_2$ treatment is then applied by one of the methods described above. The ideal solution would be the containment of the overall device production within the same process. Metal organic chemical vapour deposition (MOCVD) can, in principle, achieve this goal but the critical step of depositing $CdCl_2$ by MOCVD has not previously been demonstrated.

MOCVD has been extensively used for optoelectronic devices such as cadmium mercury telluride (CMT) infrared detectors [9], where the fine control of electrical, physical and chemical properties of the layers is paramount. In 1990, Chu et al. [10] showed that CdTe, grown by MOCVD, could be used for the photovoltaic application. Good photovoltaic conversion efficiencies have been obtained using MOCVD for CdS while using CSS for CdTe [11]. The potential for depositing the full CdTe/CdS junction by MOCVD using alkyl precursors was first reported in 1998 [12]. Since then, improved p-type activation of

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* Corresponding author. Tel.: +44 1248 382 235; fax: +44 1248 370 528.
  E-mail address: v.barrioz@bangor.ac.uk (V. Barrioz).

the CdTe absorber layer has been achieved using arsenic (As) doping without $CdCl_2$ treatment [13].

In this paper, the novel deposition of $CdCl_2$, on glass and silicon substrates, by atmospheric pressure MOCVD and subsequent *in situ* annealing, on CdTe PV cells, is investigated and characterised using scanning electron microscopy (SEM), X-ray diffraction (XRD) and *in situ* interferometry. Preliminary current–voltage (*J–V*) characteristics of an all-in-one MOCVD process for activated p–n junctions, using the *in situ* $CdCl_2$ treatment, are also reported in this paper and compared with untreated CdTe solar cells.

2. Experimental

2.1. MOCVD of $CdCl_2$

The deposition of $CdCl_2$ was carried out in a horizontal MOCVD reactor at atmospheric pressure with hydrogen as a carrier gas. Dimethylcadmium (DMCd) and tertiarybutylchloride (tBuCl) or *n*-hexylchloride (*n*-HexCl) alkyl precursors were used, respectively, for the cadmium (Cd) and chlorine species. The calibration of the partial pressure of the precursors was carried out using an Epison II from Thomas Swan. The partial pressure of DMCd was kept constant at 28.4 Pa, when using tBuCl, and at 20.3 Pa while using *n*-HexCl. The II:VII precursor ratio was either Cl rich (0.29 or 0.45) while using tBuCl or Cd rich (2) when using *n*-HexCl. Using the *n*-HexCl, it was not possible to achieve a Cl rich precursor ratio due to the flow limitation from the mass flow controllers used, combined with the low saturated vapour pressure of *n*-HexCl. The metal organic precursors were introduced inside the reactor for 50 min for each run. $CdCl_2$ was deposited on both glass substrates and silicon wafers 3° off (111). The substrates were placed on a non-rotating graphite susceptor. The stable substrate temperature (T_s) during deposition was achieved using a graphite resistive heater able to reach 600 °C.

2.2. Analytical apparatus and techniques

The deposition of all layers was monitored using an *in situ* triple-wavelength reflectometer operating normal to the sub-
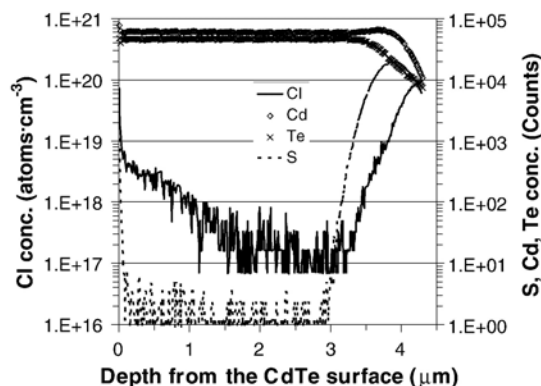

Fig. 1. SIMS depth profile of a CdTe/CdS structure after Cd–Cl post-treatment using *n*-HexCl and DMCd as precursors. There is evidence of chlorine diffusion into the CdTe layer.
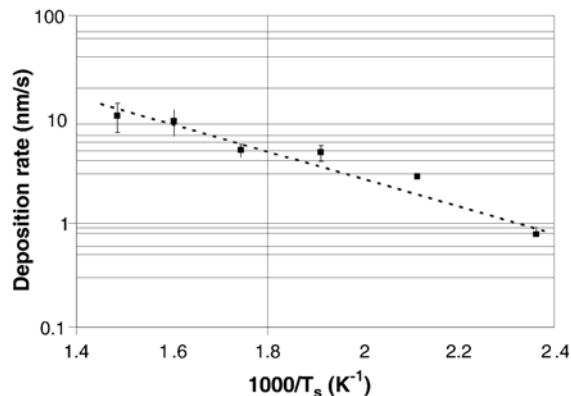

Fig. 2. The Arrhenius graph of the deposition rate of $CdCl_2$ using DMCd and tBuCl as precursors in a total gas flow of 3500 cm^3 min^{-1}. The partial pressure of DMCd was 28.4 Pa with a II:VII precursor ratio of 0.29. The solid squares represent the experimental data. The line is fitted to determine the activation energy (E_a) of the reaction.

strate surface. The layer thickness, deposition rate and material properties can be determined using the Fabry–Perot interference equation [14]. The use of different laser wavelengths (i.e. 532 nm, 635 nm, and 980 nm) allows different band gap materials to be monitored without losing the interferometer oscillations.

The SEM, used to examine surface morphology, was a S-520 from Hitachi. The samples studied were pre-coated with a sputtered thin gold layer to provide electron conduction from the sample surface to the stud. Using cross-sectional mounted samples, it was also possible to measure the thickness of the layers and consequently deduce their deposition rates. Three cross-sectional pictures per sample were used to calculate the average value of the layer thicknesses and their standard deviations, using 10 data points each time. The error bars in the graphs are the calculated standard deviation values.

The powder XRD was a PW3040/60 X'Pert PRO from Philips. Due to the hygroscopic nature of $CdCl_2$, the XRD spectra were completed within 5 h of the sample being open to ambient air. The X'pert HighScore software was used to determine the indexing of the $CdCl_2$ layers.

The *J–V* characterisation was carried out with a set of 4 halogen lamps to provide a constant 100 mW cm^{-2} light power density over a 2.5 cm^2 activated cell area, measured using a broadband thermopile power meter from Melles Griot. *J–V* characteristics, for 30 different devices, from this setup were compared with those of a solar simulator from ORIEL (300 W), calibrated for an AM 1.5 global spectrum using a calibrated cell, at the University of Durham. It was found that cell efficiencies were on average 63% lower than for our setup with the highest difference coming from the J_{sc}. This difference was corroborated by a comparison of the different spectral irradiance of the halogen lamps with an AM 1.5 spectrum, taking into account the spectral range for high quantum efficiency of a CdTe solar cell. A Keithley 2400 source/meter was used to sweep the voltage and measure the current density. The device PV characteristics were obtained from these curves. After the *in situ* $CdCl_2$ treatment, a 5 second bromine–methanol etch, with