

# The effect on CdS/CdTe solar cell conversion efficiency of the presence of fluorine in the usual CdCl<sub>2</sub> treatment of CdTe



O.K. Echendu <sup>a, b, \*</sup>, I.M. Dharmadasa <sup>a</sup>

<sup>a</sup> Electronic Materials and Sensors Group, Materials and Engineering Research Institute, Sheffield Hallam University, S1 1WB Sheffield, United Kingdom

<sup>b</sup> Solar Energy and Materials Science Group, Department of Physics, Federal University of Technology, P. M. B. 1526 Owerri, Nigeria

## HIGHLIGHTS

- CdCl<sub>2</sub> + CdF<sub>2</sub> treatment.
- n-CdS/n-CdTe solar cell.
- Improved solar cell performance.

## ARTICLE INFO

### Article history:

Received 17 October 2014

Received in revised form

7 February 2015

Accepted 7 March 2015

Available online 14 March 2015

### Keywords:

Chalcogenide

Electronic material

Semiconductor

Thin film

Heat treatment

Electrochemical technique

## ABSTRACT

The addition of CdF<sub>2</sub> to the CdCl<sub>2</sub> solution used in the well-known CdCl<sub>2</sub> treatment of CdS/CdTe solar cells has been observed to drastically improve the conversion efficiency of fully fabricated CdS/CdTe solar cells. The observed improvement is as a result of further enhancement of structural and optoelectronic properties of the CdCl<sub>2</sub> + CdF<sub>2</sub>-treated CdTe layers compared to the CdCl<sub>2</sub>-treated CdTe layers. A set of CdS/CdTe samples were grown by electrochemical deposition under different conditions and each sample was divided into two. One set of these parts was treated with only CdCl<sub>2</sub> solution while the other set was treated with the CdCl<sub>2</sub> + CdF<sub>2</sub> mixture. Both sets were annealed at 450 °C for 15 min and the solar cells completed by evaporating Au back contact on the CdTe layers after chemical etching. The results of the device measurements show drastic improvements in all the solar cell parameters (open-circuit voltage, short-circuit current density, fill factor and conversion efficiency) for the devices treated with CdCl<sub>2</sub> + CdF<sub>2</sub> mixture compared to those treated with only CdCl<sub>2</sub>. The conversion efficiencies increased from (1.0–3.0)% with CdCl<sub>2</sub> treatment to about (5.0–7.0)% with CdCl<sub>2</sub> + CdF<sub>2</sub> treatment. The observed improvements have been attributed to the unique properties of fluorine.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

CdCl<sub>2</sub> treatment has been known to drastically improve the solar energy conversion efficiency of CdTe-based solar cells at least since the 1990s [1–3]. Apart from generally improving the efficiency of CdTe-based solar cells, this treatment has been said to result in the conversion of as-grown n-type CdTe thin films to p-type CdTe [4,5] and in the improvement of n-type conductivity of CdTe layers [6]. There are also recent reports of conversion of p-type CdTe to n-type [3,5,7] or at least the conversion of thin outer layer of p-type CdTe grains to n-type [8] and thin outer layer of n-CdTe to p-type [7]. These cases however, depend on the nature of

the defect distribution in the as-grown CdTe material [7].

The CdCl<sub>2</sub> treatment process involves covering the surface of as-grown CdTe layer with a layer of CdCl<sub>2</sub> from a solution of CdCl<sub>2</sub> in methanol or in water. Alternatively this is done by evaporating dry CdCl<sub>2</sub> powder (or crystal) onto the CdTe layer. In the case of CdCl<sub>2</sub> solution, the solution is allowed to dry afterwards. In any case, the CdTe layer with a layer of dry CdCl<sub>2</sub> is then annealed at temperatures up to 450 °C in air atmosphere. After cooling, the dry CdCl<sub>2</sub> residue on CdTe is washed off with de-ionised water or methanol. The solar cell device fabrication is then completed by etching the CdTe surface with suitable etchants (in some cases) and evaporating appropriate back metal contact onto the etched CdTe surface. Some researchers have however carried out this all-important chloride treatment in slightly different ways. For example, Cunningham et al. reported the incorporation of chloride into CdTe layers during the electrodeposition process by adding CdCl<sub>2</sub> into

\* Corresponding author.

E-mail address: [oechendu@yahoo.com](mailto:oechendu@yahoo.com) (O.K. Echendu).

the deposition electrolyte and therefore carried out post-deposition annealing of CdTe without applying CdCl<sub>2</sub> on the CdTe surface again [9]. Mazzamuto et al. also reported the annealing of CdTe layers in the presence of CHF<sub>2</sub>Cl in close-space sublimation chamber and this represented CdCl<sub>2</sub> treatment [10].

From the foregoing, it is clear that the incorporation of chlorine or more generally, halogens, is crucial in obtaining high efficiency solar cells based on CdTe. We have therefore combined the addition of CdCl<sub>2</sub> and CdF<sub>2</sub> into our CdTe electrodeposition electrolyte and the post-deposition annealing of CdTe layers with (CdCl<sub>2</sub> + CdF<sub>2</sub>) treatment, to achieve enhanced solar cell efficiency of CdTe-based solar cells. The results of a comparative study of the effects of post-deposition (CdCl<sub>2</sub> + CdF<sub>2</sub>) treatment and the conventional CdCl<sub>2</sub> treatment on the conversion efficiency of CdTe-based solar cells are presented and discussed in this paper.

## 2. Experimental procedure

The CdS and CdTe thin films used in this work were both electrodeposited from acidic aqueous electrolytes using simple two-electrode system with carbon and platinum counter electrodes respectively. The electrolyte for the deposition of CdS contains 0.3 M CdCl<sub>2</sub>·H<sub>2</sub>O and 0.03 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O in 800 ml of de-ionised water. Both chemicals were laboratory reagent grade purchased from Fisher Scientific, UK. Prior to the deposition of CdS, the aqueous solution containing only 0.3 M CdCl<sub>2</sub>·H<sub>2</sub>O was electro-purified for 48 h at a cathodic potential slightly lower than that for the deposition of Cd. These voltage values were established from a cyclic voltammogram obtained for this solution also using the two-electrode system with a computerised GillAC potentiostat. After electro-purification, 0.03 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O was then added and the resulting electrolyte was stirred for 24 h. The pH of the electrolyte was adjusted to 1.80 ± 0.02 using dilute HCl and NH<sub>4</sub>OH after which another cyclic voltammogram was recorded to determine the cathodic deposition potential range for CdS. The substrate used for all voltammetry and electro-purification in this work was cleaned glass/FTO supplied by Pilkington Group Ltd, UK. After depositing some CdS samples on glass/FTO substrates across the identified deposition voltage range and characterising them using optical absorption, X-ray diffraction (XRD), photoelectrochemical (PEC) cell and scanning electron microscopy (SEM), the best cathodic deposition voltage of 1450 mV was established. Using this growth voltage, a set of CdS layers was then deposited on different substrates and annealed at 400 °C for 20 min after CdCl<sub>2</sub> treatment. The substrates used were glass/FTO, glass/FTO/Al–ZnO and glass/ITO/i–ZnO all supplied by Pilkington Group Ltd, UK.

For CdTe deposition, the electrolyte contains 1 M CdSO<sub>4</sub> (99% purity), 1 mM TeO<sub>2</sub> (99.999%), 1000 ppm CdCl<sub>2</sub> (99.999%) and 1000 ppm CdF<sub>2</sub> (99.999%) all purchased from Sigma–Aldrich, UK. The aqueous solution containing only 1 M CdSO<sub>4</sub> was first electro-purified (due to its relative low purity level) following similar steps as in the case of CdS above. From the solution containing only CdSO<sub>4</sub> and TeO<sub>2</sub> at a pH of 2.00 ± 0.02, the cathodic deposition voltage range for CdTe was obtained from cyclic voltammograms recorded using the GillAC computerised potentiostat in two-electrode configuration with Platinum counter electrode. CdCl<sub>2</sub> and CdF<sub>2</sub> were then added as sources of Cl and F for n-type doping of CdTe. After depositing some samples on glass/FTO substrates across the identified deposition voltage range and characterising them using optical absorption, X-ray diffraction (XRD), photoelectrochemical (PEC) cell and scanning electron microscopy (SEM), the best cathodic deposition voltage for CdTe was established as 2038 mV with respect to Pt counter electrode as reported recently [11].

CdTe layers were deposited on the previously annealed CdS

layers. Each CdS/CdTe structure was then divided into two halves. One set of these halves was dipped in a saturated solution of CdCl<sub>2</sub> in 50 ml of de-ionised water and allowed to dry. The other set was dipped in the same CdCl<sub>2</sub> solution but also containing about 0.1 g of CdF<sub>2</sub> and then allowed to dry. Both sets of samples were then annealed in air at 450 °C for 15 min using a furnace. After cooling, these samples were etched in a dilute aqueous solution of (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub>) for 5 s, rinsed in de-ionised water, etched again in a warm aqueous solution containing 0.5 g each of NaOH and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> for 2 min and rinsed in de-ionised water. After drying in a stream of N<sub>2</sub>, the solar cell fabrication was completed by vacuum-evaporating 100 nm-thick Au back metal contacts of 2 mm diameter on the etched CdTe surfaces. Further details of these processes are contained in a recent publication [11].

The resulting solar cells were assessed for their performance using current–voltage (I–V) characteristics obtained using a Keithly 619 Electrometer/Multimeter and a solar simulator with a power density of 100 m Wcm<sup>-2</sup>. The results of the materials characterisation and device assessment are presented and discussed in the next section.

## 3. Results and discussion

Fig. 1 shows typical XRD pattern and optical absorption spectrum of the electrodeposited CdS layer annealed at 400 °C for 20 min after CdCl<sub>2</sub> treatment. Fig. 1(a) shows the polycrystalline nature of the CdS layers with preferred crystallite orientation along the (002) crystal plane. Fig. 1(b) shows the absorption edge of this material as well as the characteristic high absorption coefficient of CdS. The energy bandgap of the layer obtained from  $(\alpha h\nu)^2$  vs.  $h\nu$  plot is 2.42 eV (Not shown here for brevity). Since the main focus of this paper is centred on CdTe, the rest of the results and discussion will concentrate on CdTe and the resulting solar cells. However, full characterisation of electrodeposited CdS layers using two-electrode system can be found in a recent publication by Diso et al. [12].

Photoelectrochemical (PEC) cell measurement was used to establish the electrical conductivity type of the CdTe layers deposited on glass/FTO substrates in both as-deposited and annealed conditions. The PEC principle relies on the depletion region formed at solid/liquid junction between the semiconductor (CdTe in this case) and a suitable electrolyte (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in this case). The difference between the open-circuit voltages across this depletion region under illumination ( $V_L$ ) and under dark condition ( $V_D$ ) gives the PEC signal. The sign of the PEC signal shows the electrical conductivity type of the semiconductor involved while

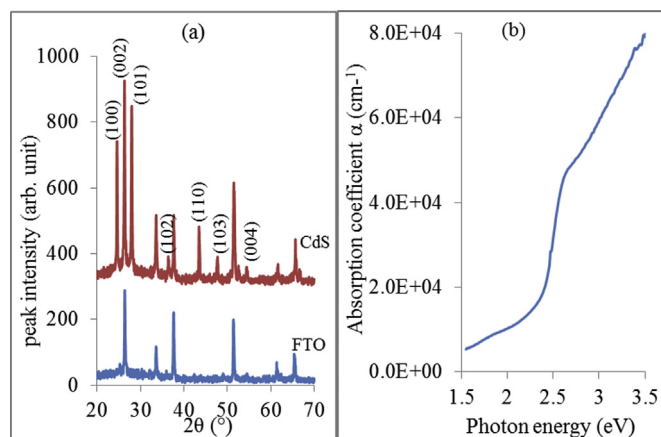


Fig. 1. Typical (a) XRD pattern and (b) Optical absorption spectrum of electrodeposited CdS layer annealed at 400 °C for 20 min after CdCl<sub>2</sub> treatment.

Download English Version:

<https://daneshyari.com/en/article/1521360>

Download Persian Version:

<https://daneshyari.com/article/1521360>

[Daneshyari.com](https://daneshyari.com)