HIGH EFFICIENCY CDTE SOLAR CELLS BY LOW TEMPERATURE DEPOSITION WITH MGZNO HRT LAYER

Daniele Menossi, Elisa Artegiani, Francesco Bittau[1], Marco Barbato[2], Matteo Meneghini[2], Gaudenzio Meneghesso[2], Jake W. Bowers[1], John M. Walls[1], Fabio Piccinelli[3] and Alessandro Romeo.
Laboratory for Photovoltaics and Solid State Physics, Department of Computer Science, University of Verona, Strada Le Grazie 15, 37134 Verona, Italy
[1]Centre for Renewable Energy Systems Technology (CREST), Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK
[2]Department of Information Engineering, Via Gradenigo 6/B, 35131 University of Padova, Italy
[3]Department of Biotechnology, University of Verona, Verona, 37123, Italy

ABSTRACT: CdTe solar cells have shown high efficiency and the technology is scalable. As a result thin film CdTe modules are competitive with crystalline silicon modules.
Thin film CdTe devices with efficiency above 22% have been reported using high substrate temperatures during the deposition process. It is known that high substrate temperatures result in large grain size with a reduced number of grain boundaries and this is believed to contribute to the high efficiency. However, use of high temperature requires robust substrates and excludes the use of most flexible substrate materials. It also involves higher energy consumption and more complicated machinery.
In this work we present a process for high efficiency solar cells with an improved front contact, by introducing magnesium-doped zinc oxide high resistance transparent layer. By optimizing the fabrication process we have achieved a conversion efficiency exceeding 16%, which is one of the highest reported for substrate temperatures below 500°C.

Keywords: CdTe, TCO Transparent Conductive Oxide, Buffer Layer

1 INTRODUCTION

CdTe solar cells are manufactured on a large scale and with high efficiency by vapour transport deposition (VTD) with a record cell efficiency exceeding 22% [1].

VTD together with Close Space Sublimation has delivered the highest efficiencies using high substrate temperature avoiding re-evaporation of the material.

Although no explanation has been provided for the high current density produced in the champion cell it is speculated that the junction has been optimized by the reduction of absorption in the CdS as well as optimization of the back contact with a back reflector. Back contacts as ZnTe:Cu have been introduced since the beginning of the 2000s [2].

16,7% efficiency by VTD has been obtained by inserting a Cd_2SnO_4 transparent conducting oxide as transparent conductive oxide (TCO) and a Zn_2SnO_4 high resistance transparent (HRT) layer. High efficiency devices exceeding 18% were presented by Sites et al. [3] by introducing a MgZnO buffer layer and other improvements including a broadband antireflection coating and a Te compound as a back reflector.

In this work we study the introduction of a Mg doped ZnO HRT layer to replace our standard insulating ZnO layer. ITO/MZO layers were fabricated at Loughborough with different substrate temperatures and their physical properties have been studied. Finished solar cells have been fabricated on the prepared TCOs and physical and electrical properties have been analysed.

Devices show different performance according to the different substrate temperature deposition. A larger amount of Mg results with higher substrate temperature and consequently a higher band gap is registered.

This optimized process has delivered solar cells with efficiencies up to 16.2%. This results to be the highest value measured in our lab, and would give, if verified in a certified laboratory, the highest efficiency for low substrate temperature deposited CdTe devices.

2 EXPERIMENTAL

2.1 TCO preparation

At Loughborough University, Indium-doped Tin Oxide and Mg doped ZnO thin films were deposited on soda lime glass by Radio-Frequency (RF) magnetron sputtering. The films were deposited using an Orion 8 HV magnetron sputtering system (AJA international, USA) equipped with an AJA 600 series RF power supply.

The 3" diameter ITO target (90% In_2O_3 and 10% SnO_2) and 3" diameter MZO target (11% MgO and 89% ZnO) were rotated at 10 rpm during deposition to assure uniformity. Both targets were sputtered at a constant power density of 3.5 Wcm^{-2} and at an Argon pressure of 133.3 Pa. 1% O_2 in Ar atmosphere was added for the MZO deposition. Substrate temperature was set to 450 °C for ITO deposition, while for MZO deposition substrate temperatures from 20 °C up to 400 °C were applied.

2.2 Solar cell fabrication

At the University of Verona the ITO/MZO substrates were coated with CdS and CdTe by thermal evaporation in a vacuum chamber at a pressure of 10^{-4} Pa with a Edwards XDS10 roughing pump and a Edwards ST-451 turbo-molecular pump.

CdS is evaporated from a tungsten crucible at a deposition rate of 5 Å/sec. During deposition the substrate was kept at 150 °C with halogen lamps. Before and after CdS deposition, the stack is annealed in vacuum at 450 °C for 30 minutes, this allows the polycrystals of ITO/MZO and the deposited CdS to crystallize and increase robustness for the depositions and treatments that follow. CdTe was deposited from a special graphite Knudsen cell at an evaporation rate of 10 Å/sec. The rate was controlled by piezoelectric quartz crystal with an

Intellemetrics IL-150 controller.

The CdTe activation treatment was carried out by deposition of $CdCl_2$ in methanol solution. This is prepared by dissolving the $CdCl_2$ powder (previously dried in a furnace at 0.1 Pa) in methanol to form a saturated solution. The liquid is then deposited in the form of drops on the CdTe surface. A typical amount of 250 µl is calculated. Finally the stack is annealed in air at 380-400 °C for 30 minutes after a 25 minutes ramp from room temperature.

The $CdCl_2$ treatment improves the electrical properties of the absorber (also by the passivation of the grain boundaries), enhances CdS/CdTe intermixing reducing the lattice mismatch and enlarges the grain size by one order of magnitude thereby reducing the density of grain boundaries [4]. In our laboratories we also have developed alternative activation treatment by application of chlorine containing compounds such as difluorochloromethane [5] or $MgCl_2$ [6]. However the $CdCl_2$ wet deposition delivers the highest performance.

The back contact consists of Cu/Au deposited on top of the CdTe layer, which was previously treated with a solution of bromine (50 µl) and methanol (40 ml) to clean the surface and remove $CdCl_2$ residuals to form a Te-rich layer. 2 nm thick Cu and 50 nm thick Au films were subsequently deposited by thermal evaporation at room temperature in a specific chamber with a vacuum of 10^{-3} Pa. Final annealing of the structure for 20 min at 190 °C in air, is necessary to obtain high efficiency.

2.3 Characterization methods

The morphological properties of the CdTe layers were studied by atomic force microscopy (AFM) with a NT-MDT Solver Pro in semi-contact mode.

X-ray diffraction analysis (XRD) of the CdTe layers has been performed by means of a Thermo ARL X'TRA powder diffractometer, operating in Bragg-Brentano geometry equipped with a Cu-anode X-ray source (Kα, k =1.5418 Å) and using a Peltier Si(Li) cooled solid state detector. Current density-voltage (JV) characteristics of the completed cells were measured with a Keithley Source Meter 2420, using a halogen lamp calibrated with a silicon solar cell under an irradiation of 100 mW/cm^2.

Light transmission measurements of TCO layers were performed by a Unicam UV2 UV/Vis spectrometer. Finally external quantum efficiency measurements (EQE) have been performed with a commercial LOANA (PV-Tools GmbH) solar cell analysis system. The EQE were calibrated with a silicon reference sample with known response using an incident spotlight of 1mmx 2 mm area.

3 RESULTS

Different solar cells have been prepared with MZO deposited at different temperatures.

Bittau et al. have already observed that in these layers higher substrate deposition temperatures result in higher amount of Mg into the HRT layer; this provides a larger band gap and, consequently, a higher transparency [7].

Cells with MZO deposited at temperatures above 300°C have resulted in a superior conversion efficiency compared to the standard process with ITO/ZnO solar cells.

Different annealing temperatures of the $CdCl_2$ activation treatment were applied to optimize the fabrication process. Most of the devices had superior efficiency, in the range of 14 % to 16 %. However, the best results were obtained by annealing the CdTe at 390 °C (as described above) and by a reduction of the CdS thickness.

In Figure 1, the current density-voltage (JV) characteristic of a 16.2% efficiency solar cell is shown with a V_{oc}= 852 mV, J_{sc}= 25,8 mA/cm^2 and a F.F.= 74 %. The parameters indicate a higher fill factor and current density, compared to our best ITO/ZnO devices (efficiencies are in the range of 15%) [8].

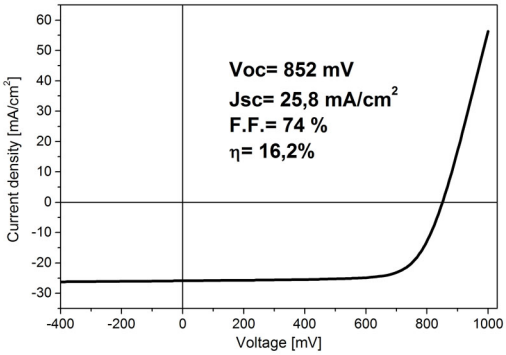

Figure 1: Current density-voltage characteristic of the highest efficiency CdTe solar cell with MZO/ITO front contact.

CdTe grown on CdS/MZO/ITO show a similar morphology irrespective of the MZO temperature and slight different recrystallization (see figure 2). CdTe grain size is almost equal for the MZO (deposited at 200 °C and 400 °C) and for the ITO/ZnO cases. On the other hand the orientation of the crystals shown on the XRD spectra slightly change their preferred orientation.

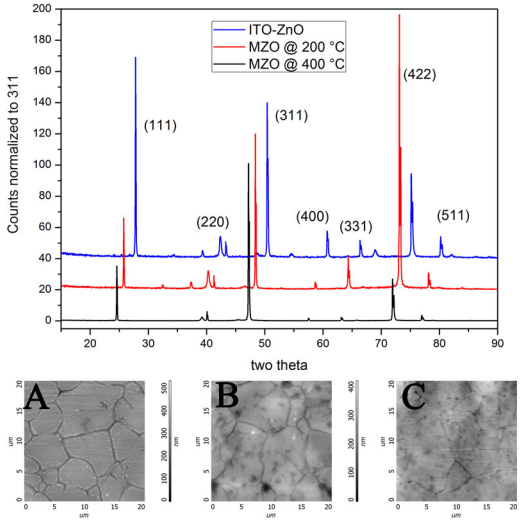

Figure 2: Comparison of XRD spectra of CdTe deposited on CdS and on ITO/ZnO or ITO/MZO (top) and morphology of CdTe deposited on CdS/ZnO/ITO (A), on CdS/MZO/ITO with MZO deposited at 200°C (B) and at 400 °C (C).

As already mentioned the application of MZO/ITO may result in higher transparency of the TCO layer (see figure 3). However, the improved performance is not entirely connected to an increased amount of photons absorbed in the CdTe. In fact quantum efficiency measurement (shown in figure 4) shows a different

response according to the different TCOs, and the insertion of the MZO layer improves the response across the entire wavelength range and in particular in the long wavelength region. This is not connected to a reduced absorption in the TCO and CdS layers.

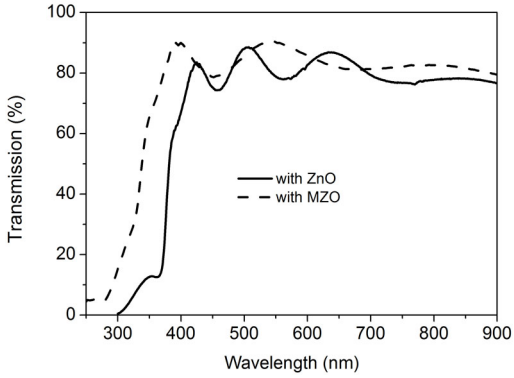

Figure 3: Comparison of transmission spectra of the new ITO/MZO stack with our standard ITO/ZnO stack.

It is possible to explain this phenomenon if we consider that the intermediate layer is not only preventing pin-holes in case of ultra thin CdS layers, or limiting diffusion of impurities from the front contact [9] but also, as mentioned by Klein et al. [10], reducing the band offset between ITO and CdS.
Moreover Rao et al. have shown that MZO has an increased match with CdS compared to ZnO [11] and Kephart et al have demonstrated that it is even possible to tune the MZO band gap and electron affinity in a way to have an optimum match with CdTe, forming MZO/CdTe heterojunction [12].

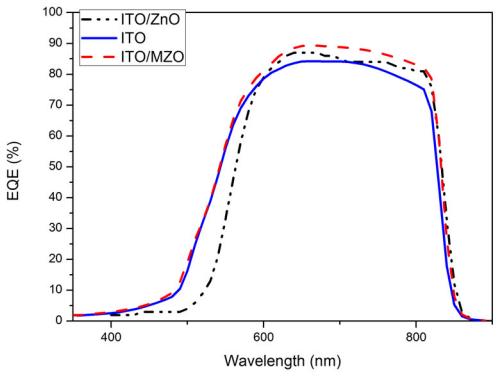

Figure 4: External quantum efficiency of CdTe solar cells made with only ITO and with ITO/MZO front contact (in this case CdS is thicker than record efficiency cells).

4 CONCLUSIONS

Thin film CdTe solar cells have been prepared using a low temperature substrate deposition process by thermal evaporation in vacuum. The process has been optimized for a front contact with insertion of high resistance transparent HRT layer of Mg-doped ZnO.

MZO substrate deposition temperature has been optimized in order to have the ideal band gap and produce a better match with the CdS buffer layer. Various $CdCl_2$ activation treatment temperatures have been used to optimize the fabrication process. The majority of devices have delivered high efficiency (from 14 to 16 %). The highest efficiency of 16,2% is a record for vacuum evaporated CdTe solar cells. The improvement of performance is not justified by the increased transparency of MZO but can be explained by an improved band alignment with the CdS buffer layer, compared to ITO or ITO/ZnO stacks.

5 ACKNOWLEDGMENTS

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