Photovoltaic performance of CdS/CdTe junctions on ZnO nanorod arrays

G. Kartopu[a,*], D. Turkay[b,c], C. Ozcan[b,d], W. Hadibrata[b,c], P. Aurang[b,c], S. Yerci[b,c,d], H.E. Unalan[b,c,e], V. Barrioz[f], Y. Qu[f], L. Bowen[g], A.K. Gürlek[a], P. Maiello[f], R. Turan[b,c,h], S.J.C. Irvine[a]

[a] Centre for Solar Energy Research, College of Engineering, Swansea University, OpTIC Centre, St. Asaph Business Park, LL17 0JD, UK
[b] Centre for Solar Energy Research and Applications (GÜNAM), Middle East Technical University, 06800 Ankara, Turkey
[c] Department of Micro and Nanotechnology, Middle East Technical University, 06800 Ankara, Turkey
[d] Department of Electrical and Electronics Engineering, Middle East Technical University, 06800 Ankara, Turkey
[e] Department of Metallurgical and Materials Engineering, Middle East Technical University, 06800 Ankara, Turkey
[f] Department of Mathematics, Physics and Electrical Engineering, Ellison Building, Northumbria University, Newcastle Upon Tyne NE1 8ST, UK
[g] G.J. Russell Microscopy Facility, Durham University, South Road, Durham DH1 3LE, UK
[h] Department of Physics, Middle East Technical University, 06800 Ankara, Turkey

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ABSTRACT

One-dimensional nanostructures, such as nanorod (NR) arrays, are expected to improve the photovoltaic (PV) response of solar cells with an ultrathin absorber due to an increased areal (junction) density and light trapping. We report on the deposition of CdS and CdTe:As semiconductor thin films on ZnO NR arrays by means of metalorganic chemical vapour deposition (MOCVD). The change in optical properties of the ZnO NRs upon the growth of CdS shell was monitored and compared to the simulated data, which confirmed the presence of strong light scattering effects in the visible and near infrared regions. The PV performance of nanostructured *vs.* planar CdS/CdTe solar cells (grown using the material from the same MOCVD run) showed similar conversion efficiencies (~ 4%), despite the current density being lower for the nanostructured cell due to its thicker CdS window. A clear improvement in the quantum efficiency was however observed in the near infrared region, resulting from the light trapping by the ZnO/CdS core-shell NR structure. We also showed that reduction of surface defects and use of high absorber carrier density would boost the efficiency beyond that of planar CdTe solar cells. The reported device performance and the direct observation of light trapping are promising towards optimisation of extremely-thin-absorber CdTe PV devices.

1. Introduction

Cadmium telluride (CdTe) based photovoltaic technology is increasing its promise for large scale solar electricity production, with new record efficiencies of 22.1% for solar cells and 18.6% for modules [1]. Although, only 1 μm thick CdTe is sufficient to capture more than 95% of the solar spectrum above the CdTe bandgap (1.45 eV), typically more than 2 μm thick CdTe is used to realise high efficiency planar devices. Attempts to reduce the CdTe thickness to less than 1 μm so far ended with severe losses in cell performance [2].

Electrically conducting ZnO nanorod (NR) arrays would form an interesting front contact for superstrate CdTe solar cells with an extremely-thin-absorber (eta). A combination of the improved areal density of the semiconductor junction (due to the large surface area of the NR array available for deposition) and also the light trapping effects observable in such nanostructures [3] are expected to improve the

photocurrent and spectral response. However, a survey of the related literature on solar cells involving NR arrays (Table 1) suggests this is not straightforward to realise. In practice, there seems to be many technical issues related to material properties and deposition uniformity, resulting in poor and even non-functional one-dimensional PV structures. The best result was obtained by depositing a thick CdTe layer, via chemical vapour deposition, onto CdS nanopillars sticking out of a porous anodic alumina nano-template [9]. However, this process is very complicated involving many fabrication steps. Simplified structures to be deposited by highly conformal deposition methods, such as atomic layer deposition (ALD), metalorganic chemical vapour deposition (MOCVD), and successive ionic layer adsorption and reaction (SILAR), would be of interest to advance one-dimensional CdTe photovoltaics.

This paper presents a study into the effects of using a ZnO NR scaffold on the growth and performance of CdS/CdTe solar cells,

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Table 1
Comparative performance of CdTe based one-dimensional photovoltaics.

Substrate	Structure	Absorber		J_{sc} (mA cm^{-2})	η (%)	Ref
		Growth method	Thickness (μm)			
Various	Dense CdTe NR	MS	0.1	0.04	–	[4]
FTO/glass	ZnO/CdTe NR	CSS	0.05–0.1	0.35	0.01	[5]
ITO/glass	ZnO/CdTe NR	ED	~0.1	5.9	–	[6]
FTO/glass	ZnO/CdS/CdTe NR	SILAR	~0.2	~8	0.7	[7]
Mo/glass	CdTe/CdS/ZnO/ITO NR	VLS (via CSS)	0.05–0.2	13.9	2.49	[8]
AAO/Al	CdS/CdTe NR	CVD	1	21	6	[9]

TF, Thin Film; NR, Nanorod; ITO, Indium Tin Oxide; FTO, Fluorine-doped Tin Oxide; Mo, Molybdenum; AAO, Anodic Aluminium Oxide; Al, Aluminium; MS, Magnetron Sputtering; ED, Electro-chemical Deposition; CSS, Closed-Space Sublimation; VLS, Vapour-liquid-solid growth; CVD, Chemical Vapour Deposition.

deposited by MOCVD. A ZnO/CdS/CdTe core-shell NR based device structure, modelled using the finite-difference time-domain (FDTD) method for light-trapping prediction, was fabricated using hydrothermal and MOCVD methods for the deposition of ZnO and CdS/CdTe, respectively. The deposition characteristics of the CdS/CdTe shells on the ZnO NRs, as well as their material properties were assessed. Nanostructured solar cells, with comparable performance to planar cells and displaying light trapping characteristics are reported. Thin film properties and device performance issues are discussed for the future optimisation of eta-CdTe cells.

2. Experimental and simulation details

ZnO NRs aligned perpendicularly to the substrate were synthesized via a hydrothermal method [10]. First, a ~ 10 nm thick ZnO film, serving as the self-catalytic seed layer for the ZnO NR growth, was deposited by radio-frequency magnetron sputtering (6 sccm Ar flow, 40 W power, 25 mTorr pressure) onto a commercial indium tin oxide (ITO)/boro-aluminosilicate glass (Delta Technologies, 4–8 Ω/sq. with 83% transparency at 550 nm). The seed layer coated substrate was then dipped into the hydrothermal solution containing 19 mM zinc acetate dihydrate [Zn(O$_2$CCH$_3$)$_2$(H$_2$O)$_2$], 1 mM aluminium acetate [Al (C$_2$H$_3$O$_2$)$_3$] and 20 mM hexamethylene tetramine (C$_6$H$_{12}$N$_4$), and kept at 80 °C for 45–180 min. The substrates taken from the solution were washed in de-ionised water and dried under N$_2$ gas. The growth duration determines the length of NRs, where the amount of hexamethylene tetramine determines the rod diameter. Using this method one can easily grow ZnO NR array films over relatively large areas (few cm^2) with high uniformity (in rod height and diameter), as depicted in Ref. [10]. In this study, the NR length was controlled in the range of 0.5–1.4 μm.

A conventional (horizontal, atmospheric pressure) MOCVD reactor was used to deposit CdS/CdTe layers as well as to perform CdCl$_2$ activation treatment for the devices. The CdS film was deposited without pre-treatment on the ZnO NRs using ditertiarybutylsulphide and dimethylcadmium organometallic precursors and hydrogen (H$_2$) carrier gas at 315 °C. CdTe films were deposited at 390 °C with ~ 10^{19} atoms cm^{-3} arsenic (As) dopant atoms incorporated. The precursors for As and Te were tris(dimethylamino)arsenic and diisopropyltelluride, respectively. Device activation was performed in two steps; first, a CdCl$_2$ layer was deposited onto the CdTe surface at 200 °C, using tertiarybutylchloride as the Cl source, and annealed for 3 min at 420 °C (in H$_2$ atmosphere), and second, the sample was annealed in air at 170 °C for 90 min after being taken out of the MOCVD chamber. Further experimental details on MOCVD growth and device activation can be found in Refs. [11,12].

Solar cells were defined by evaporating Au through a shadow mask onto the air-annealed CdTe surfaces. The cells were typically dot contact type with a diameter of 2 mm (3.14 mm^2 area), but larger ones with 5 mm × 5 mm (25 mm^2 area) dimensions were also used for spectral response measurements. AM1.5G *J-V* curves were collected

using an Abet Technologies Ltd. solar simulator with the light power density calibrated using a GaAs reference cell. External quantum efficiency (*EQE*) measurements were carried out using a Bentham spectral response system under unbiased conditions over the spectral range 300–1000 nm. The system response was corrected by scanning the output of a c-Si reference detector. Arsenic atom concentration depth profiling was carried out via secondary ion-mass spectroscopy (SIMS) using a Cameca IMS-4f instrument with Cs$^+$ ion source operating with 10 keV energy and 20 nA current. UV–Vis spectroscopy (Shimadzu UV-2600, Varian Cary5000) was used to measure both transmittance and haze of the ZnO NRs before and after CdS deposition. Electrical properties of the ZnO NRs/ITO substrates were characterised by four point probe (for sheet resistance) and the Hall effect (for carrier density and mobility) measurements at room temperature. Prior to electrical measurements, the samples were spin coated with a dilute poly(methyl methacrylate) (PMMA) solution in chlorobenzene at 3000 rev min^{-1} and allowed to dry in air, in order to partly fill the gaps between NRs for complete electrical isolation of the underlying ITO film. Scanning electron microscopy (Tescan Mira 3, Zeiss EVO HD 15, FEI Helios NanoLab) and transmission electron microscopy (JEOL JEM 2100F) were used in combination with high resolution/low voltage energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments X-Max Extreme) to characterise the structure and composition of the samples. For TEM analysis, samples were scraped off the ITO substrates, sonicated in isopropanol and drop casted onto copper grids.

The optical simulations of the structures were performed using a commercially available finite-difference time-domain (FDTD) simulation tool, LUMERICAL™. A full-field electromagnetic wave calculation was carried out. The size of the unit cell was set to be 2000 nm × 2000 nm. Plane waves were normally directed into the structure in the z-direction (i.e. from the glass side). Bloch periodic boundary conditions were set in x- and y-direction. Meanwhile, perfectly matched layers (PMLs) were utilized in the direction of propagation of the plane waves. The haze simulations of ZnO rods and CdS/ZnO rods were carried out in three-dimensional layouts with cubic mesh size of 5 nm. This structure consists of randomized rods, whose coordinates were generated using a randomization algorithm with minimum separation between each rod specified at 100 nm.

In optical simulations of CdTe solar cells, the geometrical parameters of the cell structure were extracted from the cross-sectional EDS images. The ZnO NR diameters were measured as 100 nm with an average height of 470 nm and the average deviation of the NRs from the surface normal was measured as ~ 20°. The average CdTe layer thickness was found to be 830 nm. The conformal CdS window layer of 20 nm thickness was built around the ZnO NRs. The CdTe layer is thick enough to 'bury' all the ZnO/CdS NRs, yielding an excess layer of 360 nm. Optical simulations for planar solar cells were performed for comparison. For the planar cells, ZnO and CdS thicknesses were kept as 10 nm and 20 nm, respectively, as in the NR-based cells. The CdTe thickness was chosen by considering the equivalent volume of CdTe used in the NR-based cells. The corresponding planar CdTe thickness