The backing layer dependence of open circuit voltage in ZnO/polymer composite solar cells

N.O.V. Plank ^a, M.E. Welland ^a, J.L. MacManus-Driscoll ^b, L. Schmidt-Mende ^{c,*}

^a *Nanoscience Centre, The University of Cambridge, Department of Engineering, 11 JJ Thomson Avenue, Cambridge, CB3 0FF, UK*

^b *Department of Materials Science, Pembroke Street, Cambridge CB2 3QZ, UK*

^c *Department of Physics and Center for NanoScience (CeNS), Ludwig-Maximilians University (LMU), Amalienstr. 54, 80799 Munich, Germany*

Abstract

Different layered ZnO/MEH:PPV composite solar cells have been fabricated to assess the role of the ZnO backing layer on the open circuit voltage of nanowire composite solar cells. Comparisons between cells using a ZnO layer prepared by spray pyrolysis and by sputtering and oxidising a Zn layer are compared. Cells with a sputtered Zn layer which is then oxidised show a significantly improved open circuit voltage compared to cells with a blocking layer prepared by spray pyrolysis. The thickness dependence of the blocking sputtered blocking layer is investigated. A 130 nm ZnO layer gives in a cell configuration with MEH PPV an open circuit voltage of 0.41 V, which decreases with thicker ZnO layers to 0.28 V at 650 nm. Simultaneously the EQE reduces from 7.2% at 130 nm ZnO to 2% for the 650 nm thick films. The increase in open circuit voltage of sputtered and oxidised layers of Zn compared to spray pyrolysis ZnO layers is attributed to a dense and pinhole free film for sputtered films, whilst the reduction in EQE is attributed to charge carrier reductions in the thicker films. The sputter ZnO/MEH:PPV devices have been shown to have reproducible I-V characteristics over many pixels indicating the high quality of the sputtered ZnO films.

Keywords: Hybrid solar cells; Open circuit voltage; ZnO; Polymer

1. Introduction

There is a great deal of scientific interest in ZnO due potential applications of the material, such as, field effect transistors [1], sensors [2–5], and in optoelectronic devices such as LEDs [6–11] and solar cells [12–14]. ZnO is a wide bandgap (3.3 eV) [15] material which can be easily fabricated in a variety of different morphologies, ranging from thin films to nanorods, nanobelts and nanoflowers, at low cost and with a high level of control [16] at low temperature solution based synthesis. Here we are looking at ZnO structures for semiconductor/polymer composite solar cells. Device characteristics such as the open circuit voltage and short circuit currents, which determine the power efficiency of the working solar cells, have to be

optimised. There are still several challenges to overcome which currently limit the solar cell efficiency. It is assumed that the efficiency can be increased by improving splitting efficiently of photogenerated excitons at an interface between two semiconductors with offset energy levels. Fast recombination of the excitons takes place over length scales of 4–20 nm [17] and may be shorter than the distance to the closest interface, where charge separation can take place before the charges can be collected at the electrodes. A possible solution is the optimised geometry of nanowire composite solar cells (NWCS). Nanowire arrays with nanowire distances smaller than the exciton diffusion length would ensure more efficient charge separation. ZnO nanowires are inherently n-type semiconductors [18] which can be used as an active component of nanowire composite solar cells together with a conductive polymer such as poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH:PPV), which serves as the hole transporting material of the device.

NWCS cells consist of an array of highly ordered crystalline ZnO NWs with a conducting polymer evenly dispersed within the NW array. The resulting geometry allows for an increased

* Corresponding author. Tel.: +44 1223 331693; fax: +44 1223 331693.

E-mail addresses: novp2@cam.ac.uk (N.O.V. Plank), mew10@eng.cam.ac.uk (M.E. Welland), jld35@hermes.cam.ac.uk (J.L. MacManus-Driscoll), L.Schmidt-Mende@physik.uni-muenchen.de (L. Schmidt-Mende).

junction area between the polymer and the semiconducting wire, allowing for greater efficiencies in the charge collection before the exciton recombination lengths of the order of 10 nm [17]. Although such structures have attracted a great deal of interest, both in the form of dye sensitized solar cells, [19–22] and nanowire composite cells [23–25] it is noted that there is often a problem with low open circuit voltages. For dye sensitized devices, V_{oc} ranges from 0.67 V [19], 0.74 V [21], 0.78 V [20] and 0.71 V [22], with power efficiencies of 0.3%, 0.5%, 1.2% and 0.5% respectively have been measured. In dye sensitized solar cells the dye is the absorber medium and is regenerated by a liquid electrolyte redox couple. The amount of dye molecules is restricted to the surface area covered by these molecules. Therefore nanowire dye sensitized solar cells are disadvantageous compared to nanoparticle cells, which have a much higher surface area for the dye to attach to. In nanowire dye sensitized solar cells usually only a small fraction of the incoming light is absorbed. Therefore nanoporous ZnO films outperform nanowire-structured devices. In contrast NWCS incorporate an organic hole-transporter material, which absorbs most of the incoming light, and this semiconducting organic layer is not limited to a monolayer as in the case of the dye. Therefore NWCS with a thickness of around 200 nm already absorb most of the incoming light at the wavelength where the organic material absorbs. However, these cells have produced low open circuit voltages of 0.3 V [24], 0.2 V [25] and 0.44 V [23], with power efficiencies of 0.2%, 0.2% and 0.53% respectively. Although the NWCS at present show lower power efficiencies and poor V_{oc} , the simplicity of the device architecture and the potential to create very low cost, high yield solar cells make them a worthwhile prospect for research and development. However, in order for these devices to be commercially useful V_{oc} needs to be between 0.5 and 1.2 V [17]. Also the reproducibility of these cells has to be improved. A possible mechanism for the low open circuit voltages may be in the poor quality of the backing layer fabricated prior to the growth of the NWs.

To determine the role of the backing layer in the NWC devices thin film ZnO solar cells were made by depositing MEH:PPV directly onto flat layers of ZnO in a systematic study. The ZnO layers were deposited by three different methods. Firstly, spray pyrolysis of a zinc acetate solution in ethanol, secondly a thin ZnO film made by oxidising Zn naphthenate and finally by oxidation of sputtered Zn metal films. On all resulting backing layers successful growth of surface ordered ZnO nanowires was subsequently demonstrated by hydrothermal methods [26,27].

2. Experimental methods

ITO films on glass substrates were cleaned in acetone and IPA following standard substrate cleaning procedures in a cleanroom environment. Three different methods of ZnO deposition were employed for the solar cell tests. 1. A 0.01 M solution of zinc acetate in ethanol was prepared [27]. The zinc acetate solution was then deposited onto the substrate surface by spraying directly at onto the substrates held at 400 °C on a

Fig. 1. A schematic of the ZnO/polymer composite solar cell.

hotplate. The substrates were left on the hotplate for 5 min to allow full evaporation of the solvent. 2. A solution of zinc naphthenate was produced as in reference [28]. The substrate was spray coated with the naphthenate at 200 °C then annealed in an oven at 450 °C for 1 h. 3. ZnO films were made by directly sputtering Zn onto the ITO substrates and oxidising the structures in DI water at 92 °C. Zn was sputtered for different times to produce films with the thicknesses of 130 nm, 250 nm, 300 nm, 330 nm, 580 nm and 650 nm respectively.

To fabricate the solar cells, a solution of MEH:PPV was prepared at 6 g/l concentration in chloroform. The solution was then spin coated onto the various ZnO films by drop coating 50 μ L of the solution onto the substrate surface and spin coating at 4000 rpm for 60 s. 80 nm Au contacts were then evaporated by thermal evaporation, using a direct contact shadow mask onto the polymer film surface. Each device consisted of 8 separated pixels of $\sim 2.25 \text{ mm}^2$ active area. A schematic of the final device structure is shown in Fig. 1.

The solar cells were characterized using a tungsten lamp in combination with a monochromator and Keithley 237 SMU. The current as a function of incident wavelength was recorded and the external quantum efficiency calculated using a Si diode as the standard reference. Scanning electron microscopy was carried out using a LEO 1530 VP SEM.

3. Results and discussion

An important characteristic of a working solar cell is the open circuit voltage (V_{oc}), where the I – V is at open circuit condition and no current flow is detected. The V_{oc} along with the short circuit current (J_{sc}), the current at short circuit condition ($V=0$), are important parameters of a solar cell. The efficiency of the solar cell directly depends on these values. Previous predictions that the V_{oc} is the difference between the work functions of the top and bottom electrode are too simplistic [29,30], and it has been shown that a model considering the charge separation, diffusion and drift currents is needed. As such, the backing layer and the ability for charges to separate in these devices are critical to controlling the solar cell characteristics and to maximise the power efficiency. Another important parameter of the solar cell device is the external quantum efficiency (EQE) which relates the conversion of incident photons into mobile charges in the conducting polymer.

Several different backing layers have been investigated for ZnO solar cells: ZnO layers fabricated by spray pyrolysis, ZnO films made by annealing Zn naphthenate and ZnO films made by oxidation of sputtered Zn films. All ZnO/MEH:PPV polymer

devices resulted in solar cells with EQEs up to 7.2%. An example of the output current and the EQE of a 130 nm sputtered and oxidised Zn film solar cell over 375–700 nm wavelengths is shown in Fig. 2. There is a maximum current at 525 nm due to the absorption of light by MEH:PPV, which is effective over 350–650 nm wavelengths [17], whilst the EQE peaks at 475 nm. Shown for comparison is the fraction of absorbed light by a MEH:PPV film deposited onto oxidised sputtered ZnO. The film shows broad absorption over the visible spectrum with the maximum close to 500 nm.

The spray pyrolysis method for ZnO films produced excellent nanowire structures when used as a seed layer for ZnO NW growth. In the literature, this method is often used to fabricate a seed layer for aqueous solution growth. However, solar cells made with spray pyrolysis backing layers did not show any reliable open circuit voltage. Looking at the SEM image in Fig. 3(a) it is observed that although the seed layer is smooth and uniform, there are nanoscale islands of approximately 20–40 nm in diameter visible. The thickness of the layer is around 20–40 nm. Such discrete islands could lead to a leakage path directly from the conducting polymer into the ITO. An improvement to the device characteristics was made using the Zn naphthenate films. Fig. 3(b) shows the top view of a ZnO film produced with Zn naphthenate. The film is thicker than the sprayed seed layers by an order of magnitude and has an average thickness of 160 nm. An open circuit voltage of 0.32 V was observed for a basic device. However, the device characteristics were not always uniform, nor reproducible. The most reliable backing layer fabrication process is to deposit a sputtered layer of Zn metal followed by *in situ* oxidation during the hydrothermal growth process for ZnO NWs. The resulting ZnO film shows nanoscaled features, similar to the initial growth stage of ZnO nanowires, Fig. 3c. Even though the film shows some structured features, it seems to be densely packed and pinhole-free. The surface structures seen in Fig. 3c are smaller than the overall thickness of the film, which suggest that the film is pinhole-free, hence leading to higher open circuit voltages. Another reason for the increased efficiency might lie in the higher interfacial area between the ZnO and the polymer,

Fig. 2. The fraction of absorbed light and EQE over the visible light spectrum for a device with an MEH:PPV film on 250 nm ZnO film prepared by sputtering and oxidising a Zn layer.

Fig. 3. SEM image of (a) a spray pyrolysis ZnO seed layer, (b) a ZnO film made by oxidising Zn naphthenate and (c) a ZnO film prepared by wet oxidation of sputtered Zn.

induced by the nanosized features. Further increase in the interfacial area is expected to result in further increase in the solar cell device performance.

In addition the effect of the thickness of the backing layer of sputtered Zn oxidised on the Voc was investigated. Fig. 4(a) shows the open circuit voltage against the thickness (varied by the sputter time) of the initial Zn layer. It is seen that the open circuit voltage reduces with increasing thickness of the ZnO layer, from 0.41 V at 130 nm oxide thickness to 0.28 V at

Fig. 4. Voc and EQE of devices with sputtered and oxidised Zn layers as a function of oxide thickness, taken with incident light at 550 nm. The characteristic for a Zn naphthenate solar cell is shown for comparison.

650 nm oxide thickness. The origin of this decrease is not fully understood and needs to be addressed further. Optical interference effects strongly depending on the ZnO layer thickness might have some influence. The sprayed seed layers usually showed Voc close to zero, although occasional pixels could give up to 0.11 V, whilst a typical naphthenate film characteristic is plotted in Fig. 4 for comparison to the sputtered layers. Here a 160 nm ZnO thick film leads to a Voc of 0.32 V. The EQE decreases with increasing thickness of the zinc oxide layer, Fig. 4, as does the short circuit current (not shown). Such an effect can be explained by several mechanisms. There is the possibility of reduced intensity of light reaching the MEH:PPV layer due to the light scattering that may be caused by the increased thickness of ZnO. Also, the conduction path of electrons through the ZnO will meet more resistance in the thicker layer causing a reduction in conversion efficiency. However, reducing the ZnO layer thickness significantly, as in the case of the spray pyrolysis films, leads to low open circuit voltages, probably due to pinholes in the film.

The ZnO polymer composite devices made with oxidised sputtered zinc films show high reproducibility of the open

Fig. 5. I-V characteristics of the pixels of a device with a ~330 nm sputtered and oxidised Zn film taken with incident light at 550 nm. The open circuit voltage is observed to remain almost constant across the different pixels at the device.

Fig. 6. The I-V characteristics of the same device as in Fig. 5 under solar simulation (AM 1.5 G), at 550 nm illumination and in the dark.

circuit voltage and similar I-V curves across the measured range on all pixels. Fig. 5 shows the I-V characteristics of all pixels on one 330 nm thick (40 s) sputtered ZnO device measured at a light illumination at 550 nm. It is noted that although some pixels do outperform others and have higher fill factors, overall the pixels are similar, which is an indication for a homogenous film formation of the full sample. Also the variation from device to device is very small for the sputtered Zn film devices. With an average Voc at 0.4 V for ~100 nm thick oxidised Zn layers, these devices have already shown higher Voc than comparable NWCS in the literature [23–25], even though this is only the open circuit voltage at single wavelength illumination at low intensity. When exposed to solar simulation illumination (AM 1.5) the Voc increases further to over 0.5 V, as shown in Fig. 6. The device characteristics show the performance under standard solar conditions (AM 1.5 global, ~100 mW/cm²), the performance at 550 nm and the diode behaviour at dark current. There is a dramatic increase in the short circuit current under solar illumination as expected with the increase of intensity of the incident light.

Improvements to the device characteristics can still be made by optimising the concentration and thickness of the MEH:PPV layer or by changing the polymer used altogether, to a P3HT/PCBM blend [23] for example, or by using different top electrode materials. The control and reproducibility of using sputtered Zn films to form the backing layer for ZnO NW devices show exceptional promise for the development of highly efficient solar cells, in particular due to the ease of scaling up the substrate area. An interesting approach to improve the open circuit voltage has been recently introduced by Olson et. via band-offset engineering [31]. This method is not directly and easily applicable to sputtered films. However, it might be advantageous to use a combination of sputtered film and a spray pyrolysis prepared film on top, which can be doped.

4. Conclusion

We show that Zn sputtered and oxidised layers form a good backing layer for NWSCs, outperforming ZnO layers prepared by spray pyrolysis or other methods. However, the film made by

spray pyrolysis was significantly thinner, which might be one reason for the lower performance. It has been clearly observed that the quality and thickness of the ZnO backing layer influence the device performance of simple geometry flat junction semiconductor and polymer composite solar cells. Uniform, pinhole-free oxide films are essential for the fabrication of working solar cells and to ensure reproducibility of results. With increasing ZnO thickness Voc and EQE decrease similarly, showing that the best case backing layers for ZnO NW solar cell devices is a ~100 nm ZnO layer prepared by oxidising sputtered Zn.

Acknowledgements

The authors would like to thank EPSRC, Marie Curie Excellent Grant, MC-EXT – 014156, and the Royal Society for funding. Also the members of the optoelectronics group in Cavendish led by Sir Richard Friend for their useful discussions and access to measurement equipment.

References

- [1] Z. Fan, P.C. Chang, J.G. Lu, E.C. Walter, R.M. Penner, *Appl. Phys. Lett.* 25 (2004) 6128.
- [2] H.T. Wang, B.S. Kang, F. Ren, L.C. Tien, P.W. Sadik, D.P. Norton, S.J. Pearton, J. Lin, *Appl. Phys. Lett.* 86 (2005) 243503.
- [3] L.C. Tien, P.W. Sadik, D.P. Norton, L.F. Voss, S.J. Pearton, H.T. Wang, B.S. Kang, F. Ren, J. Jun, J. Lin, *Appl. Phys. Lett.* 87 (2005) 222106.
- [4] C.S. Rout, A.R. Raju, A. Govindaraj, C.N.R. Rao, *Solid State Commun.* 138 (2006) 136.
- [5] Z. Fan, J.G. Lu, *Appl. Phys. Lett.* 86 (2005) 123510.
- [6] J. Bao, M.A. Zimmler, F. Capasso, X. Wang, Z.F. Ren, *Nano Lett.* 6 (2006) 1719.
- [7] G.T. Du, W.F. Liu, J.M. Bian, L.Z. Hu, H.W. Liang, X.S. Wang, A.M. Liu, T.P. Yang, *Appl. Phys. Lett.* 89 (2006) 052113.
- [8] R. Könenkamp, R.C. Word, C. Schlegel, *Appl. Phys. Lett.* 85 (2004) 6004.
- [9] R. Könenkamp, R.C. Word, M. Godinez, *Nano Lett.* 5 (2005) 2005.
- [10] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [11] K. Govender, D. Boyle, P. O'Brien, D. Binks, D. West, D. Coleman, *Adv. Mater.* 14 (2002) 1221.
- [12] I. Bedja, P.V. Kamat, X. Hua, A.G. Lappin, S. Hotchandani, *Langmuir* 13 (1997) 2398.
- [13] K. Keis, C. Bauer, G. Boschloo, A. Hagfeldt, K. Westermark, H. Rensmo, H. Siegbahn, *J. Photochem. Photobiol., A* 148 (2002) 57.
- [14] K. Keis, E. Magnusson, H. Lindström, S.E. Lindquist, A. Hagfeldt, *Sol. Energy Mater. Sol. Cells* 73 (2002) 51.
- [15] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc, *Appl. Phys. Rev.* 98 (2005) 041301.
- [16] Z.R. Tian, J.A. Voigt, J. Liu, B. McKenzie, M.J. McDermott, M.A. Rodriguez, H. Konishi, H. Xu, *Nat. Mater.* 2 (2003) 821.
- [17] K.M. Coakley, M.D. McGehee, *Chem. Mater.* 16 (2004) 4533.
- [18] L. Huang, C.M. Lieber, *Pure Appl. Chem.* 76 (2004) 2051.
- [19] J.B. Baxter, A.M. Walker, K. van Ommering, E.S. Aydil, *Nanotechnology* 17 (2006) S304.
- [20] J.B. Baxter, E.S. Aydil, *Sol. Energy Mater. Sol., C* 90 (2006) 607.
- [21] J.B. Baxter, E.S. Aydil, *Appl. Phys. Lett.* 86 (2005) 053114.
- [22] M. Law, L.E. Greene, J.C. Johnsons, R. Saykally, P. Yang, *Nat. Mater.* 4 (2005) 455.
- [23] D.C. Olson, J. Piris, R.T. Collins, S.E. Shaheen, D.S. Ginley, *Thin Solid Films* 496 (2006) 26.
- [24] A.M. Peiró, P. Ravirajan, K. Govender, D.S. Boyle, P. O'Brien, D.D.C. Bradley, J. Nelson, J.R. Durrant, *J. Mater. Chem.* 16 (2006) 2088.
- [25] P. Ravirajan, A.M. Peiró, M.K. Nazeeruddin, M. Graetzel, D.D.C. Bradley, J.R. Durrant, J. Nelson, *J. Phys. Chem. B* 110 (2006) 7635.
- [26] L. Vayssieres, *Adv. Mater.* 15 (2003) 464.
- [27] L.E. Greene, M. Law, D.H. Tan, M. Montano, J. Goldberger, G. Somorjai, P. Yang, *Nano Lett.* 5 (2005) 1231.
- [28] M.S.M. Saifullah, K.R.V. Subramanian, D.J. Kang, D. Anderson, W.T.S. Huck, G.A.C. Jones, M.E. Welland, *Adv. Mater.* 17 (2005) 1757.
- [29] C.M. Ramsdale, J.A. Barker, A.C. Arias, J.D. MacKenzie, R.H. Friend, *J. Appl. Phys.* 92 (2002) 4266.
- [30] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, T. Fromherz, M.T. Rispens, L. Sanchez, J.C. Hummelen, *Adv. Funct. Mater.* 11 (2001) 374.
- [31] D.C. Olson, S.E. Shaheen, M.S. White, W.J. Mitchell, M.F.A.M. van Hest, R.T. Collins, D.S. Ginley, *Adv. Funct. Mater.* 17 (2007) 264.