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Nanowire Solar Cell Sensitized with II-VI Quantum Dot Layer

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ABSTRACT

We report first results on a new solar cell consisting of a p-i-n hetero-junction formed between n-type transparent nanowires, undoped semiconductor quantum dots and a wide bandgap p-type polymer layer. The overall structure is $\text{SnO}_2/\text{ZnO}/\text{CdSe}/\text{MEH-PPV}$ with MEH-PPV standing for poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]. Microscopic studies on the structure of the quantum dot layer before and after anneal indicates a morphology change from a quantum dot assembly to a continuous polycrystalline thin film. The charge transfer between the absorber layer and the adjacent layers is improved as the layer is converted from the quantum dot assembly towards a polycrystalline thin film structure. In optimized devices the spectral photocurrent response shows contributions from the ZnO , the CdSe and the MEH-PPV, covering the spectral range from 300 to 700nm with an external quantum efficiency between 30 and 40%. The overall energy conversion efficiency approaches 1%.

INTRODUCTION

Nanostructured solar cells have recently attracted considerable interest as they offer enhanced interface areas for carrier separation, improved optical light trapping and very simple fabrication procedures (1). Incorporation of nanowires into these devices holds promise to improve the charge carrier transport for at least one carrier type. Molecular dye layers, polymers and ultra-thin inorganic semiconductor layers have been considered as suitable absorber materials for these cells (2-6).

Here we report on a new solar cell structure which uses a thin quantum dot layer as the precursor for the optically active absorber material. Depending on processing conditions this layer can be designed to have quantum dot character or, alternatively, it can be converted into a continuous poly-crystalline thin film. The absorber layer is deposited on n-type vertically oriented nanowires, which provide a fast electron pathway to the SnO_2 substrate. The p-type contact is a polymeric hole conductor, MEH-PPV, and an evaporated Au layer. The deposition processes are carried out at temperatures below 100C, but a number of intermittent annealing steps are provided at temperatures between 100C and 400C. While the quantum dot layer shows quantum confinement properties in the as-grown state and after moderate anneal, exposure to high temperatures converts the quantum dot layer into to a continuous, polycrystalline thin film with bulk-like properties. In the latter case the confinement effects are found to be absent in the solar cell characteristics. These results show that the quantum dot layer can be used as a useful precursor to obtain conformal film coverage in deep nanostructures. The solar cell efficiency is highest for continuous thin film layers due to the more efficient charge transfer.

a)

b)

c)

d)

Figure 1 a: CdSe quantum dot layer after deposition. Single quantum dots are visible in the TEM micrograph; b: high resolution micrograph showing crystallinity of single quantum dots with average size of ~ 7 nm, corresponding to their size in the colloidal solution; c: conformal coverage exhibit by quantum dot layers after annealing at 380 °C in CdCl_2 ; d: high resolution micrograph after 24 h anneal. The crystallite size is now larger than 100 nm. The location of the crystallite is near the nanowire tip.

EXPERIMENT

ZnO nanowires were grown on fluorine doped SnO₂ substrates in electrodeposition at 90°C using a standard 3-electrode electrochemical cell with Pt counter and Ag/AgCl reference electrodes. Before deposition the substrates were cleaned ultrasonically in acetone and methanol with subsequent rinsing in HNO₃ and distilled H₂O. The deposition used aqueous solutions of 0.1 M KCl and 0.3 mM ZnCl₂ saturated with O₂ gas. Al doping was provided by addition of AlCl₃ to the solution. More details on the deposition process are given in ref. 7. The nanowires were typically 1-2 μm long, 100-200 nm in diameter and their orientation was within +/- 30° from the substrate vertical. CdSe quantum dots capped with various organic ligands were obtained commercially and dissolved in toluene at a concentration of 2 g/l. The quantum dot solutions were drop coated in a sequence of 2-4 depositions, and annealed in a mixture of air and CdCl₂ vapor at temperatures of 380°C for durations from 30 min to 30 h. The CdSe/ZnO heterostructures were then provided with a p-type contact consisting of a thin MEH-PPV layer and an evaporated Au contact. The completed devices were annealed in vacuum for 5-8 h at 125°C.

Figure 2: Improvement of solar cell performance with increasing anneal time for annealing at 380 °C in air/CdCl₂. The effects of annealing in air only are also shown.

The annealing in air/ CdCl_2 liberates the freshly deposited CdSe quantum dots from their organic ligands and promotes connectivity and grain growth in the particle layer. Depending on the duration of the anneal process the morphology of the quantum dot layer can be changed from that of a loosely connected particle arrangement to a continuous polycrystalline film with micrometer grain size. The polycrystalline films are also observed to be in conformal contact to the nanowires. Fig. 1 shows transmission electron micrographs of this morphology change. The micrographs show quantum dots of 7 nm average diameter in Fig. 1a-b, and a polycrystalline film in part c-d.

DISCUSSION

The photo-electrical characteristics of this device directly reflect the morphological changes shown in Fig. 2. The external quantum efficiency curves show very inefficient charge transfer when no annealing is carried out, indicating that the organic ligands block electron injection into the ZnO and most likely also the hole injection into the MEH-PPV. For extended anneal times the response increases markedly, as shown in Figure 2. The photocurrent onset is universally observed at a wavelength of 730nm, corresponding to the bandgap of bulk CdSe. For these bulk-like absorber films the cell efficiency is optimal and reaches 1% for illumination at an intensity of 85 mW/cm^2 with a quartz-halogen spectrum. The open-circuit voltage in these conditions is 0.52 V and the short circuit current 5.3 mA/cm^2 . Typical current-voltage curves for dark and illuminated conditions are plotted in Fig. 3. The dark characteristics of these devices exhibit excellent rectification with very low leakage currents.

Figure 3: Current-voltage plot of the SnO_2 /nanowire ZnO/CdSe/MEH-PPV/Au solar cell.

Finally, in Fig. 4 we show an approximate band diagram of the ZnO/CdSe/MEH-PPV heterojunction based on energy level values obtained from photoemission spectroscopy. While this diagram does not include band bending, it shows that the electronic levels in the three semiconductors are lined up in a fashion which supports charge separation with electron collection in ZnO and hole collection in the MEH-PPV layer. More data on doping and Fermi-level position in the various layers need to be known to include band bending and dipole effects at the interfaces.

Figure 4: Schematic band diagram of ZnO/CdSe/MEH-PPV hetero-structure.

CONCLUSIONS

We have presented a new solar cell consisting of ZnO nanowires, sensitized by a variety of CdSe thin film arrangements prepared from colloidal quantum dot solutions and contacted by a p-type polymer material. The absorber layer morphology in these devices can be varied from loosely connected quantum dot layers to continuous polycrystalline thin films with excellent surface conformality. Best conversion efficiencies are in the region of 1% and are predominantly obtained with well annealed, polycrystalline absorber films.

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