Electrochemical Deposition of ZnO Nanorods for Hybrid Solar Cells

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Abstract
ZnO nanorod arrays were grown by electrochemical deposition on ZnO-seeded indium tin oxide (ITO) and on bare ITO substrates. The seed layer was deposited via sol-gel technique from a solution of methanol and zinc acetate. The optically transparent seed layer is made up of nanoparticles around 20 nm in diameter. Nanorod arrays grown on the seeded substrates have better vertical alignment and have more homogeneous diameters compared to those grown on bare ITO. Furthermore, analysis of the photoluminescence spectra showed that there are fewer defects in the ZnO nanorod arrays grown on the seed layer. The solar cell performance of hybrid solar cells prepared from the seeded substrates were better than those prepared from the bare ITO substrates.

1. Introduction
For hybrid solar cells, the ideal structure for optimal charge collection is that of an ordered bulk-heterojunction where an inorganic film grown into an array of vertically-aligned, crystalline nanorods is encased by a polymer active layer [1]. ZnO is a popular choice for the inorganic material and can be grown with various techniques such as chemical vapor deposition and epitaxy [2]. We used electrochemical deposition to grow the nanorods in this study.

Controlling the nanostructure of the film is essential because its quality affects the performance of the solar cell. It is preferable for the nanorods to be well-aligned, thin, and closely spaced such that the distance between the rods is comparable to the diffusion length of the generated excitons. A ZnO seed layer deposited on the ITO substrate before deposition has been helpful in achieving well-ordered nanostructures [3,4]. Tena-Zaera deposited a seed layer by galvanostatic electrochemical deposition [3]. In this study, we followed a modified version of Anthony’s method of seed layer deposition where the sol-gel technique is employed using a solution of methanol and zinc acetate [4]. We then proceeded to grow ZnO nanorod arrays on ZnO-seeded and bare ITO substrates by electrochemical deposition in a potassium chloride (KCl) and zinc chloride (ZnCl₂) electrolyte solution. We compared the nanostructure, optical properties, and photoluminescence properties of ZnO films grown on ZnO-seeded and bare ITO substrates. Hybrid solar cells were fabricated from these films and their performances were measured.

2. Experimental
ZnO seed layer and nanorod growth
ZnO nanorod arrays were grown by electrochemical deposition on clean bare ITO substrates and on ZnO-seeded ITO substrates. The ZnO seed layer was deposited by spin-coating a filtered solution of zinc acetate and methanol (0.1g/mL) onto ITO substrates followed by baking at 350 °C for 30 min.

Electrochemical deposition was carried out on a rotating disk electrode (RDE) set-up and on a stationary electrode set-up. ZnO growth was carried out potentiostatically at constant voltages of either -1.0 V or -1.1 V vs. SCE in a 0.1 M KCl and 5 mM ZnCl₂ electrolyte solution kept at 70 °C during deposition. A platinum wire was used as the counter electrode. The electrolyte solution was saturated with bubbling oxygen from a glass frit for least 20 min prior to deposition. A Hokuto Denko HSV-110 voltammetry system was used to control the potential source. After deposition, the samples were cleaned with deionized water to wash away remaining salts and were dried at 150 °C.

Characterization
The nanostructure of the ZnO films were observed under SEM. Optical characterization was carried out by measuring the UV-Vis transmittance spectra with JASCO V-530. Photoluminescence (PL) spectra were measured with a PMA-50 spectrometer.

Hybrid solar cell fabrication
Hybrid solar cells were fabricated from the samples and JV curves were measured. The hybrid solar cell has an ordered bulk-heterojunction structure where the ZnO nanorod array serves as the ordered inorganic component and an active layer of poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁-butyric-acid-methyl ester (PCBM) acts as the organic component. The active layer was deposited by spin-coating from a solution of P3HT and PCBM at a 2:1 ratio in chlorobenzene (15 mg/mL) onto the ZnO layer. For the top electrode, a thin film (~10 nm) of MoO₃ and a film of Au were deposited by vapor deposition through a shadow mask.

3. Results
ZnO nanorod arrays
The nanostructure of the electrochemically-deposited ZnO films on seeded and bare ITO using the stationary electrode can be seen in Fig. 1. The nanorods grown on the
ZnO-seeded substrates have better vertical alignment and the diameters of the nanorods are homogeneous, about 50 to 70 nm. The nanorod density is high and the nanorods are closely spaced but not compact. In comparison, the ZnO film grown on the bare ITO substrate is composed of larger nanorods growing in a less-ordered manner. The diameters of these structures vary from about 100 to 500 nm. Consequently, the optical properties of the films grown on the ZnO-seeded layer had higher transmittance.

As expected, the solar cell performance of the devices fabricated from ZnO-seeded substrates is better compared to those fabricated from bare ITO substrates. There were cases in the bare ITO samples where the ZnO did not grow on the ITO surface during deposition, leaving it exposed. These exposed ITO areas create short circuit paths detrimental to solar cells and results in an ohmic JV curve as shown in Fig. 3. Because the ZnO seed layer covers the entire ITO surface, it also serves as an effective hole blocking layer.

The PL spectra of the films are compared in Fig. 2. PL spectra are analyzed to assess defect types and concentrations [5]. The larger intensity of the PL spectra for the films grown on bare ITO indicates a larger concentration of defects. It can also be seen that the peaks are different for either the ZnO-seeded and bare samples suggesting that growing on different substrates produces defects that are characteristic to that method.

4. Conclusions

ZnO nanorod arrays have been grown on ZnO-seeded and bare ITO substrates by electrochemical deposition. The ZnO seed layer deposited via sol-gel was observed under the SEM to be composed of densely-packed nanoparticles about 20 nm in diameter. The nanorods grown on the seeded substrates had better vertical alignment and homogeneous diameters about 50 to 70 nm whereas the nanorods grown on bare ITO had diameters ranging from 100 to 500 nm. The PL spectra indicate a larger concentration of defects in the films grown on bare ITO substrates. The performance of the solar cells fabricated from the ZnO-seeded substrates were better. The ZnO seed layer acts as an effective hole-blocking layer as well as provides preferable surfaces for nucleation and growth of nanorods.

References