Carbon nanotubes grown on $\text{In}_2\text{O}_3:\text{Sn}$ glass as large area electrodes for organic photovoltaics

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The authors report the growth of multiwall carbon nanotubes directly onto indium tin oxide glass via chemical vapor deposition as large area semitransparent electrodes for organic solar cell applications. The rate of nanotube growth on this ternary oxide is greatly reduced as compared to that of silicon dioxide and glass substrates enabling a high degree of control over nanotube height. The strong potential of this nanostructured semitransparent substrate as an interpenetrating hole-extracting electrode in bulk-heterojunction organic solar cells is also demonstrated. © 2007 American Institute of Physics. [DOI: 10.1063/1.2431437]

In recent years, organic solar cells have been the focus of significant research interest owing to their potential as a low cost path to harvesting energy from sunlight. At present, the efficiencies and lifetimes are inferior to their conventional semiconductor counterparts and too low for commercial viability. To date, the most efficient low cost organic solar cells have been built upon the bulk-heterojunction concept, comprising phase separated blends of solution processed donor and acceptor molecules.^{1,2} Power conversion efficiencies as high as 5% under simulated AM 1.5 solar illumination have been reported,¹ with several reports showing that processing parameters such as drying time^{2,3} and postdeposition annealing¹ are key to realizing high efficiency.

One of the limiting factors affecting power conversion efficiency is the low short circuit current density (J_{sc}) which relies on the ability of the photoactive material(s) to efficiently absorb photons, dissociate excitons, and transport charge carriers to the respective electrodes. Disordered organic materials are, however, widely known for their poor exciton diffusion lengths and low charge carrier mobilities,⁴ which seriously limit the J_{sc} . While the issue of short exciton diffusion length is largely solved in bulk-heterojunction structures exhibiting nanoscale phase separation,⁵ the low charge carrier mobility—particularly that of holes—remains a limiting factor. The simplest means of overcoming this problem is to reduce the active layer thickness. Unfortunately this approach reduces the optical absorbance resulting in a commensurate reduction in the light harvesting capability of the device.⁶ An alternative approach is the use of an interpenetrating electrode which extends into the active organic layer, extracting charge carriers close to the point of generation.

Carbon nanotubes (CNTs) offer a possible route to realizing high area, interpenetrating electrodes in organic solar cells. Multiwall carbon nanotubes (MWCNTs) confined to the donor layer of bilayer solar cells have been utilized as the hole-extracting electrode,^{7,8} where they have been shown to reduce cell series resistance and increase fill factor.^{8,9} Conversely single wall carbon nanotubes (SWCNTs) have been utilized as the electron acceptor and electron extracting electrode in heterojunction organic solar cells.^{10,11} Freestanding

SWCNT films have also been demonstrated as a low cost alternative to indium tin oxide (ITO) glass in bulk-heterojunction organic solar cells.^{12–14}

This letter reports the controlled growth of MWCNTs directly onto ITO coated glass using chemical vapor deposition (CVD) to realize large area electrodes with high optical transparency suitable for organic solar cell applications. The primary advantages of this approach over simply mixing MWCNTs with the active organic matrix are threefold: (i) the MWCNTs are directly bonded to the ITO substrate enhancing the mechanical stability of the contact; (ii) this approach guarantees that all MWCNTs are in direct contact with the underlying ITO electrode ensuring a continuous pathway to the external circuit; (iii) since the MWCNTs are of controlled dimensions and are not randomly distributed within the active organic matrix it is possible to avoid problems associated with electrical shorting, such that the MWCNTs penetrate the photoactive layer without compromising the integrity of the diode. Previous reports pertaining to CNT growth on ITO glass used a thick (~ 15 nm) catalyst layer rendering the substrate virtually opaque, and therefore unsuitable for optoelectronic applications. In addition to enabling MWCNT growth on solid supports, CVD of MWCNT is arguably best suited to large area electronic applications due to the ability to produce high yields with relatively few impurities.

Devices were fabricated on commercially sourced ITO coated aluminosilicate glass ($5\text{--}15\ \Omega\ \text{sq}^{-1}$) which ensured its resistance to the elevated temperature used during nanotube growth. The ITO substrates were cleaned using a three stage ultrasonic cleaning procedure: toluene, an aqueous solution of decon-90, and acetone. Immediately prior to use, substrates were suspended in the vapor of refluxing acetone followed by microwave oxygen plasma treatment. A 5 nm film of nickel catalyst was sputter coated onto the ITO substrates. MWCNTs were grown via acetylene pyrolysis at $550\ ^\circ\text{C}$ for 50 min at 0.68 Torr using hydrogen as the carrier gas. Substrates were allowed to cool to room temperature under nitrogen before solar cell fabrication.

Poly(3-hexylthiophene) [P3HT]:[6,6]-phenyl- C_{61} butyric acid methyl ester [PCBM] $18\ \text{mg ml}^{-1}$: $18\ \text{mg ml}^{-1}$ blends in 1,2-dichlorobenzene were spin cast at 650 rpm and allowed to dry for 1 h in a covered Petri dish. LiF was deposited to a

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FIG. 1. (a) SEM image showing that MWCNTs grow very slowly on ITO as compared to the growth rate on glass under identical growth conditions (4 min, 550 °C, 2 nm Ni); (b) SEM image showing the uniform coverage of MWCNTs on ITO grown under optimized growth conditions (50 min, 550 °C, 5 nm Ni); (c) Cross-sectional SEM of MWCNT mat shown in (b).

thickness of 1.5 nm on all devices, followed by a 50 nm aluminum counterelectrode evaporated through a shadow mask to form the top electrode. Film thickness was monitored throughout deposition using a quartz crystal microbalance. The photoactive device area was typically 8 mm². Devices were tested using an Oriel solar simulator under AM 1.5 D spectral illumination of 100 mW cm⁻² (1 sun) immediately after device fabrication.

The growth of CNTs on ITO glass was very sensitive to the catalyst layer thickness. A minimum Ni layer thickness of ~5 nm was required to achieve growth due to the rapid diffusion of Ni into the polycrystalline ITO substrate at the temperatures required for acetylene pyrolysis. Notably, we also observe that the rate of CNT growth on ITO was very much slower than that of glass substrates, as shown in Fig. 1(a). We suggest that this is due to the contamination of the Ni catalyst by In and Sn from the underlying ITO, since ITO glass is known to contaminate the active organic layers in organic light-emitting diodes with these metals,¹⁵ neither of which are known to catalyze CNT growth. This reduced growth rate is advantageous in the present context since it enables the very high degree of control over CNT height required for utility in organic solar cells (<200 nm).

The scanning electron microscopy (SEM) image in Fig. 1(b) and cross-sectional image in Fig. 1(c) show that the MWCNTs grow in an unorientated fashion on ITO to form a dense mat. The transmission electron microscopy (TEM) images in Fig. 2 confirm the multiwall, defective structure of the CNTs. For the current application, defective MWCNTs are ideal since MWCNTs are intrinsically metallic in nature and the defective structure is expected to facilitate adherence to the adjacent organic semiconductor. Figures 1(c) and 2(a) also show that the MWCNTs are sufficiently short so that

FIG. 2. (a) TEM image showing an individual MWCNT removed from the ITO substrate. (b) A higher magnification TEM image of (a) where the graphitic fringes can be observed.

they penetrate extensively into the P3HT:PCBM layer without extending all the way to the counter-electrode.

The optical transmission of the ITO substrate, a 5 nm nickel coated ITO substrate and the substrate after MWCNT growth are shown in Fig. 3. The optical transmission of the ITO coated aluminosilicate glass at the maximum absorption of the P3HT:PCBM blend: ~550 nm, was ~90%. The transmission of the Ni coated substrate and MWCNT coated substrates at the same wavelength were ~75% and ~60%, respectively. Despite the ~30% reduction in the light intensity reaching the P3HT:PCBM layer in the cell incorporating MWCNTs, as compared to cells utilizing unmodified ITO glass, J_{sc} remains unchanged at ~4 mA/cm². This result cannot be attributed to a difference in the thickness of the P3HT:PCBM layer, which was measured to be ~150 nm in all cell structures using cross-sectional SEM and profilometry. This is compelling evidence that the loss in efficiency due to the 30% reduction in light entering the cell is offset by efficient hole extraction by the large area interpenetrating electrode. It is possible that geometric electric field enhancement at the MWCNT ends and sidewalls—estimated to be as much as four times the built-in electric field—may facilitate enhanced hole extraction. In addition, the 50%–60% increase in the “nanotextured” area of the MWCNT-ITO glass composite electrode, as compared to planar ITO glass, reduces the average distance holes need to travel before extraction to

FIG. 3. Transmission spectra of ITO glass, ITO glass coated with 5 nm Ni and ITO glass with grown CNTs. The absorption spectrum of P3HT:PCBM is also included for reference.

FIG. 4. Current-voltage characteristics of reference, ITO/MWCNT and ITO/Ni devices under AM 1.5 D illumination at 100 mW/cm². Inset: schematic energy level diagram.

the external circuit, thereby improving the hole-extraction efficiency. The combination of these two effects is likely to compensate for the 30% loss in light absorption and clearly points the way to improve charge transfer efficiencies in future cells.

The inclusion of MWCNTs into the cell structure resulted in a very small (~ 0.05 V) decrease in V_{oc} as compared to cells utilizing unmodified ITO glass. This is consistent with the comparable work function of MWCNTs (~ 4.3 eV) (Ref. 16) and the microwave plasma treated ITO glass, measured in our laboratory using ultraviolet photoemission spectroscopy to be ~ 4.4 eV [Fig. 4 (inset)]. Devices fabricated with a 5 nm Ni layer on the ITO surface exhibited a large (~ 0.2 V) reduction in V_{oc} . This result is somewhat counterintuitive since Ni would be expected to increase V_{oc} on account of its relatively high work function (~ 4.7 eV). However, since abrupt negative vacuum level shifts at metal-organic interface are known to modify the interfacial energy level alignment by as much as 1.5 eV,¹⁷ this result it is not entirely unexpected. Notably, Fig. 4 also shows that J_{sc} is essentially independent of V_{oc} .

The fill factor (0.47) and overall efficiency (0.93%) of MWCNT devices were reduced as compared to the reference (fill factor=0.61, efficiency=1.37%), largely due to a reduction in cell shunt resistance. From the gradient of the fourth quadrant response where it crosses the y axis, it is evident that this reduction in power conversion efficiency can be attributed to a reduction in cell shunt resistance. We suggest that through the judicious selection of an appropriate electron injection buffer layer,¹⁸ this small reduction in shunt

resistance is likely to be greatly reduced in optimized cell structures.

In summary, we report the growth of MWCNTs directly onto ITO coated glass using CVD to realize large area electrodes with high optical transparency. Crucially, the MWCNT growth rate is much slower than on glass or silica enabling a high degree of control over nanotube dimensions. We have also demonstrated the utility of this nanostructured electrode as efficient hole-extracting electrodes in organic solar cells. Importantly, the transparency of this electrode is highest at longer wavelengths, making it well matched to the solar spectrum. With the ability to pattern substrates with catalyst particles and to tailor ordered and vertically aligned arrays of CNTs, it is envisaged that this approach is a promising path to enhancing the efficiency of bulk-heterojunction organic solar cells.

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