Low vacuum process for polymer solar cells: Effect of TiO$_x$ interlayer

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Here, the effect of integration of a TiO$_x$ interlayer on low vacuum-processible organic-based solar cells is reported. Devices with an Al electrode prepared at a low vacuum condition shows lower efficiency compared to those with an Al electrode prepared at a high vacuum condition because the interface between the active layer and Al electrode is too rough. When a TiO$_x$ layer is inserted between the active layer and Al electrode of the device, the cell efficiency is regained and much less dependent on the level of vacuum during Al deposition so that it may be possible to develop low cost process. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908035]

In recent years, there has been significant progress in the development of thin film polymer solar cells, employing polymer-fullerene heterojunctions as active layers. Since the discovery of efficient electron transfer between [6,6]-phenyl C61-butyric acid methyl ester (PCBM) and conjugated polymers in bulk-hetero junction (BHJ) polymer-based solar cells, considerable attention has been directed toward increasing the performance of these systems. Photogenerated free holes and electrons in these systems are transported through the donor and acceptor phases toward the electrodes, resulting in an external photocurrent density. As a result, the photocurrent does not solely depend on the photogeneration and transport properties of the electrons and holes but also depend on the interface between the active layer and electrodes.

Generally, to obtain good interfacial properties between the active layer and electrodes, a device with a spin-coated active layer is placed in a high vacuum condition ($\sim$10$^{-7}$ torr) and an Al film ($\sim$100 nm) is deposited on top of the BHJ layer. It is well known that, in general, a reduction in vacuum pressure is accompanied by increases in aluminum film conductivity and density, and a decrease in surface topography. This implies that there is a strong relationship between the solar cell performance and vacuum condition for cathode preparation. High vacuum process is an expensive and time-consuming process. Therefore, a new cell structure that yields the same cell efficiency without requiring a high vacuum condition to prepare the metal cathode is necessary for the commercialization of polymer-based solar cells.

Recently, a polymer solar cell containing a thin TiO$_x$ layer has been prepared by the Heeger group with an efficiency of 5%. The TiO$_x$ layer in this device has been served as an optical spacer. Other group has investigated a similar structured solar cell by introducing a functional TiO$_x$ layer as a hole blocking layer in the BHJ solar cell.

The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital energy levels of TiO$_x$ are 4.4 and 8.1 eV, respectively. TiO$_x$ is expected to perform both as a hole blocking layer and an exciton blocking layer because TiO$_x$ has its LUMO level near the Fermi level of Al and possesses a large band gap. Here, we present another effect of integration of a TiO$_x$ interlayer in a polymer-based solar cell: the cell efficiency of the solar cell with a TiO$_x$ interlayer was less dependent on the vacuum condition for deposition of a metal cathode compared to a solar cell without the TiO$_x$ interlayer.

Indium tin oxide glass was cleaned and then treated with oxygen plasma before use. A conducting polymer poly(3,4-ethylenedioxythiophene:poly(styrene sulfonate) (Baytron P) was then spin coated to a thickness of ~35 nm. An active layer of the reference device consisting of P3HT and PCBM was then spin coated from chlorobenzene solvent at 900 rpm for 10 s. The device was subsequently heated on a hotplate at 200 °C for 5 min. The active layer thickness is about 220 nm. The metal electrode (Al) was thermally deposited with a thickness of 150 nm. This process was performed under various pressures: 6.5 × 10$^{-5}$, 1.5 × 10$^{-5}$, 6.5 × 10$^{-6}$, 1.5 × 10$^{-6}$, and 6.5 × 10$^{-7}$ torr. The deposited Al electrode area defines the active area of the devices as 4−5 mm$^2$. Thermal annealing was next carried out by directly placing the fabricated devices on a digitally controlled hotplate at 150 °C for 30 min. All thermal annealing processes (preannealing and postannealing) were performed in an inert-gas filled glove box. For preparation of a solar cell with a TiO$_x$ layer, the

![](image)

**FIG. 1.** J-V curves of reference devices fabricated at various vacuum pressures (☐: 6.5 × 10$^{-5}$ torr, ⊙: 1.5 × 10$^{-5}$ torr, △: 6.5 × 10$^{-6}$ torr, ▽: 1.5 × 10$^{-6}$ torr, and ◆: 6.5 × 10$^{-7}$ torr).
TiO$_x$ layer (~6.5 mm) on the preannealed active layer was prepared by spin coating an isopropyl alcohol solution of titanium (IV) isopropoxide at 2500 rpm for 40 s. A metal electrode was then thermally deposited with a thickness of 150 nm. In the case of the device with TiO$_x$, post-thermal annealing was not performed because the cell efficiency is greatly reduced by this process (see supporting data). The J-V curves were measured at AM 1.5 illumination using a Keithley 2400 source measure unit. A 1000 W xenon lamp (Oriel, 91193) served as the light source and its intensity was calibrated using a Si reference cell (Fraunhofer ISE, certificate no. C-ISE269).

Figure 1 shows J-V curves of reference devices fabricated under various vacuum pressures. These devices were fabricated without a TiO$_x$ layer and with postannealing after Al deposition. As expected, the performance of the device decreases as the vacuum pressure increases: $V_{oc}$ of the device decreases from 0.61 to 0.51 V and $J_{sc}$ of the device decreases from 9.43 to 7.61 mA/cm$^2$. The fill factor (FF) of the device decreases from 0.508 to 0.408 and this efficiency decreases from 2.91% to 1.61%. Given that all processes before Al deposition are identical, it can be concluded that factor reducing the performance of the device is the structure of the deposited Al depending on the vacuum pressure.

As noted above, Al electrode deposition at low vacuum pressure yields a rougher interface between the active layer and Al electrode relative to that prepared at high vacuum pressure. This rougher interface disturbs the contact between the active layer and Al electrode and decreases the performance of the device. To confirm this, scanning electron microscopy (SEM) images of the Al electrodes deposited on the active layer were obtained and are presented in Fig. 2. Figure 2(a) is an image of an Al electrode deposited at 6.5 $\times$ 10$^{-5}$ torr and Fig. 2(b) is an image of an Al electrode deposited at 6.5 $\times$ 10$^{-7}$ torr. While some defects on the surface of the Al electrode deposited at 6.5 $\times$ 10$^{-5}$ torr can be easily observed in Figure 2(a), there are few or no defects on FIG. 2. SEM image of Al film deposited at 6.5 $\times$ 10$^{-5}$ torr (a) and 6.5 $\times$ 10$^{-7}$ torr (b) (x150,000).

FIG. 3. J-V curves of devices with TiO$_x$ layer fabricated under various vacuum pressures (□: 6.5 $\times$ 10$^{-5}$ torr, ○: 1.5 $\times$ 10$^{-5}$ torr, △: 6.5 $\times$ 10$^{-6}$ torr, ▽: 1.5 $\times$ 10$^{-6}$ torr, and ◇: 6.5 $\times$ 10$^{-7}$ torr).

FIG. 4. Normalized values of $V_{oc}$, $J_{sc}$, FF, and efficiency of the reference devices (■) and the devices with a TiO$_x$ layer (○) fabricated at various vacuum pressures.
the surface of the Al electrode deposited at $6.5 \times 10^{-7}$ torr, in Fig. 2(b).

Figure 3 shows $J$-$V$ curves of devices fabricated under various vacuum pressures. These devices are fabricated with a TiO$_x$ layer between the active layer and Al electrode. Before spin coating the TiO$_x$ layer, preannealing is performed and postannealing is not performed after Al deposition. As the vacuum pressure increases, the performance of the device decreases. However, while all factors decrease in the reference devices, $V_{oc}$ of devices with a TiO$_x$ layer is maintained at about 0.62 V and FF of the devices with a TiO$_x$ layer slightly changes near 0.50. The factor that critically decreases efficiency of the devices with a TiO$_x$ layer is $J_{sc}$. $J_{sc}$ of the device with the TiO$_x$ layer decreases from 9.60 to 7.27 mA/cm$^2$. Furthermore, the efficiency of the device with the TiO$_x$ layer decreases from 3.31% to 2.07%. From these results, we can conclude that interfacial effect, which is degraded by the rough surface of the Al electrode deposited at low vacuum pressure, is overcome by inserting a TiO$_x$ layer between the active layer and Al electrode.

Figure 4 shows normalized values of $V_{oc}$, $J_{sc}$, FF, and efficiency of the reference devices and the devices with a TiO$_x$ layer fabricated at various vacuum pressures. As the vacuum pressure is increased, $V_{oc}$ of the device with TiO$_x$ is very close to that of the reference device and the FF of the device with the TiO$_x$ layer only slightly decreases compared to the reference device. On the other hand, $J_{sc}$ of the reference device and the device with the TiO$_x$ layer decrease by almost the same ratio. The efficiency of the device with the TiO$_x$ layer only slightly decreases under a low vacuum, whereas the efficiency of the reference device dramatically decreases under the same fabrication environment. In order to explain this effect, it is necessary to look at the interface between TiO$_x$/Al electrode in detail. Up until now, several studies concerning Al–O–C bonds between a conducting polymer and Al interface have been reported.\textsuperscript{12–14} This chemical bond originated from the small amount of oxygen in the carbonyl groups in polymer chains. The oxygen directly bonded to an Al atom during thermal evaporation process. The formation of oxygen bridging complexes such as C–O–Al possibly increases the interface adhesion. From these previous studies, we could expect that the formation of C–O–Al complex and Ti–O–Al complex in active layer/Al interface and TiO$_x$/Al interface, respectively, resulting in the enhancement of the interface adhesion. Because TiO$_x$ layer have much more oxygen compared to active layer more enhanced interface adhesion would be expected between TiO$_x$ layer and Al cathode. Thus, the effective area for electron transporting paths is increased so that it could compensate for the poor contact between the active layer and Al electrode prepared at low vacuum condition.

In conclusion, it is found that insertion of a TiO$_x$ layer between the active layer and Al electrode prepared under a low vacuum condition would compensate for the poor contact between the active layer and Al electrode of the device. Integration of a TiO$_x$ layer between the active layer and Al electrode of the device makes it possible for an organic solar cell fabrication process under low vacuum with less cost. This technology is certainly expected to play an important role in the practical application of the roll-to-roll process/nanoimprinting process.

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