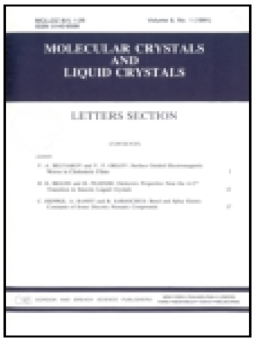

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Solution-Processed NiO Layers for PTB7: $PC_{71}BM$ Organic Solar Cells

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Nickel oxide (NiO) has become attractive as a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT :PSS) substitute in solar cells' hole transport layers (HTLs). However, solar cells with NiO HTLs based on poly[[4,8-bis[(2-ethylhexyl) oxy]benzo [1,2-b:4,5-b′]dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno[3,4-b]-thiophenediyl] (PTB7) and [6,6]-phenyl C_{71} *butyric acid methyl ester (*$PC_{71}BM$*) remain poorly characterized. We report the effects of NiO-layer thickness on the performance of glass/ITO/NiO/PTB7:*$PC_{71}BM$*/LiF/Al-structured solar cells. Thickness was optimized by changing nickel acetate tetrahydrate concentration in 2-methoxyethanol solution used for spin-coating deposition. We achieved a power conversion efficiency of 5.14% at 0.2 M of nickel acetate tetrahydrate. Solar cells with NiO HTLs exhibited improved long-term reliability.*

Keywords Organic solar cells; PTB7; $PC_{71}BM$; HTL; NiO

1. Introduction

Demands for sustainable energy sources are increasing all over the world. Recently, organic photovoltaics (OPVs) have attracted significant attention owing to their lightweight, low-cost solution processing, and flexibility [1]. They have become a viable source of renewable energy after the advantages of polymer organic bulk hetero-junction (BHJ) solar cells were delineated [2]. Organic BHJ solar cells usually consist of a transparent indium tin oxide (ITO) anode, a hole transport layer (HTL), a photoactive layer, and a top cathode. The HTLs must have high optical transparency, good chemical stability, large ionization potential, and good electron-blocking capability.

In a typical polymer solar cell, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is used as the HTL, and its work function (Φ) is 5.2 eV. However, its acidity, tendency to absorb water, and inability to block electrons effectively cause inferior device performance and poor long-term stability [3]. Accordingly, metal oxides have been extensively investigated as an alternative for PEDOT:PSS [4–7]. Amongst these metal

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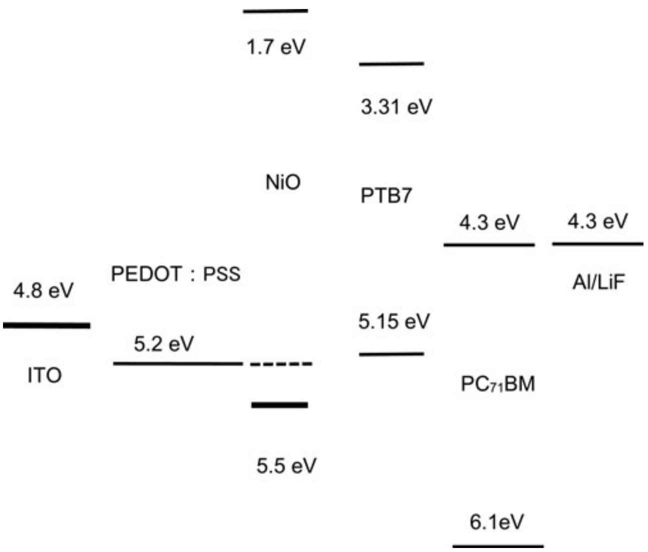

Figure 1. Energy band diagram for the investigated solar cell structures.[8, 21]

oxides, nickel oxide (NiO) was shown to exhibit excellent performance as a HTL [8–13]. This is because stoichiometric NiO is an excellent insulator at room temperature with a conductivity on the order of 10^{-13} S cm^{-1} [8, 14], while non-stoichiometric NiO is a wide bandgap p-type semiconductor [8, 15–19].

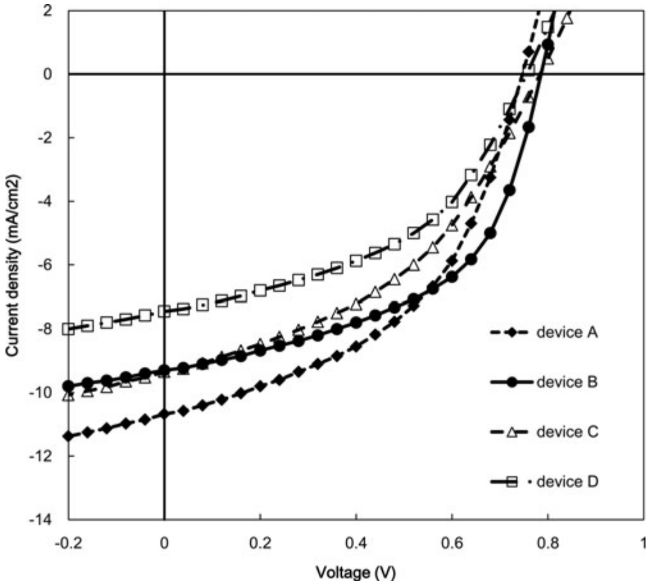

Figure 2. *J-V* characteristics of BHJ solar cells with different NiO HTL layers for different concentrations of NAT:MEA dissolved in 2-methoxyethanol: device A (0.1 M), device B (0.2 M), device C (0.3 M), and device D (0.4 M). All devices were fabricated at the spin-coating frequency of 800 rpm for 30 s, and were solvent-annealed for 30 min.

Table 1. Average solar cell parameters for BHJ solar cells, obtained for different precursor concentrations

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)
A (0.1M)	0.76	10.4	0.47	3.69	19.6	288
B (0.2M)	0.78	9.6	0.51	3.78	17.3	370
C (0.3M)	0.77	8.3	0.44	2.85	33.6	340
D (0.4M)	0.72	8.1	0.40	2.3	42.3	284

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Irwin et al. first demonstrated enhanced performance of polymer solar cells with a NiO electron-blocking layer deposited via pulsed laser deposition [12]. Recently, solution-processed NiO was also used in BHJ-solar-cells fabrication [8–10, 13], and under ambient conditions, NiO-based devices have been reported to be more air-stable than PEDOT:PSS-based devices. In addition, organic BHJ solar cells using poly[[4,8-bis[(2-ethylhexyl)oxy]benzo [1,2-b:4,5-b']dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7) and [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) attracted significant attention owing to their extremely high power conversion efficiency (PCE) that could reach 9% [20–22]. Solar cells with NiO HTLs based on PTB7:$PC_{71}BM$ remain poorly characterized. Therefore, we investigated glass/ITO/NiO/PTB7:$PC_{71}BM$/LiF/Al structured BHJ solar cells. In this paper, we determined the optimal concentration of NiO precursor, and then investigated the PCE degradation characteristics of the solar cells with NiO HTLs stored in air and compared these characteristics with those of control solar cells with PEDOT:PSS as an HTL.

2. Experimental

Fabrication of solar cell devices

We fabricated BHJ solar cells with NiO HTLs deposited using different precursor concentrations as well as solar cells with PEDOT:PSS HTLs that served as a reference. All films were deposited onto electrode-patterned ITO substrates (Techno Print). The substrates were cleaned in de-ionized water, acetone, and isopropanol, respectively for 15 min each in an ultrasonic bath. All dried substrates were UV-ozone cleaned for 15 min. To fabricate the reference device, a layer of PEDOT:PSS (Aldrich) was spun on the substrates at 3000 rpm, followed by annealing at 130°C for 20 min.

Devices with NiO film HTLs were fabricated as follows. The cleaned ITO substrates were baked at 150°C for ~20 min. The NiO films were deposited by spin coating the NiO precursor at 4000 rpm for 30 s, followed by annealing on a hot plate in air at 350°C for 90 min. Next, UV-ozone cleaning was performed for 2 min. To prepare the precursor solution, nickel acetate tetrahydrate (NAT) ($Ni(OAc)_2{\cdot}H_2O$) and mono ethanolamine (MEA) were dissolved in 2-methoxyethanol. The NAT:MEA molar ratio was maintained at 1:1. Devices A, B, C, and D were fabricated using the precursor solutions with NAT:MEA concentrations of 0.1, 0.2, 0.3, and 0.4 M, respectively. The active layer was deposited using a solution in which 10 mg of PTB7 and 15 mg of $PC_{71}BM$ were dissolved in a 1:1.5 ratio by weight in 1 ml of 1,2-dichlorobenzene. For active layer deposition, the spin-coating speed and duration were 800 rpm and 30 s, respectively. After coating the PTB7:$PC_{71}BM$ layer,

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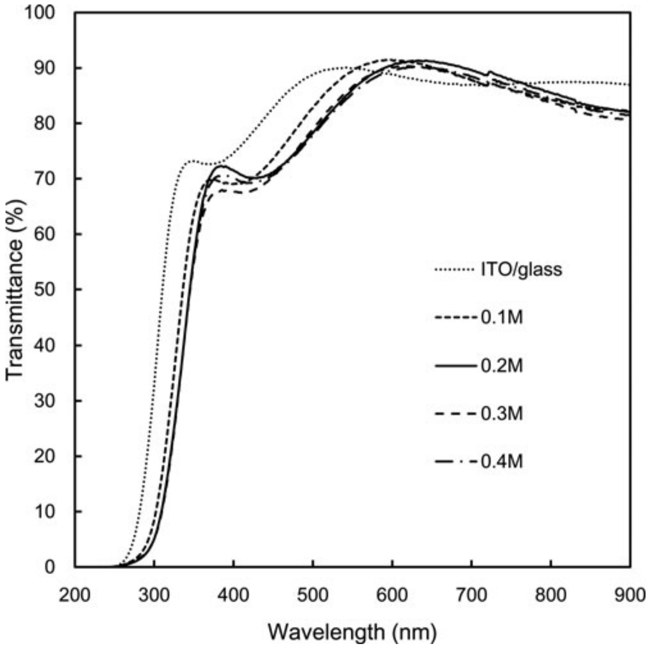

Figure 3. Optical transmittances of NiO films on ITO-coated glass substrates, for NAT:MEA concentrations of 0.1 M, 0.2 M, 0.3 M, and 0.4 M.

the substrate was solvent-annealed in a Petri dish under dry nitrogen ambient conditions for 30 min before being transferred to a vacuum system for depositing the cathode layers. Finally, a 2-nm thick LiF and 90-nm thick Al layers were deposited under 4×10^{-4} Pa by thermal evaporation through a shadow mask. The fabrication conditions for solar cells based on PTB7:$PC_{71}BM$ were described in details in our previous publications [23, 24]. The active area of the fabricated solar cell device was 4 mm^2. The current density–voltage (J–V) characteristics of the solar cell devices were measured by using a Keithley 2400 source meter under simulated solar illumination conditions and light intensity of 100 mW/cm^2. The optical transmittance spectra of the NiO films were recorded on a Shimadzu UV-3700 spectrophotometer. All measurements were performed under atmospheric conditions.

3. Results and Discussion

The energy band diagram of the BHJ solar cells with NiO HTLs is shown in Fig. 1. This energy band diagram was drawn based on previously published works [8, 21]. The valence band of NiO is lower than the highest occupied molecular orbital (HOMO) of PTB7, and the conduction band of NiO is higher than the lowest unoccupied molecular orbital (LUMO) of PTB7. The electron flow from PTB7 to ITO is blocked. The hole flow from PTB7 to ITO is limited by tunneling. Thus, it is expected that the hole current will be reduced when the NiO layer thickness is increased.

Figure 2 shows the J-V characteristics of the NiO devices with different NiO layer thickness, as controlled by the precursor concentrations. The short-circuit current density (J_{sc}) decreased from 10.4 mA/cm^2 to 8.1 mA/cm^2 as the precursor concentration increased from 0.1 M to 0.4 M. This may be attributed to the hole tunneling current reduction with

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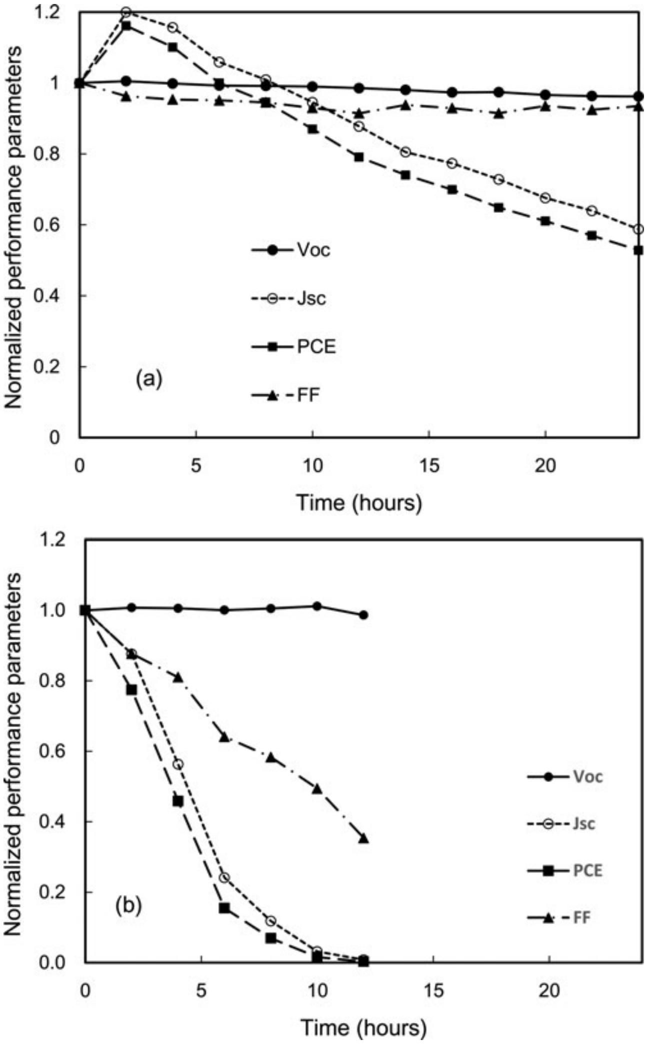

Figure 4. Temporal changes of solar cell parameters for BHJ solar cells with NiO layer (0.2 M) and PEDOT:PSS layer. The spin-coating frequency and duration for the PTB7:PC$_{71}$BM solution were 800 rpm and 15 s, respectively, and solvent annealing lasted 30 min.

increasing NiO layer thickness. The BHJ solar cell performance was highest at the NiO precursor concentration of 0.2 M. Table 1 summarizes the average parameters for each device.

Series and shunt resistances were calculated by taking the inverse slopes at V_{oc} and J_{sc}, and their values are also listed in Table 1. The series resistance increased with increasing NiO film thickness. These phenomena were similar to those reported previously [9]. These results suggest that the NiO films thickness should be optimized for better organic solar cell performance.

Figure 3 shows optical transmittances of the NiO films on ITO-coated glass substrates deposited using the precursors with different NAT:MEA concentrations. Interestingly, the transmittances of the NiO films on the ITO/glass substrates were similar, although a spectral

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shift toward larger photon wavelengths was observed. Therefore, the J_{sc} change in NiO devices was not related to the optical transmission influenced by the NiO layers.

Although the BHJ solar cell performance peaked at the NiO precursor concentration of 0.2 M, we found that the performance of these solar cells could be significantly improved by changing the spin-coating time from 30 s to 15 s at 800 rpm. The improved J-V characteristics of NiO HTL solar cells obtained by using 0.2 M of precursor and of PEDOT:PSS film solar cells, fabricated at the PTB7:PC$_{71}$BM spin-coating time of 15 s. All other process parameters were the same. The solar cell parameters V_{oc}, J_{sc}, FF, and PCE for the device with NiO (0.2 M) were 0.78 V, 13.3 mA/cm^2, 0.50, and 5.14%, respectively. The corresponding solar cell parameters for the device with PEDOT:PSS were 0.77 V, 11.1 mA/cm^2, 0.50, and 4.31%. These results show that the device that uses PTB7/ PC$_{71}$BM as the active layer with NiO film performs better than the device with PEDOT:PSS.

Furthermore, we investigated the NiO HTLs influence on the degradation of these devices stored in air. It has been reported that NiO BHJ solar cells are more stable than solar cells with a PEDOT:PSS [8, 9, 11]. However, the degradation properties of BHJ solar cells with PTB7:PC$_{71}$BM active layers have not been reported. To validate the stability, we compared the non-encapsulated NiO- and PEDOT:PSS-based devices stored in air and in dark in the laboratory ambient conditions. Figure 4(a) shows the temporal changes of the solar cell parameters for the NiO-based solar cell with 0.2 M, as well as the temporal changes of the solar cell parameters for the PEDOT:PSS-based solar cell that was reported in Fig. 4(b). The PCE of the PEDOT:PSS device approached zero after 12 hours of storage, as shown in Fig. 4(b). On the other hand, the NiO-based device exhibited much slower degradation. The V_{oc} and FF of the NiO-based solar cell did not change. Only the J_{sc} slightly increased within the first 5 hours, and gradually decreased after that. It should be noted that the PCE degradation of the NiO-based solar cell was mostly caused by the decreasing J_{sc}. On the other hand, the J_{sc} and FF of the PEDOT:PSS-based solar cell rapidly decreased with time, and were responsible for the rapid decrease of PCE with time. In a previous report, it was shown that the acidity and hygroscopic nature of PEDOT:PSS corrodes the ITO electrode and the PEDOT:PSS itself [25]. The acidity and hygroscopic nature of PEDOT:PSS introduce interfacial HTL degradation.

4. Conclusion

We studied the performance of organic solar cells by using solution-based NiO films and PTB7:PC$_{71}$BM as active layers. The NiO-layer thickness was optimized by varying the concentration of nickel acetate tetrahydrate in 2-methoxyethanol solution used for spin-coating deposition. The NiO HTL device exhibited better stability and performance compared with the PEDOT:PSS-based device. The maximum PCE of 5.14% was achieved at a nickel acetate tetrahydrate concentration of 0.2 M. These results suggest that the studied NiO films could be used as a promising alternative to PEDOT:PSS.

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